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Analisis de la demanda de equipo y maquinaria para la Industria Química en México para 1977-1982"

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Esta es la segunda de una serie de monografías cuyo propósito es ilustrar los estudios metodológicos y su aplicación práctica que ha venido desarrollando el Grupo de Desarrollo de Tecnología. División de Estudios Superiores, Facultad de Química de la Universidad Nacional Autónoma de México, con el soporte técnico y económico de Du-Pont,S.A. de C.V., el Consejo Nacional de Ciencia y Tecnología y la Organización de Estados Americanos.

Como se indica más adelante, el presente trabajo es la aplicación de una metodología para planear de una forma racionalizada la fabricación de equipo y maquinaria necesaria para la industria química durante 1977 a 1982.

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Quiero agradecer de manera muy especial al Ing. José Giral y al Lic. Antonio Bolívar su colaboración en la realización de este trabajo. Así como también a todas las personas que con su apoyo físico y moral ayudaron a que se realizara este trabajo. Una lista de estas personas seria interminable, a cada una de ellas, muchas gracias.

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SINOPSIS, OBJETIVOS Y CONCLUSIONES

Este trabajo tiene como objetivo, estudiar el problema de bienes de capital en lo que se refiere a la industria química, aplicando una metodología, propuesta por el Grupo de Desarrollo de Tecnología de la UNAM la cual se detalla más adelante.

El trabajo se ha dividido en dos partes:

En la primera parte, marco general, se habla de un panorama general en la industria de bienes de capital en México, importaciones, demanda y producción nacional; se detallan las diferentes clasificaciones que existen en las publicadas en la literatura para equipo y maquinaria y se propone una clasificación que de acuerdo a los propósitos de este trabajo es la más adecuada. De acuerdo a la clasificación propuesta se describe brevemente cada uno de sus apartados, poniendo en un capítulo aparte a la industria química. Se hace una breve descripción de los equipos considerados en este trabajo y de acuerdo a los apartados de la clasificación se habla de estandarización de equipo, métodos de fabricación y materiales para fabricación de equipo.

La segunda parte, análisis de la demanda de bienes de capital para la industria química en México en 1977 - 1982, contiene los objetivos, una amplia explicación de la metodología y las conclusiones y recomendaciones del trabajo.

Por último se incluyen tablas y apendices y una serie de diagramas de flujo, que sirvieron de base para este estudio y que son los proyectos que se esperan para 1977 - 1982 en la industria química en México. En las tablas se incluye el desglose de la inversión esperada para la industria, tipo de tecnología y por tipo de insumos de acuerdo a los incluidos en el desarrollo de un proyecto.

Las principales conclusiones y recomendaciones de este trabajo son las derivadas de las tablas como los coeficientes tecnológicos de la inversión, desglose de la inversión esperada, análisis de los equipos y maquinarias de proceso más comunes en los proyectos considerados.

Se recomienda a instituciones específicas relacionadas con el tema que lleven a cabo un estudio basado en esta metodología ya que ellos cuentan con mayores recursos tanto humanos como económicos para poderlo efectuar y obtener datos más exactos.

PRIMERA PARTE

MARCO GENERAL

1. PLANTEAMIENTO Y CONSIDERACIONES GENERALES

Antecedentes.

En varios países actualmente en desarrollo, el proceso de industrialización se inició después de la segunda guerra mundial, con la fabricación de bienes de consumo inmediato tales como alimento, vestido y calzado. A medida que se fué integrando esta etapa se avanzó también en la sustitución de importaciones de bienes de consumo duradero, bienes intermedios y materias primas, para lo cual se otorgaron subsidios y facilidades para la importación de equipos para industrias. Se llegó a contar así con una industria que permite satisfacer la demanda interna de la mayor parte de bienes de consumo e intermedios, pero se desalentó la fabricación de maquinaria y equipo.

Con lo anterior se puede considerar que las dos primeras etapas del proceso de industrialización quedaron prácticamente cubiertas. La tercera etapa de desarrollo industrial, relativa a la fabricación de bienes de capital, es la que concierne a este trabajo; dicha tercera etapa se inició parcialmente en los años sesenta con la fabricación de los primeros bienes de capital producidos en forma sistemática, entre los cuales se puede mencionar maquinaria agrícola, maquinaria para la industria de la construcción, montacargas, taladros eléctricos de mano, compresoras de aire y gas, herramientas neumáticas de corte y equipo de transporte, que se puede considerar como el subsector de bienes de capital más desarrollado en México.

Importancia de los bienes de capital en México.

La demanda de equipo y maquinaria está directamente relacionada con la instalación y expansión de plantas industriales, así como con la compra de equipo en otros sectores de la economía. En este sentido México ha experimentado una demanda elevada y constante debido a su alta tasa de inversión interna, del orden del 20% mayor que la de Estados Unidos y Reino Unido así como respecto a la de varios países en vías de desarrollo, aunque otros países como Japón, Francia y España la han superado.

La participación de la industria, excluyendo la minería, en el PIB, aumento de 32.4% en 1970 a 33.7% en 1974. El crecimiento real que estas cifras implican es del 7% anual, superior al de la economía en su conjunto, que fué del 6%. Lo anterior significa que el sector industrial es uno de los más dinámicos de la economía, y a consecuencia de ésto es que la demanda de bienes de capital ha crecido ininterrumpidamente. (4).

La demanda interna total de estos bienes, que en 1974 fué de 121,115 millones de pesos y en 1970 de 77,126 millones de pesos a precios de 1974, con una tasa de crecimiento promedio de 12%, lo cual incluye a todo el sector metalmecánico que comprende: el grupo de productos metálicos, principalmenente productos de pailería, calderas, quemadores, intercambiadores de calor y otros productos intermedios. El grupo de maquinaria no eléctrica incluye principalmente maquinaria y equipo para la industria petrolera, de construcción y minería, maquinaria para trabajos metales, maquinas-herramientas, maquinaria para la industria de alimentos y bebidas, rodamientos, filtros, algunas bombas y válvulas. El grupo de maquinaria eléctrica, donde los más importantes son motores, generadores, transformadores y ciertos equipos industriales. Y por último el grupo de equipo de transporte.

Al rápido crecimiento de la industria debe sumarse el aumento de precios.

Por el año de 1985 se ha calculado una demanda de equipo de 423,923 millones de pesos (también a precios de 1974) y se estima que el país deberá realizar un gasto al exterior de 247,000 millones de pesos, o sea casi la mitad del total.

Frente a la demanda señalada, la producción interna de equipo y maquinaria, a pesar de su rápido incremento en la primera mitad de esta década, es aún reducida; el valor agregado alcanzó los 10,715 millones de pesos en 1974 y experimentó un crecimiento real del 10.1% anual en el período de 1970-1974. Sin embargo, para 1974 apenas constituía el 1.6% del PIB y el 4.8% del producto industrial. Comparando con otros países de nivel de desarrollo similar, el contraste es marcado. Brasil en 1959, superaba ampliamente la proporción que México logra quince años después y que actualmente es inferior a la de Chile y Argentina. En términos de valor bruto de la producción, la fabricación nacional representó 96,740 millones de pesos en 1974 y llegará a 195,625 millones de pesos en 1980. Esta situación nos indica que de mantenerse la actual estructura, cada año la fabricación de maquinaria y equipo tenderá a cubrir una menor proporción de la demanda total, con grave perjuicio para la balanza comercial y para nuestra independencia económica y política. (6)

Importaciones previstas de maquinaria y equipo.

Al analizar las importaciones de equipo y maquinaria se observa una tendencia acelerada hacia el alza. Las compras crecieron a una tasa promedio anual de 14.5% durante 1970 a 1974, de los 16,865 millones de pesos a 28,077 millones de pesos. Esto se debe a un aumento tanto en precios como en volúmen, sin embargo se considera que en términos reales la tasa de incremento ha sido alrededor del 12% anual. Las importaciones de equipo y maquinaria, representaron el 65% del total de las importaciones.

Las proyecciones de producción interna en el sector metalmecánico para el año de 1985 (a precios de 1974), dan una cifra de 350,361 millones de pesos. El desglose de importaciones para 1985 a precios de 1974 será:

	millones de pesos
Sector metalmecánico	96,997
Grupo productos metálicos	4,863

	millones de pesos
Grupo maquinaria no eléctrica	46,759
Grupo maquinaria eléctrica	15,045
Grupo material y equipo de transporte	30,330

Todo lo anterior nos demuestra que a pesar de los esfuerzos realizados, los resultados que se han logrado son insuficientes y dada la magnitud de las cifras de importación señaladas, así como la dificultad de que el país genere divisas que se requieren para satisfacer estas necesidades de importación de los bienes que no se producen o se producen en forma insuficiente para cubrir la demanda, es de gran importancia el impulsar la fabricación de bienes de capital. (6)

Este sector es de gran importancia porque provee la maquinaria que servirá de base a los demás sectores de la industria, así como a la agricultura y los servicios. Así mismo su configuración económica tendrá gran repercusión sobre el resto de la economía, además de que su demanda de insumos require de una mezcla de tecnología avanzada con alto contenido de ingeniería de diseño, de mano de obra calificada y de capital, que combinados logran una mayor eficiencia en la producción.

Aspectos tecnológicos.

La tecnología incorporada a los bienes de capital importados, así como la que se adquire por medio de la inversión extranjera directa y en acuerdos de transferencia, constituyen la base tecnológica sobre la cual opera la industria nacional, dado que es insignificante su generación en el país.

Lo anterior aunado a la importación directa de equipo crea una fuerte dependencia tecnológica.

La industria se puede clasificar en cuatro categorías tecnológi gicas:

1. Industrias de conversión física. Básicamente tecnología de equipo;
2. Industria de producto. Básicamente tecnología de proceso;
3. Industrias de proceso. Básicamente tecnología de operación.
4. Industrias de operación. Básicamente tecnología de operación.

En dos de ellas (la basada en tecnología de equipo y la basada en tecnología de operación) la tecnología se adquiere generalmente en paquetes que incluyen el equipo. En las otras dos categorias (la basada en tecnología de proceso y en tecnología de producto) las bases del diseño están tan relacionadas a la adquisición de la tecnología que no es extraño que el 60% del equipo se tenga que adquirir en el país licenciador de la tecnología. (7)

Algunos obstáculos a la fabricación local de bienes de capital.

Todo lo que se ha dicho anteriormente refuerza el porqué de la situación que prevalece en México y otros países en desarrollo en torno a los bienes de capital. Sin embargo, hay que analizar los problemas que se presentan a la fabricación local de estos bienes, unos están relacionados con las características peculiares de laproducción de equipo y maquinaria y otros son relativos a los sectores usuarios.

A) Las empresas oferentes de tecnología, que normalmente son empresas productivas situadas en los países industrializados, no están interesadas en participar en proyectos en países en desarrollo, o bien aprovechan su situación de ventaja de diferentes maneras: cobrando regalías muy altas, vendiendo el equipo caro y/o innecesario, controlando la distribución, o bien, debido al mejor conocimiento del proceso de fabricación, tratando de retener partes componentes del equipo o algunos puntos estratégicos de la tecnología.

B) Los empresarios nacionales han mostrado falta de interés por participar en empresas que produzcan equipo y maquinaria. De hecho, la mayor parte de las empresas que operan en el país tienen una alta participación extranjera, cumpliendo muchas de ellas una función principalmente de ventas de equipo importado. Esta falta de interés se puede explicar por la baja rentabilidad que ofrecen estos proyectos, la cual va asociada con algunos factores como son: largas curvas de aprendizaje que hacen los proyectos sean de lenta maduración, poca protección con respecto a otras actividades económicas, altos riesgos, elevados costos de la tecnología y la inseguridad de la demanda, la que muchas veces es generada por una o dos empresas solamente. Esta última situación origina que se presenten grandes variaciones de la demanda con el tiempo, con la consiguiente necesidad de un financiamiento especial para inventarios, el que debe ser en condiciones muy favorables.

C) Los consumidores nacionales, constituidos en su mayor parte por grandes empresas, presentan muchas veces resistencias a la instrumentación de políticas de sustitución de importaciones de equipo y maquinaria.

Las razones parecen obvias, ya que estas empresas, por lo menos al inicio de la fabricación nacional, tendrían que comprar los equipos más caros y posiblemente con inferior calidad, además de perder parcialmente la libertad de elección en cuanto a proveedor, fechas de entrega y otros aspectos de la adquisición. Este problema se presentará también a las empresas del sector público que están encargadas de realizar un programa de inversiones, en un tiempo determinado y con un presupuesto fijo.

D) Existen además otros factores de índole institucional, como son: el grado reducido de prortección que se les otorga a los proveedores de equipo y maquinaria; las reglas de financiamiento que fijan algunos organismos internacionales, los que permiten a las grandes empresas productoras de equipo de los países desarrollados competir por abajo de sus costos medios; las prácticas de financiamiento atado que son comunes para otorgar créditos a los países en desarrollo.

Requisitos para la producción de equipo y maquinaria.

Para un país como México, la fabricación de bienes de capital tiene ventajas importantes siempre y cuando se realicen en forma apropiada. Las dos condiciones esenciales para esto son: la concentración de algunos bienes de producción y el logro de una producción eficiente, para poder vender a un precio cercano al internacional.

Lo primero es fundamental, en cuanto a que el país no debe pretender ser autosuficiente en todos los equipos que importa. En algunos casos es muy costoso producir el equipo en el país, porque el mercado es reducido, porque los insumos materiales del proceso de producción son caros, o porque se requiere de recursos con los que no se cuenta en el país.

En otros casos, la fabricación interna puede ser viable y los equipos pueden producirse a costos razonables. El bajo costo de la mano de obra, el aprovechamiento de la infraestructura o bien de instalaciones existentes, pueden contribuir a disminuir el costo de fabricación de nuevos equipos.

En países en desarrollo como México, es difícil lograr el adiestramiento de la mano de obra y la capacitación tecnológica separados de una necesidad directa para su utilización, sobre todo cuando se trata de capacitar a técnicos de nivel medio indispensables en la producción de artículos de alta precisión. Se puede enfocar esta capacitación como un servicio que se genera conjuntamente con la producción de equipo y maquinaria. El país se vería obligado de esta manera a canalizar más recursos para la calificación de mano de obra.

En cuanto al segundo punto, un precio elevado de la maquinaria producida en el país puede provocar una baja en la inversión industrial general, pues se aumenta el costo de los bienes de capital en relación al flujo de ingreso futuro que generan. Es cierto que el precio internacional de algunos bienes de este tipo se encuentra subsidiado por los propios gobiernos de los países exportadores y a un fabricante nacional tal vez no le sea posible sostener esos precios, pero esos bienes hay que distinguirlos de los demás.

Las ventajas de producir algunos bienes de capital en el país, incluyen el logro de una mayor independencia económica, además de cultural y política. Aunque el déficit de la balanza comercial, provocado en gran parte por la importación de bienes de capital, se ha podido financiar hasta la fecha, la producción interna de maquinaria y equipo libera a la formación de capital de restricciones de balanza de pagos. Además, dado que los insumos para la industria son nacionales en su mayor parte, la inversión tendrá un multiplicador interno mayor.

Uno de los objetivos de este trabajo, es el de tratar de ayudar a la solución del problema demostrando la aplicación de una metodología para la planeación de la fabricación racionalizada de equipo y maquinaria para México y países en desarrollo.

2. CLASIFICACION Y CARACTERIZACION DE LOS BIENES DE CAPITAL

Existen muchas formas de definir y clasificar los bienes de capital. Una definición adecuada para nuestros propósitos, podría ser la siguiente: Bienes de Capital son equipos para la producción en la industria metalúrgica, mecánica, eléctrica y de equipo de transporte.

Las clasificaciones de equipo más usadas son las siguientes:

- La Clasificación Uniforme de Comercio Internacional (CUCI) de las Naciones Unidas, en la sección 7 dedicada a maquinaria y material de transporte abarca los siguientes capítulos:

  CAPITULO 7.1 Maquinaria, excepto la eléctrica.
  CAPITULO 7.2 Maquinaria, aparatos y utensilios eléctricos.
  CAPITULO 7.3 Material de transporte.

  En la sección 6, que corresponde a artículos manufacturados, clasificados principalmente según el material, se incluyen muchos artículos que encajan, por sus funciones, dentro de los productos a considerar en el sector bienes de capital.

- Nomenclatura Arancelaria de Bruselas (NAB).- Su finalidad es esencialmente arancelaria y no contempla, como la anterior, fines estadísticos, agrupa los productos en orden progresivo, ésto es: desde materias primeras hasta el producto elaborado; en diferentes secciones y capítulos. Por ejemplo, en la sección XV se incluye metales comunes y manufacturas de estos metales en la sección XVI incluye máquinas, aparatos y material eléctrico; en la sección XVII materiales de transporte y en la Sección XVIII, instrumentos, equipo científico, etc.

- Clasificación Internacional Industrial Uniforme (CIIU). Su principal objetivo es agrupar e identificar las actividades industriales, tampoco clasifica especialmente los bienes de capital, sino que se encuentran ubicados en los capítulos 35: manufacutras de productos de metal, excepto maquinaria y equipo de transporte; 36: Manufactura de maquinarias; excepto eléctrica; 37: maquinaria eléctrica, aparatos y partes; 38: manufactura de equipo de transporte y 39: otras manufacturas diversas.

- Clasificación en Grandes Categorías Económicas (CGCE). Esta clasificación ha sido preparada por la Oficina de Estadística de las Naciones Unidas, en base a las secciones de la CUCI, que integran 19 Categorías destinadas a proporcionar elementos en la clasificación CGCE que permitiesen a los usuarios obtener agregados más comparables, dentro de lo posible, a los de las tres clases fundamentales del sistema de Cuentas Nacionales: Bienes de Capital, Intermedios y de Consumo. En ésta clasificación los bienes de capital se agrupan en lo esencial dentro de la categoría 4 que incluye Maquinaria, otros bienes de capital excepto equipo de transporte y accesorios. Permite sin embargo, con facilidad agrupar los bienes de capital, aparte del material de transporte industrial.

- Clasificación según uso o Destino Económico (CUODE). Esta es otra clasificación preparada por las Naciones Unidas, también con fines estadísticos, que agrupa los bienes de capital de acuerdo con la actividad económica a que se destinan: a agricultura, industria y transporte.

Estas clasificaciones son las que se tienen a nivel internacio-- nal. A continuación se indican clasificaciones de bienes de capital que se han elaborado en México.

- En México la Mejor Inversión (EMMI). No se ha tratado en particular la importación de bienes de capital sino que se ha considerado dentro de los diferentes sectores industriales. El criterio que usaron para esta clasificación está fundamentado en la tarifa del impuesto general de importación; analizando básicamente los capítulos 82 y 84, se llegó a clasificar 19 sub-sectores o familias y que presentan en detalle las importaciones realizadas en el sector maquinaria y equipo, excepto lo eléctrico, indicando además si se produce o no en México, y si ésta producción es o no suficiente para cubrir la demanda nacional. Estos son:

1. Herramientas.
2. Calderas y turbinas.
3. Equipo de bombeo y compresión.
4. Equipo para el tratamiento têrmico.
5. Filtros y centrífugas.
6. Equipo para el manejo de materiales.
7. Maquinarias de construcción.
8. Maquinaria e implementos agrícolas.
9. Maquinaria para la industria alimentaria.
10. Maquinaria para las industrias del papel y las artes gráficas.
11. Maquinaria textil.
12. Maquinaria para la industria metalúrgica.
13. Maquinarias - herramienta.
14. Maquinaria para el trabajo de minerales.
15. Maquinaria para la industria del plástico.
16. Cajas de fundición y moldes.
17. Rodamientos.
18. Maquinaria para empacar.
19. Válvulas.

- Clasificación del Grupo ONUDI-NAFINSA. La Gerencia de Proyectos y programación de Nacional Financiera, con la colaboración de expertos de la Organización de las Naciones Unidas para el Desarrollo Industrial, ha emprendido un estudio extenso, encaminado a programar y promover proyectos de inversión para el desarrollo del sector productor de bienes de capital.

Este grupo ha tomado como base para la clasificación de bienes de Capital, la definición que aparece al comienzo del capítulo y la definición de CUCI llegando a lo siguiente: equipo eléctrico, mecánico y otro equipo no eléctrico y sus principales partes y componentes utilizados para la producción en ramas selectas de la economía; se excluyen equipos utilizados para otras ramas, como equipo para la industria de transporte, bienes que no se utilizan directamente para la producción, como maquinas de oficina y equipo auxiliar como tubería, alambre y accesorios. Esta definición tiene como ventaja la de concentrar la atención en la maquinaria y equipo que requiere promoverse en el país.

Para identificar las lagunas en la producción del sector de bienes de capital, tomaron como base los datos de las proyecciones que llevaron a cabo para el período de 1976 - 1980 con base en macroproyecciones de demanda e importaciones, para bienes de capital específicos, modificados a la luz de varios propuestos de expansión y nuevos proyectos que se estan actualmente considerando o implementando. Estas proyecciones se llevaron a cabo para 26 grupos de bienes de capital, lo cual proporciona una identificación razonable de aquellas ramas de bienes de capital en las que habrá mayor demanda y como consecuencia importaciones sutanciales. Por lo tanto se puede considerar que es una clasificación adecuada de bienes de capital, específicamente para México, ya que se está haciendo énfasis en los que realmente son necesarios y además hay posibilidades de que sean producidos.

Dichos bienes se han clasificado en 26 grupos, bajo tres encabezados principales:

a) Equipo no eléctrico usado en varios sectores de producción:

1. Equipo no eléctrico para generación de energía.
2. Maquinas-herramienta.
3. Maquinarias para trabajos sobre metal.
4. Maquinaria para empaque, básculas y rociadoras.
5. Equipo para calefacción y enfriamiento.
6. Bombas, compresoras y centrífugas.
7. Equipos para carga, transporte y elevación.
8. Otras máquinas.
9. Partes de maquinaria y accesorios

b) Equipo no eléctrico usado en sectores específicos de producción:

10. Equipo para la manufactura de hierro, acero y metales no ferrosos.
11. Equipo para minería, construcción y producción de cementos.
12. Equipo para producción de pulpa y papel.
13. Equipo para azúcar y alimentos.
14. Equipo para productos químicos y fertilizantes.
15. Equipo para textiles.
16. Equipo para la agricultura.
17. Maquinaria partes y accesorios.

c) Equipo eléctrico:

18. Maquinaria para generación de energía eléctrica.
19. Transformadores, interruptores, motores y aisladores.
20. Aisladores de porcelana, chumaceras, para alto voltaje.
21. Equipos para telecomunicaciones.
22. Medidores eléctricos e instrumentos de control.
23. Equipo eléctrico, y otras herramientas.

24. Hornos eléctrico, aparatos eléctricos para soldar y cortar.
25. Otros equipos eléctricos.
26. Bienes de capital no identificados especificamente.

El Grupo de Desarrollo de Tecnología ha venido haciendo investigaciones en los diferentes aspectos de la industria, entre los cuales entra el presente trabajo sobre bienes de capital y debido a la cantidad de información que se necesita, se ha tenido que recurrir a elaborar una clasificación para cumplir sus propósitos. Se hizo esta clasificación de acuerdo a las necesidades de éste trabajo, ya que las clasificaciones que existen están hechas siguiendo el enfoque de actividad comercial, como puede ser la importación y exportación. La clasificación que se propone está enfocada a la planeación de un programa para la fabricación racionalizada de bienes de capital y que sirva de referencia para:

- Organizar la información estadística de usos, costo y vida promedio, para cada tipo de equipo.

- Identificar y analizar las diferntes alternativas de equipo para un mimo uso.

- Evaluar diferentes técnicas para la manufactura de cada pieza principal de equipo.

- Analizar las posibilidades de estandarización, importación, mercado, usos y fabricación de las principales piezas de equipo.

Como bienes de capital se consideran todos aquellos equipos y maquinarias, que producen entradas de dinero al país.

Para los fines de éste trabajo la clasificación es la siguiente:

A. Usos

En este primer punto se consideran los equipos de acuerdo al tipo de industria a que son destinados, basándonos en la clasificación de industrias por sus características tecnológicas, la cual se menciona en la introducción.

- Agricultura. En este punto se cuentan los siguientes:

1. Maquinaria y aparatos para preparar, trabajar y cultivar la tierra.
2. Maquinaria y aparatos para recolección, trilla y clasificación d eproductos agrícolas.
3. Tractores, excepto aquellos para la combinación tractor-remolque.
4. Maquinaria y artefactos mecánicos para la agricultura.
5. Prensas usadas en vinicultura, etc.
6. Otras máquinas para la agricultura

Transportación. En este renglón se consideran los siguientes componentes:

1. Construcción y reparación de embarcaciones.
2. Construcción y reparación de equipo ferroviario.
3. Vehículos automotrices, tractocamiones para trailers, accesorios y refacciones.
4. Motocicletas, vehículos de tracción animal y propulsión a mano y refacciones.
5. Aviones y sus partes.

Minería, petrólero y construcción.

1. Apisonadoras mecánicas.
2. Excavadoras, aplanadoras, perforadoras, etc.
3. Trituradoras, clasificadoras, moldeadoras, etc.
4. Maquinaria para trabajar vidrio.

- Industria de transformación.

a) Industria del papel y artes gráficas.
   1. Maquinaria para la fabricaicón y acabado de pasta celulósica del papel y del cartón.
   2. Guillotinas para papel y otras maquinarias para fabricación de artículos de pasta de papel y cartón.
   3. Maquinaria para encuadernar.
   4. Maquinaria para fundir y componer tipos.
   5. Otras máquinas de imprenta.

b) Industria química. Se consideran como industria química, los presentados en la clasificación por características tecnológicas, y se trata por separado.

c) Industria de trabajo sobre metal.
   1. Máquinas y herramientas para trabajo sobre metal.
   2. Máquinas para trabajar metal que no sean máquinas - herramientas.
   3. Convertidores, calderas de colados, lingoteros y máquinas de colar.
   4. Trenes de laminar y sus cilindros.
   5. Máquinas y aparatos de gas para soldar, colar, etc.

d) Industria del cuero.
   1. Máquinas para separar o rebajar.
   2. Máquinas para igualar, cortar o dividir.
   3. Máquinas para achaflanar, adelgazar o rebajar.
   4. Máquinas para reforzar, acanalar o ranurar, o moldear.
   5. Máquinas para restirar, montar o engrapar.
   6. Máquinas que ejecuten dos o mas operaciones.
   7. Máquinas para la preparación y trabajo de los cueros.
   8. Máquinas para fabricación de calzado.

e) Industria eléctrica.

1. Maquinaria para generación de energía eléctrica.
2. Transformadores, interruptores.
3. Aisladores de porcelana, bushings, etc, para alto voltaje.
4. Equipos para telecomunicaciones.
5. Medidores eléctricos e instrumentos de control.
6. Equipos eléctricos y otras herramientas.
7. Hornos eléctricos, aparatos eléctricos para soldar y cortar.
8. Otros equipos eléctricos.

f) Oficina.

1. Máquinas de escribir, y máquinas para autentificar cheques.
2. Máquinas calculadoras, para contabilidad y máquinas análogas con mecanismos calculadores, incluso computadoras electrónicas.
3. Máquinas de estadística que calculan a base de tarjetas perforadoras o cintas.
4. Copiadoras, impresoras de sobreescritos, etc.

B. Grado de Estandarización

Estándar, producción en Masa.
Semi-estándar, línea de producción.
Fabricación individual.

C. Método de Fabricación

Fundición.
Maquinado.
Metalistería.
Otros.

D. Materiales de Construcción

Acero.
Acero noxidable.
Aleaciones especiales.
Madera.
Mampostería.
Plástico.

En el primer punto de la clasificación, relativo a usos, se enumeran las industrias que abarca cada sector. Los siguientes puntos de la clasificación, que son estandarización, métodos de fabricación y materiales de construcción, se describen en el capítulo de análisis de fabricación de equipo y maquinaria.

3. SITUACION ACTUAL DE LAINDUSTRIA DE BIENES DE CAPITAL EN MEXICO

En este capítulo se describe brevemente la industria en general indicando algunos datos sobre demanda, prducción e importaciones de bienes de capital. En esta parte no se incluye a la industria química, ya que se le dedica un capítulo por separado.

Se consideró de interés incluir esta parte, porque nos da un panorama mas amplio para poder situar a la industria química y ver cual es su situación con respecto a las demás industrias.

- Agricultura.

Maquinaria e implementos agrícolas:
Tomando en cuenta la producción actual, las importaciones en este sector durante 1974 fueron de 2,495 millones de pesos, distribuidos en máquinas e implementos para el cultivo y preparación de suelos y en máquinas cosechadoras y trilladoras, a pesar de que ya los implementos, maquinarias y equipos son fabricados en México con alto grado de integración.
Existen ocho compañías, la mayoría de las cuales reciben asistencia técnica de firmas extranjeras. Estas empresas producen tractores, arados rastras, cosechadoras y otros, y están cubriendo casi toda la demanda, excepto la de máquinas de mayor tamaño, como se mencionó antes. (6)

- Material y equipo de transportación.

De acuerdo a las importaciones, la demanda, de este sector en 1974 fué de 41,300 millones de pesos, teniendo mayor participación el renglón automotríz y tractocamiones para trailers, con 23,157 millones de pesos, siguiendo en importancia el renglón de construcción y reparación de equipo ferroviario, con 2,961 millones de pesos, construcción y reparación de embarcaciones con 2,031 millones de pesos, aviones y sus partes 690 millones de pesos, el resto (113,061 millones de pesos) está comprendido por carrocerías, motores, accesorios y refacciones, motocicletas y similares vehículos de atracción animal y propulsión a mano.

Se aprecia que, conforme a las proyecciones para 1980 la demanda en este sector será de 83,557 millones de pesos y la producción de 71,900 millones de pesos con lo que no se podrá cubrir la demanda y se prevee que las importaciones serán de 16,575 millones de pesos. (6)

- Minería, Petróleo y Construcción.

Equipo para minería:

La importación en 1974 de este sector representó un monto de más de 700 millones de pesos, siendo los principales rubros, máquinas trituradoras, clasificadoras, cribadoras y lavadoras. Existe producción nacional de algunos equipos, sin embargo, ésta no alcanza a satisfacer la demanda presentada principalmente por las industrias minera, cementera y siderúrgica.

Equipo para la construcción.

La maquinaria para la construcción de todos tipos se construye en México por compañías que emplean tecnología extranjera. Sin embargo, las importaciones en 1974 alcanzaron la cifra de más de 600 millones de pesos, principalmente en máquinas escarciadoras de concreto, raspadoras y explanadoras entre otras, es obvio que este mercado tiene un gran atractivo y se puede empezar su conquista por medio de ensamble inicialmente y una integración programada. Se debe alentar a las compañías exitentes y a nuevos inversionistas, para facilitar el incremento de la producción y cubrir rápidamente el crecimiento de la demanda y exportación, para la que se considera que hay buenas posibilidades. La normalización de tipos y medidas contribuirá al mejo ramiento de la producción. (3)

Equipo para producción de cementos.
Mientras ciertos componentes simples del equipo para fabricar cemento se producen en México, la mayor parte del equipo de alimentación, como quebradoras primarias, molinos de bolas, hornos rotatorios (excepto para pequeñas y medianas plantas), filtros y enfriadores de clinker no se producen. Durante los años 1976 - 1980 se requerirá de 2 a 3 molinos con una capacidad de 1,500 a 2,500 Ton. por día. El valor de la maquinaria a producir se estima a razón de 150 millones de pesos por año, lo que justificará la inversión estimada de alrededor de 150 millones de pesos para la primera etapa de 1976 - 1980 y posibles expansiones para después de 1980. Esto corresponde a una tasa de crecimiento anual de 7% de la producción de cemento. (7)

- Industria de transformación

a) Equipo para papel y artes gráficas.
Se espera que la demanda de pulpa y papel crezca rápidamente; y a menos que se establezcan nuevas fábricas, la importación tendrá un aumento muy importante. De acuerdo con los requerimentos máximos, se estima que durante 1976 - 1980 , será necesaria la instalación de 3 plantas con capacidad cada una de 300 Ton. por día. Este aumento de la capacidad corresponde a una fábrica de papel periódico y dos de papel kraft, semi-kraft, de imprenta y de escribir. La maquinaria para un programa de esta magnitud, se valúa a razón de 250 millones de pesos por año, para lo que probablemente se requerirá tecnología extranjera.

Las importaciones de estos equipos representaron en 1974 fuga de divisas del orden de casi 800 millones de pesos, correspondiendo principalmente a equipos para producir papel o cartón, pulpa, máquinas para la manufactura de artículos de papel y cartón, maquinaria para la composición, impresión y encuadernación; se estima que el mercado mas accesible es de aproximadamente 250 millones de pesos. (7)

b) Industria Química.
Se tratará por separado.

c) Trabajos sobre metal.
La industria de maquinas-herramienta está dando sus primeros pasos, aunque existen en México alrededor de 25 empresas fabricantes, estas no son suficientes para atender la demanda que crece a un ritmo muy acelerado; así se sabe que para 1974 se importaron equipos por valor de 2,070 millones de pesos.

Este grupo se analiza bajo dos aspectos: 1) Máquinas-herramienta con arranque de viruta y 2) Máquinas-herramienta sin arranque de viruta. Se estima una demanda no satisfecha con demanda interna de 680 millones por año, que se considera persista durante el período 1976 - 1980. Sobre una base de cubrir el 50% de este déficit, el valor de la producción sería de 344 millones de pesos por año, lo que requeriría una inversión de cerca de 413 millones de pesos entre 1976-1980.

Para el segundo grupo, o sea sin arranque de viruta, tal como prensas hidráulicas, guillotinas y dobladoras, se estima una demanda de 229 millones de pesos por año durante 1976-1980. Cerca del 85% de las máquinas son grandes y muy especializadas, por lo que no es factible fabricarlas económicamente en México por lo menos en algún tiempo. Para el 15% restante, o sea 30 millones de pesos anuales se requiere una inversión de 42 millones de pesos.

Herramientas, partes de máquinas y accesorios.
Una gran parte de la herramienta, tanto manual como de corte es producida en México.

En el primer caso, la producción nacional cubre aproximadamente el 60% de la demanda interna e incluso algunos tipos se importan, en el segundo caso, aunque la producción nacional se ha incrementado en los últimos años, se sigue recurriendo a la importación, principalmente de dados y troqueles, que sumados a otros rubros representaron en 1974 importaciones por valor casi de 400 millones de pesos, de los cuales se considera que existen productos promivibles aproximadamente por 140 millones de pesos, siendo principalmente peines para roscar, escariadores, fresas para herramientas de mano, brocas de carburo de tungsteno, matrices y troqueles entre otros. (5)

Se considera que el desarrollo de la industria de bienes de capital dependerá en mucho de ciertas actividades como: la fundición de acero gris para piezas hasta de 15 Ton. con una producción anual de 595 millones de pesos y una inversión de 655 millones de pesos; fabricación de engranes, incluyendo reductores, multiplicadores y forjas de precisión con una producción de 275 millones e inversión de 385 millones de pesos; utensilios de desgaste como herramientas, dados, guías, accesorios, escantillones, etc., cuya producción sería de 50 millones y la inversión de 65 millones de pesos; herramientas de medición como escuadras, reglas, calibradores de todos tipos, etc., con producción de 30 millones e inversión de 42 millones de pesos, lo cual sumado daría una producción total de 950 millones de pesos y una inversión de 1147 millones de pesos. Como se dijo al principio, la producción de todos estos artículos es escasa, por lo que debe tomarse en consideración su fabricación.

Se estima que ninguno de los fabricantes existentes en estas líneas estará en posibilidades de cubrir la demanda y que la tecnología extranjera podría requerirse para algunos de estos renglones. (7)

Cajas de fundición y moldes; estos se consideran dentro de las partes y accesorios para máquinas y como es sabido, tienen una importancia determinante en la calidad y precio de los productos termiandos. Aunque se ha presentado un considerable aumento en la manufactura de estas partes en México, las importaciones de estas en 1974, alcanzan la cifra de 115 millones de pesos, contribuyendo con esta cifra las partes hechas para los moldes de acero para máquinas de inyección entre otras.

Rodamientos. Los rodamientos, ya sea de bola o de rodillos cónicos, cilíndricos, etc., son partes esenciales en muchas maquinarinas, siendo de muchos tipos y tamaños los que se utilizan en la fabricación de maquinaria y equipo para diversas industrias. Aunque existe fabricación de estas partes en el país, no se cubre satisfactoriamente la demanda, por lo que en 1974 se importaron 300 millones de pesos de las mismas, este mercado tiene un índice de crecimiento muy elevado. (5)

Válvulas. Este es uno de los rubros que quizás satisfaga con más amplitud la demanda del país, en virtud de que el consumo de estos componentes es de manufactura nacional en un 85%, además de que permite exportar a varios mercados, principalmente latinoamericanos.
Ahora bien, se siguen importando grandes cantidades de vál-

vulas, debido al gran desarrollo de la industria petrolera del país, lo que motivó en 1974 a importar alrededor de 350 millones de pesos. (6)

- Industria Eléctrica

La fabricación de equipo eléctrico considerado como bienes de capital es distinta a la fabricación de bienes de consumo y comprende: Sistemas de generación, transmisión y distribución de energía eléctrica; fabricación de motores; acoplamientos, equipos de control, transformadores, rectificadores e interruptores.

La generación de energía eléctrica ha crecido y se estima que seguirá creciendo a una tasa de 12% anual. Debido a este aumento, se demandarán cantidades importantes de equipo pesado y especializado. Se estima que la CFE importará cerca de 10000 millones de pesos en equipo para el período de 1976-80. En el país se produce equipo solo para distribución de energía, por lo que la capacidad manufacturera del equipo para generación y transmisión de energía muestra un déficit de cerca del 80% expresado en valor. Ciertos tipos de transformadores, motores e interruptores de mediana magnitud se producen en cantidades limitadas y todo el equipo pesado se importa. Se considera como resultado del estudio, que ciertos artículos pueden fabricarse en el país.

Maquinaria para la generación de energía eléctrica. Las necesidades futuras de equipo de México en cuanto a generación de energía eléctrica, comprenderán sobre todo plantas térmicas y adicionalmente plantas nucleares, pues los recursos hidroeléctricos estarán completamente aprovechados en 1980. Por lo tanto, será necesario establecer instalaciones para fabricar calderas grandes de alta presión, turbinas de vapor turbogeneradores y equipo auxiliar para una capacidad de 300 - 500 megavatios, lo que va de acuerdo con los planes de la CFE. Se considera que la producción de calderas de alta presión se justifica desde todos los puntos de vista. Instalaciones con una inversión de 350 millones de pesos darían una producción anual de 300 millones de pesos en 1980. Se estima que para años venideros la fabricación de componentes simples para generación nuclear como intercambiadores de calor también será posible.

La producción de grandes turbinas de vapor para generadores de energía no se considera deseable en el presente, en vista de la alta especialización que implica su producción y la necesidad de importar más del 80% de los componentes (tales como moldes, forjas, hojas, etc.) por largo tiempo. La producción de reactores y otro equipo para las plantas atómicas no es justificable en esta fase. Las empresas existentes en el sector de industrias metálicas podrían instalar sus propias plantas generadoras. (7)

Transformadores, interruptores, motores y aisladores.
A pesar de que la producción interna de transformadores pequeños de distribución satisface plenamente la demanda, la producción nacional cubre solo una pequeña parte de la demanda de transformadores medianos y grandes, elaborada por una sola compañía. Tomando en cuenta la demanda futura de transformadores de 230 KV y 400 KV, se justificaría el establecimiento de nuevas industrias productivas para la manufactura de transformadores para cubrir una demanda adicional de 4,000 MVA anuales para 1980. Esto implicaría una inversión de unos 150 millones de pesos, generando un valor de producción anual de 160 millones de pesos en 1980.

Como no existen instalaciones productivas para la elaboración de interruptores de alto voltaje, ni de muy alto voltaje, el establecimiento de nuevas instalaciones para esta línea de producción se justificaría necesitándose una inversión en capital de unos 150 millones de pesos, para lograr una producción anual con valor de 150 millones en 1980.

La industria de motores eléctricos, incluyendo generadores medianos y pequeños, están en una etapa de desarrollo inicial. Solamente se producen partes y pequenos motores utilizables en bienes de consumo duraderos. Dos o tres firmas están elaborando algunos tipos de motores sencillos de tamaño mediano hasta de 2,000 caballos de potencia. Existe un déficit muy importante en este campo, el cual será mayor a medida que los planes para las industrias de bienes de capital tomen forma, pues esto implicará una mayor demanda de estos productos. La creación de nuevas instalaciones con una inversión de 150 millones de pesos parece necesaria. Con esta inversión sería posible ontener una producción anual equivalente a unos 170 millones de pesos para 1980. Mientras se planean estas instalaciones, será necesario no perder de vista la posibilidad de iniciar la manufactura de grandes turbogeneradores a partir de 1980.

La producción de generadores y motores para locomotoras diesel y de motores para el sistema de transporte colectivo en México parece tener posibilidades atractivas. Las nuevas instalaciones para este propósito podrían ser combinadas con las de otras fabricas o establecerse por separado. Se estima que se requerirá una inversión de 100 millones de pesos para una producción de equipo de tracción eléctrica con un valor de 100 millones de pesos anuales para 1980.

Aisladores de porcelana, chumaceras, para alto voltaje. El sistema de distribución de energía necesita para sus líneas de distribución, grandes cantidades de aisladores y forros de porcelana para alto voltaje, además de otras partes para transformadores, interruptores y otros aparatos eléctricos. Solamente existen dos productores que elaboran aisladores de porcelana para los sistemas de bajo voltaje. De aquí que haya una justificación para establecer nuevas instalaciones para la manufactura de productos de porcelana para alto voltaje, lo que implicaría una inversión de capital de aproximadamente unos 100 millones de pesos, para una producción anual de 150 millones de pesos. (7)

Equipo eléctrico restante.

Un número de conceptos de equipo diverso como: clabe, alambre, rectificadores, capacitores, herramientas eléctricas e instrumentos medidores de control se producen parcialmente o totalmente por fabricantes nacionales. Algunos de los productos son bienes de consumo duraderos y algunos son partes o componentes marginales de bienes de capital muy complejos y pesados. Se espera que la demanda futura para estos bienes sea satisfecha a través de la expansión normal de las compañías existentes.

En el campo de las telecomunicaciones, la capacidad de producción existente parece adecuada con excepción de la dedicada a la producción de equipo de microondas y de equipo del tipo de alta frecuencia (VHF), el cual está siendo importado en su totalidad y se cree que la iniciación de la producción interna puede tener alguna justificación.

Se estima que la demanda del equipo eléctrico referido se cubra dividiéndola en un 50% con nuevos fabricantes, 25% de importaciones, y 25% por expansiones de las empresas actuales. (7)

4. SITUACION ACTUAL DE LA INDUSTRIA QUIMICA

Debido a los intereses de este trabajo se ha querido dar mayor énfasis a la industria química y a los problemas existentes dentro de esta industria con respecto a la fabricación de equipo y maquinaria. A continuación se darán datos de estadística y datos de importaicón y demanda de algunos equipos y ramos industriales.

Industria metalúrgica

Para satisfacer la demanda de la expansión de la producción de acero, el país requirió importar en 1974 equipo por valor de 280 millones de pesos, demanda que irá en aumento, debido a las ampliaciones de las empresas csnsumidoras de estos equipos, ya que por los planes de expansión los próximos 15 años serán de grandes inversiones.

Dentro de estas importaciones destacan por su valor las que se realizan en trenes y rodillos de laminación, convertidores, cucharones y máquinas para fundición.

Se estima que la demanda de equipo para la producción de hierro y acero (fierro esponja, hierro en lingotes, acero en lingotes y productos rolados, para 1976 - 80, será aproximadamente de 1,123 millones de pesos. Para las industrias del aluminio y del cobre se estiman cantidades de 319 y 242 millones respectivamente. (7)

Industria azucarera y alimentaria

En la actualidad se calcula que el 60% de las necesidades de equipo para ingenios azucareros se produce en México. Los renglones importantes foráneos son centrífugas, turbinas, engranes y algunos equipos de molienda de grandes dimensiones.
Las importaciones en su mayoría son hechas por la industria azu-

carera y alcanzaron un valor de 170 millones de pesos.

La industria de alimentos ocupa un lugar muy importante en la economía. La maquinaria requerida para los años de 1976 - 80 se estima en cerca de 5,575 millones de pesos que equivalen a un promedio de 1,115 millones de pesos anuales. Se espera una producción sustancial estimada en un 76 a 86% con las instalaciones existentes. Para la diferencia que representan ciertos equipos especializados como mezcladoras, máquinas para fabricar pasta, secadores, pasteurizadores y otros renglones, se justifica el establecimiento de nuevas instalaciones, las que requieren de colaboración extranjera. Estas instalaciones se preven para una producción anual de 150 millones de pesos, con una inversión de 150 millones de pesos. (7) (5)

Aunque gran cantidad de estos equipos se producen en el país, e inclusive estos equipos son ya exportados, las importaciones que se realizan bajo este rubro son del orden de 183 millones de pesos, destacándose maquinarias para los procesos de la industria láctea y derivados.

Productos químicos, petroquímicos y fertilizantes

Estas industrias están creciendo rápidamente y los requerimentos de maquinaria en el período 1976 - 80 serán importantes. La demanda promedio anual se calcula en 1,600 millones de pesos. Existe una docena de empresas que están fabricando varios renglones de este eqipo mediante diseños proporcionados por sus clientes o principales contratistas. Las firmas mexicanas no cuentan con diseñadores de fábricas completas y emplean una cantidad importante de partes importadas. Por esta causa se aprecia la necesidad de establecer una organización de diseño e ingeniería en México en sociedad con una o mas firmas consultoras de ingeniería extranjeras. (7)

Industria textil

Este subsector tiene particular importancia, ya que la mayor parte de la maquinaria textil se importa por la necesidad de modernización de la industria actual, las importaciones durante 1974 alcanzaron más de 1,600 millones de pesos, destacando las máquinas para la preparación de hilados, torcedoras, tejedoras, entre muchas mas considerándose un mercado de productos promovibles de mas de 1,000 millones de pesos. (4)

La demanda proyectada pra 1976 - 80 se calcula en cerca de 1,600 millones de pesos anuales. Se estima un crecimiento de 8 a 10% anual a partir de 1980. En el periodo de 1976 - 80 se podría cubrir un 50% de la demanda considerando los renglones mas simples lo que equivale a una producción con valor de 685 millones de pesos. Se calcula que la inversión para producir este equipo es de 750 millones de pesos. Como estas maquinarias son altamente especializadas se requerirá de colaboración extranjera adecuada. A partir de 1980 se preve la fabricación de máquinas mas complejas y por lo tanto, la exportación de éstas tendrá alcances considerables. (7)

Industria de plásticos

Existen varias empresas en el país que fabrican máquinas para el tratamiento de hules y plásticos, siendo básicamente inyectoras para plástico, moldeadoras de termoplásticos y extrusoras de tuberías de plástico. Las importaciones que se realizaron bajo este renglón en 1974 fueron de 260 millones de pesos, destacándose por su importancia las máquinas sopladoras, granuladoras, inyectadoras y extrusoras. (5)

Equipo no eléctrico para la generación de energía
Calderas y turbinas para propósitos industriales y máquinas de

combustión inerna, están siendo producidas por tres compañías con asesoría de firmas extranjeras. Las turbinas de tipo industrial no se fabrican en México, aún cuando es justificable su producción ya que las importaciones en 1974 alcanzaron la cifra aproximada de 550 millones de pesos de los cuales es factible sustituir importaciones por valor de casi 300 millones de pesos con una inversión que se puede considerar relativamente baja con respecto a este mercado.

Una gran laguna está en máquinas diesel de 100 - 600 H.P. para la generación de energía, bombeo y usos marinos, se estima su demanda en 200 millones de pesos. En una segunda etapa, que sería a partir de 1980 sería necesario obsorber un crecimiento de la demanda que incluye exportación de 10 a 15% de la capacidad de producción.

La inversión aproximada para la primera etapa se estima en 200 millones de pesos.

Máquinas de empaque, básculas y rociadoras

Tres compañías de magnitud media están produciendo la mayor parte de los equipos para empaque, con excepción de equipo muy específico y complejo. Los tipos simples para equipo de rociado se producen en México y se cree que las mismas compañías podrían cubrir una variedad más amplia.

En relación a las básculas hay dos importantes productores que cubren la mayoría de los renglones, con excepción de tipos muy específicos, que corresponden a las que tienen indicador automático e impresión con capacidad de 1,000 kg. Sin embargo se puede ver que en 1974 se importaron equipos por valor de 270 millones de pesos, lo que significa que la producción existente no alcanza a satisfacer mas que una parte de la demanda interna.

Los principales equipos que se importaron bajo este renglón fueron máquinas para lavar y secar recipientes, máquinas para envasar y empaquetar derivados de leche, máquinas cerradoras, básculas y máquinas etiquetadoras. (5)

Equipo para calefacción y enfriamiento

Aunque este es un rubro en el cual la producción nacional de equipo es cada vez más sofisticado se han venido sustituyendo las importaciones observando que en 1974 estas alcanzaron un valor de 735 millones de pesos, considerando que la plànta industrial nacional ha venido abasteciendo equipos de gran tamaño y capacidad, además de equipos para usos especiales, gracias al dominio de técnicas y al conocimiento profundo de su tecnología, personal especializado, se puede pensar que una parte de la demanda interna con valor aproximado de 285 millones de pesos se puede cubrir satisfactoriamente con las empresas que están operando en el país. (5)

Bombas compresores y centrífugas

Bombas y compresores de varios tipos y capacidades son producidas en México por más de 10 plantas manufactureras, sin embargo, en 1974 se importó más de 300 millones de pesos, siendo 100 millones de pesos posibles de sustituirse con producción nacional, correspondiendo un 30% aproximadamente a empresas ya establecidas y en operación, el 70% restante son inversiones tanto para ampliaciones como para el establecimiento de nuevas industrias, en las cuales se incluye tecnología y capital de firmas reconocidas en el mercado internacional. (5)

Las centrífugas industriales no se producen en México. Se cree que la fabricación de bombas y centrífigas debe considerarse en conjunto, pues requieren el mismo equipo de producción, por lo que la sola expansión de la capacidad existente permitirá producir las centrífugas con excepción de ciertos tipos especiales, los cuales se seguirán importando. El faltante de capacidad durante los años de 1976 - 80, se evalúa en 60 millones de pesos por año para bombas y centrífugas. Se estima una inversión adicional de 72 millones de pesos para prever expansiones futuras después de 1980. (7).

Equipo para manejo de materiales

Existe una producción nacional elevada, con alto grado de integración en los renglones de montacargas, equipo de transportación y gatos hidraúlicos, sin embargo una gran demanda se aprecia en los renglones de partes principales y componentes de grúas de puente, equipo para puertas y grúas torre, cuya demanda conjunta asciende a unos 200 millones de pesos anuales, durante los años de 1976 - 1980. Lo cual requerirá de una inversión de 200 millones de pesos.

En el renglón de los polipastos, grúas autopropulsadas, tornos y cabrestantes se importaron en 1974 450 millones de pesos. Esto es debido a que muchos fabricantes nacionales solo fabrican las partes estructurales de acero importando los componentes tales como transmisiones, controles y sistemas hidraúlicos además de los ya mencionados.

Esto puede corregirse solo si las empresas actuales intervienen también en la producción de componentes o si establecen otras empresas auxiliares que en base a una nacionalización produzcan estos componentes en forma económica, pero sin detrimiento de su calidad. Estas empresas tendrían garantizado un mercado de aproximadamente 150 millones de pesos. (7) (5)

5. ANALISIS DE LA FABRICACION DE EQUIPO Y MAQUINARIA

En este punto se efectúa un estudio sobre los métodos de fabricación, y tipos de materiales con que se construyen, diferentes tipos y tamaños de equipos.

Equipo de proceso. Se consideran como tales lo que se fabrican bajo pedido y son:

Cambiadores de calor
Los cambiadores se construyen en un sinúmero de formas y diseños, pero tres son los tipos más comunes: cambiadores de serpentines sumergidos, en el líquido, cambiadores de calor tubulares, formados por tupos soportados por placas, una de las cuales está suelta con el objeto de permitir la expansión entre los tubos y la coraza, cambiadores de doble tubo, que consisten en dos tubos concéntricos, uno para cada fluido.

Su diseño puede ser de tubos lisos o bien por superficies extendidas por medio de aletas en los casos en que el coeficiente de transmisión de un fluido sea muy bajo.

Existen patrones para el diseño de cambiadores de calor, por ejemplo en el comercio se encuentran tuberías de 2.40, 3.60 y 6.0 m. Los tamaños de las cubiertas llegan hasta 60 cm de diámetro, usándose placas roladas cuando se necesitan diámetros mayores, el espacio mínimo entre tubos es de 5 cm. o una quinta parte del diámetro interno de la coraza, mientras que la menor distancia en la disposición de los tubos es de 1 1/4 veces el diámetro externo del tubo. Por lo que hay que considerar algunas limitaciones al diseñar cambiadores y hay que procurar usar tamaños normales, lo cual repercutirá en el costo, tanto de fabricación como de mantenimiento de los mismos.
El material de construcción mas usado es acero en la coraza y

acero dulce para los tubos. La coraza va soldada. Otros materiales usados son acero admiral, duriron, durclor, acero inoxidable niquel y aleaciones de niquel, para ácidos grasos se usan tubos de inconel y monel.

Columnas y torres

Una torre o columa se puede llenar de empaques, o bien esta última se puede fabricar con un cierto número de platos separados por una distancia fija, para una operación de contacto escalonado. Este tipo de columnas solas o en serie, se especifican generalmente para absorsión de gases, destilación, extracción y humidificación. Los platos se fabrican en los siguientes tipos: casquetes de burbujeo, platos perforados y platos con emparrillado romboidal.

El empaque es usado en las torres, puede consistir en anillos, sillas de Berl, colchonetas de fibra de vidrio o hélices. Las torres empacadas se usan solo para operaciones en pequeña escala, para diámetros menores de 60 cm.

Las torres de enfriamiento son de dos tipos: de tiro natural y de tiro forzado.

Un tipo simple de construcción son las de secciones de fierro forjado, un plato por sección.

Las mejores torres de acero son las que llevan juntas soldadas.

Las columas son fabricadas también de cobre, con platos y casquetes de cobre, las columnas para destilación de cerveza se fabrican con madera y casquetes de fierro forjado o cobre. Se usan de muchos otros materiales incluso vidrio refractario, para líquidos corrosivos se usan torres de acero recubierto con aleaciones resistentes a la corrosión.

Las torres de platos se construyen en todos tamaños desde algunas muy grandes hasta pequeñas con solo algunas pulgadas de diâmetro y 10 pies de altura.

El número de platos varía; por ejemplo en la industria petrolera, una columna con 30 a 50 platos es la comunmente usada para fraccionamiento de productos de refinación convencionales, para super fraccionamientos, las columnas pueden tener hasta 150 platos o mas.

Recipientes a precisión

Los recipientes para resistir altas presiones son casi siempre cilíndricos, en algunos casos se emplean también recipientes esféricos, principalmentepara almacenar grandes cantidades de fluidos a presiones relativamente bajas, y que se construyen de diversas maneras: rolado de placa con remaches; el mas usual es el soldar las juntas longitudinales y las costuras de los extremos con las cuales se unen los fondos, sobre todo para presiones mayores de 21 kg/cm^2. Los recipinetes soldados autógenamente son el tipo mas comun de recipientes de gran tamaño para presiones hasta de 100 kg/cm^2. Para recipientes pequeños de presiones hasta de 210 kg/cm^2 se usa soldadura o costura, estos recipientes se hacen comunmente por un procedimiento de embutido y estirado.

Para los recipientes grandes de 100 a 140 kg/cm^2 de presión se usan recipientes forjados o de múltiples capas. Estos son los métodos de construcción mas comunes: para los materiales de construcción, además de temperatura y presión es muy importante considerar la resistencia a la corrosión , son usados principalmente, acero al carbón acero al cromo, acero cromo-niquel y otras aleaciones de acero, de espesor sencillo, suplementados por cons trucciones de paredes multicapas. El desarrollo de soldaduras, especialmente la soldadura ppor fusión, ha proporcionado métodos adicionales de fabricación; el examen por medio de rayos X de las juntas soldadas detecta cualquier defecto en ellas, las cuales pueden ser reparadas o reemplazadas.

Tanques atmosféricos

Los tanques son usados no solo para almacenamiento de materias primas sino también de algún producto intermedio, si son usados durante la fabricación del producto se les denomina tanques de proceso, por lo que según su uso hay tanques para disolución, mezclado, para tratamientos y muchas veces los tanques son partes principales de otros equipos, como espesadores, marmitas, clasificadores, fermentadores y algunos otros.

Para construcción de tanques es muy usada la madera, debido a que no es atacada por un gran número de soluciones; se usa lámina de acero soldada de varios espesores. En tanques horizontales es muy usado el recubrimiento de diferentes materiales como vidrio o esmalte vidriado, hule plomo, acero inoxidable, niquel y otros; otro material usado es el haveg, que es muy resistente a la acción de algunos ácidos y sales en solución.

Los tanques cilíndricos de madera, se construyen de tablas verticales, las cuales se unen con varillas de fierro, generalmente acero bajo en carbón, monel, acero inoxidable y otras aleaciones los tanques de acero son los más comunmente usados para almacenamiento, ya que son los mas fuertes y prácticamente indestructibles y en tiempos normales tienen ventaja en el costo. Generalmente van soldados.

Los tanques se construyen en gran variedad de espesores, tamaños y capacidades.

Reactores

Los reactores se fabrican en tipos muy variados, pudiendo ser desde un tanque atmosférico con agitación o mezclado, hasta complicadas unidades de alta presión, enchaquetados, con unidades de refrigeración o calentamiento.

Se clasifican principalmente en dos grupos: reactores intermitentes o autoclaves y convertidores o reactores continuos.

Los reactores intermitentes se construyen generalmente con palastro soldado autógenamente y tapas semiesféricas o semielipsoidales, cierre de brida y empaquetadura de asiento. Prácticamente no hay autoclaves estándar, solo algunas pequeñas para laboratorio.

Los reactores continuos, son generalmente largos tubos forjados para altas presiones o construidos con tubos sin soldadura o costura o para presiones mas bajas de palastro soldado autógenamente.

Como los recipientes a presión se construyen en diferentes tamaños, capacidades y materiales. Estos últimos pueden ser de acero inoxidable, niquel, aleaciones con diferentes metales, pueden ser también vidriados o esmaltados según lo amerite el caso.

Condensadores

Muchos condensadores se construyen siguiendo los lineamientos específicos para cambiadores de calor. Los tipos de condensadores mas usados son: condensadores barométricos, y de superficie. Ambos tipos de condensadores, se construyen generalmente de acero soldado, también se usa como material de construcción el acero dulce, everdur y acero inoxidable.

Evaporadores

Existen varios tipos de evaporadores: de circulación natural, tipo calandria, de canasta, de tubos horizontales y de circulación forzada. Los accesorios internos, pueden ser fundidos, soldados o atornillados a las paredes del cuerpo del evaporador.

Los materiales mas usados para su fabricación son principalmente fierro fundido y acero, para casos especiales se usan materiales que son un poco mas costosos como: niquel monel, inconel, para la industria azucarera, se usan tubos de cobre y bronce fundido, acero niquel-clad, acero recubierto de hule, plomo (generalmente fundido) y aluminio. Las dimensiones de los evaporadores pueden ser de 100 a 1000 ft^2 de superficie de calentamiento, para evaporadores de un solo efecto.

Secadores

Los principales tipos de secadores se enumeran a continuación: continuos de bandeja; continuos de material en hoja o lámina; transportadores neumáticos; rotatorios; por pulverización; de circulación transversal; de tunel; cilíndricos de tambor; con transportador de tornillo sin fin; rotatorio de tubos con vapor de bandejas vibrantes; de pailas con agitación; liofilizadores; rotatorios con vacio; de bandejas al vacio. Debido a la gran variedad de secadores, se fabrican de diferente forma y materiales; algunos de los cuales pueden ser de: acero galvanizado, acero inoxidable, fierro fundido o semi-acero bronce.

Hornos

Las retortas, estufas o los hornos de tempraturas de 540°C o menores, no presentan ningun problema en la construcción ni en el mantenimiento. Las dificultades se presentan en los hornos a medida que se eleva la temperatura y aumenta la afinidad química entre el recubrimiento y la carga. El material de construcción comunmente usado es el ladrillo refractario de silice o alúmina. Los materiales metálicos de construcción del interior tienen que adaptarse de acuerdo a la temperatura; el acero ordinario o sin aleación se oxida a temperaturas superiores a 537°C; para temperaturas superiores se usa la fundición o bien aleaciones de hierro-cromo y niquel, a mayor temperatura debe usarse menos hierro. Los tamaños de hogares se clasifican de acuerdo a su capacidad de producir vapor y van desde 950 kg/hora hasta 202 000 kg/hora.

Cristalizadores

Existen diferentes tipos de cristalizadores, siendo los mas usados el cristalizador intermitente con agitación que además está provisto de un sistema de enfriamiento, existiendo variaciones en la forma delos serpentines y la forma de agitación; cristalizadores de tubería doble usados en la separación de cera de aceite en la industria petrolera; evaporador abierto de paila larga para cloruro de sodio; con paila de vacio para la industria azucarera, también se utilizan cristalizadores de vacío.

Los cristalizadores suelen fabricarse de acero; cuando se trata de materiales corrosivos llevan hule.

Maquinaria de proceso. Aquí se consideran aquellos equipos que se fabrican en serie como son:

Filtros

La operación de filtrado en cualquiera de sus variantes está basada en el aprovechamiento de diferencia de fases, mediante la aplicación de diferencia de presiones.
Existe gran variedad de filtros: rotatorios, de placas intermi--

tentes o continuas y el mas adecuado debe elegirse de acuerdo a la naturaleza de las partículas, al tipo de operación, a la cantidad, al interés del producto (fluido, sólido o ambos). Cualquier filtro puede colocarse dentro de alguna de las siguientes clasificaciones:

- filtros por gravedad
- filtros por presión
- filtros a vacio
- filtros centrífugos

Los filtros se emplean en una gran variedad de circunstancias, y en los trabajos de la industria química es necesario construirlos de materiales resistentes a la corrosión. Cada solución o substancia manipulada presenta un problema que exige el empleo de materiales especiales de construcción.

Para soluciones cáusticas y álcalis, los filtros se construyen de fundición usando aleaciones como acero inoxidable y monel, para tornillos, tuercas, accesorios y el medio filtrante.

Para condiciones ácidas, las placas y marcos y los filtros de vacio se hacen de madera. Los accesorios pueden ser cubiertos con plomo o fabricados con aleaciones especiales.

El plomo se usa como recubrimiento interior para los filtros de presión del tipo de envolvente cerrada y para los tanques de los filtros de vacio, cuyos tambores pueden ser de plomo fundido. El hule es apropiado para trabajos en condiciones muy ácidas, pero sus aplicaciones están limitadas por la temperatura que pueden resistir. Se emplean también plásticos sintéticos.

Para los medios filtrantes, se usa mucho la fibra de vidrio y las telas de monel, hay casos especiales en los que se usan telas de fibras de asbesto, de vidrio, de algodón nitrado o hule.

Agitadores y mezcladores

El mezclado mas que ninguna otra operación unitaria química, es todavía un arte, ya que tiene muy pocas bases científicas. Por este motivo se han desarrollado numerosos tipos de mezcladores, muchos de los cuales distan de ser satisfactorios. Se han agrupado unos 40 tipos de mezcladores como sigue: mezcladores de flujo, de paleta o brazos, de hélice o helicoidales, incluyendo los transportadores de tornillo, de turbina o de impulsor centrífugo, coloidales y homogeneizadores, tipos misceláneos, incluyendo los mezcladores de lodos, de masas, de sólidos y los de tambor.

Un gran núemro de piezas específicas del proceso tienen mezcladores de uno u otro tipo, generalmente para estimular una reacción. Entre estas piezas de equipo pueden mencionarse las autoclaves, los equipos de blanqueo, cloradores, digestores, tanques de solución, emulsificadores, extractores, reactores, nitradores, percoladores, retortas, reductores y sulfonadores.

Como ya se ha indicado, la selección del mezclador puede basarse en la experiencia anterior o en experimentaciones.

Prácticamente, cualquier material de construcción puede emplearse en un mezclador; el acero dúctil es el material mas usado, aunque pueden usarse casi todos los metales y aleaciones especiales, así como los recubrimientos no metálicos.

Ventiladores y sopladores

Los términos ventilador y soplador pueden ser intercambiables, pero soplador no es lo mismo que aspirador. Un ventilador puede funcionar como soplador o como extractor. Como soplador introduce aire dentro de ductos o tuberías, como extractor saca el aire a través de ductos o tuberías, y lo libera en el exterior. El mismo ventilador puede servir en ambas instalaciones. La gran mayoría de los ventiladores trabajan a bajas presiones.

Los ventiladores se dividen principalmente en ventiladores centrífugos y ventiladores de flujo axial.

Algunos de los materiales usados en la fabricación de ventiladores es el acero al carbón, hierro fundido y el acero inoxidable.

Centrífugas

Las centrífugas, son máquinas cuyo propósito es el de separar sólidos de líquidos por medio de una fuerza centrífuga. Hay dos tipos principales de centrífugas; una tiene una canasta perforada que gira rápidamente. El líquido sale por las perforaciones. El otro tipo tiene una canasta sólida donde el líquido se desborda por los bordes dela canasta, debido a la rápida rotación.

La canasta perforada se construye de dos manera.s Un método consiste en una pared de material ligero, reforzada con anillos, esta es la forma antigua y la más adecuada ya que proporciona mas area para drenaje. Los materiales que se usan son bronce, acero inoxidable, o aleaciones especiales como acero inoxidable con cromo y niquel; todas las partes usadas en la construcción de la canasta son templadas antes de la fabricación. Después de su completa fabricación y maquinado es tratada con ácido, se le aplica un tratamiento térmico a 1950°F, y sumerge en agua.

Las canastas sin perforación se construyen de manera muy similar a las anteriores.

Estandarización de equipo y maquinaria

Las ventajas y la necesidad de estandarizaicón son ya muy conocidas, por lo tanto se hará solo una descripción breve y se analizará el problema.

Lo importante en un equipo estándar no son básicamente sus dimensiones o sus características mecánicas, sino más bien su campo de aplicación, siendo este último el principal problema de la estandarización. Pueden existir dos casos; uno en el que se tenga un campo de aplicación pequeño y que se tenga una gran variedad de equipos estándares y otro en el cual exista un gran campo de aplicación y los equipos estándares sean pocos, lo cual puede actuar en contra de la economía.

En el primer caso porque al tratar de hacer el número total de aparatos posibles se tiende a eliminar la estandarización. Y en el segundo caso porque cuando un equipo cubre un mayor campo de aplicación que para el que fue diseñado, operará a un costo muy elevado.

Frente al problema de proporcionar un equipo para un servicio determinado, se consideran básicamente dos casos:

a) El equipo que se diseña especialmente, ya sea totalmente o en sus partes, esto es fabricación sobre pedido.
Como ejemplos podemos citar: cambiadores de calor, torres y columnas, recipientes, reactores, condensadores, evaporadores, secadores, hornos, etc.

b) La maquinaria de proceso, la cual se elige entre elementos estándares. Los principales equipos de esta categoría son: Filtros, agitadores y mezcladores, ventiladores y sopladores, centrífugas, extrusores, molinos, cribas vibratorias, etc.

Las ventajas de usar equipos o partes estandarizadas, en comparación de los de diseño especial son los siguientes:

- Reducción en el costo de fabricación debido a la producción en serie.
- Facilidad en conseguir partes de repuesto.
- Reducción en la inversión de capital.
- Reducción en el tiempo del proyecto y a consecuencia reducción en 1 de los costos.
- Rapidez y facilidad en la compra y entrega de equipos y partes.

Las ventajas mencionadas son obviamente recíprocas, tanto para el fabricante como para el usuario. Es importante consideár que el tiempo de obsolencia de una planta es generalmente menor que la duración de un equipo, por lo que al disponer de equipo y maquinaria estándar estos se pueden volver a usar para el nuevo proceso.

Criterios de estandarización

En base a lo mencionado anteriormente se analizará el grado de estandarización de algunos equipos, como son:

- Equipos totalmente estandarizados: bombas.
- Equipos parcialmente estandarizados: cambiadores de calor, columnas y torres y recipientes.

Bombas

El problema de estandarización para los diferentes tipos de bombas es el mismo. Lo primero es determinar los diferentes usos y tratar de cubrirlos con una serie de bombas funcionales, sin necesidad de tener todos los tipos y tamaños. La segunda parte consiste en la selección de partes como: flechas, carcaza, cojinetes y combinarlos a manera de obtener la bomba mas adecuada con un mínimo número de tipos.

Cambiadores de calor

Los tipos principales de cambiadores son:

- Cabezal fijo. Los tubos se pueden limpiar mecánicamente pero la coraza no.
- Tubos en U. Es posible la limpieza mecánica de la coraza, pero no de los tubos.
- Cabezal flotante. Tiene la ventaja de los dos anteriores pero a un costo mayor aproximadamente en un 20 - 25%.

Componentes estándar de los cambiadores de calor

a) Tubos. Es sabido que conforme se reduce el diámetro de los tubos, se reduce el costo del cambiador; contrariamente, la reducción del diámetro hace dificultosa la limpieza mecánica del interior. La combinación de los factores anteriores se usa como criterio de selección del mínimo diámetro adecuado.

b) Coraza. Generalmente se encuentra unida a los tubos, por medio de placas fijas y dotados de un cuerpo flanqueado en el cabezal flotante.
Para los tubos en U, el cuerpo va soldado directamente a la coraza. Normalmente los diámetros de tubos para las corazas se han unificado y varían de 6 a 60 cm.

c) Mamparas y platos de soporte. Los tipos estándares son los siguientes:
  - Mamparas transversales: segmentos, disco-anillo, disco anillo modificado, interno.
  - Mamparas longitudinales.

Otras partes que generalmente son estándares son: flancos principales, guarniciones y soportes.

Columnas y torres

Los tipos principales son dos: de platos y empacadas.

Partes estandarizadas de columnas y torres:

a) Platos. Los tipos más usados son: de campaña, de válvula y perforados, siendo los de válvula y perforados los mejores, por las siguientes razones:

- Los platos perforados y de válvula son mas ligeros, menos costosos y mas fáciles de instalar.
- Tienen una pérdida de carga inferior.
- Tienen una cpacidad mayor para manejar líquidos y vapores.
- Su mantenimiento es mas sencillo por lo que tienen un costo menor.

Platos perforados. La necesidad de limitar los diferentes diámetros de las perforaciones, se debe a que para cada diámetro se necesita disponer de punzones y accesorios relativos. El diámetro de las perforaciones se selecciona esencialmente en base al servicio que la columa debe realizar. Las perforaciones grandes son mas difíciles de obturar, pero con perforaciones pequeñas se obtiene un mejor funcionamitnto. El diámetro de las perforaciones tiene además una limitación de tipo mecánico, que depende del espesor de la lámina y del tipo de material. Como regla general se puede decir que para perforar acero al carbón o inoxidable, el espesor del plato debe ser aproximadamente no mayor de la mitad del diámetro de la perforación.

La separación de las perforaciones se expresa en têrminos de la relación entre el paso y el diámetro del hoyo que varía de 1 a 5. En general el paso es triangular. Los diámetros de la perforación usados se eligen de acuerdo a las condiciones de uso.
El porciento de área perforada, en general, varía del 5 al 15%.

Platos de válvulas. Se usan normalmente dos tipos, uno para columnas de vacio y otro para columnas a presión.

El diámetro de la perforación es de unos 38 mm y los pasos son normalmente triangulares con espacios entre filas de 2.5 in. y la distancia entre válvulas en la misma fila de 3, 4.5 y 6 pulg.

Para los tres tipos de platos se han estandarizado también:
- Las trabes de soporte y sus soportes.
- Elementos de fijación de platos a las trabes.
- Anillos de soportes de platos.
- Boquillas y diagramas.
- Juntas antivibración.
- Otros accesorios internos.

b) Fondos de columnas. Los tipos normalmente usados son los siguientes:

- Tipo neto sin junta (análogo al tipo gross)
- Tipo neto con junta.
- Tipo mixto.

Los factores que influyen en la selección del fondo son de construcción y funcionales.
Para el primer tipo se presentan limitaciones en la construcción.y Se prefiere adoptarlo para diámetros inferiores a 1,000 mm. para diámetros mayores se prefieren los otros dos tipos.
El segundo tipo es conveniente para diámetros de aproximadamente 1,500 mm. mientras que el tercero para diámetros superiores a 1,500 mm.

Otras partes de columnas que están estandarizdas son:
- Grilletes de soporte para columnas empacadas.
- Cojinetes antivibracionales y tros grilletes.

- Platos de distribución y redistribución.
- Otras partes como soportes, pasarelas, etc.

Los diámetros internos de las columnas normalmente aconsejados para valores menores a 600 mm. son los de tubos unidos. Mientras que de 600 mm. en adelante varían entre 100 pulg y 100 mm. Esta estandarización permite diseñar menos y en el caso de columnas de construcción estándar y de los cambiadores, es posible hacer los cálculos por computadoras.

Reactores y tanques

En general se ha tratado de estandarizar todo tipo de reactores y recipientes donde la única exigencia es la capacidad volumétrica.

Para la estandarización es importante tomar en cuenta las siguientes normas de ejecución:
- Puertas de inspección y pasos de hombre especiales.
- Soportes de la coraza.
- Soportes en el techo.
- Escotilla de acceso.
- Descarga de fondo.
- Soportes para difusores de espuma.
- Plataformas, barandillas y rejas.
- Soportes para serpentines de enfriamiento.
- Espejos.
- Sellos para depósitos horizontales.

Es importante tener presente además, en la selección del diámetro del recipiente que los fondos disponibles son de tres tipos: semiesféricos, policéntricos 1/10 y elípticos 2:1 y están estandarizados para diámetros entre 400 y 3,00 mm. con variaciones entre 100 pulg y 100 mm.

La altura y el diámetro elegidas para el recipiente se derivan de consideraciones de tipo económico como son:

- Dimensiones estándar de lámina comercial.
- Reducción al mínimo posible del peso total del recipiente, para un volumen dado.
- Exigencias de transportación.

Es bueno hacer notar que la mayor parte de las estandarizaciones que se han mencionado, han sido las adoptadas por "Montedison" y no corresponden necesariamente a las normas oficiales.

Se puede decir que de un campo estrictamente dimensional se ha pasado a un campo más vasto de una verdadera normatividad.

Métodos de fabricación de equipo y maquinaria

Una de las ventajas de la estandarización, es una mayor eficiencia en la fabricación, por lo que se considera importante hacer algunas observaciones en los métodos de fabricación.

Considerando los principales procesos de metalistería, es muy difícil clasificarlos en forma rigurosa, ya que un proceso de fabricación puede incluir una o varias operaciones de metalistería. Sin embargo para fines de simplicidad se han clasificado de la siguiente forma:

Fabricación en campo. Básicamente se consideran las operaciones de corte y soldadura, armado de estructuras y armado de tanques grandes, el rolado y el alivio de esfuerzos que esto implica se efectúan previamente en taller.

Fabricación en taller. Aquí se consideran las operaciones de rolado y soldado que principalmente se usan en la fabricación de pailería, además de fundición, maquinado, forjado, vaciado y remachado.

A continuación se describen brevemente las principales operaciones de metalistería:
Corte. Existen mayor número y variedades de procesos de corte que de cualquier otra operación de metalistería, entre los cuales se incluyen corte con herramientas de mano como serrucho, formón y lima así como corte con todo tipo de maquinas-herramientas como taladro, prensa, torno, cepillo mecánico y máquinas fresadoras.

Rolado. El rolado se usa para formar largas piezas de sección uniforme como barras de diferentes secciones, rieles, platos, algunas secciones estructurales como vigas en U, doble T y ángulos. El rolado puede hacerse en caliente para una gran reducción en sección o en frio para exactitud en tamaño y control de grano.

Soldado. Existen tres tipos principales de soldadura: soldadura con estaño-plomo, soldadura con latón o bronce, soldadura autógena y eléctrica. La soldadura con latón y estaño se usa para unir dos partes de metal, usando un metal de aporte cuya temperatura de fusión sea menor que la de los metales que se van a unir. El latón y el bronce se usan como metales de aporte duros, que son usados para soldar y formar uniones resistentes. Esta soldadura es muy efectiva en hornos ya que forma uniones muy fuertes y puras. La soldadura autógena es usada para formar uniones permanentes en partes construidas como sustitutos para piezas fundidas o forjadas, para reemplazar uniones remachadas o atornilladas y en la reparación de secciones de partes rotas o gastadas.

Fundición. La fundición en arena requiere de moldes separados para cada pieza. La fundición en moldes de metal puede ser usada para metales con punto de fusión relativamente bajo; se usan moldes de metal que pueden ser usados para producir muchas piezas fundidas. La fundición con troquel se usa en producción masiva de pequeñas partes hechas de aleaciones de punto de fusión bajo.

Forjado a mano en máquina. Se usan martillos de potencia para hacer partes cuya forma requiere ser trabajada con materiales en estado semiplástico, o cuando se desea controlar una estructura interna en cuanto a tamaño y dirección de grano.

Materiales para fabricación de equipo

Los materiales para la construcción de plantas químicas se dividen básicamente en dos grupos: metálicos y no metálicos. Los metálicos pueden ser puros o bien aleaciones.

La selección de materiales de construcción para la fabricación de equipo y maquinaria en la industria química, se basa principalmente en la resistencia a los medios corrosivos.

Entre los materiales de construcción usados para la producción de bienes de capital en México, son de mayor importancia tanto por su contenido en peso como por su proporción en costos: las fundiciones de hierro y acero, las de aluminio y las de acero.

Hierro gris. En México el 50% de la producción de hierro gris, está destinado a la industria automotríz; el 20% a la industria siderúrgica y el 30% restante es absorbido por otras industrias.

Una parte muy importante de la producción procede de un reducido número de plantas, ya que abundan los pequeños talleres carentes de recursos para desarrollarse.

Para efectos del desarrollo de la industria de bienes de capital es conveniente señalar que solo 12 de un total de 80 fundiciones están en condiciones de producir piezas de más de una tonelada de peso y con un aceptable nivel de calidad; sin embargo, todas ellas están trabajando a su capacidad total.

Hierro maleable. La necesidad de piezas fundidas con ciertas características o propiedades mecánicas, tales como la resistencia a la fatiga, mayor maquinabilidad y otras, abrió en un momento dado un amplio campo al uso del hierro maleable.

Cerca del 90% de la producción nacional de hierro maleable, corresponde al grado SAE M-3210 con una estructura metalográfica ferrítica. La calidad del material producido es aceptable desde el punto de vista metalográfico y de pruebas físicas.

Hierro Nodular. La producción de este material se inició en México hace una década. Hoy día existen en el país una docena de fundiciones que lo fabrican, sin embargo, no son más de 8 las que lo producen en volúmenes industriales y con controles de proceso adecuados.

Este material ha venido ganando una enorme penetración en el sector del mercado que tradicionalmente estaba cubierto por el hierro maleable y muy específicamente por la forja.

Sus propiedades mecánicas son superiores a las del hierro maleable y muy similares, aunque inferiores a la forja. Sus principales ventajas radican en la eliminación de la necesidad de tratamientos térmicos prolongados y costosos, si se le compara con el maleable y del mínimo costo de los herramentales, si la comparación se hace con las forjas.

Es conveniente señalar que, por ejemplo, en la industria automotríz, el hierro nodular ha sustituido a la forja en aplicaciones tan críticas como el cigueñal, el árbol de levas, las masas de rueda y existe una marcada tendencia a fabricar también con nodular el brazo de la dirección y algunos otros componentes del tren motríz.

En otras áreas industriales, como la construcción de equipo para manejo de materiales, el hierro nodular ha sustituido también con éxito al maleable y a la forja. Un caso típico son los eslabones para cadenas.

El tipo de nodular de más frecuente uso es el correspondiente al grado SAE- D-4512, cuya estructura metalográfica es ferrítica perlítica. El futuro de este material dependerá fundamentalmente de la celeridad con que se logren avances tecnológicos que permitan una mayor absorción del magnesio por el baño, lo cual contribuirá a abatir los costos y eliminar totalmente la necesidad de tratamientos térmicos cuando se trate de obtener estructuras total o casi totalmente ferríticas.

Acero. Las pocas fundiciones de acero existentes están dedicadas primordialmente a la fabricación de partes de repuesto para la maquinaria y el equipo en operación y solo en casos excepcionales a la producción de componentes para la manufactura de nuevos equipos.

Por otro lado, varios de los fabricantes de equipo y maquinaria que se han instalado en México, han preferido seleccionar aquellos diseños en que predomina la técnica de la placa soldada, en lugar de los que requieren de piezas fundidas, en virtud de que para bajos volúmenes de producción, la técnica de placa soldada es económica, porque se evita la inversión en moldes de fundición, cuya amortización resultaría en detrimento de los costos de fabricación.

A pesar de todo lo anterior, desde el punto de vista de peso y costo, es la materia prima más importante en la fabricación de bienes de capital.

Si bien es cierto que algunas estadísticas muestran que el acero ha perdido algún terreno por la penetración que en los primeros años de esta década registraron los plásticos y el aluminio, también lo es el hecho de que en ese periodo la escasez de acero y algunos otros factores cíclicos y aleatorios, operaron en detrimento de la posición de este material en el mercado.

Por otro lado, para que la industria petrolera pueda desarrollarse al ritmo que reclaman las necesidades del mundo actual, será necesario emplear muchos millones de toneladas de acero en la fabricación de equipo de perforación, bombeo, oleoductos, gasoductos, tanques de almacenamiento y refinerías.

Se requieren 29.6 veces más energía eléctrica para producir una tonelada de aluminio a partir de alúmina, que para producir igual peso de acero a apartir de chatarra.

Algunos de los avances tecnológicos significativos ocurridos en los últimos 25 años son: el amplio uso dado al oxígeno en los procesos de refinación de acero, que desembocó en el proceso B.O.F. y los desarrollos relacionados con el uso de pellets como material de carga en los altos hornos, han mejorado el volumen de producción de metal líquido por tonelada de carbón empleada.

Por otra parte, los avances logrados en las técnicas de reducción directa, entre los cuales, el proceso HYL es uno de los más aceptados, han revolucionado algunos conceptos tradicionales en la producción del acero.

El uso de fuentes de poder de mayor capacidad para la operación de hornos eléctricos; la difusión que ha alcanzado el uso de hornos de inducción; el empleo del desgasificado al vacío que ha permitido mejorar considerablemente la calidad de ciertos tipos de acero, principalmente los de alta aleación; el uso de los sistemas de colada continua.

En relación con los avances de la industria siderúrgica mencionados, México cuenta con la mayoría de ellos; siendo la excepción más importante, la ausencia de sistemas de desgasificado al vacío.

Sin embargo, desde el punto de vista de los productos elaborados, México padece algunas deficiencias que son causa de las altas importaciones de productos siderúrgicos que afectan su balanza de pagos y que de no resolverse a corto plazo significarían un grave impedimento en la fabricación de equipo y maquinaria.

Láminas de acero al silicio

El acero al silicio, grano orientado se emplea en la manufactura de equipos eléctricos, tales como transformadores, motores, reactores y una amplia variedad de equipo de control eléctrico. Se estima que el volumen de las importaciones es cercano a las 30,000 toneladas anuales. Esta cifra no incluye el material contenido en motores de gran caballaje y especiales que se importan.

Laminados planos de acero inoxidable

En 1974 el volumen de importaciones alcanzó una cifra superior a las 20,00 ton, existe un proceso que contempla una producción inicial cercana a las 40,000 ton. usando en la primera etapa rollos de acero laminado en caliente importados como materia prima.

Barras sólidas de aceros especiales

La producción de éstas se inició en México a fines de la década de los años 50. Desde entonces, el volumen de las importaciones ha disminuido en relación al volumen del mercado. Subsisten algunos problemas de suministro en lo que se refiere a rollos de diámetro inferior a 13 mm. y de barras forjadas con diámetro mayor de 533 mm. y en largos superiores a 6 m debido a las limitaciones de los hornos de tratamiento térmico de que disponen los productos nacionales.

Barras huecas de aceros especiales

Aunque el volumen de las importaciones de este material es relativamente bajo, su fabricación en México tiene algunos inconvenientes debido a la baja demanda y amplia variedad de tipos de acero y dimensiones que se requieren, una empresa abastece la demanda, sin embargo, la solución a fondo demorará varios años.

Estas son las principales materias primas de origen siderúrgico necesarias para el desarrollo de la industria dedicada a la producción de equipo y maquinaria. Además de estos existen muchos otros materiales como pueden ser: cobre, niquel, plomo, aleaciones especiales, vidrio, plásticos, hule, madera, carbón estructural y muchos otros. Desafortunadamente no se contó con la información pertinente sobre estos materiales, pero en el apéndice se proporcionan unas tablas con algunos datos generales.

SEGUNDA PARTE

ANALISIS DE BIENES DE CAPITAL PARA LA INDUSTRIA QUIMICA EN MEXICO PARA 1977 - 1982

6. OBJETIVOS

El trabajo que se presenta a continuación forma parte de un proyecto que lleva a cabo el Grupo de Desarrollo de Tecnología (GDT) de la Facultad de Química de la UNAM.

El proyecto tiene por tema general el desarrollo de una base teórica y de una metodología de implementación, así como la evaluación cuantitativa, de sistemas de planeación tecnológica tanto a nivel nacional como a nivel de empresa.

En la bibliografía se presenta una relación de las publicaciones que el GDT ha realizado sobre los avances a la fecha tanto en el campo metodológico como en la evaluación cuantitativa.

Los estudios más recientes, de los que ésta tesis es una secuencia lógica, se han avocado a analizar los pronósticos de desarrollo de la industria química en el período de 1977 a 1982, no solo a un nivel agregado, o macro, sino también a un nivel desagregado, proyecto por proyecto, de los 154 proyectos más probables, que representan 84% de la inversión esperada. La elaboración de este sólido banco de datos ha permitido refinar las proyecciones de demanda de recursos financieros y de recursos humanos en distintas especialidades así como las necesidades de negociación, transferencia y adaptación de tecnología en forma cuantitativa y desagregada (3).

Como complemento a lo anterior el estudio presente analiza la demanda de equipo que tendrá la industria química de México en el período de 1977 a 1982 y sus posibilidades de fabricación.

Hasta la fecha, la fabricación de bienes de capital se ha enfocado en México solamente desde el punto de vista comercial, ya que se ha dependido principalmente de la importación. Se quiere ahora analizar las necesidades de equipo desde el punto de vista de su fabricación y las ventajas de planear una industria local para ese fin.

El objetivo funcional y práctico de este trabajo es ilustrar la aplicación de una metodología concreta, propuesta por el GDT, para determinar la demanda de equipo y maquinaria en la industria química. Esta metodología, que se detalla en el Apéndice I, consiste en pocas palabras en: 1) Clasificación y caracterización de equipos; 2) Análisis de la demanda futura de los mismos; 3) Estudio de su posible fabricación local y 4) Análisis de los mecanismos para proteger y promover el diseño y fabricación locales de equipos.

La evaluación cuantitativa de esta metodología se aplicó al caso de México para el período de 1977 - 1982, con el objetivo de demostrar la validez de la teoría metodológica, así como ilustrar un caso de aplicación a una industria de la que se dispone de una base de información amplia, con números sólidos y confiables.

Ahora bien, la prudencia sugiere tomar en cuenta el riesgo de posible error en la evaluación individual de un proyecto, error que puede deberse a un cambio tecnológico, a un cambio en planes industriales o a un cambio de tipo financiero o económico, cambios que pueden modificar sustancialmente al proyecto bajo estudio. Esto, unido a la discreción necesaria al tratar la información que afecta directamente los planes confidenciales de muchas empresas, nos ha hecho inclinarnos por una presentación de los resultados a nivel agregado, con el propósito de satisfacer dos objetivos: la confiabilidad estadística de los datos agregados es mucho mayor, por compensación de variancias, y de esta manera se protege la confiabilidad de los proyectos individuales.

Se considera que el método de análisis que se presenta aquí para el equipo de la industria química puede aplicarse a la demanda de equipo de otros sectores industriales y, con ello, se contribuirá a asentar las bases para la planeación de una industria local sana, en el renglón de fabricación de equipo y maquinaria.

7. METODOLOGIA

La metodología usada en este trabajo fué propuesta en el artículo "Diseño de equipo apropiado para países en desarrollo" presentado por J. Giral en la reunión de Viena, durante Mayo de 1977 (Ver Apêndice I); y se aplicó de acuerdo al listado de proyectos para 1977-1982 del artículo "Demanda Tecnológica en la Industria Química", presentado por J. Giral y S. González Passini en la XVII Convención Anual del IMIQ en Octubre de 1977 (Ver Apêndice II).

Dicha tecnología se describe a continuación:

a) Clasificación de equipo. Se estudiaron diferentes clasificaciones para equipo y maquinaria, como son: La Clasificación Uniforme de Comercio Internacional (de enfoque comercial), La Nomenclatura Arancelaria de Bruselas (de enfoque fiscal), La Clasificación Internacional Industrial Uniforme (usada para identificar las actividades industriales), La Clasificación en grandes categorías económicas de la ONU (de enfoque comercial), la Clasificación según uso o Destino Económico de la ONU (usado para identificar las actividades económicas). Se estudiaron también las clasificaciones elaboradas en México: La hecha para "En México la mejor inversión" (de enfoque comercial) y la del grupo ONUDI-NAFINSA (basada en la C.U.C.I. de enfoque comercial); encontrándose que los enfoques de estas clasificaciones no son adecuados para el presente trabajo. Requiriéndose un enfoque funcional, se optó por la clasificación propuesta en el Apéndice I.

b) Análisis de proyectos probables. Se tomaron en cuenta proyectos para 1977 - 1982 (Ver Apéndice II) y la inversión requerida para cada uno de ellos; estando clasificados de acuerdo al monto de dicha inversión (grande, mediana o pequeña) y de acuerdo al tipo de tecnología correspondiente, ya sea Tecnología de proceso, de producto, de operación o de equipo, se determinaron los tipos principales de equipo indicados para cubrir las necesidades de los proyectos.

c) Determinación de la participación del costo del equipo en la inversión total. De acuerdo a la experiencia práctica y por medio de encuesta directa en varias firmas de ingeniería e industrias químicas que han operado en México durante los últimos 50 años, se hizo un análisis del desglose típico de la inversión en sus renglones fundamentales (equipo, maquinaria, gastos de instalación, diseño, etc.) para proyectos grandes, medianos y pequeños y, en cada caso, con tecnología de proceso producto, operación y equipo (*). De esta manera se obtuvieron doce matrices de coeficientes tecnológicos del desglose de la inversión correspondientes a cada uno de estos doce grupos, obtenidos según se indica en (b) más arriba.

d) Análisis de diagramas de flujo. Se hizo una recopiliación (por medio de investigación bibliográfica y de consultas con expertos en el campo) de los diagramas de flujo de gran parte de los proyectos considerados, mismos que representan el 70% de la inversión total de la industria química para el lapso indicado. En el apêndice III se relacionan los diagramas obtenidos y los no obtenidos.

Se analizó cada diagrama y se hizo una lista de equipo para cada uno de ellos, indicando la cantidad de equipos para cada tipo; este análisis es un tanto subjetivo, debido a la escasa información contenida en los diagramas de flujo e información complementaria de la literatura. De acuerdo con la frecuencia de aparición de cada equipo se obtuvo una lista final de prioridades de fabricación.

El análisis de los diagramas de flujo se presenta por medio de una serie de tablas en el apêndice.

8. RESULTADOS, CONCLUSIONES Y RECOMENDACIONES

1. Coeficiente tecnológico de la inversión

La tabla 1 muestra el desglose típico de la inversión en un proyecto según el tipo de tecnología. Estos coeficientes tecnológicos de inversión se basan en la experiencia de un centenar de proyectos representativos de las cuatro categorías tecnológicas, con un valor de más de 500 millones de dólares actuales.

Por considerar que la muestra no era suficientemente amplia no se calculan factores diferentes para empresas grandes, medianas y pequeñas sino que se decidió tomar promedios.

Se recomienda pulir esta información, revisar posibles cambios por tendencias tecnológicas y de uso de equipo en los planes futuros de inversión, y desglosar los coeficientes por tamaño de empresa y cualquier otro parámetro relevante tanto como lo permita la confiabilidad estadística.

Una matríz de coeficietes de este tipo, como la que se ilustra en la tabla 1, puede constituir una valiosísima herramienta de planeación tanto a nivel nacional como a nivel empresarial, ya que permitirá desglosar las proyecciones generales de inversión en sus componentes principales y evaluar lo que, por ejemplo, un cambio de planes de inversión de Pemex, puede significar en cuanto a la demanda de equipo.

Se cree que la Asociación Nacional de Firmas de Ingeniería podría recoger esta idea y desarrollarla ampliamente, poniéndola a la disposición de los grupos de planeación del gobierno y del sector empresarial.

2. Desglose de la inversión esperada

La tabla 2 muestra el desglose de la inversión esperada para la indus tria química en el período 1977 - 1982 según el tipo de tecnología y el tamaño de la industria (3).

Se recomienda que la Secretaría de Patrimonio y Fomento Industrial Química, mantengan actualizada esta información. El GDT, donde se han llevado a cabo estos trabajos, podría colaborar en la obtención y preparación de estos datos.

Se utilizaron como base para los estudios subsiguientes de este trabajo por razones de consistencia y uniformidad y por considerar que en este momento constituyen el banco de datos sobre la industria química de México en los próximos cinco años.

Como puede verse en dicha tabla los ambiciosos planes de Pemex hacia la industria petroquímica, que en su casi totalidad corresponde a la categoría de industria de inversión grande y tecnología de proceso, representan la mayor parte de la inversión pronosticada, siguiéndoles de cerca los planes de empresas privadas en petroquímica secundaria, que cae dentro de la misma categoría.

Estos planes de inversión a futuro son muy dinámicos y cambian rápidamente.

3. Análisis de insumos de la inversión esperada

Las tablas 3, 4 y 5 muestran un desglose de la inversión esperada o programada, según se describe en la sección 2 anterior, aplicando los coeficientes tecnológicos de la inversión que se describen en la sección 1.

Estos cálculos se comprobaron en forma cruzada para aquellos renglones de los que se dispone información. Por ejemplo, todos aquellos que se refieren a mano de obra y, en especial a personal calificado, se cotejaron con estimados del Instituto Mexicano del Petróleo, de la Asociación Nacional de Firmas de Ingeniería y de trabajos previos del GDT (ver bibliografía) encontrándose un nivel aceptable de confiabilidad.

Por falta de recursos y por no haber tenido información confiable no se han podido cotejar las estimaciones agregadas en los renglones de equipo, maquinaria y materiales de instlación.

Se recomienda que el Grupo de Estudio de Bienes de Capital que ha estado trabajando en Nacional Financiera coteje estos datos y los rectifique o ratifique.

4. Análisis de los equipos y maquinarias de proceso más comunes en los proyectos considerados.

Una de las partes más laboriosas de este trabajo ha sido la que se describe en esta sección. Se localizaron en la bibliografía diagramas de flujo y descripciones de procesos, que representan un 70% de la inversión total esperada.

Por otro lado se seleccionó de varios estudios y artículos sobre bienes de capital (ver bibliografía) una lista de equipo y maquinaria de proceso comunmente usados en la industria química. La lista final que se seleccionó, y que aparece en la primera columna de - la tabla # 6 es coherente con los estudios previos de Jorge Carbajal, José M. López Rodríguez y José de J. Sánchez. Aplicación de técnicas de deescalación a la adaptación de tecnología del GDT, lo que permitirá capitalizar la información presentada en dicho trabajo en cuanto a procedimientos de fabricación del equipo y maquinaria a su morfología y a los materiales de construcción usados, así como a la sensibilidad de su costo de fabricación en función de la capacidad del equipo, consideración sumamente importante en la industria química, que es de las más sensibles a la escala de operación.
Del análisis de cada uno de los procesos estudiados, según las lis-

tas de equipo y maquinaria descritas más arriba, se elaboraron cuadros básicos de diseño. La tabla # 6 presenta una sinopsis de estos resultados.

Confiamos en que esta información aunque sea pobre y limitada, represente una contribución al estudio de bienes de capital de Nacional Financiera en lo que se refiere a industria química, ya que consideramos que a menos que se haga un estudio con este enfoque metodológico y con este nivel de detalle sería muy difícil información relativamente confiable en cuanto a qué conviene fabricar en México.

Creemos que la recopilación de diagramas de flujo y descripciones de proceso que se efectuó para este trabajo es un primer paso en un camino que es muy importante caminar, ya que representa la única compilación que conocemos de la tecnología nueva o adicional que va a usar la industria química en los próximos cinco años.

En este sentido quisiéramos hacer las recomendaciones siguientes:

1. A INFOTEC, para que con mejores recursos que los que teníamos a nuestro alcance, complete esta compilación y haga un número de copias para su distribución a los interesados.

2. Al Registro Nacional de Transferencia de Tecnología para que, con base a su experiencia de los últimos cuatro años, prepare un análisis sobre las formas más recomendables de seleccionar, negociar y transferir esta tecnología.

3. Al CONACYT, para que utilice esta información para normar sus criterios tanto en la formación de recursos humanos como en el apoyo a la investigación aplicada y desarrollo experimental.

4. Al grupo de Desarrollo de Tecnología, para que prosiga con sus planes en esta línea de trabajo, en concreto con la idea de apli

car la Teoría de Módulos Básicos al estudio de esta recopilación de procesos.

5. Recomendaciones generales

La tabla 7 muestra una sinopsis del análisis del gasto en equipo, maquinaria, bombas y compresores y equipo auxiliar por tipo de tecnología y tamaño de empresa.

Se recomienda tener especial cuidado en la elaboración de fabricación local de bienes de capital, ya que un excesivo apresuramiento o un proteccionismo indebido puede dar lugar a deficiencias cuyas repercusiones económicas pueden ser serias.

Por otro lado, que un desarrollo y adaptación de un acervo tecnológico apropiado a nuestras condiciones no se puede llevar a cabo si no se dispone de la capacidad de diseñar y fabricar bienes de capital apropiados a esas condiciones, por lo que es altamente deseable disponer en México de esa capacidad y utilizarla en forma racional y eficiente.

Al llevar a cabo el presente trabajo y en el caso de otros, nos hemos encontrado siempre con el problema de la falta de información o que la que existe se encuentra dispersa en diferentes lugares. Un ejemplo es el caso de los diagramas de flujo, se localizaron algunos en las fuentes más comunes y para buscar los faltanes se recurrió a instituciones especializadas en información suponiendo que ellos contarían con una amplia colección de ellos. La carencia de los diagramas de flujo en el apéndice es una indicación más de la pobreza de nuestras fuentes de información en México.

México se encuentra en una etapa de desarrollo en la que es fundamental hacer una planeación basada en el análisis concienzudo de los componentes desagregados de la inversión, tanto para el caso de los bienes de capital (como la metodología cuya aplicación se usa en este trabajo) como para el de los otros insumos clave: recursos humanos, tecnología, financiamiento e inversión, etc.

Para poder llevar a cabo estos estudios es urgente enriquecer los acervos de fuentes de información como INFOTEC, SECOBI, etc.

APENDICE I

DISEÑO DE EQUIPO APROPIADO PARA PAISES EN DESARROLLO*

ANTECEDENTES

Durante los años posteriores a la Segunda Guerra Mundial los países en vías de desarrollo concentraron sus recursos en la manufactura de bienes intermedios y de consumo, subsidiando, o al menos facilitando la importación de equipo (bienes de capital). Esta política, regularmente generalizada en la mayoría de los países del tercer mundo, ha conducido en los primeros años de la década de los 70s a una situación no deseable porque:

1. Los bienes de capital (equipo) son unos de los artículos de mayor cantidad importada y causan una considerable sangría en el intercambio exterior. México solo importó dos mil millones de dólares en 1974 y se espera que importe 3.5 mil millones de dólares en 1980. Venezuela importó cerca de mil millones de dólares en 1975 y se espera que triplicará sus importaciones en 1984.

2. La importación de equipo tiende a empeorar la dependencia tecnológica. Considerando las cuatro categorías tecnológicas de la industria (ver anexo A) en dos de ellas (Tecnología basada en equipo y Tecnología basada en operaciones) la tecnología es usualmente adquirida como un paquete incluyendo el equipo; y en una tercera categoría (Tecnología basada en proceso) las bases para el diseño de equipo están tan fuertemente relacionadas a la adquisición de tecnología, que no es sorprendente que más del 60% del equipo es comprado en el país donde la tecnología es licenciada.

3. La manufactura de equipo es, o puede ser, una industria que utiliza

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* Resumen en español del Artículo de J. Giral.

relativamente abundante mano de obra, Un tamizado selectivo de oportunidades de manufactura local de equipo conduciría a la creación de muchos empleos necesitados.

PROPOSITO DE ESTE TRABAJO

Muchos países en desarrollo, a través de las consideraciones expresadas anteriormente, están tratando de adentrarse en la manufactura de equipo. Mientras que esto puede traer muchas de las ventajas deseadas (ahorros en intercambio exterior, menor dependencia tecnológica, más empleos), puede ser a costa de una ineficiente industria manufacturera de equipo, ya sea por calidad deficiente, baja posibilidad de seleccionar una mezcla de productos o altos costos.

Nosotros sentimos que al desarrollar una estrategia de diseño y fabricación de equipo debemos considerar la experiencia que hemos adquirido en los pasados 30 años cuando se trató de acelerar la industrialización de bienes intermedios y de consumo, y entonces tratar de evitar las fallas de una industria sobreprotegida, eso sería mucho más dañino en el caso de la industria de fabricación de equipo por su impacto en productividad más directo.

El propósito de este trabajo es presentar algunas ideas generales y consideraciones a ser tomadas en cuenta por un comité de expertos de las Naciones Unidas cuando recomienden el trabajo de estudio adicional a realizarse para desarrolar una estrategia de industrialización para la industria de fabricación de equipo. Las ideas han sido agrupadas en cuatro áreas de recomendación.

1. Clasificación y caracterización de equipo,

2. Evaluación de la demanda de cada categoría de equipo.

3. Fabricación local de equipo.

4. Mecanismos para protección y promoción de la industria de diseño y fabricación de equipo.

1. CLASIFICACION Y CARACTERIZACION DE EQUIPO

Existen varias clasificaciones para equipo, orientadas principalmente a actividades comerciales, pero ninguna de ellas es adecuada para los propósitos de planear un programa racional para manufactura de equipo.

Tal clasificación es muy necesaria para establecer un marco para:

- Organizar la información estadística sobre uso y costo, y vida promedio, de cada tipo de equipo.
- Identificar y analizar equipos alternativos para el mismo uso.
- Evaluar alternativas de técnicas para manufacturar cada pieza importante de equipo.
- Analizar posibilidades de estandarización de importación, mercado, uso y fabricación de piezas de equipo importante.

Se sugiere, como prioridad inmediata para un programa patrocinado por las Naciones Unidas, promover el diseño y desarrollo de un modelo para clasificación y caracterización de equipo, siguiendo los siguientes lineamientos:

A. USO:

- AGRICULTURA
- TRANSPORTACION
  - Agua
  - Aire
  - Tierra
    - Individual
    - Colectiva
- MINERIA Y PETROLEO
- INDUSTRIA MANUFACTURERA
- CONSTRUCCION
- ELECTRICIDAD

OFICINA
OTROS

B. GRADO DE ESTANDARIZACION:

ESTANDAR, PRODUCCION EN MASA
SEMI-ESTANDARIZADO, PRODUCCION EN LINEA
FABRICACION INDIVIDUAL — PAQUETE DISEÑADO ESTANDAR
HECHO SEGUN ESPECIFICACIONES

C. METODO DE FABRICACION:

FUNDICION MAQUINADO
MAQUINADO
METALISTERIA
OTROS

D. MATERIALES DE CONSTRUCCION:

ACERO
ACERO INOXIDABLE
ALEACIONES ESPECIALES
MADERA
MASONERIA
PLASTICOS

2. EVALUACION DE LA DEMANDA DE CADA CATEGORIA DE EQUIPO

La evaluacion de la demanda puede hacerse siguiendo uno o ambos enfoques complementarios siguientes:

A) Estudio de tendencias históricas.
B) Análisis de la demanda futura.
Una vez que el modelo de clasificación y caracterización produzca

una nomenclatura aceptable, las Naciones Unidas propondrían su adopción internacional, y equipos de estudio coordinados pueden clasificar la importación histórica y la fabricación de equipo en cada país. Esto desmenuzará la demanda histórica y actual en elementos de significado para la selección de una mezcla de equipo apropiado.

La mayor parte de los países en desarrollo poseen algún grado de planeación para su industrialización. Una tarea complementaria a la descrita anteriormente sería caracterizar para cada proyecto de industrialización las principales alternativas tecnológicas, en términos de sus necesidades de equipo. Un enfoque similar al uso de criterios de plausibilidad para la selección de tecnología debe ser desarrollado (ver anexo B).

Esta caracterización proveerá una buena referencia para selección de tecnología desde el punto de vista de la mezcla de equipo más apropiada, junto con otras consideraciones, tales como el uso de materias primas locales, sensibilidad a la escala, etc. El uso de técnicas que impliquen gran cantidad de mano de obra puede ser visto desde dos puntos de vista: fabricación del equipo y operación del equipo, y para cada uno el costo relativo puede ser evaluado.

Al desarrollar esta interacción entre selección de tecnología y un campo más promisorio de oportunidades puede ser abierto: el diseño de equipo nuevo y la selección de equipo apropiado a condiciones locales. Para poder generarla creatividad necesaria en esta área, la primera tarea es la definición de las especificaciones mínimas adecuadas para cada tipo de equipo importante. Esto requiere una combinación de habilidades sociológicas, económicas y técnicas, específicamente orientadas a generar creatividad a través de la preparación de algunos ejemplos ilustrativos en cada categoría.

3. FABRICACION DE EQUIPO

Una vez que la mezcla de equipos apropiados ha sido seleccionada y/o diseñada y su volúmen ha sido evaluado, el paso siguiente sería el diseño del mejor enfoque de fabricación, al hacer esto la siguientes consideraciones deben tenerse en mente:

- El costo de fabricación por unidad decrece significativamente conforme el número de unidades se incrementa. Esto hace muy importante la estandarización, puesto que ésta incrementará el número de unidades similares al ser fabricado.

- La estandarización tiene que ser vista no solo en términos del equipo final producido, sino también en términos de los métodos de fabricación, para consolidar la fabricación similar tanto como sea posible. Esto facilitará la instalación de nuevas plantas para manufactura de equipo y el entrenamiento del personal requerido para operar esas plantas.

- La estandarización debe ser vista también en términos de los materiales de construcción, para facilitar la fabricación del equipo y el entrenamiento del personal, así como para simplificar el desarrollo de fuentes locales de materias primas para los materiales de construcción. Al diseñar las especificaciones mínimas adecuadas de cada equipo, como se indica en el número 2 anteriormente, es también muy importante verificar la necesidad de usar aleaciones sofisticadas y caras en comparación con los materiales sintéticos nuevos, de bajo costo, sencillos de trabajar que han sido desarrollados en años recientes.

- Idealmente, al proyectar la mezcla de equipo más apropiada, se debería comenzar por la selección de la tecnología más apropiada, y entonces rediseñarla para hacer el mejor uso de las diferencias básicas del país. Sin embargo, debe tenerse en mente que los países que encaran la necesidad de generar una industria local de fabricación de equipo han dependido tradicionalmente en la importación de tecnología y en los bienes manufacturados en países industrializados, lo que implica una estructura de Investigación y desarrollo mucho más sofisticada para reorientar esta tendencia.

RECURSOS

Notablemente el elemento simple más importante para asegurar un exitoso desarrollo local de la industria de fabricación de equipo es la disponibilidad de recursos humanos entrenados. Estos pueden ser vistos en tres diferentes niveles:

a) Artesanos hábiles
b) Supervisores y diseñadores de fabricación
c) Diseñadores de equipo nuevo

Se ha dicho lo suficiente en la literatura acerca de la necesidad de gente capaz en las categorías a) y b) para llevar a cabo nuestro propósito.

La clase de gente a que se refiere la categoría c) prácticamente no existe hoy día. Entrenarla y desarrollarla es una tarea de al menos 5 años que debía ser comenzada inmediatamente. Esta debe ser gente que enteienda el medio donde el equipo será usado, para desarrollar un diseño apropiado, y hacer el mejor uso de la mano de obra local y de las materias primas al fabricar y operar tales piezas de equipo. No debe haber muchos generalistas, a menos que sean especialmente dotados. Un diseñador de equipo para la industria de procesos químicos debe entender qué sucede dentro del proceso y cuáles grado de libertad tiene al diseñar una pieza de equipo apropiada para lograr especificaciones mínimas adecuadas. Lo mismo se aplica para cualquier otro sector industrial. El también debe ser suficientemente conocedor de las técnicas de fabricación de equipo, para poder visualizar alternativas de abatimiento de costos e interactuar con la gente descrita bajo la categoría b) anteriormente.
Las Naciones Unidas debían considerar la identificación de centros

de estudio para desarrollar una estructura de esta categoría c) de especialistas.

4. MECANISMOS PARA LA PROTECCION Y PROMOCION DE LA INDUSTRIA DE DISEÑO Y FABRICACION DE EQUIPO

Los últimos 30 años de industrialización de bienes de consumo y bienes intermedios han proporcionado mucha experiencia relevante en términos de lo que sucede cuando se abusa del proteccionismo. Al menos una lección es evidente: las ineficiencias resultantes, la baja productividad, la baja calidad y el alto costo no son compensados con la creación de empleos y actividad local.

El desarrollo de una industria de fabricación de equipo ineficiente y sobre-protegida tendría un efecto mucho más dañino.

A continuación se citan algunas ideas generales a considerarse en esta área:

- No hay incentivo para diseñar y desarrollar equipo apropiado excepto la sustitución de importaciones por licenciamiento de la tecnología de fabricación por parte de un país industrializado. No obstante que no sea la mejor alternativa para el país, (la más plausible), usualmente es la mejor alternativa para la compañía involucrada (la más factible) y la del menor riesgo.
  Para compensar por el tiempo mayor, más alto costo y riesgo más alto de diseñar y desarrollar equipo apropiado es necesario proporcionar mecanismos temporales tales como:

  . Ante la presentación (y aprobación)de un programa de diseño y y desarrollo local para un tipo de equipo, el gobierno local debía considerar dar a la compañía una posición privilegiada para importar y vender equipo equivalente para ayudar a financiar el programa local de diseño y desarrollo y al mismo tiempo adquirir experiencia más práctica en aplicaciones y valor en uso para ese equipo.

. Para esos diseños con un alto índice de plausibilidad, ambos, las Naciones Unidas y el Gobierno local debían considerar un enfoque de fondos conjuntos para financiar el programa de diseño y desarrollo.

. Se debían dar consideraciones a incentivos por medio de impuestos, tales como deducciones y reembolsos, en la forma usada por el gobierno mexicano para incentivar la exportación (CEDIS) con objeto de promover programas locales de desarrollo técnico.

- Para ayudar a incrementar el volumen de fabricación de una pieza de equipo en particular un fuerte soporte gubernamental debe ser dado a los acuerdos de trueque al usar las categorías, siguiendo el enfoque usado por México con partes de la industria automotríz.

- Puesto que la industria de fabricación de equipo es considerada un buen candidato para aumentar la creación de empleos, debían ser desarrollados mecanismos fiscales específicos para promover creación de empleos junto con la industria de fabricación de equipo misma, así como para subsidiar las alternativas de equipo que, en su operación, requerirán un amplio uso de mano de obra.

ANEXO B

ANALISIS DE PLAUSIBILIDAD

En la planeación industrial a nivel nacional normalmente se utilizan criterios macroeconómicos y la mayoría de las empresas utilizan criterios financieros. Esto ha llevado a crear industrias tecnológicamente ineficientes en el país, sólo porque en alguna ocasión representaron una engañosa posibilidad de ahorro de divisas, o porque las políticas del gobierno de evitar importaciones competitivas o de incentivos fiscales hicieron el proyecto financieramente atractivo para el inversionista.

Sin embargo, si el objetivo es una selección racional de tecnologías de base, es obvia la necesidad en todos los niveles de planeación de una combinación de criterios tecnológicos, macroeconómicos y financieros. En vista de que los proyectos seleccionados con estos criterios serían de interés social para la nación (o dignos de aplauso) se utiliza el término "criterios de plausibilidad" para definirlos, a diferencia de "criterios de factibilidad" que funcionan desde un punto de vista estrictamente económico. O sea, los criterios de plausibilidad son usados para evaluar la contribución social del proyecto y su congruencia con los planes nacionales de desarrollo industrial. Estos criterios se han clasificado como sigue:

1. Criterios de Mercado

   a) Substitución de importaciones.
   b) Demanda nueva.
   c) Exportación
   d) Elasticidad de la demanda.

2. Criterios Macroeconómicos
   a) Beneficios regionales (descentralización, distribución del ingre

so, uso de materias primas de la región, etc.).

b) Generación de actividad económica.
c) Competencia similar o equivalente (duplicación de inversiones).
d) Integración del proyecto a los planes nacionales.
e) Generación de empleos (costo de generar cada empleo).

3. Criterios Financieros

a) Inversión (tipo, origen, composición, magnitud).
b) Insumos nacionales y valor agregado.
c) Rotación del capital (ventas/inversión total).
d) Liquidez (capital de trabajo/inversión fija).
e) Costeo incremental.

4. Criterios Tecnológicos

a) Disponibilidad de la tecnología (número de licenciantes y de licenciatarios, alternativas existentes, antiguedad de las patentes, etc.).
b) Sensibilidad a la escala y relación de capacidades.
c) Características de la tecnología (potencial de adptación, de asimilación, dependencia futura, grado de sofisticación).
d) Elasticidad de la tecnología (especificaciones mínimas adecuadas del producto, del proceso y de las materias primas).
e) Impacto ecológico de la tecnología (contaminación, manejo de materiales tóxicos, carcinogénicos o peligrosos, aspectos eco-sociales).

Como muchos de estos criterios son de apreciación subjetiva, es conveniente fijar de antemano una escala de calificación (1, 2, 3; de 0

NOTA: Otra clasificación similar es usada en el "Manual para Desarrollo Transferencia y Adaptación de Tecnología Química Apropiada". J. Grial. UNAM. Facultad de Química, División de Estudios Superiores México, 1974.

a 10; de - 2 a + 2), con objeto de que diferentes personas en la industria y en el gobierno puedan ser congruentes en la calificación.

APENDICE II

Para la evaluación de la demanda de equipo se tomó como base la información desarrollada por el GDT (3). A continuación se transcriben las listas de proyectos que sirvieron de base.

PROYECTOS DE INVERSION GRANDE
(mayor a 10 millones de dls.)

Con Tecnología de Proceso

Urea
Acido acético
Dimetil formamida, metilaminas
Poliestireno
Politereftalato de etilen glicol
Acido Tereftálico
Furfural (2 proyectos)
Acido sulfúrico
Proyectos de Guanomex (11 proyectos)
Acetaldehido
Acrilonitrilo
Amoniaco y anhídrido carbónico
Azufre
Benceno
Cumeno
Cloruro de vinilo, dicloroetano
Dodecilbenceno, alquilarilo pesado
Estireno, etil benceno
Etileno
Plantas criogénicas
Plantas endulzadoras
Metanol
Oxido de etileno
Percloroetileno
Paraxileno
Polietileno
Tetrâmero
Tetracloruro de carbono
Acido acrílico

Con Tecnología de Proceso

Oxido de propileno
Propileno
Polipropileno
Butadieno
Ortoxileno
Tolueno

Con Tecnología de Producto

Aminoácidos
Carburo de silicio
Pentraeritritol
Formaldehido, pentaeritritol, formiato de sodio
Diferilmetano diisocianato
Etilen, propilen glicoles y eter glicoles

Con Tecnología de Operación

Parathion nitrofenol
Negro de humno
Pulpa de celulosa
Gases de uso industrial
Electrodos de grafito
Cloro y sosa cáustica

Con Tecnología de Equipo

Filamento de polipropileno

TOTAL DE INVERSIONES GRANDES: $ 3,335.94 Millones de Dólares

PROYECTOS DE INVERSION MEDIANOS
(Entre 1 y 10 millones de dólares)

Con Tecnología de Proceso

Aminas alifáticas, sales de amonio
Poliuretano
Poliacrilato de nitrilo
Acrilatos de metilo, etilo, butilo y 2 etil-hexilo
Mono, di, tri-etilen glicol

Con Tecnología de Producto

Acidos grasos
Resinas Epóxicas
Acrilonitrilo, estrireno butadieno
Acido 2, 4 diclorofenoxiacético
Anilina
Paratoluidina, antraquinona, ácidos diversos y derivados
Resinas poliestireno, copolimeros y terpolimeros
Gliceria y ácidos grasos

Con Tecnología de Operación

Polimero de caprolactama
Hule de guayule

Con Tecnología de Equipo

Oxígeno, argon, nitrógeno
Productos de plástico
Productos de hule
Plásticos
TOTAL DE PROYECTOS DE INVERSION MEDIANA: $ 71,87 millones de dls.

PROYECTOS DE INVERSION PEQUEÑA
(Menos a 1 millón de dólares)

Con Tecnología de Proceso

Gramoxone
Parafinas cloradas
Carboximetil celulosa
Cloropropilatos, monocrotóforos
Poliamidas
Melamina y fenolformaldehido

Con Tecnología de Producto

Resinas epóxicas
Cloroparafina
Propilen-glicol, fenoles bloqueados, detergentes no iónicos y polietilen glicol
Diebenzoato de propilen glicol
Ciclohexano, peroxido acetil sulfónico
Fenatos, detergentes e inhibidores
Acido monocloroacético
Anhídrido ftálico
Formoldehido
Alfa-beta naftol
Ftalato de dioctilo
Acrilamida
Alcohol polivinilico
Ftalatos de dialquilo
Alquil fenoles
Plastificantes

Con Tecnologías de Operación
Productos químicos de vegetales

Con Tecnologías de Operación

Insecticidas, fertilizantes agrícolas
Pinturas industriales

Con Tecnología de Equipo

Poliestireno
Aceites para industrias
Aceites lubricantes
Nylon, partes.

TOTAL DE PROYECTOS PEQUEÑOS: $ 12.50 Millones de Dólares

APENDICE III

La información que a continuación se presenta, está basada en los diagramas de flujo presentados en el trabajo (apendice IV).

La interpretación de dichos diagramas, es en muchos casos subjetiva y pueden haber errores, por lo que se creyó conveniente adjuntar un resumen de las hojas de trabajo.

Tabla de contenido:

TIPO DE TECNOLOGIA

	PROCESO			PRODUCTO			OPERACION			EQUIPO			TOTAL		
	MO	M	T	MO	M	T	MO	M	T	MO	M	T	MO	M	T
1.1 Equipo Proceso	3	17	20	4	26	30	2	8	10	2	8	10			
1.2 Maq. Proceso	-	10	10	-	15	15	-	25	25	-	30	30			
1.3 Bombas y Compr.	-	5	5	-	5	5	-	10	10	-	10	10			
1.4 Equipo Auxiliar	2	8	10	1	4	5	3	12	15	2	8	10			
1. TOTAL EQUIPO	5	40	45	5	50	55	5	55	60	4	56	60			
2.1 Inst. civil/Mec	2	-	2	3	-	3	5	-	5	3	-	3			
2.2 Tub. Valv. acc.	4	6	10	4	3	7	2	1	3	1	1	2			
2.3 Aislam/pintura	1	1	2	1	1	2	1	-	1	1	-	1			
2.4 Intr./control	2	8	10	1	3	4	-	1	1	1	2	3			
2.5 Inst. eléctrica	2	3	5	2	2	4	3	4	7	4	4	8			
2. TOTAL INSTAL. EQUIPO	11	18	29	11	9	20	11	6	17	10	7	17			
3. EDIF. Y ESTRUC.	8	3	11	10	3	13	6	2	8	10	5	15			
4. DISEÑO	8	-	8	6	-	6	7	-	7	4	-	4			
5. ADMON. OBRA	7	-	7	6	-	6	8	-	8	4	-	4			
TOTAL	39	61	100	38	62	100	37	63	100	32	68	100			

Tabla 1, Desglose típico en porciento de la inversión de un proyecto según el tipo de tecnología.

Fuente: Experiencia privada - Firmas de ingeniería y empresas químicas.
MO = Mano de Obra, M = Material, T = Total,

TIPO DE TECNOLOGIA	INVERSION GRANDE	INVERSION MEDIANA	INVERSION PEQUEÑA	TOTAL
DE PROCESO	3,573.9	52.0	4.7	3,630.6
DE PRODUCTO	79.9	64.4	17.4	162.2
DE OPERACION	244.8	36.7	2.5	284.0
DE EQUIPO	14.4	22.5	5.2	42.1
TOTAL	3,913.0	176.1	29.8	4,118.9

Tabla 2. Desglose por tipo de tecnología y tamaño de industria de la inversión esperada en 1977-1982 en la industria química en México. Datos en millones de dólares de 1977.

Fuente: Análisis de la demanda tecnológica de la industria Química en México, 1977 - 1982, José Giral B. y Sergio González P. GDT, Octubre de 1977.

INVERSION GRANDE

TIPO DE TECNOLOGIA

	PROCESO			PRODUCTO			OPERACION			EQUIPO			TOTAL		
	MO	M	T	MO	M	T	MO	M	T	MO	M	T	MO	M	T
1.1 Equipo Proceso	107.2	607,6	714,8	3,2	20,8	24,0	4.9	19,6	24,5	0,3	1,2	1.5	115.6	649.2	764.8
1.2 Maq. Proceso	-	357.4	357,4	-	11,9	11,9	-	61,2	61,2	-	4.3	4.3	-	434.8	434.8
1.3 Bombas y Compr.	-	178,7	178,7	-	3,9	3,9	-	24,5	24.5	-	1,4	1,4	-	208,5	208.5
1.4 Equipo Auxiliar	71.5	285.9	357,4	0,8	3,2	4,0	7,4	29.4	36,8	0,3	1,2	1,5	80,0	319.7	399.7
1. TOTAL EQUIPO	178,7	1429,6	1608.3	4,0	39.8	43,8	12,2	134,7	146.9	0.6	8.1	8.7	195,6	1612,2	187.8
2.1 Inst. civil/Mec	71,5	-	71,5	2,4	-	2,4	12,2	-	12,2	0,4	-	0,4	86.5	-	86.5
2.2 Tub. Valv. acc.	142,9	214,4	357.3	3,2	2.4	5,6	4,9	2,4	7.3	0.1	0,1	0,2	151.1	219.3	370.4
2.3 Aislam/pintura	35,7	35,7	71,4	0,8	0.8	1,6	2.4	-	2,4	0.1	-	0,1	39.0	36,5	75,5
2.4 Intr./control	71,5	285,9	357.4	0.8	2.4	3,2	-	2,4	2,4	0,1	0,3	0.4	72,4	291.0	363,4
2.5 Inst. eléctrica	71.5	107,2	178.7	1.6	1,6	3,2	7.3	9,8	17,1	0,6	0,6	1,2	81.0	119,2	200.2
2. TOTAL INSTAL. EQUIPO	393,1	643,2	1036.3	8,8	7,2	16.0	26.8	14.6	41,4	1.3	1.0	2,3	430.0	666.0	1096.0
3. EDIF. Y ESTRUC.	285,9	107,2	393.1	8,0	2,4	10,4	14.7	4,9	19.6	1,4	0,7	2.1	310,0	115.2	425.2
4. DISEÑO	285,9	-	285,9	4,8	-	4.8	17,1	-	17,1	0.6	-	0,6	308,4	-	308.4
5. ADMON. OBRA	250,2	-	250,2	4,8	-	4,8	19.6	-	19,6	0,6	-	0.6	275,2	-	275,2
TOTAL	1393.8	2180.0	3573,8	30,4	49.4	79.8	90,4	154,2	244.6	4.5	9.8	14,3	1519,2	2393,4	3912.6

Tabla 3. Desglose de la inversión programada en industrias grandes según el tipo de tecnología y por tipo de insumo - en millones de dólares de 1977.

Fuente: Ver tablas 1 y 2.

INVERSION MEDIANA

TIPO DE TECNOLOGIA

	PROCESO			PRODUCTO			OPERACION			EQUIPO			TOTAL		
	MO	M	T	MO	M	T	MO	M	T	MO	M	T	MO	M	T
1.1 Equipo Proceso	1,6	8.8	10.4	2.6	16.9	19.5	0.7	2.9	3.6	0,5	1.8	2,3	5.4	30.4	35.8
1.2 Maq. Proceso	-	5.2	5.2	-	9.7	10.3	-	9.2	9,2	-	6,8	6,8	-	30.9	30.9
1.3 Bombas y Compr.	-	2.6	2,6	-	3.2	3,2	-	3,7	3,7	-	2,2	2,2	-	11.7	11.7
1.4 Equipo Auxiliar	1,0	4.2	5,2	0,6	2.6	3,2	1,1	4.4	5,5	0,5	1,8	2,3	3,2	13.0	16.2
1. TOTAL EQUIPO	2,6	20.8	23.4	3,2	32.4	35,6	1.8	20.2	22.0	1,0	12,6	13.6	8.6	86.0	94.6
2.1 Inst. civil/Mec	1,0	-	1.0	1,9	-	1,9	1,8	-	1,8	0.7	-	0,7	5,4	-	5.4
2.2 Tub. Valv. acc.	2,1	30.1	5.2	2,6	1.9	4,5	0,7	0.4	1,1	0,2	0.2	0.4	5.6	5.6	11.2
2.3 Aislam/pintura	0,5	0.5	1.0	0.6	0,6	1,2	0,4	-	0.4	0,2	-	0,2	1.7	1.1	2.8
2.4 Intr./control	1,0	4.2	5.2	0,6	1.9	2,5	-	0,4	0,4	0,2	0,5	0,7	1,8	7,0	8.8
2.5 Inst. eléctrica	1,0	1.6	2.6	1,3	1.3	2,6	1,1	1,5	2,6	0,9	0,9	1,8	4,3	5,3	9.6
2. TOTAL INSTAL. EQUIPO	5,6	9.4	15,0	7,0	5.7	12,7	4.0	2,3	6,3	2,2	1,6	3,8	18,8	19,0	37.8
3. EDIF. Y ESTRUC.	4,2	1,6	5,8	6,5	1,9	8,4	2,2	0,7	2,9	2,2	1.1	3,3	15.1	5,3	20,4
4. DISEÑO	4,2	-	4,2	3.9	-	3,9	2.6	-	2,6	0,9	-	0,9	11,6	-	11.6
5. ADMON. OBRA	3,6	-	3.6	3,9	-	3,9	2,9	-	2,9	0,9	-	0,9	11,3	-	11.3
TOTAL	20.2	31,8	52,0	24,5	40,0	64,5	13,5	23.2	36,7	7,2	15.3	22,5	65,4	110.3	175.7

Tabla 4. Desglose de la inversión programada en industrias medianas según el tipo de tecnología y por tipo de insumo - en millones de dólares de 1977.

Fuente: Ver tablas 1 y 2.

INVERSION PEQUEÑA

TIPO DE TECNOLOGIA

	PROCESO			PRODUCTO			OPERACION			EQUIPO			TOTAL		
	MO	M	T	MO	M	T	MO	M	T	MO	M	T	MO	M	T
1.1 Equipo Proceso	0.14	0.79	0,93	0.69	4,52	5.21	0,05	0,20	0.25	0.10	0.42	0.52	0.98	5,93	6.91
1.2 Maq. Proceso	-	0.47	0.47	-	2.61	2.61	-	0.63	0.63	-	1.56	1.56	-	5.27	5.27
1.3 Bombas y Compr.	-	0.24	0.24	-	0.87	0,87	-	0.25	0.25	-	0.52	0.52	-	1.88	1.88
1.4 Equipo Auxiliar	0.09	0.38	0.47	0.17	0.69	0,86	0,08	0.30	0.38	0.10	0.42	0.52	0,44	1.79	2.23
1. TOTAL EQUIPO	0,23	1.88	2.11	0.86	8,69	9.55	0,13	1.38	1,51	0.20	2.92	3,12	1,42	14.87	16.29
2.1 Inst. civil/Mec	0,09	-	0.09	0. 52	-	0.52	0.13	-	0,13	0.16	-	0.16	0,90	-	0.90
2.2 Tub. Valv. acc.	0.19	0.28	0.47	0.69	0.52	1.21	0,05	0.03	0.08	0,05	0,05	0,10	0,98	0.88	1.86
2.3 Aislam/pintura	0.05	0.05	0.10	0,17	0,17	0,34	0,03	-	0.03	0,05	-	0.05	0.30	0,22	0.52
2.4 Intr./control	0,09	0.38	0,47	0,17	0,52	0.69	-	0,03	0.03	0,05	0,10	0.15	0.31	1.03	1.34
2.5 Inst. eléctrica	0,09	0.14	0,23	0,35	0,35	0.70	0,08	0.10	0,18	0,20	0,20	0.40	0.72	0.79	1.51
2. TOTAL INSTAL. EQUIPO	0.51	0.85	1,36	1,91	1.56	3,46	0,29	0.16	0.46	0,51	0.35	0,86	3.21	2.92	6.13
3. EDIF. Y ESTRUC.	0,38	0.14	0.52	1.74	0,52	2,26	0.15	0,05	0.20	0,52	0.26	0,78	2.79	0.97	3.76
4. DISEÑO	0,38	-	0.38	1,04	-	1.04	0,18	-	0,18	0,20	-	0,20	1.80	-	1,80
5. ADMON. OBRA	0,33	-	0.33	1,04	-	1,04	0.20	-	0,20	0.20	-	0,20	1.77	-	1.77
TOTAL	1.83	2,87	4,70	6,59	10,77	17.35	0,95	1.59	2.55	1,63	3,53	5.16	10.99	18.76	29.76

Tabla 5. Desglose de la inversión programada en industrias pequeñas según el tipo de tecnología y por tipo de insumo.
Fuente: Ver tablas 1 y 2.

PROYECTO DE INVERSION
GRANDE

TECNOLOGIA DE PROCESO

	EQUIPO DE PROCESO												MAQUINARIA DE PROCESO					
	Cambiadores de calor	Columnas y torres	Tanques atmosféricos	Recipientes a presión	Reactores	Condensadores	Evaporadores	Secadores	Hornos	Cristalizadores	Transportadores	Decantadores	Filtros	Agitadores y mezcladores	Ventiladores y sopladores	Centrífugas	Extrusores	Molinos y quebradoras
Acetaldehido	X	X		X	X													
Acido acético	X	X			X													
Acido acrílico	X	X			X				X									
Acido fosfórico	X	X	X	X		X	X		X				X					
Acido sulfúrico	X	X		X	X								X		X			
Acrilonitrilo	X	X			X													
Acido tereftálico	X	X			X			X					X					
Amoniaco	X			X	X	X			X				X					
Amoniaco CO_2	X	X			X													
Azufre	X	X	X	X	X													
Benceno	X	X			X				X									
Butadieno	X	X			X				X									
Cloruro de vinilo	X	X		X	X				X									
Criogénicas	X	X		X	X	X												
Cumeno	X	X	X	X	X													
Dimetilformamida	X	X	X		X	X	X											
Dodecilbenceno	X	X	X		X			X					X					
Endulzadoras	X	X				X		X					X					
Estireno	X	X	X	X	X													
Etilbenceno	X	X	X	X	X													
Etileno	X	X		X	X			X	X									
Furfural	X	X	X										X					
Hexaclorobenceno	X	X	X		X	X												
Metanol	X	X	X	X	X	X												
Metilaminas	X	X	X				X											
Nitrato de amonio - HNO_3	X	X		X	X		X	X					X		X			
Oxido de etileno	X	X		X														
Oxido de propileno	X	X			X													
Percloroetileno	X	X		X	X			X				X						
Poliestireno alto P.M.	X	X	X		X													
Poliestireno bajo p.m.	X	X	X		X						X		X					
Polietileno alta densidad	X	X	X		X	X		X				X		X		X	X	
Polietileno baja densidad	X	X	X		X			X										
Polipropileno			X	X	X			X										
Propileno	X	X		X				X										
Sulfato de amonio	X	X	X	X	X			X		X								
Tetrámero	X	X		X														
Tetracloruro de carbono	X	X		X	X	X												
Tolueno	X	X		X														

TABLA 6. Sinopsis de los equipos y maquinarias de proceso más comunes en los procesos considerados.

TABLA 6. Continuación.

	EQUIPO DE PROCESO												MAQUINARIA DE PROCESO					
	Cambiadores de calor	Columnas y torres	Tanques atmosféricos	Recipientes a presión	Reactores	Condensadores	Evaporadores	Secadores	Hornos	Cristalizadores	Transportadores	Decantadores	Filtros	Agitadores y mezcladores	Ventiladores y sopladores	Centrífugas	Extrusores	Molinos y quebradoras
PROYECTO DE INVERSION GRANDE																		
TECNOLOGIA DE PROCESO																		
Urea	X	X	X	X	X	X												
O-Xileno	X	X			X				X							X		
P-Xileno	X	X		X	X													
PROYECTOS DE INVERSION GRANDE																		
TECNOLOGIA DE PRODUCTO																		
Aminoácidos	X	X	X			X			X					X				
Etilenglicol	X	X			X		X											
Formaldehido	X	X		X	X		X											
Glicol éteres															X			
Pentaeritritol			X	X	X		X	X		X			X	X				
PROYECTOS DE INVERSION GRANDE																		
TECNOLOGIA DE OPERACION																		
Cloro-sosa	X	X	X	X		X	X	X										
Negro de humo	X								X									
PROYECTOS DE INVERSION MEDIANA																		
TECNOLOGIA DE PROCESO																		
Butilacrilato	X	X		X	X													
Etilacrilato	X	X			X		X											
Etilenglicol	X	X			X		X											
Furfural	X	X	X			X	X						X					
Metilmetacrilato	X	X		X														
Poliacrilonitrilo	X		X		X									X				
Sales de amonio			X		X								X	X				

NOTA: Estas tablas están incompletas en lo referente a maquinaria de proceso, ya que los diagramas de flujo y las descripciones de proceso no son muy explícitos. Se incluyen solo por el valor que pudiese tener la información parcial.

TABLA 6. Continuación

	EQUIPO DE PROCESO	Cambiadores de calor	Columnas y torres	Tanques atmosféricos	Recipientes a presión	Reactores	Condensadores	Evaporadores	Secadores	Hornos	Cristalizadores	Transportadores	Decantadores	MAQUINARIA DE PROCESO	Filtros	Agitadores y mezcladores	Ventiladores y sopladores	Centrífugas	Extrusores	Molinos y quebradoras
PROYECTOS DE INVERSION MEDIANA																				
TECNOLOGIA DE PRODUCTO																				
Ac. 2, 4 Diclorofenoxiacético					X	X					X							X		
Acidos grasos				X		X														
Acrilonitrilo		X	X			X														
Anilina		X	X			X	X	X					X							
Antraquinona		X	X			X	X	X								X				
Butadieno-estireno		X	X	X	X	X														
Glicerina		X	X	X	X	X										X				
Poliestireno		X		X					X										X	X
Resinas epoxi		X			X											X				
PROYECTOS DE INVERSION MEDIANA																				
TECNOLOGIA DE OPERACION																				
Caprolactama		X	X	X	X	X					X				X	X				
Celulosa		X	X	X		X			X			X								
Guayule				X		X		X	X			X			X					X
Hidrógeno		X	X		X															
PROYECTOS DE INVERSION PEQUEÑA																				
TECNOLOGIA DE PROCESO																				
Carboximetilcelulosa						X			X							X				X
Cloro parafinas		X	X			X														
Fenol-formaldehido				X	X	X	X					X				X				X
Melamina		X	X				X													
PROYECTOS DE INVERSION PEQUEÑA																				
TECNOLOGIA DE PRODUCTO																				
Acido cloro-acético		X	X	X	X		X			X							X			
Acrilamida					X	X			X		X							X		
Alcohol polivinílico				X		X			X			X				X				
Anhídrido ftálico		X	X			X	X		X							X			X	
Beta-naftol		X	X	X	X										X					X

TABLA 6. Continuación

	EQUIPO DE PROCESO	Cambiadores de calor	Columnas y torres	Tanques atmosféricos	Recipientes a presión	Reactores	Condensadores	Evaporadores	Secadores	Hornos	Cristalizadores	Transportadores	Decantadores	MAQUINARIA DE PROCESO	Filtros	Agitadores y mezcladores	Ventiladores y sopladores	Centrífugas	Extrusores	Molinos y quebradoras
PROYECTO DE INVERSION PEQUEÑA																				
TECNOLOGIA DE PRODUCTO																				
Ciclohexano		X	X	X	X	X			X											
Cloro parafinas		X	X			X														
Formaldehido		X	X		X	X		X									X			
Plastificantes		X	X	X	X		X								X	X				
Polietilenglicol		X	X			X	X													
Resinas epoxi		X			X											X				
PROYECTOS DE INVERSION PEQUEÑA																				
TECNOLOGIA DE OPERACION																				
Fertilizantes		X	X				X	X	X						X	X				X
Pinturas industriales				X		X						X				X	X			X
PROYECTOS DE INVERSION PEQUEÑA																				
TECNOLOGIA DE EQUIPO																				
Aceites lubricantes		X	X	X																

EQUIPO DE PROCESO

TECNOLOGIA DE

INVERSION	PROCESO Mill. dls	 %	PRODUCTO Mill. dls	 %	OPERACION Mill. dls	 %	EQUIPO Mill. dls	 %	TOTAL Mill. dls	 %
GRANDE	607.6	88.7	20.8	3.0	19.6	2.9	1.2	0.2	649.2	94.8
MEDIANA	8.8	1.3	16.9	2.5	2,9	0.4	1.8	0.2	30.4	4.4
PEQUEÑA	0.8	0.1	4.5	0.7	0.2	0.02	0.4	0.1	5.9	0.9
TOTAL	617.2	90.1	42,2	6.2	22.7	3.32	3,4	0.5	685.5	100.1

MAQUINARIA DE PROCESO

TECNOLOGIA DE

INVERSION	PROCESO Mill. dls	 %	PRODUCTO Mill. dls	 %	OPERACION Mill. dls	 %	EQUIPO Mill. dls	 %	TOTAL Mill. dls	 %
GRANDE	357.4	75.8	11.9	2.5	61.2	12.9	4.3	0.9	434.8	92.1
MEDIANA	5.2	1.1	9.7	2.0	9.2	2.0	6.8	1.4	30.9	6.6
PEQUEÑA	0.5	0.1	2.6	0.6	0.6	0.1	1.6	0.3	5.3	1.1
TOTAL	363.1	77.0	24.2	5.1	71.0	15.0	12,7	2,6	471.0	99.8

Tabla 7. Sinopsis del análisis de gastos en equipo, maquinaria, bombas y compresores y equipo auxiliar por tipo de tecnología y tamaño de empresa.

BOMBAS Y COMPRESORAS

	TECNOLOGIA DE									
	PROCESO		PRODUCTO		OPERACION		EQUIPO		TOTAL	
INVERSION	Mill. dls	%	Mill. dls	%	Mill.dls	%	Mill. dls	%	Mill. dls	%
GRANDE	178.7	80.4	3.9	1.7	24.5	11.0	1.4	0.6	208.5	93.8
MEDIANA	2.6	1.2	3.2	1.4	3.7	1.6	2.2	1.0	11.7	5.3
PEQUEÑA	0.2	0.1	0.8	0.4	0.3	0.1	0.5	0.2	1.9	0.8
TOTAL	181.5	81.7	7.9	3.5	28.5	12.7	4.1	1.8	222.1	99.9

EQUIPO AUXILIAR

TECNOLOGIA DE

	PROCESO		PRODUCTO		OPERACION		EQUIPO		TOTAL	
INVERSION	Mill. dls	%	Mill. dls	%	Mill. dls	%	Mill. dls	%	Mill. dls	%
GRANDE	285.9	85.5	3.2	1.0	29.4	8.8	1.2	0.4	319.7	95.6
MEDIANA	4.2	1.3	2.6	0.7	4.4	1.3	1.8	0.5	13.0	3.9
PEQUEÑA	0.4	0.1	0.7	0.2	0.3	0.1	0.4	0.1	1.8	0.5
TOTAL	290.5	86.9	6.5	1.9	34.1	10.2	3.4	1.0	334.5	100.0

TABLA 7. Continuación

TABLA 8.

*Resistencia química de plásticos a varios disolventes **

Clave de la designación para resistencia química

S = satisfactorio hasta 30°C
S1 = satisfactorio hasta 60°C
S2 = satisfactorio por encima de 60°C
A = adecuado
I = insatisfactorio

	PVC rígido	*PVC plastificado*	*Polietileno*	*Polipropileno*	*Metacrilatos*	*Poliésteres*	*Epoxis*	*Fluorocarburos*	*Poliestireno*	*Polímeros ABS*	*Poliacetales*	*Fenolformaldehído*	*Policarbonato*	*Cl poliéter*	*Furano*	*"Saran"*
Aceites lubricantes	S1	S	S	S	S	S	S2	S2	A	S	S	S	S1	S2	S	S1
Acetato de etilo	I	I	I	I	I	I	A	S2	I	I	. . .	I	I	S	S	A
Acetona	I	I	S	S	I	I	A	S2	I	I	S1	I	S	S	A	S
Alcohol metílico	S	S1	S1	S1	S	S1	S	S2	S	S1	S1	A	S1	S2	S	S1
Alcohol etílico	S	S1	S1	S1	S	S1	S	S2	S	S1	S1	A	S1	S2	S	S1
Alcohol butílico	S	S1	S1	S1	S	S1	S	S2	S	S	S1	A	S1	S2	S	S1
Anilina	I	I	S	S	. . .	. . .	S	S2	S	I	. . .	I	. . .	A	I	I
Benceno	I	I	I	I	I	S1	S	S2	I	I	S	S	I	S	S	A
Ciclohexanona	I	I	. . .	. . .	. . .	. . .	. . .	S2	. . .	I	. . .	. . .	. . .	. . .	. . .	I
Dicloruro de etileno	I	I	I	I	I	I	A	S2	I	I	S	S	I	S2	. . .	S
Eter etílico	I	I	S	S	I	. . .	S	S2	I	I	S1	S	S1	S2	S	I
Hexano	S	I	A	A	S	S	S	S2	I	A	S	S	S1	S	S	S1
Keroseno	S	S1	S	S	S	S	S	S2	I	A	S	S	S1	S	S	S1
Naftaleno	I	I	S	S	I	S	S	S2	I	I	S	S	A	S2	S	S1
Tetracloruro de carbono	I	I	I	I	I	S1	S	S2	I	I	S1	S	I	S2	S	S
Trietanolamina	S1	S	S	S	. . .	. .	. . .	S2	. . .	I	. . .	. . .	. . .	S2		
Xileno	I	I	I	I	I	S2	S	S2	I	I	S1	S	I	S	S	A

TABLA 9.

Resistencia a la corrosión de materiales de construcción *

Clave de la designación para resistencia a la corrosión

A = aceptable, puede usarse con éxito
C = cuidado, la resistencia varía dependiendo de las condiciones; úsese si se puede tolerar algo de corrosión
X = inaceptable
. . = no se dispone de información

Clave de la designación para los materiales de empaque

a = asbesto blanco (comprimido o tejido)
b = asbesto azul (comprimido o tejido)
c = asbesto (comprimido y ahulado)
d = asbesto (tejido y ahulado)
e = GR-S o hule natural
f = "Teflón"

	Metales								*No metálicos*					
			Acero inox.											
Producto químico	*Hierro y acero*	*Hierro vaciado (resist-Ni)*	*18-8*	*18-8 Mo*	*Níquel*	*Monel*	*Bronce rojo*	*Aluminio*	*Vidrio industrial*	*Carbón (Karbate)*	*Resinas fenólicas*	*Resinas acrílicas*	*Cloruro de vinilideno*	*Materiales no metálicos de empaque aceptables*
Acetona	A	A	A	A	A	A	A	A	A	A	C	X	C	a,e,f
Ac. acético anhidro	C	C	A	A	A	A	X	A	A	A	A	X	C	b,c,d,f
Ac. acético crudo	C	C	C	C	C	C	C	A	A	A	A	A	C	b,c,d,f
Ac. acético puro	X	X	C	A	C	A	X	A	A	A	A	A	X	b,c,d,f
Ac. bórico	X	C	A	A	A	A	C	A	A	A	A	. . .	A	a,c,d,e,f,
Ac. carbónico	C	C	A	A	A	A	C	A	A	A	A	A	A	a,e,f
Ac. cítrico	X	C	C	A	C	A	C	A	A	A	A	A	A	b,c,d,e,f
Ac cloracético	X	. . .	X	X	C	C	X	C	A	. . .	A	. . .	. . .	b,f
Ac. clorhídrico	X	X	X	X	C	C	X	X	A	A	A	A	C	b,c,d,f
Ac. crómico	C	C	C	C	C	C	X	C	A	X	X	X	A	b,f
Ac. esteárico	C	A	A	A	A	A	C	A	A	A	A	. . .	. . .	a,e,f
Ac. fluorhídrico	C	X	X	X	C	C	X	X	X	A	C	. . .	C	b,f
Ac. fórmico	X	. . .	C	C	C	C	X	X	A	A	A	. . .	A	b,c,e,f
Ac. fosfórico	C	C	C	A	C	C	X	X	C	A	A	. . .	A	b,c,f
Ac. láctico	X	C	C	A	C	C	A	C	A	A	A		. . .	a,b,c,d,e,f
Ac. nítrico	X	C	C	C	X	X	X	C	A	C	C	. .	C	b,f
Ac. oleico	C	C	A	A	A	A	C	A	A	A	A	. . .	A	a,e,f
Ac. oxálico	C	C	C	C	C	A	C	C	A	A	A	. .	. . .	b,c,d,e,f
Ac. sulfúrico (75-95%)	A	C	X	X	X	C	X	X	A	C	X	X	C	b,f
Ac. sulfúrico (10-75%)	X	C	X	X	C	C	X	X	A	A	C	C	A	b,f
Ac. sulfúrico (<10%)	X	C	X	C	C	C	C	C	A	A	C	A	A	a,b,c,e,f
Ac. sulfuroso	X	. . .	C	A	X	X	C	C	A	A	A	. . .	C	b,c,d,e,f
Acidos grasos	C	C	A	A	A	A	C	A	A	A	A	. . .	A	a,c,f
Alumbres	X	C	C	A	C	A	X	A	A	A	A	A	A	a,c,d,e,f
Amoniaco anh.	A	A	C	A	A	A	X	C	A	. . .	A	. . .	C	a,f
Anhidrido acético	C	C	A	A	A	A	X	A	A	A	A	X	C	b,c,d,f
Anilina	A	A	A	A	. . .	A	X	. . .	A	A	C	. . .	C	a,f
Azufre	A	C	C	C	C	C	C	C	A	A	A	. . .	. . .	a,c,f
Benceno	A	A	A	A	A	A	A	A	A	A	A	. . .	C	a,f
Bióxido de azufre	C	C	C	C	C	C	C	A	A	A	A	. . .	A	a,f
Bisulfato de sodio	X	C	A	A	A	A	C	C	A	A	A	. . .	A	b,c,d,e,f
Bromo	X	C	C	C	C	C	C	. . .	A	C	X	. . .	X	b,f
Carbonato de sodio	A	A	A	A	A	A	C	C	C	A	A	X	. . .	a,c,d,e,f
Cloro húmedo	X	X	X	X	X	X	X	X	A	C	A	. . .	X	b,c,f
Cloro seco	A	A	C	A	A	A	A	A	A	A	A	. . .	X	b,e,f
Cloruro de aluminio	X	C	X	X	C	C	A	A	A	A	A	. . .	A	a,c,e,f
Cloruro de amonio	C	A	C	C	A	A	C	C	A	A	A	A	A	b,c,d,e,f
Cloruro de calcio	C	A	C	C	A	A	C	C	A	A	A	A	A	b,c,d,e,f
Cloruro de cinc	C	C	C	X	A	A	X	C	. . .	. . .	A	A	. . .	b,c,d,e,f
Cloruro de magnesio	C	C	C	C	A	A	C	C	A	A	A	. . .	A	b,c,e,f
Cloruro de sodio	A	A	C	C	A	A	C	C	A	A	A	. . .	. . .	a,c,d,e,f
Cloruro férrico	X	X	X	C	X	X	X	X	A	C	A	. . .	A	b,c,f
Etanol	A	A	A	A	A	A	A	A	A	A	A	. . .	A	a,c,e,f
Etilen-glicol	A	A	A	A	A	A	A	A	A	A	A	A	C	a,c,e,f
Fenol (ac. carbólico)	C	A	C	A	A	A	C	A	A	A	C	A	C	a,f
Formaldehído	C	C	A	A	A	A	C	A	A	A	A	. . .	A	a,c,e,f
Fosfato dibásico de amonio	C	A	A	A	. . .	A	C	C	A	A	A	. .	. . .	a,c,d,e,f
Fosfato monobásico de amonio	X	C	A	A	. . .	C	X	X	A	A	A	. . .	. . .	b,c,d,e,f

TABLA 9.

Resistencia a la corrosión de materiales de construcción (continúa)

	Metales								No metálicos					
			Acero inox.											
Producto químico	*Hierro y acero*	*Hierro vaciado (resist-Ni)*	*18-8*	*18-8 Mo*	*Níquel*	*Monel*	*Bronce rojo*	*Aluminio*	*Vidrio industrial*	*Carbón (Karbate)*	*Resinas fenólicas*	*Resinas acrílicas*	*Cloruro de vinilideno*	*Materiales no metálicos de empaque aceptables*
Fosfato tribásico de amonio	A	A	A	A	A	A	X	C	A	A	A	...	...	a,c,d,e,f
Glicerina	A	A	...	A	A	A	A	A	A	A	C	A	C	a,c,e,f
Hidrocarburos alifáticos	A	A	A	A	A	A	A	A	A	A	A	A	C	a,c,d,f
Hidróxido de amonio	A	A	A	A	C	C	X	C	A	...	A	A	C	a,c,d,f
Hidróxido de calcio	A	A	A	A	...	A	C	...	...	...	...	...	...	a,c,d,e,f
Hidróxido de potasio	C	C	A	A	A	A	X	X	...	...	...	...	C	a,c,f
Hidróxido de sodio	A	A	A	A	A	A	C	X	C	A	A	A	C	a,c,d,f
Hipoclorito de calcio	X	C	C	A	C	C	C	C	A	A	C	...	C	b,c,d,f
Hipoclorito de sodio	X	C	C	A	C	C	C	X	A	C	X	...	A	b,c,d,f
Metanol	A	A	A	A	A	A	A	A	A	A	A	...	A	a,c,e,f
Nitrato de sodio	A	A	A	A	A	A	C	A	A	A	A	...	...	b,c,d,e,f
Peróxido de hidrógeno	C	...	C	C	C	C	C	A	A	A	A	A	C	a,e,f
Sulfato de aluminio	X	C	C	A	C	C	X	A	A	A	A	A	A	a,c,d,e,f
Sulfato de amonio	C	A	C	C	A	A	C	A	A	A	A	A	A	b,c,d,e,f
Sulfato de cinc	C	A	A	A	A	A	C	C	...	...	...	...	...	b,c,d,e,f
Sulfato de cobre	X	C	A	A	C	C	X	X	A	A	A	X	...	b,c,d,e,f
Sulfato de magnesio	A	A	A	A	A	A	A	A	A	...	A	...	A	b,c,e,f
Sulfato de sodio	A	A	A	C	A	A	A	A	A	A	A	...	A	a,c,d,e,f
Sulfato férrico	X	X	C	A	C	C	X	C	A	C	A	...	A	b,c,e,f
Sulfato ferroso	C	A	A	A	A	A	C	C	A	A	A	...	C	
Sulfito de sodio	A	A	A	A	A	A	C	C	A	A	A			
Sulfuro de sodio	A	A	C	A	A	A	X	X	C	A	A	...	...	a,e,f
Tetracloruro de carbono	C	C	C	A	A	A	C	C	A	A	A	A	C	a,f
Tiosulfato de sodio	C	...	A	A	A	A	C	C	A	A	A	...	A	a,c,d,e,f
Tricloroetileno	C	A	C	A	A	A	C	C	A	A	A	..	C	a,f

TABLA 10 .

*Costo comparativo de distintos metales en lámina**

Material	*Relación* = $\frac{\text{costo por kg del metal}}{\text{costo por kg de acero al carbón}}$
Acero al carbón, calidad para bridas	1
Acero laminado con acero inox. 304	5
Acero laminado con acero inox. 316	6
Aluminio (99 +)	6
Acero inoxidable 304	7
Cobre (99.9 +)	7
Acero laminado con níquel	8
Acero laminado con monel	8
Acero laminado con Inconel	9
Acero inoxidable 316	10
Monel	10
Níquel	12
Inconel	13
Hastelloy C	40

TABLA 11.

*Costo de instalación del equipo como porcentaje de su costo de compra**

Tipo de equipo	*Costo de instalación*
Separadores centrífugos	10-35
Compresores	20-60
Secadores	50-150
Evaporadores	10-40
Filtros	25-45
Cambiadores de calor	10-35
Cristalizadores mecánicos	30-50
Mezcladores	10-20
Bombas	10-50
Torres	25-50
Cristalizadores de vacío	40-55
Tanques de madera	30-60
Tanques metálicos	20-40

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* Estas tablas se sacaron del Libro: Giral B., J. , F. Barnés y A. Ramírez. Ingeniería de Procesos, Facultad de Química, UNAM, México, 1977.

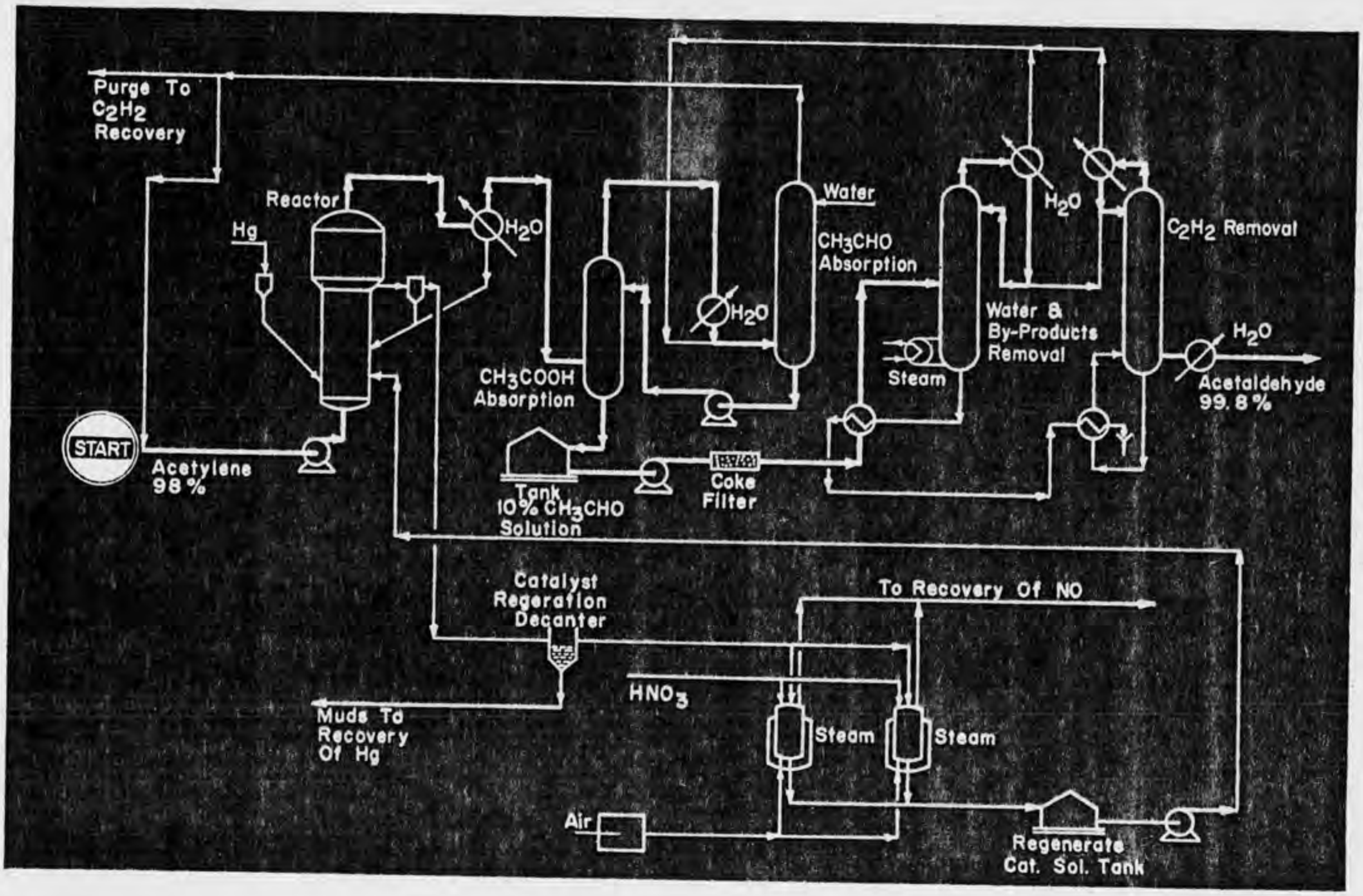
APENDICE IV

La colección de diagramas de flujo que se presenta a continuación se obtuvo de la literatura disponible.

De la relación de proyecto que constituyen el programa de inversión para la industria química en 1977 - 1982 (apéndice II) no se incluyen todos los diagramas de flujo por no disponer de la información necesaria, y debido a ésto el análisis sólo se basó en los diagramas de flujo disponibles.

Esta colección, se ha fotocopiado de las fuentes originales, la mayoría en inglés, por carecer de tiempo y recursos, para la traducción y redibujado de los mismos y por considerarse que tendría un -- cierto valor el disponer de una recopilación de breves descripciones de la mayor parte de las tecnologías que serán usadas por la industria química en México los primeros cinco años.

PROYECTO DE INVERSION GRANDE
TECNOLOGIA DE PROCESO



Acetaldehyde—MONTECATINI

Application: A process for manufacturing acetaldehyde by means of catalytic hydration of acetylene

Charge: Acetylene, 98 percent pure.

Product: Acetaldehyde having a purity of 99.8 percent.

Description: Acetaldehyde is obtained by direct hydration of acetylene, according to the following equation:

$$CH \equiv CH + H_2O \rightarrow CH_3 \cdot CHO$$

This reaction, catalyzed by mercuric ion, takes place by injecting gaseous acetylene into a mercuric sulphate solution, acidified by H_2SO_4.

During the process, owing to secondary reactions, a progressive reduction of mercuric ions, which are catalitically active, takes place to metallic mercury which is catalitically inactive.

In order to prevent the reduction of mercuric salts to metallic mercury, ferric sulphate is continuously added to the catalyst solution; the ferric compound is reduced to ferrous sulphate during the process.

The catalyst therefore must be continuously replaced for reoxidization of ferrous sulphate to ferric sulphate.

To this aim the catalyst solution is continuously withdrawn and sent to the regenerator, after removal of mercury-containing muds; said muds are periodically hot-treated in order to recover metallic Hg. Regeneration of catalyst solution comprises a hot-treatment with nitric acid in the presence of an air stream blown in the solution.

Nitrogen oxide is produced; ferrous ion is oxidized to ferric ion.

The regenerated catalyst is recycled to the acetylene hydration reactor. The latter operates adiabatically and the residence time of acetaldehyde in the catalytic solution is calculated in such a way to minimize side-reactions.

Acetaldehyde vapors, mixed with steam and unreacted acetylene overflow from the top of the reactor. The effluent mixture is then first cooled to about 60 °C; the condensate consists almost entirely of water which is sent back to the reactor. The gaseous mixture is then admitted into a column in which acetic acid is absorbed by the acetaldehyde solution flowing from the bottom of the successive acetaldehyde absorption tower. The gaseous mixture is further cooled, after the acetic acid absorption step, to about 30 °C in a final cooler.

From here the gas is sent to the absorption tower in which acetaldehyde is recovered as a crude aqueous solution.

Unreacted acetylene, together with inert gas contained in the starting gas feed flows from top of absorption tower and is sent back to reactor, while a small portion of it is continuously purged.

The purged gases, still containing acetylene, are sent to acetylene recovery which can be carried out by conventional means: in case the acetaldehyde unit is coupled to a methane cracking unit for the production of acetylene, the purged gases are sent to the main raw acetylene gasholder; thus they follow the concentration process of the pure acetylene production unit.

From the bottom of the absorption tower an acetaldehyde aqueous solution of 10 percent strength is obtained; this is sent first to the acetic acid absorption tower and then to mercury settling tanks.

Crude acetaldehyde solution is pumped, through a coke filter for separation of residual mercury and a pre-heater, to the distillation tower.

The distilled acetaldehyde is then purified from acetylene by a heating step in an acetylene stripping tower.

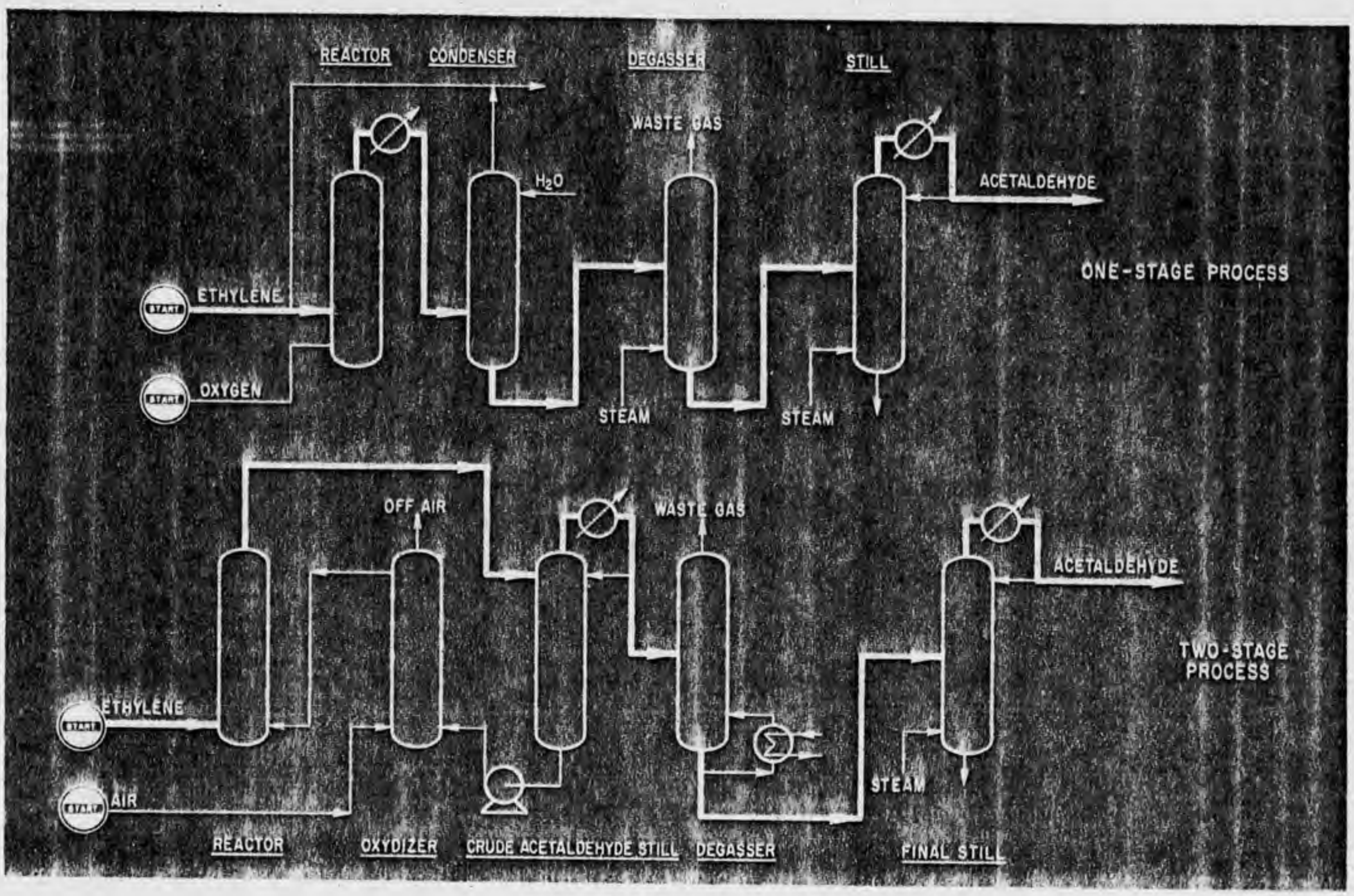
The final product has an acetaldehyde content of 99.8 percent.

Uncondensed gases flowing from the top of the acetaldehyde distillation tower are mixed with acetaldehyde vapors and acetylene leaving the top of the acetylene stripping tower and are recycled to the bottom of the column in which acetaldehyde vapors are first absorbed in water. From the bottom of the distillation tower a mixture of water and by-products is continuously drained off.

Operating conditions: The reactor operates at a temperature of about 85 °C. and the plant is run substantially at gasometric pressure.

Yields: Total yield of acetaldehyde is 95 percent based on acetylene consumption.

Commercial installations: A large industrial plant is in operation at the Montecatini Works in Novara, Italy.



Acetaldehyde from Ethylene (Aldehyd GmbH)—HOECHST-UHDE CORP.

Application: A process for acetaldehyde production by direct oxidation of ethylene. There are two variations of the process, one using oxygen and the other using air. The choice depends on local conditions such as oxygen cost, utility prices, and ethylene purity.

Description: The process employs a catalytic solution of copper chloride containing small quantities of palladium chloride. The reactions may be summarized as follows:

$$C_2H_4 + 2CuCl_2 + H_2O \xrightarrow{PdCl_2} CH_3CHO + 2HCl + 2CuCl$$

$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2CuCl_2 + H_2O$$

In the reaction, palladium chloride is reduced to elemental palladium and HC1 and is re-oxidized by cupric chloride. During catalyst regeneration, the cuprous chloride is reoxidized. The reaction and regeneration steps can be conducted separately or together. See Acetone (Aldehyd GmbH) for two-stage (air) process description.

Single-Stage Oxidation With Oxygen: Ethylene and oxygen are fed into a vertical reactor which is filled with catalyst solution. The reaction takes place under a slight pressure and at the boiling temperature of the aqueous solution. The reaction is exothermic by 58 kcal per mole acetaldehyde produced. This heat is removed by water evaporation, and the concentration of the catalyst solution is kept constant by means of a corresponding water supply. Acetaldehyde produced is condensed and scrubbed with water from unreacted gas, which is recycled.

Crude acetaldehyde thus obtained is separated from byproducts and water by a two-stage distillation.

Plant Cost: The total investment for a 75,000 ST/year plant, with either the one-stage process including the oxygen plant, or the two-stage process including air compression, is about $4 million.

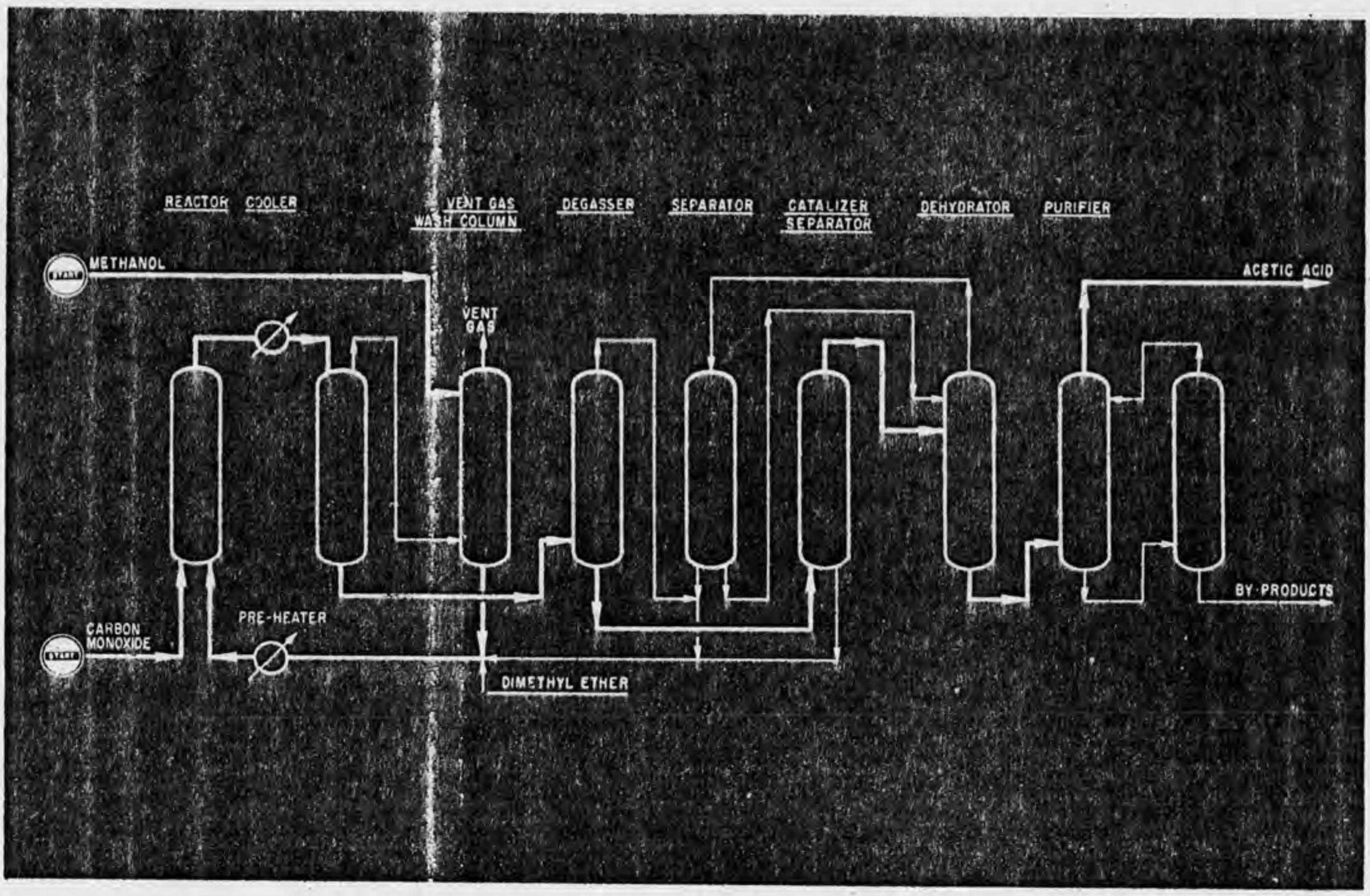
Operating Requirements Per Short Ton of Acetaldehyde

Raw Materials and Utilities	One-Stage*
Ethylene (100%) 120 psig, min., 99.8 Vol.%	1,340 lb.
Oxygen (100%) 120 psig, min., 99.5 Vol.%	9,460 scf
Catalysts (Approximate)	$0.90
HCl (31%)	30 lb.
Cooling Water, 68° F	48,000 gal.
Cold Water, 54° F	1,700 gal.
Demineralized Water	120 gal
Steam	2,100 lb.
Electric Power	15 kwh
Personnel 1 supervisor and 1 foreman per day, 3-4 men per shift	
Yield (Based on Ethylene)	95%

* Oxygen plant utilities not included

Commercial Installations: There are 19 plants throughout the world, with total annual capacity of one million short tons.

References: Further information is available from Hoechst-Uhde Corp., 550 Sylvan Avenue, Englewood Cliffs, N. J. 07632.



Acetic Acid—BADISCHE ANILIN-& SODA-FABRIK AG

Application: A continuous high-pressure process for production of acetic acid from methanol and carbon monoxide according to W. Reppe.

Description: The reaction proceeds as follows:

$$CH_3OH + CO \rightarrow CH_3COOH$$

$$CH_3OCH_3 + H_2O + 2CO \rightarrow 2CH_3COOH$$

The conversion takes place at about 250° C and 650 atm. in liquid phase in the presence of water. The catalyst is dissolved cobaltous iodide.

In the high-pressure synthesis section, the reactor is continuously supplied with a feed containing methanol and, if desired, dimethyl ether, and with carbon monoxide. 530,000 kcal of reaction heat is released per ton of acetic acid produced, which is absorbed by the cold feed and gas. A slight heat deficit is compensated by preheating the feed to 40-80° C. The crude acid and the unreacted gas are withdrawn at the top of the reactor and, after cooling, expanded down to 10 atm. gage in the medium-pressure section. The crude acid is transferred to the working-up section. Methyl iodide in the unreacted gas is recovered by washing the vent gas with the feed methanol. The methanol is combined with the other components forming the feed without any further treatment, and the washed gas is used for fuel.

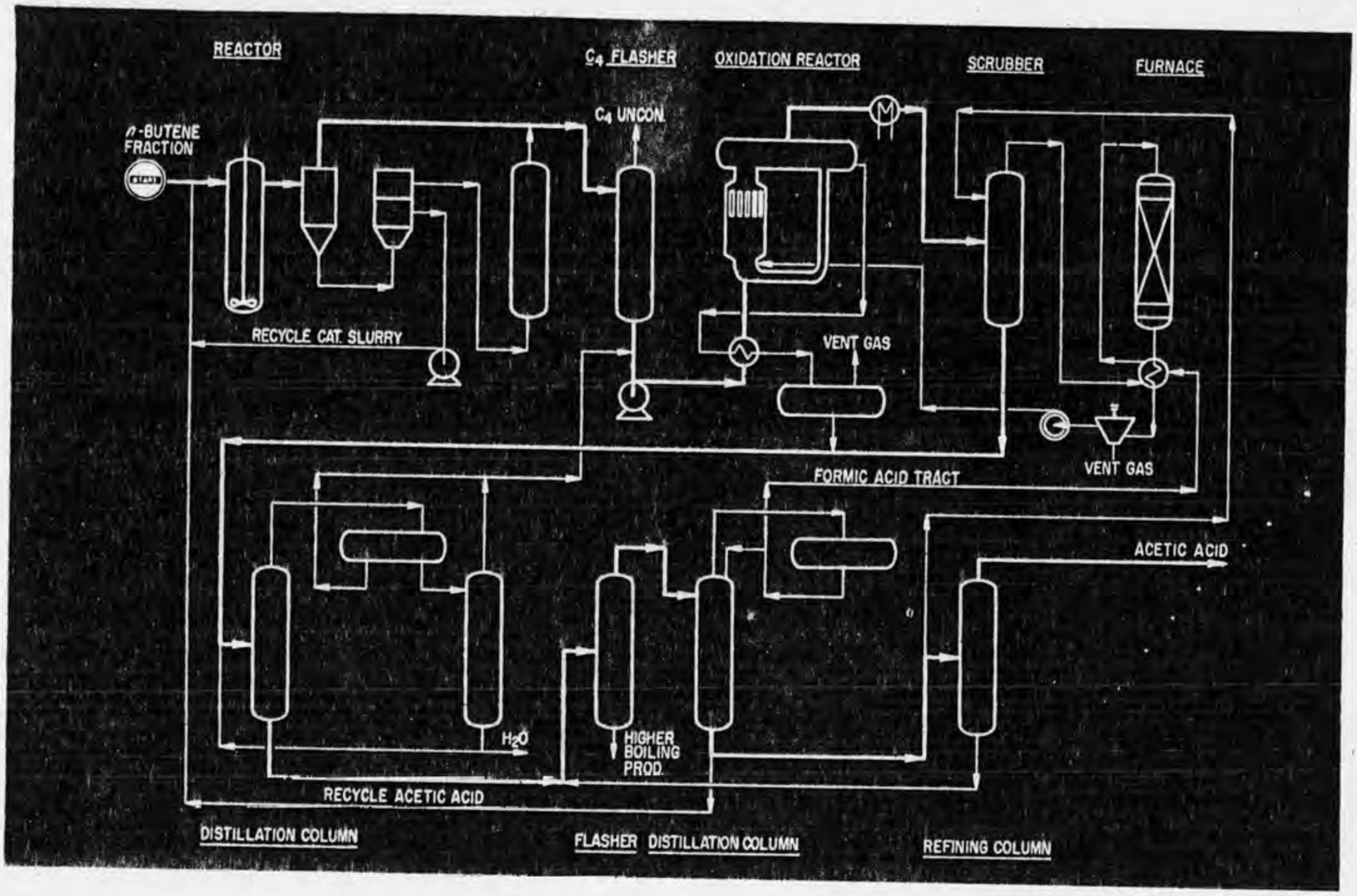
In the working-up section the acetic acid and the byproducts having a higher boiling point than acetic acid are separated from the crude acid and withdrawn. All other components of the crude acid are mixed with the methanol leaving the vent gas wash column. The mixture is supplied continuously to the reactor as feed.

The crude acid is degassed and freed from low-boiling components in a first distillation and then in the catalyst separation freed from cobaltous iodide that is removed from the column in aqueous acetic solution as bottoms. The catalyst-free crude acid is dehydrated and purified in the dehydrator column by means of azeotropic distillation. The entrainer used is a steam-volatile byproduct mixture which is formed in the reaction and which separates in the separator as the upper phase. In the bottom of the dehydrator column acetic acid free of water and formic acid is recovered, which is processed in the following two columns to pure acetic acid of over 99.8% purity, and a byproduct mixture that is free of acetic acid.

Yield: The requirements for the production of 100 kg of acetic acid are: 61 kg of pure methanol and 63m^3 (S.T.P.) CO.

Commercial Plants: 11,000 ton/year plant at BASF, 15,000 ton/year plant in the United States.

Reference: Chemie-Ingenieur-Technik, 37, 383-388 (1965), *Hydrocarbon Processing*, 45, 141-144 (Nov. 1966).



Acetic acid — BAYER AG

Application: A process for producing acetic acid from n-butene fractions.

Description: n-Butenes are first reacted with acetic acid to form sec-butyl acetate irregardless of the position of the double bond. Liquid phase oxidation of sec-butyl acetate yields acetic acid.

$$n\text{-Butene} + \text{Acetic acid} \rightarrow \text{sec-butyl acetate} + 2\,O_2 \rightarrow 3 \text{ acetic acid.}$$

One mole of acetic acid is recycled to the first step, which ultimately yields 2 moles acetic acid from 1 mole butene, at stoichiometric ratio.

The first reaction step occurs in a reactor cascade (1) in the liquid phase at 100-120° C and 15-25 atm pressure. The catalyst (an acid ion exchange resin) is suspended in the reaction mix and, after reaction, is separated in a centrifuge (2) from the liquid reactor effluent and returned to the reactor cascade. Ahead of the centrifuge the pressure of the reaction mix is reduced to that of the subsequent column. The crude product is fed to a C_4 flasher (3) in which non-reacted C_4 hydrocarbons are separated.

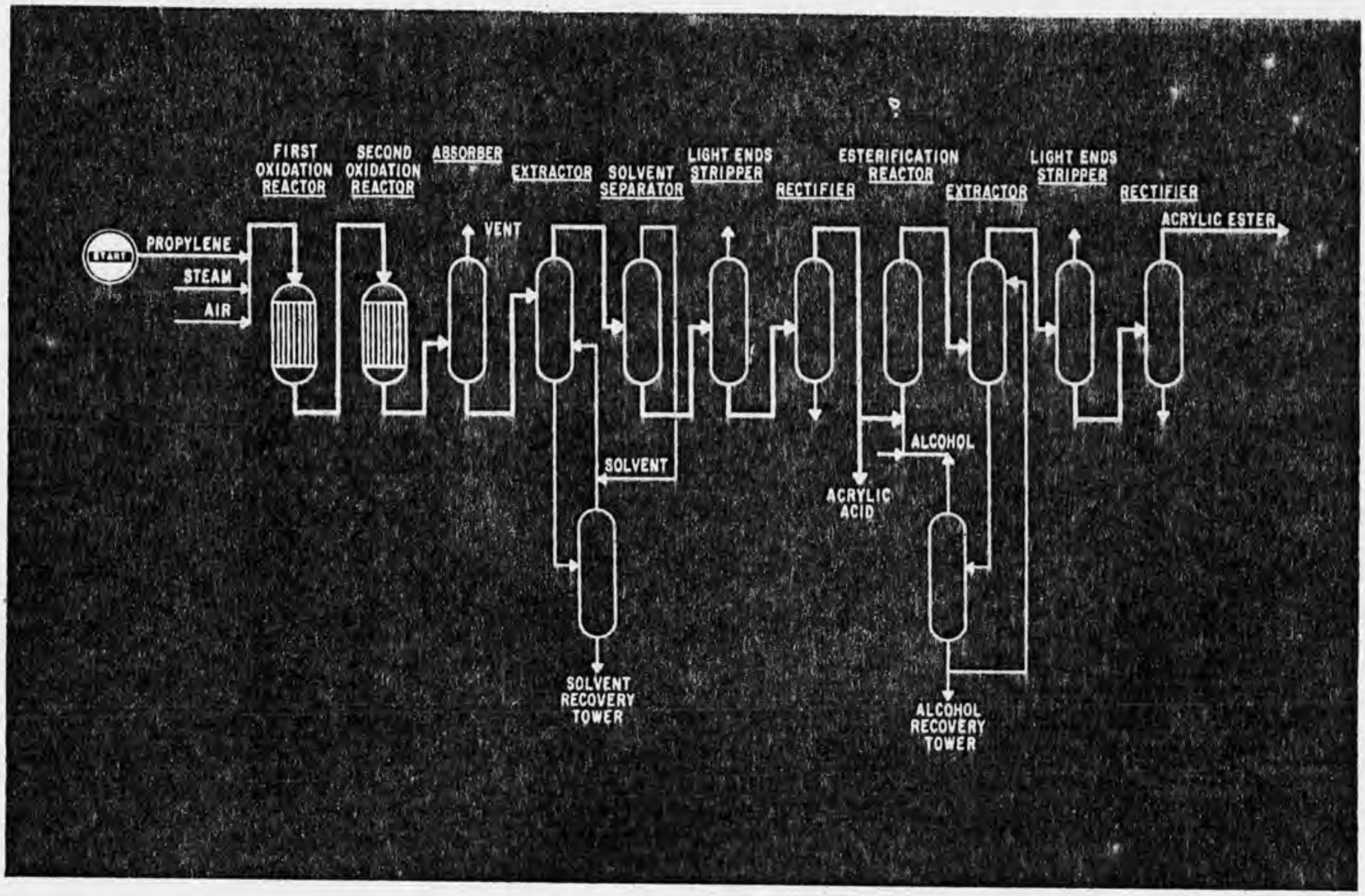
The reaction product of the first step is oxidized in the liquid phase at 200° C and 60 atm. without catalysts in the reactor (4) which is an empty tower provided with a steam generator to dissipate the heat of reaction. Air is blown into the reactor by a compressor (5). The gaseous reactor effluent after the reactor is washed with acetic acid in the scrubber (6), and the vent gas still containing oxygen is cleaned by combustion in a furnace (7) where it is simultaneously heated and subsequently pressure-released for operating the air compressor (5) turbine.

The crude acetic is withdrawn at the reactor and fed to the distillation section. Here, in a first azeotropic distillation column (8), sec-butyl acetate not reacted is drawn off with water together with volatile byproducts formed during the reaction, and is returned to the oxidation reactor. The reaction water is removed. The crude acid drawn off from the bottom product is freed from small amounts of higher boiling impurities in a flasher (9). Subsequently the formic acid formed is removed overhead off the distillation column (10), fed to the furnace (7) and in this way destroyed. The acetic acid is redistilled in the refining column (11), and bottom product of which is returned to the flasher (9). The non-redistilled acetic acid, i.e., the bottom product of the column (10), is used for the acetic acid scrubber (6) and the reaction of the n-butenes with acetic acid (1).

Yield: 0.8 metric tons n-butenes are converted per ton of acetic acid produced.

Commercial plants: None. Basic design worked out in cooperation with Lurgi Öl.

Reference: *Hydrocarbon Processing* 49 (November 1970) 117-120; The Proceedings of the Seventh World Petroleum Congress, 59-65.



Acrylic acid & esters — NIPPON SHOKUBAI KAGAKU KOGYO CO., LTD.

Application: A process for the manufacture of acrylic acid and esters from technical grade propylene, air and alcohols.

Description: Acrylic acid is produced directly from propylene in high yield by the vapor phase catalytic air oxidation process.

The reactions take place in two steps both in presence of steam as a diluent. Propylene is first oxidized to acrolein which is then oxidized to acrylic acid. The conversion of propylene is almost complete. A small amount of acetic acid is byproduced.

Air is combined with steam and propylene and the stream is fed to a series of fixed bed multi-tubular reactors which are operated at high temperatures. The pressure is atmospheric. The reaction is exothermic and the heat of reaction is removed by circulating a coolant in the shell side of the reactors and it is then recovered as steam.

The reactor effluent is introduced to an absorber where acrylic acid is scrubbed as an aqueous solution. Acrylic acid in the solution is then extracted with a solvent. After the solvent separation and light ends removal high purity acrylic acid is obtained at a final rectifier. The product acrolein may be recovered from the outlet gas of the first stage reactor through a series of distillation trains.

Methyl and ethyl esters are produced continuously in a liquid phase in the presence of a catalyst. From the reactor effluent unreacted alcohol is extracted and recycled. The high purity esters are obtained by subsequent distillations. Other higher esters are produced in separate units.

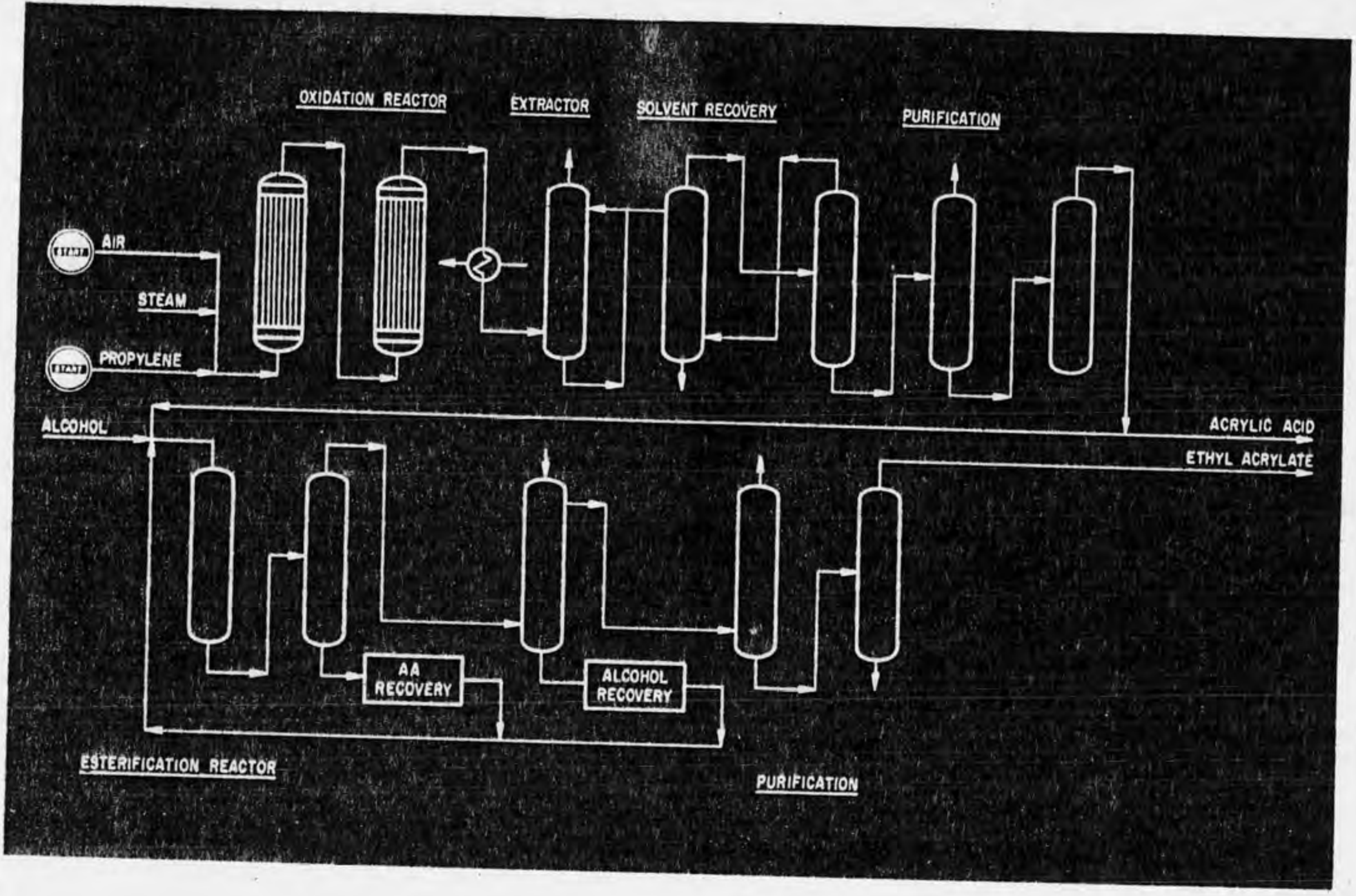
Economics:

1. B/L Capital Investment (1972, Japanese base) Acrylic acid (50,000 tons/year), 2,000 MM Yen Methyl acrylate (20,000 tons/year), 290 MM Yen
2. Raw Materials and Utilities

Acrylic acid (1 Kg)		
Propylene (100%)	0.75	kg
Catalyst & aux. chemicals	6.0	Yen
Steam	3.0	kg
Electric power	0.55	kwh
Water	50	kg
Methyl acrylate (1 kg)		
Acrylic acid	0.90	kg
Methanol	0.40	kg
Catalyst & aux. chemicals	3.0	Yen
Steam	5.5	kg
Electric power	0.04	kwh
Water	20	kg

Commercial installations: 35,000 tons/year at Nippon Shokubai's Himeji plant, Himeji, Japan. The process has been licensed to Produits Chimiques Ugine Kuhlmann, France, and Rohm and Haas Co., U.S.A., with a total capacity of some 500 million pounds/year.

Reference: *Hydrocarbon Processing,* November 1971, Vol. 50, No. 11, p. 117.



Acrylic acid/acrylic esters — MITSUBISHI PETROCHEMICAL, LTD.

Application: A process for catalytic oxidation of propylene to acrylic acid and esterification with various alcohols.

Description: Propylene, mixed with air and steam, is charged to a series of two oxidation reactors where propylene is catalytically oxidized to acrylic acid with high selectivity. The multitubular reactors use a circulating heat transfer media to remove the large quantities of reaction heat. To suppress unwanted side reactions, the reactor effluent is quenched and sent to the recovery and purification system. The purified acrylic acid is charged with the appropriate alcohol to the esterification reactor. The product is separated from the unreacted acrylic acid and the unreacted alcohol which are recycled. A conventional set of columns are used to further purify the acrylate.

Economics: Typical economic data for the Mitsubishi DAE process for 17,000 metric tons/yr of acrylic acid and for 5,000 metric tons/yr ethyl acrylate are:

	Acrylic acid 17,000 t/y	Ethyl acrylate 5,000 t/y
Raw materials		
Propylene, ton/ton	0.879	. . . .
Acrylic acid, ton/ton	. . . .	0.768
Ethyl acrylate, ton/ton	. . . .	0.495
Utilities, Yen/ton	7,350	5,600
Chemicals Yen/ton	2,835	1,560
Investment, MM Yen*	1,782	355

* Japanese basis in 1972

Commercial installations: The first commercial plant went onstream in Mitsubishi Petrochemical Co., Ltd., Yokkaichi.

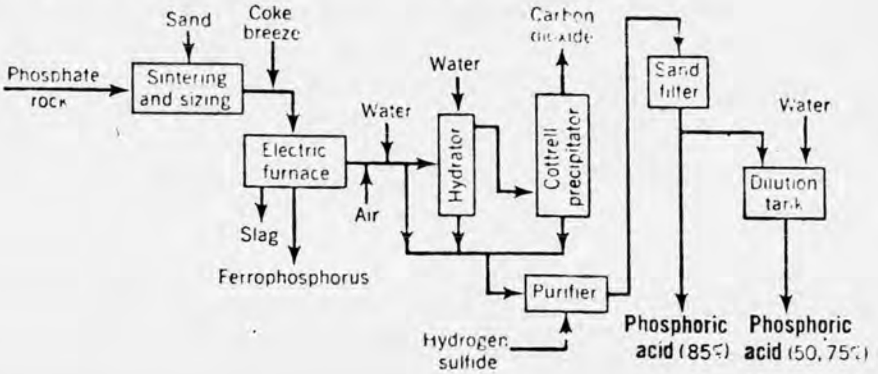
Licensor: Mitsubishi Petrochemical Co., Ltd.

PHOSPHORIC ACID

(ORTHOPHOSPHORIC ACID)

H_3PO_4

From Phosphate Rock by Electric Furnace



Reaction

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 2P + 5CO + 3CaSiO_3$$

$$2P + 5CO + 5O_2 \rightarrow P_2O_5 + 5CO_2$$

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

87–92% yield

Material Requirements

Basis—1 ton phosphoric acid (100%)
plus 4,600 lb slag

Phosphate rock (70 BPL)	4,900 lb	Carbon electrode consumption	17 lb
Sand (silica)	1,495 lb	Air (minimum)	100,000 cu ft
Coke breeze	880 lb	Electricity	4,070 kw-hr

Process

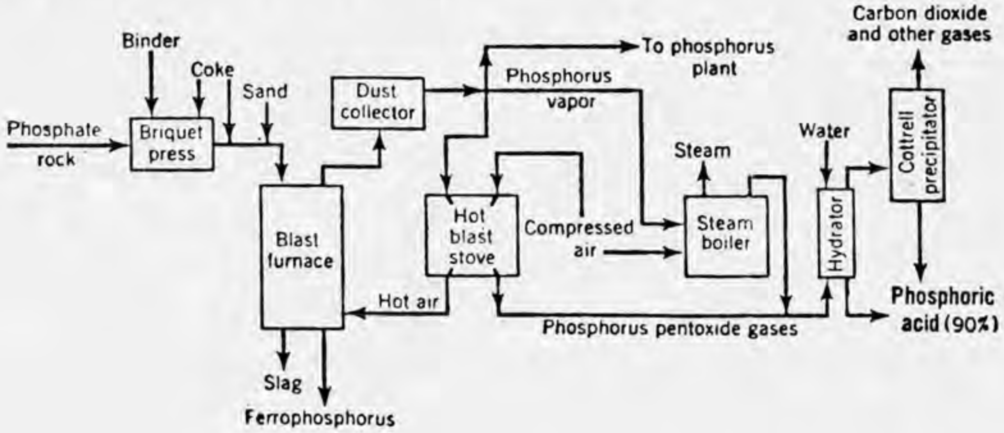
In the electric-arc-furnace process, phosphate rock is reduced to elemental phosphorus by the action of coke and heat in the presence of sand. Subsequent oxidation by air to phosphorus pentoxide followed by hydration yields phosphoric acid.

Phosphate rock is charged into a sintering oven, where it is nodulized to facilitate escape of phosphorus vapors in the electric furnace and to prevent the entrainment of dust or fines (in the vapors). The raw material is sized, and the fines are returned to the sintering oven. Coke (generally in the form of breeze) and sand are added in carefully controlled ratios, determined by rock analysis, to the sintered rock, and the mixture is charged into the shaft of an electric furnace. In the shaft hang three carbon electrodes, which are connected to a three-phase alternating current. The charge, on reaching the level of the arc, is fused at approximately 2,400°F, resulting in the reduction of the phosphate rock with liberation of elemental phosphorus vapors. Since phosphate rock usually contains fluorides as impurities, calcium fluoride and fluosilicates are also formed. The slag (mostly calcium silicate) from the furnace is usually tapped periodically and subsequently crushed for use as aggregate for road construction. Ferrophosphorus (resulting from the iron impurities) runs out with the slag. The amount of this material produced may be increased by adding iron slugs to the furnace charge. The ferrophosphorus is separated from the slag and marketed.

The gases from the furnace, phosphorus and carbon monoxide, are withdrawn from the furnace by means of a fan. In the one-step system, a current of air is drawn down through the charge by the suction induced by the fan. The two-step method produces phosphorus, which is stored for subsequent processing (see *Phosphorus*). The two currents (reaction gases and air) mix in the flue at a temperature sufficient to burn the phosphorus to phosphorus pentoxide (P_2O_5) and the carbon monoxide to the dioxide. The gases pass into a tall packed tower, where they are sprayed with water (forming a mist of phosphoric acid), and thence through a Cottrell electrostatic precipitator made of graphite (to resist the action of hydrofluoric acid) to remove any remaining phosphoric acid.

The crude phosphoric acid (85 per cent) is generally purified with respect to arsenic by the action of hydrogen sulfide. Depending on conditions, the acid may be purified further by adding sulfuric acid to remove calcium salts. Sufficient sulfuric acid is used to precipitate calcium sulfate and also to leave a slight excess to inhibit the corrosive action of the phosphoric acid. This slight excess of sulfuric acid permits the use of lead-lined equipment. Residual hydrofluoric acid may be removed by the addition of finely powdered silica. These purification steps usually take place before arsenic removal. The excess silica, calcium sulfate, arsenic trisulfide, and any suspended material are removed by passage of the acid through a sand filter. The clarified phosphoric acid (85 per cent) may be diluted with water to yield 75 per cent and 50 per cent acid. An over-all yield of about 90 per cent is realized on the calcium phosphate content of the rock raw material.

From Phosphate Rock by Blast Furnace



Reaction

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 2P + 5CO + 3CaSiO_3$$

$$2P + 5CO + 5O_2 \rightarrow P_2O_5 + 5CO_2$$

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

85–90% yield

Material Requirements

Basis—1 ton phosphoric acid (100% H_3PO_4)
(equivalent to 72% P_2O_5)

Phosphate rock (27% P_2O_5)	5,050 lb	Coke	7,000 lb
Sand (silica)	1,500 lb	Briquette binder	500 lb
		Air	450,000 cu ft

Process

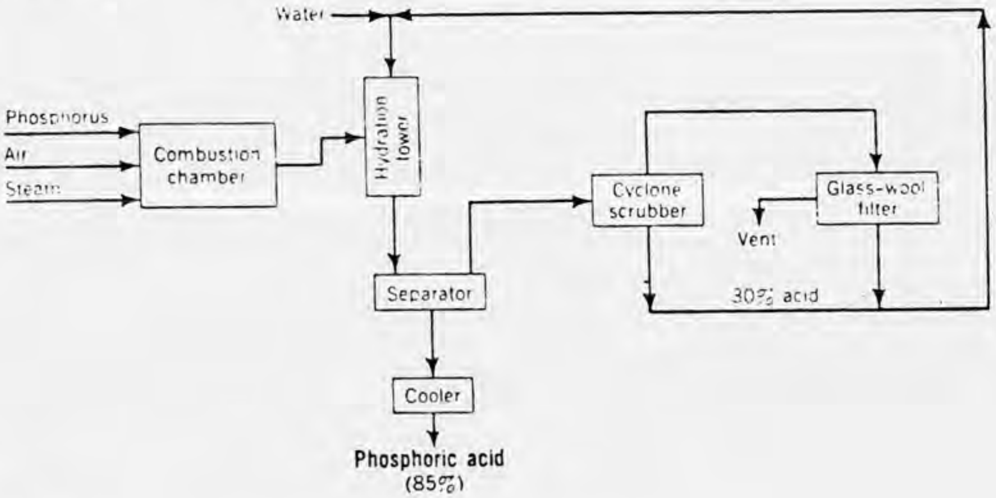
The raw materials and reactions in the blast-furnace process are essentially the same as those of the electric-furnace process. The shaft furnace used is similar in appearance to the blast furnaces used by the steel industry.

Phosphate rock is pulverized and mixed with ground coke, which serves as the reducing agent. A binder is added, and the mixture is compressed at about 5,000 psi into briquettes, which are dried (to a moisture content of less than 1 per cent) in a continuous dryer. The briquettes, sand (as flux), and additional coke are charged into the top of the shaft of the blast furnace. Preheated air (from the hot blast stoves) is blown in at the bosh (the lower part of the furnace). The blast develops a temperature of 2,400 to 2,500°F, which furnishes the necessary reaction heat. Slag (consisting chiefly of calcium silicate) is tapped from the furnace hearth once an hour, and the heavier ferrophosphorus (formed from the iron impurities in the rock and coke) is tapped every 12 hr.

The gas, containing phosphorus, carbon monoxide, and nitrogen, passes from the top of the shaft through cyclone dust collectors and special fume collectors. The clean gas may be split into two or three portions. One portion may be passed through phosphorus condensers to produce the elemental product and anhydrous phosphorus pentoxide. See *Phosphorus* for details. A second portion may be passed into special boilers for steam generation. The phosphorus pentoxide formed in the steam boiler is added to the main gas stream.

The third portion (generally the largest) is passed into hot blast regenerative stoves, where it is oxidized to phosphorus pentoxide. The stoves furnish the preheated air for the furnace blast. The gaseous products from the stoves and steam boilers are led into hydrating towers for hydration and cooling and thence through Cottrell precipitators for entrained phosphoric acid removal. The condensed acid (85 to 95 per cent H_3PO_4) may be purified (arsenic removed) by treatment with hydrogen sulfide and subsequent filtration. About 95 per cent of the phosphorus in the rock raw material is volatilized, giving a yield of about 90 per cent based on the phosphorus pentoxide content of the raw material and product.

From Phosphorus by Oxidation and Hydration



Reaction

$$2P + 2\tfrac{1}{2}O_2 \rightarrow P_2O_5$$

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

94–97% yield

Material Requirements

Basis—1 ton phosphoric acid (100% H_3PO_4)

Phosphorus	665 lb
Air	46,000 cu ft (STP)
Steam and water	Variable

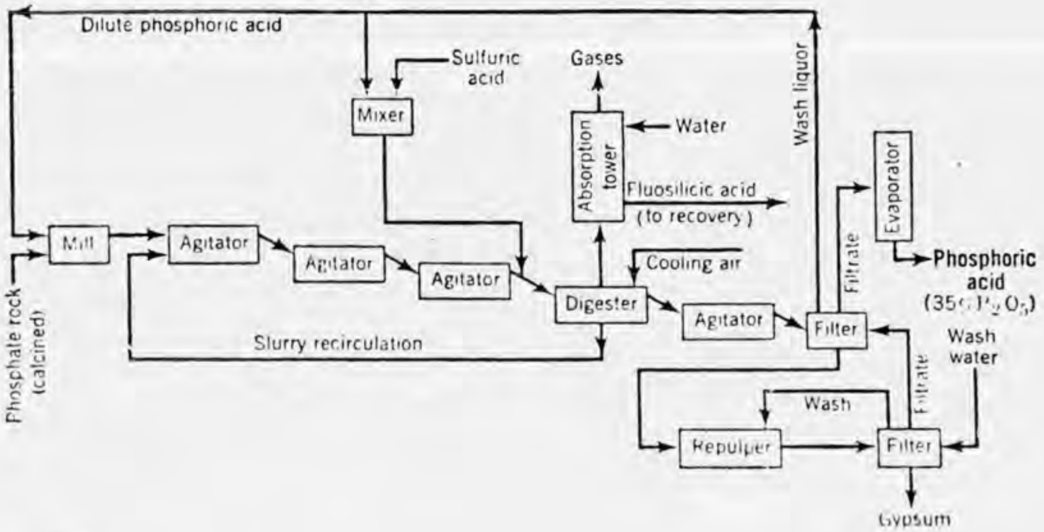
Process

Elemental phosphorus is often converted to phosphoric acid at locations other than the original point of production. The conversion involves oxidation of molten phosphorus to phosphorus pentoxide and subsequent hydration of the oxide to phosphoric acid.

Molten phosphorus is sprayed into a combustion chamber along with air and steam. Flame temperature approaches 3,600°F. Chamber design varies from one plant to another, but construction materials are usually limited to acid-proof brick, structural carbon, and stainless steel. Both vertical and horizontal chambers are used. In either case some glassy metaphosphoric acid is formed and drops to the bottom of the chamber.

The effluent gases leaving the chamber (P_2O_5, steam, nitrogen, and some oxygen) are mixed with a spray of dilute phosphoric acid in the hydration tower. If the tower is externally cooled, it too may be built of stainless steel. By proper adjustment of reacting streams, various strengths of phosphoric acid (as high as 116 per cent—equivalent to 84% P_2O_5) may be produced. The usual product is in the range of 75 to 85% H_3PO_4. Some acid mist leaves the hydrator and must be recovered by appropriate means, such as packed tower or electrostatic precipitators. In the process shown in the flow diagram a combination cyclone scrubber and glass-wool filter is used.

From Phosphate Rock by Dorr Strong-Acid Process



Reaction

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4 \cdot 2H_2O)$$

92–93% yield

Material Requirements

Basis—1 ton phosphoric acid (100%)

Phosphate rock (70 BPL)	4,880 lb
[illegible]	[illegible]

Process

The sulfuric acid or wet process produces phosphoric acid by the action of sulfuric acid on phosphate rock accompanied by the precipitation of calcium sulfate.

Phosphate rock is charged into a special ball mill, where it is ground in a dilute solution of phosphoric acid obtained as a filtrate from an ensuing operation. The slurry passes through a series of Dorr agitators, where reaction with sulfuric acid takes place. Separation of the resulting acid from the calcium sulfate precipitate, as well as washing of the precipitate, is carried out in a continuous-countercurrent decantation system.

The reaction system consists essentially of five agitators in series. Concentrated sulfuric acid (94 per cent), diluted with weak phosphoric acid, is introduced between the third and fourth agitators. The reaction takes place chiefly in the fourth agitator (the digester). The heat of reaction is considerable and is removed by blowing cooling air through the solution. As a result an appreciable amount of water is evaporated. The air, water vapor, and gaseous impurities are carried off into an absorber where fluosilicic acid (H_2SiF_6) is recovered by spraying the gases with water. A considerable portion of the reaction mixture is recycled from the fourth agitator (digester) back to the first agitator. The rate of recycle is adjusted to maintain correct sulfuric acid concentration and reaction time. The proper reaction time promotes formation of large crystals of calcium sulfate (gypsum) and facilitates subsequent filtration and washing operations. The temperature in the digester is maintained low enough to insure precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) rather than anhydrite ($CaSO_4$), which would subsequently hydrate and cause pipe plugging.

The slurry from the digester passes through the fifth agitator to a continuous rotary filter. The filtrate is finished phosphoric acid (about 45 per cent), which may be further concentrated by evaporation. Wash liquor from the filter is a dilute solution of phosphoric acid, which is used to dilute the sulfuric acid and to charge the ball mill.

The filter cake, after washing, is charged into a tank where it is repulped with wash liquor from a second filter in which the repulped slurry is filtered. Filtrate from this filter serves as the wash liquor for the first one. The second filter cake is washed with fresh hot water. The washed filter cake, gypsum, is discharged to waste.

The filtrate from the first filter (phosphoric acid) is charged into lead-lined evaporators containing lead steam coils. The acid is generally concentrated to 35°Bé, at which gravity it contains about 35 per cent P_2O_5 (approximately 50 per cent H_3PO_4). It may be concentrated to 70 per cent acid or to a specific gravity of 50°Bé (50 per cent P_2O_5). The evaporator must be operated below 150°C, because above this temperature orthophosphoric acid (H_3PO_4) is slowly converted into pyrophosphoric acid ($H_4P_2O_7$). By means of the process described, about 95 per cent [illegible] pentoxide content of the rock is dissolved, and, of this, 97 to 98 per cent is recovered as product.

Other Wet Processes

Several modifications of the wet process described have recently been of interest. In the *Prayon* process, ground phosphate rock is treated with sulfuric acid under conditions of temperature and concentration that yield calcium sulfate crystals of predetermined size (150 microns). The calcium sulfate is separated from the acid and washed thoroughly in a continuous horizontal rotary vacuum filter of special design. The phosphoric acid filtrate (32% P_2O_5) may be further concentrated or used as is.

In the *clinker* process, ground, dried phosphate rock is mixed with only a slight excess of 98 per cent sulfuric acid to yield a putty-like solid. The pasty mass is heated to 200 to 240°C for 20 to 60 minutes to give a hard porous clinker. The clinker may be countercurrently extracted with hot water to give phosphoric acid of 49%–50% P_2O_5 concentration. Yield is said to be 92 to 95 per cent.

Other Phosphorus-Containing Acids. Phosphoric acid (H_3PO_4) may be converted into pyrophosphoric acid ($H_4P_2O_7$) and metaphosphoric acid (HPO_3) by heating. Pyrophosphoric acid is formed at 250 to 260°C. On heating either the ortho- or pyro- to a red heat, metaphosphoric acid is formed. The latter may also be prepared by treating phosphorus pentoxide with the calculated amount of cold water.

Raw Material

Phosphate rock, also known as rock phosphate, phosphorite, and raw phosphate, is the primary source of practically all phosphatic chemicals. The rock is obtained chiefly from deposits in Florida, Tennessee, and the Western States. These deposits are classified roughly as residual, replacement, and sedimentary. Residual phosphate (for example Tennessee brown rock) is derived from phosphatic limestone. Replacement phosphate (for example Florida soft rock) is phosphatized limestone formed by the reaction of limestone and phosphoric acid of organic origin. The sedimentary phosphates, believed derived from marine organisms, are the principal deposits of which Florida land pebble, Florida hard rock (boulder phosphate) and river pebble are the chief varieties. The sedimentary deposits occur in irregular pockets of many sizes embedded in clay or sand. Western phosphates, usually found in fissure veins between walls of limestone and clay or shale, are mined by underground methods. The Florida and Tennessee phosphates are found usually in surface deposits and are worked by open-cut mining methods.

Virtually all commercial deposits of phosphate rock are amorphous, impure varieties of the mineral, fluorapatite ($Ca_{10}(PO_4)_6F_2$). The workable deposits contain from 18 to 90 per cent available tricalcium phosphate, $Ca_3(PO_4)_2$, known to the trader as BPL (bone phosphate of lime), and are

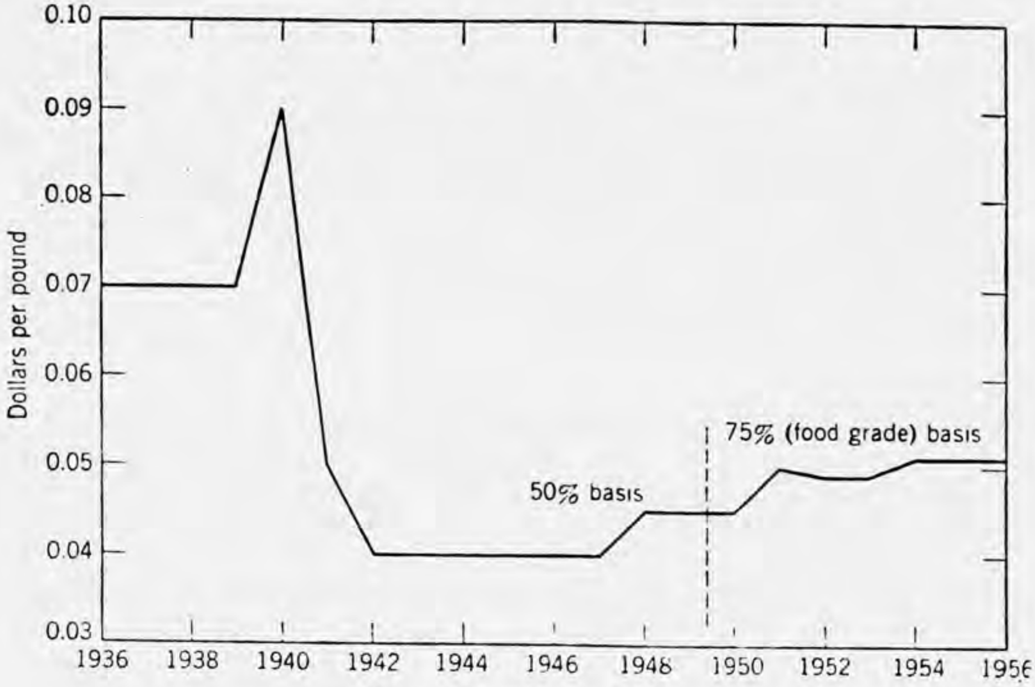
BPL, and approximately three fourths of the phosphate rock marketed contains between 70 and 76 per cent BPL. Inferior rock is processed by beneficiation procedures to raise the BPL content of the rock.

The chief impurities in domestic phosphate rock are iron, aluminum, and silicon oxides, as well as calcite, magnesite, dolomite, sand, clay, and organic matter. Most of the undesirable impurities are removed in the washing and sintering operations prior to phosphoric acid manufacture.

Production—Phosphoric Acid

Use Pattern

	1955 (est.), per cent
Fertilizer	52
Soaps and detergents	28
Animal feed	5
Food and beverages	4
Water conditioning	2
Metal cleaning	2
Misc. and export	7
	100



Price—Phosphoric Acid

Miscellaneous

Properties. Colorless, crystalline solid.

Mol. wt.	98.00	M.P.	42.35°C
Sp. gr.	1.834 (18.2°C)	B.P.	Loses ½H_2O at 213°C

Soluble in water (2,340 g per 100 ml at 20°C), and alcohol.

Commercial phosphoric acid is a clear, colorless, sparkling, mobile liquid which reaches sirupy consistency at higher concentrations (85 per cent). At 88 per cent concentration, a crystalline hydrate, $H_3PO_4 \cdot \frac{1}{2}H_2O$, separates at room temperature.

Grades. Technical (50, 75, and 85 per cent), food (50 and 75 per cent), USP (10 and 85 per cent), 90 per cent acid, 100 per cent acid (75 per cent P_2O_5), and commercial (47 and 54 per cent P_2O_5).

Containers and Regulations. Rubber-lined tank cars, tank trucks, drums, barrels, glass carboys, casks, and bottles. White ICC shipping label required.

Economic Aspects

The technology of phosphoric acid manufacture has undergone several distinct yet overlapping changes in the past 35 years. These are: (1) the shift from wet-process methods to the electric-furnace process beginning in 1920 with purer, cheaper acid as a result; (2) a shift in plant sites occasioned by development of phosphate rock deposits in the Rocky Mountain area; (3) a concurrent shift of some manufacturing facilities away from locations near the raw material to locations closer to the market (by shipment of elemental phosphorus to the point of use); and (4) a renaissance of

Phosphoric Acid The name phosphoric acid commonly refers to orthophosphoric acid, H_3PO_4. Anhydrous orthophosphoric acid is a white, crystalline solid, which melts at 42.35°C. It forms a hemihydrate, $2H_3PO_4 \cdot H_2O$, which melts at 29.32°C. Although it is possible to produce almost any desired concentration, it is common practice to supply the material as a solution containing from 75% H_3PO_4 (melting point = 17.5°C) to 85% H_3PO_4 (melting point = 21.1°C).

When phosphoric acid is heated to temperatures above about 200°C, water of constitution is lost. A series of acids is formed by the dehydration, ranging from pyrophosphoric acid, $H_4P_2O_7$, to metaphosphoric acid, $(HPO_3)_n$. Salts of the dehydrated acids are used for the preparation of certain types of liquid fertilizers and are present in many detergents in percentages up to 40%. The dehydrated acids can form water-soluble complexes with many metals, such as calcium.

One, two, or three of the hydrogens in phosphoric acid may be neutralized. When one hydrogen is replaced with sodium, the product is slightly acid, while replacement of all three hydrogens produces a highly alkaline product. The three compounds are:

	pH of 1% Solution
Monosodium phosphate, NaH_2PO_4	4.0
Disodium phosphate, Na_2HPO_4	8.3*
Trisodium phosphate, Na_3PO_4	12.0

*Not fully certain

Other phosphorous acids of little commercial significance are hypophosphorous acid, H_3PO_2; orthophosphorous acid, H_3PO_3; and pyrophosphorous acid, $H_4P_2O_5$.

Since phosphorus is essential for plant and animal life, large quantities are used, either directly or indirectly, for food production. Bones contain high percentages of tricalcium phosphate.

Uses: Total production of H_3PO_4 in the United States amounts to about 5 million tons of contained P_2O_5, while world production is estimated to be close to 10 million tons. Large quantities of phosphatic fertilizers are manufactured from phosphate rock by direct means, e.g., normal superphosphate, thus avoiding the production of H_3PO_4 as a separate material. See also **Fertilizers.**

About 80% of United States production is wet-process acid, most of which is subsequently converted into calcium phosphates or ammonium phosphates for fertilizer. Another major use is the production of sodium and potassium phosphates, either ortho or dehydrated, for use in detergents and cleaning and boiler compounds. Phosphoric acid is used as such for metal-surface treatment and in soft drinks. Other uses include the preparation of calcium phosphates for food supplements, phosphates for use in baking, and ammonium phosphates for fireproofing. Phosphates are also included in other materials, e.g., insecticides, lubricating-oil additives, toothpaste and other polishing compounds, and certain types of glass.

Raw Materials and Manufacture: The major sources of H_3PO_4 are mineral deposits of phosphate rock. Mining operations are extensive in the United States, the Mediterranean area, and Russia, with smaller operations in many other countries. Known deposits can supply world requirements for many centuries.

The major constituent of most phosphate rocks is fluorapatite, $3Ca_3(PO_4)_2 \cdot CaF_2$. Commercial rocks contain 30–38% P_2O_5 plus a variety of impurities. Of these, iron, aluminum, magnesium, silica, carbon dioxide, sodium, potassium, and sulfates may be present in appreciable quantities.

Two major methods are utilized for the production of phosphoric acid from phosphate rock. The *wet process* involves the reaction of phosphate rock with sulfuric acid to produce phosphoric acid and insoluble calcium sulfates. Many of the impurities present in the phosphate rock are also solubilized and retained in the acid so produced. While they are of no serious disadvantage when the acid is to be used for fertilizer manufacture, their presence makes the product unsuitable for the manufacture of phosphatic chemicals.

In the other method, the *furnace process*, phosphate rock is combined with coke and silica and reduced at high temperature in an electric furnace, followed by condensation of elemental phosphorus. Phosphoric acid is produced by burning the elemental phosphorus with air and absorbing the P_2O_5 in water. The acid produced by this method is of high purity and suitable for all uses with little or no treatment.

Wet Process: There are a number of proprietary processes for the manufacture of phosphoric acid. Figure P-13 is a flow sheet for a modern plant, which can be designed for capacities of up to 1,000 tons of P_2O_5 (1,100 tons of H_3PO_4) per day in a single unit. The basic reaction in this process is

$$3Ca_3(PO_4)_2 \cdot CaF_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 6H_3PO_4 + 2HF \quad (1)$$

Numerous side reactions also occur.

Phosphate rock and sulfuric acid, together with recycled weak liquors, are carefully metered to a large, stirred reactor, providing 4–8 hr retention. Conditions in the reactor are carefully controlled to maintain preselected conditions. Typical control levels are as follows:

Temperature, °C	77–83
Acid concentration, %	29–32 P_2O_5 (40–44% H_3PO_4)
Solids, %	34–40
Dissolved sulfates, %	1.5–3 (H_2SO_4)

Temperatures are controlled by removing the excess heat of reaction with a vacuum cooler or by blowing air through the phosphoric acid slurry.

The slurry, which contains precipitated gypsum, is sent to a filter, commonly a large, horizontal rotary-pan-type unit. The first filtrate is sent to further treatment or use. The gypsum is washed with water in several countercurrent steps, and weak liquor is returned to the reaction stage.

For most uses, the acid requires further concentration, normally done in vacuum evaporators,

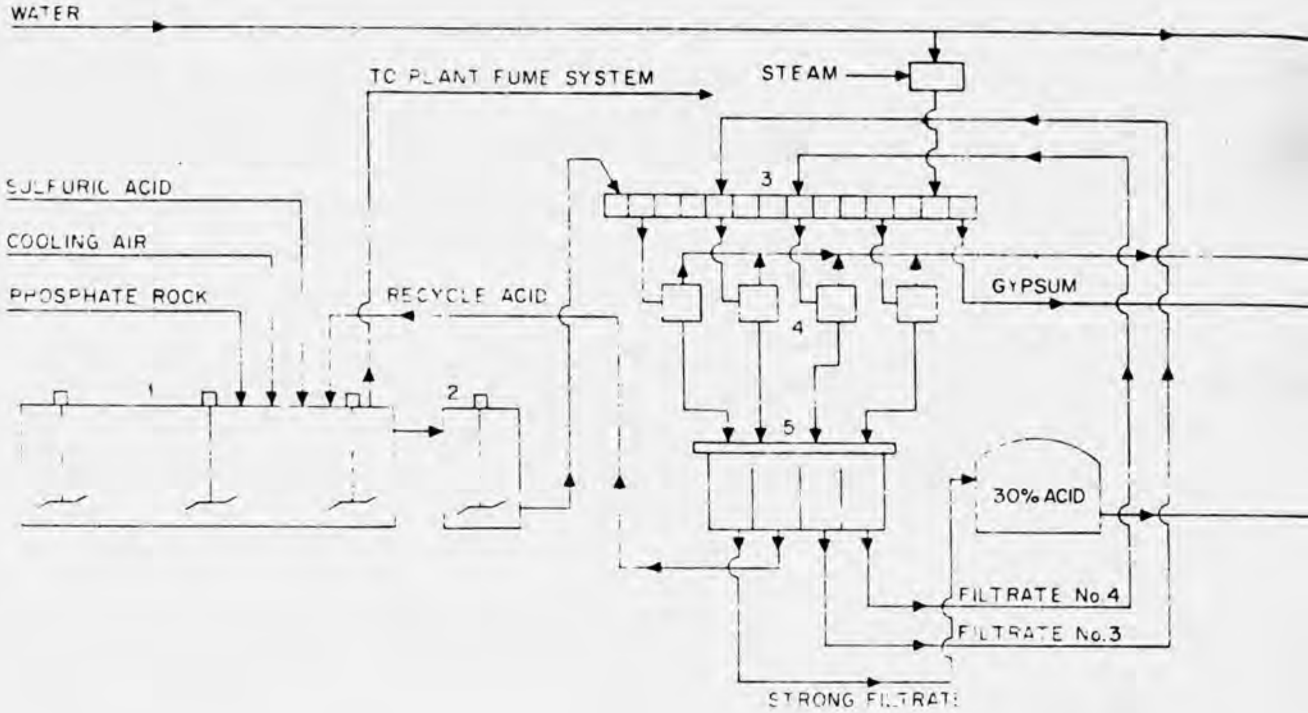


Fig. P-13. Phosphoric acid production and concentration by the wet process. (1) Digester, (2) filter feed tank, (3) filter, (4) filtrate receiver, (5) filtrate tank, (6) condenser, (7) concentrator.

operating at 2-5 in. Hg abs. Merchant-grade acid for shipping is generally concentrated to about 54% P_2O_5 (75% H_3PO_4). See also **Evaporation.**

The highly corrosive nature of the ingredients requires corrosion-resistant materials. Rubber-lined steel is frequently used for vessels and large piping. Reactors are sometimes constructed of concrete, with a rubber or mastic corrosion barrier. Carbon brick is often used to protect linings. Pumps, agitators, and other metal parts are stainless steel. Various types of plastic may be used for piping, small vessels, and other specialized equipment.

Effluents and gypsum disposal pose problems. Fluorine is evolved at various steps in the process, and scrubbers are required to reduce release to the atmosphere to acceptable levels. In the United States this is usually about 20 lb/day for large plants. Gypsum is frequently piled in diked areas or dumped into abandoned mines. In a few cases, it may be disposed of in rivers or in the ocean.

Waste water from the plant is heavily contaminated with fluorine, phosphates, sulfates, and other compounds. It is commonly impounded in large ponds, where a portion of the contaminants may precipitate or be lost by other processes. The cooled effluent from the ponds is recycled to the production unit. Any excess water must be treated with lime before it can be allowed to enter streams.

Recent developments include plants designed to precipitate the calcium sulfate in the form of the hemihydrate instead of gypsum. In special cases, hydrochloric acid is used instead of sulfuric for rock digestion, the phosphoric acid being recovered in quite pure form by solvent extraction. Solvent-extraction methods have also been developed for the purification of merchant-grade acid, which normally contains impurities amounting to 12-18% of the phosphoric acid content. Processes for recovering part of the fluorine in the phosphate rock are in commercial use.

Material and other requirements for the production of 1 ton of P_2O_5 in the form of acid containing 75% H_3PO_4 are shown in Table P-26.

Electric-Furnace Process. This process is more expensive than the wet process but has the advantage of producing acid of high purity. A single electric furnace may have a capacity of up to 300 tons/day of P_2O_5, but many installations consist of several furnaces.

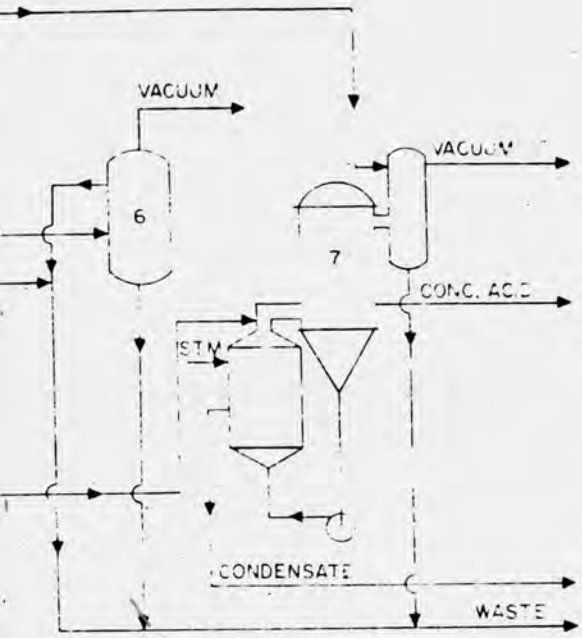


TABLE P-26. *Materials and Energy Requirements for Production of 1 Ton of P_2O_5 by Wet Process*

Phosphate rock, tons	3.0–3.5
Sulfuric acid, tons	2.6–3.0
Electric power, kWh	100–140
Water, gal	20,000–30,000
Steam, lb	4,500–5,000
Waste gypsum, $CaSO_4 \cdot 2H_2O$, tons	4.6–5.2

Figure P-14 is a simplified flow sheet of an electric-furnace plant. A mixture of coke, silica, and phosphate rock is formed into nodules by heating in a nodulizing kiln, and the resulting lump material is transferred to the electric furnace, where it is heated with an electric current introduced by means of graphite electrodes. The entire charge is melted, and elemental phosphorus is volatilized. The slag is tapped off intermittently, while the phosphorus vapor is condensed.

The liquid phosphorus is then sent to the acid plant and burned with air to form P_2O_5. The acid anhydride is absorbed in water to form phosphoric acid.

The reactions involved are basically

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4 + 10CO + 6CaSiO_3 \quad (2)$$

$$P_4 + 5O_2 \rightarrow 2P_2O_5 \quad (3)$$

$$P_2O_5 + 3H_2PO \rightarrow 2H_3PO_4 \quad (4)$$

Typical requirements for the production of 1 ton of P_2O_5 in the form of phosphoric acid are shown in Table P-27. The by-product slag is usable for light-weight building aggregate, road construction, and other minor uses.

Storage and Handling: H_3PO_4 is a strong acid, and contact with body or tissues may result in

TABLE P-27. *Materials and Energy Requirements for Production of 1 Ton of P_2O_5 by Electric-Furnace Process*

Phosphate rock, tons	3.6–4.2
Coke, tons	0.6–0.7
Silica, tons	0.7–1.3
Carbon electrodes, lb	20–30
Water, gal	18,500–20,000
Electric power, kWh	5,500

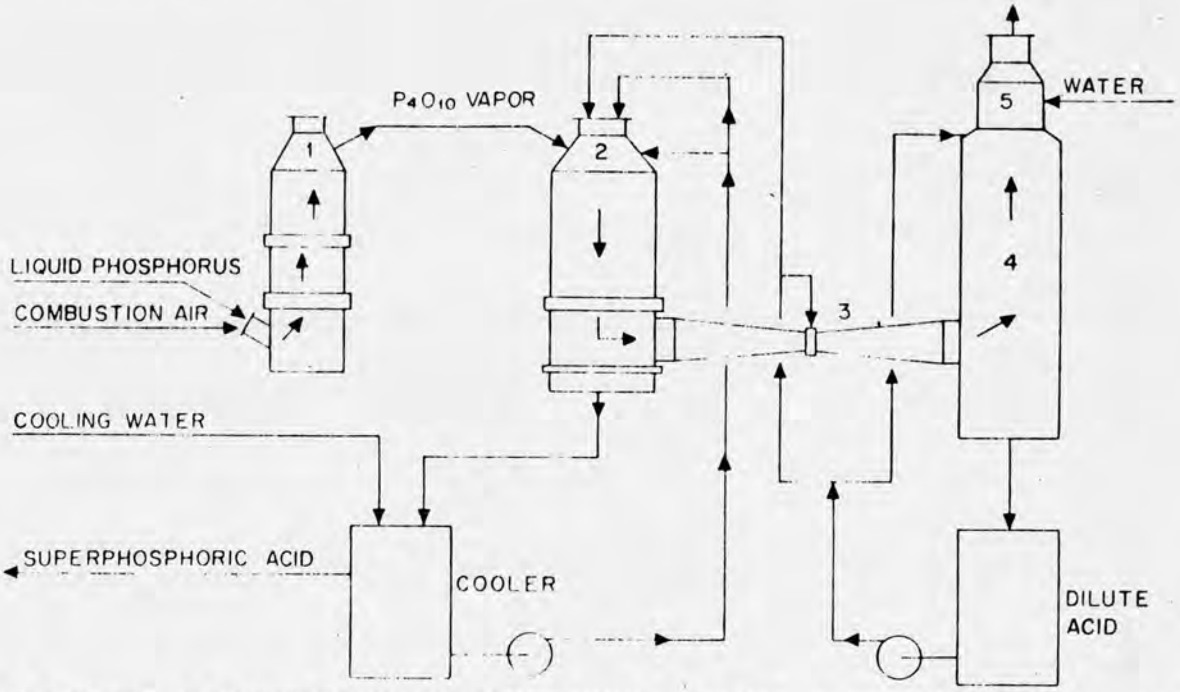


Fig. P-14. Phosphoric acid production by the electric-furnace process. Production of elemental phosphorus is not shown (see Fig. P-15). (1) Combustion chamber, (2) hydrator, (3) venturi scrubber, (4) separator tower, (5) mesh demister.

severe burns. Precautions similar to those used for handling sulfuric acid should be employed. Phosphoric acid exhibits no peculiar or systemic toxicity, and any damage is attributed to its corrosive nature.

Phosphoric acid is commonly shipped and stored in rubber-lined equipment, including tank trucks, tank cars, and specially designed ships. Stainless-steel and polyethylene containers are also used. Wet-process acid, which contains fluorine, may be corrosive to glass or coatings containing silica.

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Phosphatic Fertilizers: Properties and Processes, *Sulphur Inst. Tech. Bull.* 8, 2d ed., Washington 1966.

Phosphorus: Properties of the Element and Some of Its Compounds, *TVA Chem. Eng. Rep.* 8, 1950.

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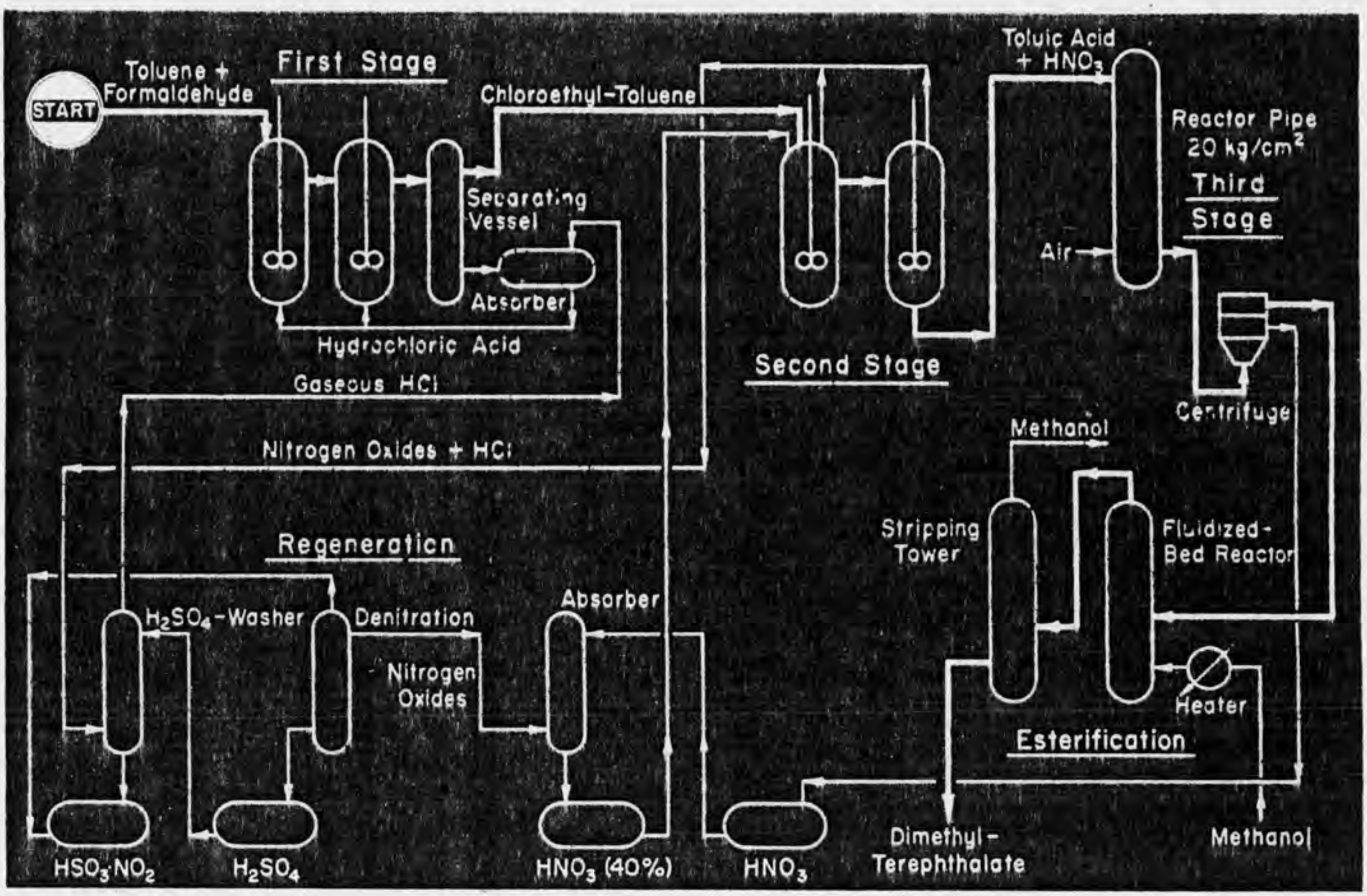
William A. Lutz, *Consulting Engineer, Louisville, Ky.*, and Enrico Pelitti, *C & I/Girdler Incorporated, Louisville, Ky.*



Terephthalic Acid — BERGBAU-FORSCHUNG

Application: A process for producing benzene carboxylic acids using toluene for terephthalic acid and xylene for pyromellitic acid.

Charge: Toluene, xylene, formaldehyde, HCl and nitric acid.

Products: Terephthalic acid, pyromellitic acid, phthalic acid and other carboxylic acids depending on charge materials and extent of processing.

Description: For the manufacture of terephthalic acid the process proceeds as follows:

First Stage: Toluene at 70° C is reacted with concentrated HCl and stoichiometric quantities of paraformaldehyde to obtain chloromethylation of about 98 percent of the toluene in two hours. Concentrated HCl (more than 33 percent) with an excess of CH_2O is circulated and the chloromethyl toluene (57 percent *p*—, 43 percent *o*—) is separated from the aqueous HCl. The HCl is reconcentrated by adding hydrogen chloride recovered by the oxidation and recycled.

Second Stage: The chloromethyl toluene is mixed with 40 percent HNO_3 and heated for one hour to 90° C resulting in a mixture of chlorine free toluic acid and HNO_3. Effluent gases are washed with H_2SO_4, nitrogen oxide going to nitrosesulfuric acid which is recovered as HNO_3 and recycled. HCl goes overhead from the H_2SO_4 washer and is also recycled.

Third Stage: After the second reaction stage the concentration of the HNO_3 is reduced for oxidation under pressure in the third stage. At a pressure of about 20 atms. and 160° C and with the addition of air, the reaction results in nitrogen oxide going to HNO_3 and an effluent of *o*-phthalic acid in solution with HNO_3 and insoluble terephthalic acid. The terephthalic acid is centrifuged and washed with water. This acid is practically free from N, Cl and *o*-phthalic acid. The *o*-phthalic acid may be recovered by recrystallization from the mother liquor.

An alternative route may be used which contacts the chloromethyl toluene with 5 percent lime milk at 120-130° C in an iron pressure reactor to convert it to methyl benzyl alcohol. HCl is lost as $CaCl_2$. The saponification product is immediately oxidized under the same conditions as the Third Stage. This alternative route of the Second Stage results in about 20 percent savings in total plant costs since the special equipment for separation of HCl and NO_2 are eliminated.

Esterfication: This step can be carried out in a newly developed fluidized bed process. Gaseous methanol, with a suitable catalyst, acts as fluidizing agent and reacting gas. The reaction mixture is separated in a stripping tower giving dimethyl terephthalate.

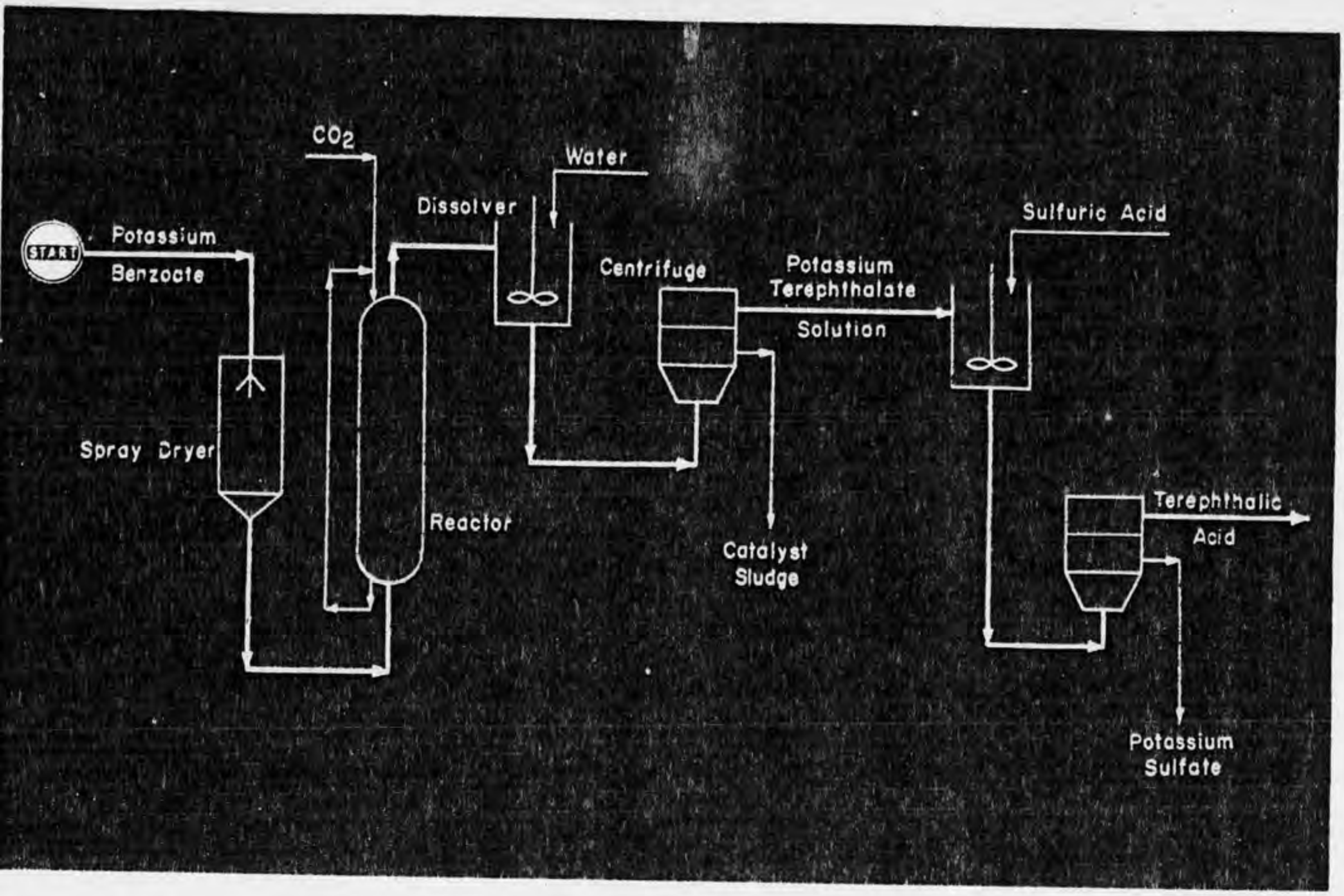
Operating Conditions: As described above.

Pilot Plant: Bergbau-Forschung operates a 200 kg pilot plant for dimethyl terephthalate. Consumption of materials for one ton of dimethyl terephthalate are:

1.0	Ton Toluene	0.5	Ton HCl (loss by saponification)
0.365	Ton Formaldehyde		
0.47	Ton HNO_3	0.4	Ton $Ca(OH)_2$
		0.375	Ton Methanol

credit can be taken for 0.7 tons of *o*-phthalic acid which is also produced.

References: U.S. Patent 2,966,514, German Patent DAS 1,082,893; 1,088,474; 1,102,128. Chemical Engineering June 13, 1960, p 71 and July 11, 1960, p 76.



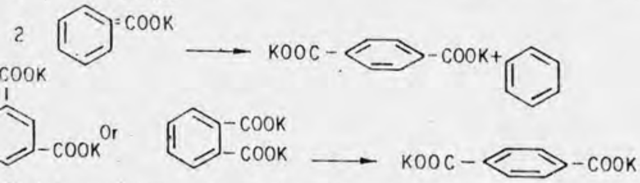
Terephthalic Acid— HENKEL & CIE

pplication: Process for making terephthalic acid.

harge: Benzoic acid, phthalic acid and other benzenecarboxylic cids, as alkali-metal salts, esp. potassium salts.

roduct: Terephthalic acid of high purity, especially suitable for aking polyester fibers.

escription: The alkali-metal salts of benzenecarboxylic acids are ansposed to terephthalates upon heating to temperatures above 50° C as follows.



Dried potassium salts of benzoic acid or of ortho- or iso- thalic acid are heated in anhydrous form to 400-430° C in the esence of a catalyst under an atmosphere of inert gas (CO_2). he reaction product is dissolved in water, the catalyst filtered f, and the terephthalic acid precipitated from the solution, for ample with dilute sulfuric acid.

A number of methods have been developed for recovering the tassium in a form in which it can be re-used directly.

For example, the terephthalic acid can be precipitated from e aqueous potassium terephthalate solution by means of the nzenecarboxylic acids used as starting materials, in which case e precipitation is preferably performed in two steps. In the st step, the less readily soluble monopotassium terephthalate precipitated. In the second step, it is converted into free ephthalic acid. Alternatively, the monopotassium terephthalate ay first be precipitated with carbon dioxide under pressure, d then reacted with the starting carboxylic acid in a second p.

uipment: The reaction may be carried on as a batch or con- uous process, using kiln, vortex-bed, continuous-belt or other ilar operation.

talyst: The most favorable catalytic activity is provided by lmium. The most advantageous forms are the benzoate, phthalate, oxide or carbonate. The corresponding zinc compounds have similar but weaker catalytic action. The cadmium is recovered from the filtered residue by roasting and appropriate beneficiation or by dissolving out with HNO_3.

Chemicals Used: If the potassium, catalyst and protective gas are recovered, the process requires no chemicals other than the starting material.

Operating Conditions: The best yields of terephthalic acid are obtained with the potassium salts. Sodium salts give poorer yields. However, an appreciable portion of the potassium may be replaced by sodium without seriously impaired yield.

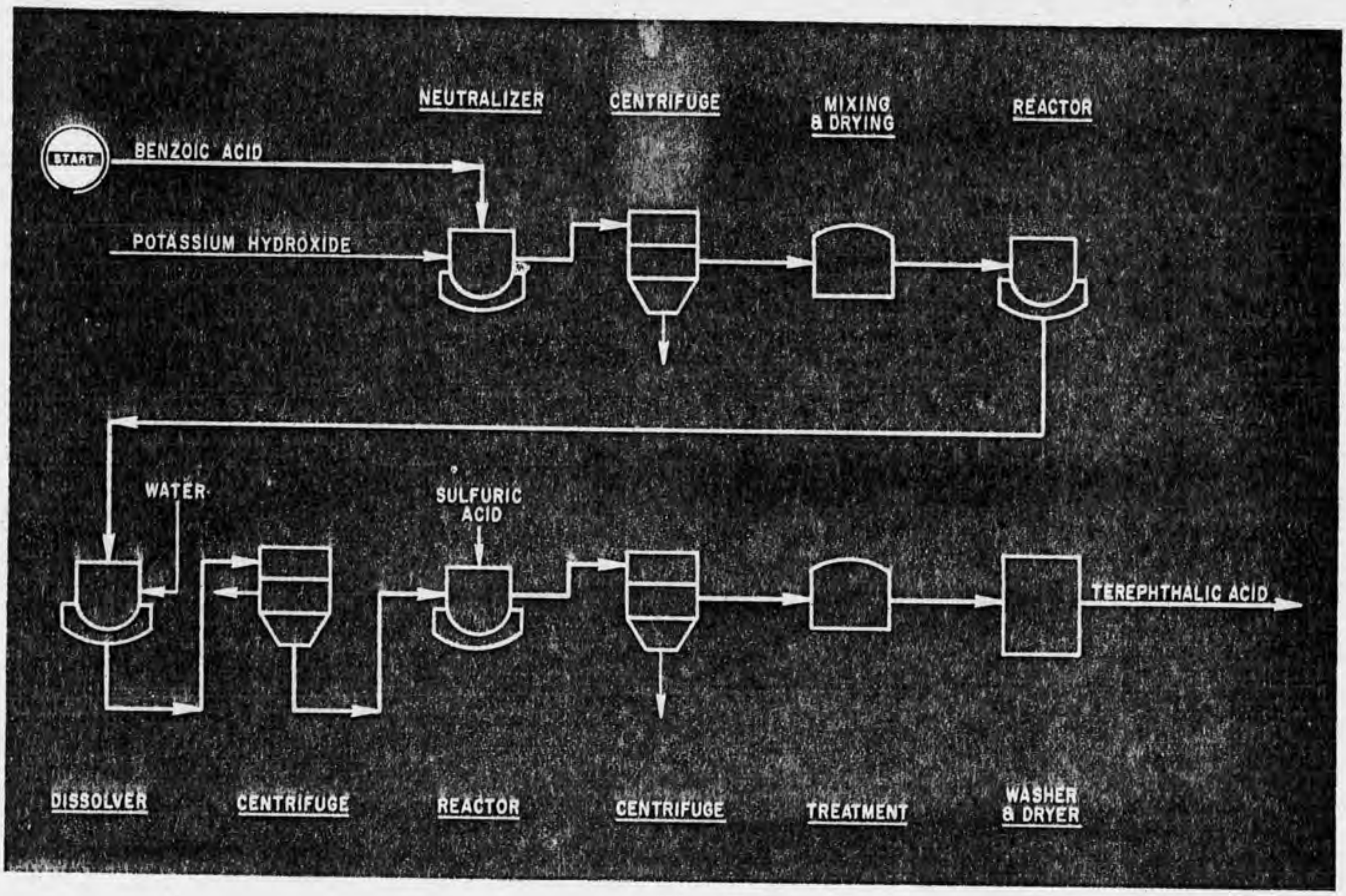
To obtain a high degree of conversion, sufficiently high temperature is essential. Although reaction begins at 350° C, temperatures above 400° C are required for commercial rates, optimum range being 410-430° C. Higher temperatures cause injurious side reactions.

Although good yields are obtainable at atmospheric pressure, the maximum yields are achieved with CO_2 under pressure. With Cadmium catalysts, 3 to 8 atm. is enough for the phthalate transposition; and 10 to 15 atm. for the benzoate reaction. Zinc catalysts require about twice the pressure. Other inert gases, such as nitrogen, give lower yields.

Water and compounds with active hydrogen atoms must be excluded from the reaction. In the preparation of the salts, therefore, care must be taken to see that equivalent quantities of starting materials are put in. Otherwise there will be diminution of yield by decarboxylation. Spray drying is most suitable for dehydrating the salts.

Yields: Under proper conditions, practically quantitative conversion is obtained, with terephthalic acid yields of 95-98 percent. The reaction product is free from ortho- and isophthalic acid. The terephthalic acid produced does not contain aldehydic or other by-products.

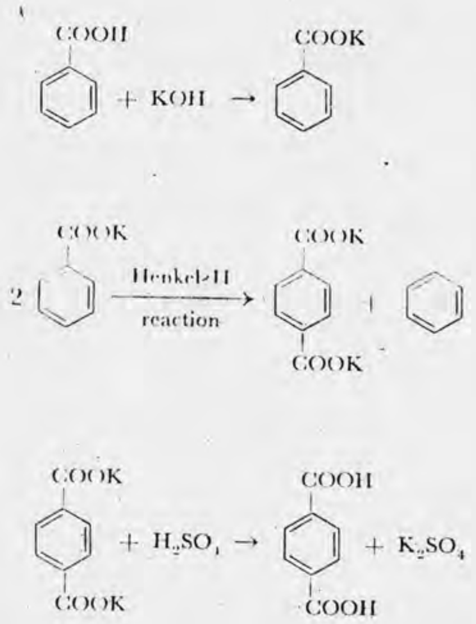
Commercial Installations: The process is in production in plants of Kawasaki Kasei Chemicals Ltd., Tokyo (Japan), and Teikoku Rayon Co. Ltd., Tokyo (Japan). A semi-commercial pilot plant is owned by the Badische Anilin- & Soda-Fabrik, Ludwigshafen-am-Rhein (Germany). The engineering know-how of the process is at the disposal of the Lurgi Gesellschaft für Mineralöltechnik m.b.H., Frankfurt-am-Main (Germany).



Terephthalic Acid— MITSUBISHI CHEMICAL INDUSTRIES LTD.

Application: A process for producing pure terephthalic acid from benzoic acid and potassium hydroxide.

Description:

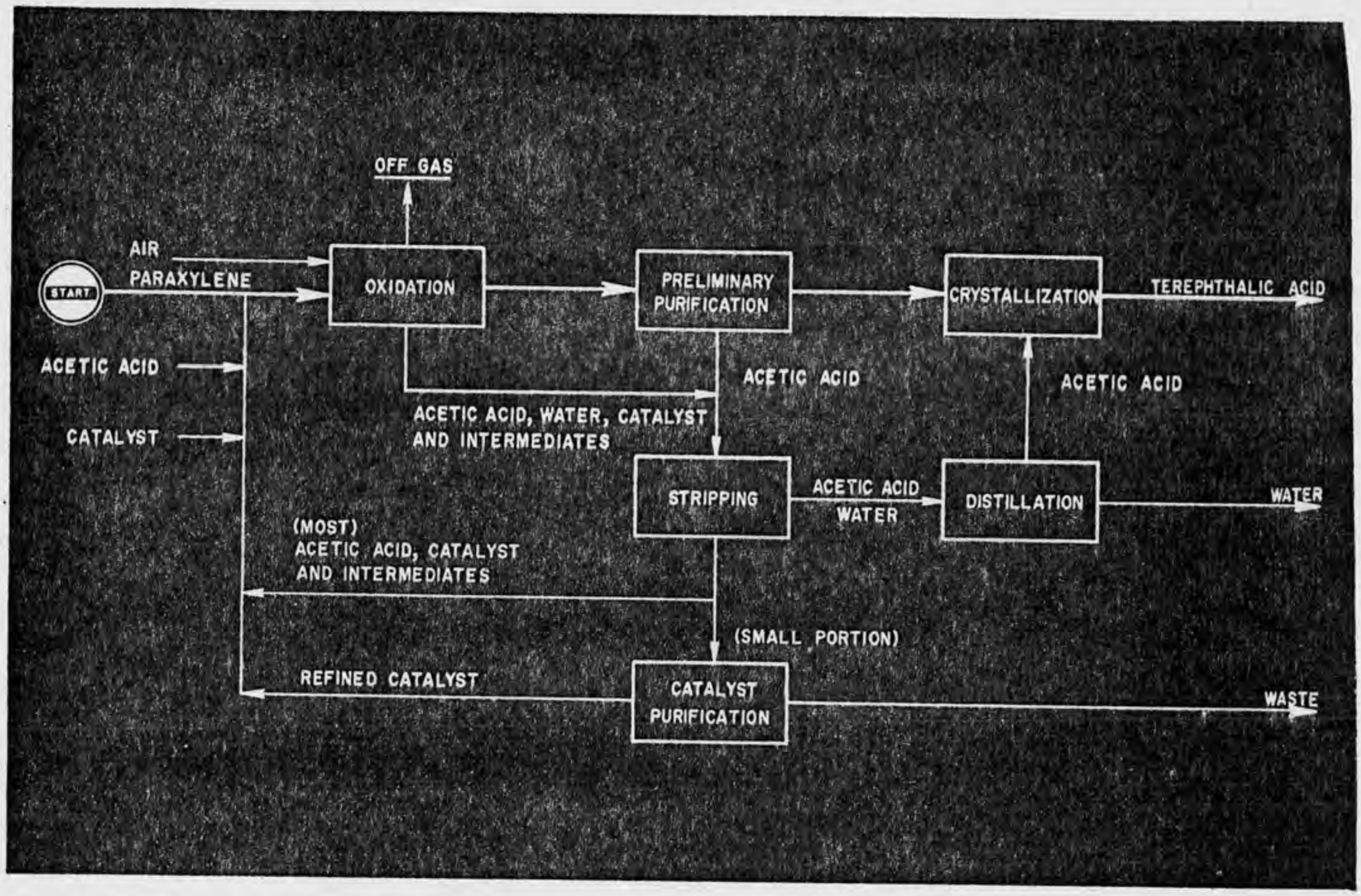


Mitsubishi Chemical Industries has developed a new technique to produce high-purity terephthalic acid which is used for direct polymerization with ethylene glycol.

This process features stable operation with continuous flow. The patent of Henkel II reaction is licensed by Messrs. Henkel & Cie. Mitsubishi Chemical Industries also has a process to produce benzoic acid by air oxidation of toluene.

Fibers made by direct polymerization of Mitsubishi's TPA are equivalent in quality to fibers made via dimethyl terephthalate and are easier to dye than fibers from TPA made by other processes.

Commercial Installation: MCI is the only manufacturer of pure TPA using the Henkel II process having a capacity of 25,200 tons annually.



Terephthalic Acid— TEIJIN LTD.

Application: A process for producing high-purity terephthalic acid (HP-TPA) by liquid phase oxidation of paraxylene with air, catalyst and acetic acid.

Description: The process consists of following three main sections:

Oxidation: Paraxylene, air, catalyst and acetic acid as solvent are charged to the liquid-phase oxidation reactor which is operated at a moderate temperature and pressure. The oxidation reaction can be carried out continuously in the presence of a considerable quantity of the cobalt compound catalyst. Crude TPA is separated from the mother liquor, which is composed of the catalyst, intermediate oxidates, water and solvent.

Purification: The crude TPA is slurried with more acetic acid and fed to a proprietary preliminary purification step. The pre-purified TPA is dissolved in acetic acid, crystallized, separated and dried to give the final, fiber-grade product.

Recovery: The mother liquors from the oxidation and purification section are fed to this section.

A portion of acetic acid and water are stripped from the mother liquor and acetic acid is purified by distillation and then recycled to the purification section.

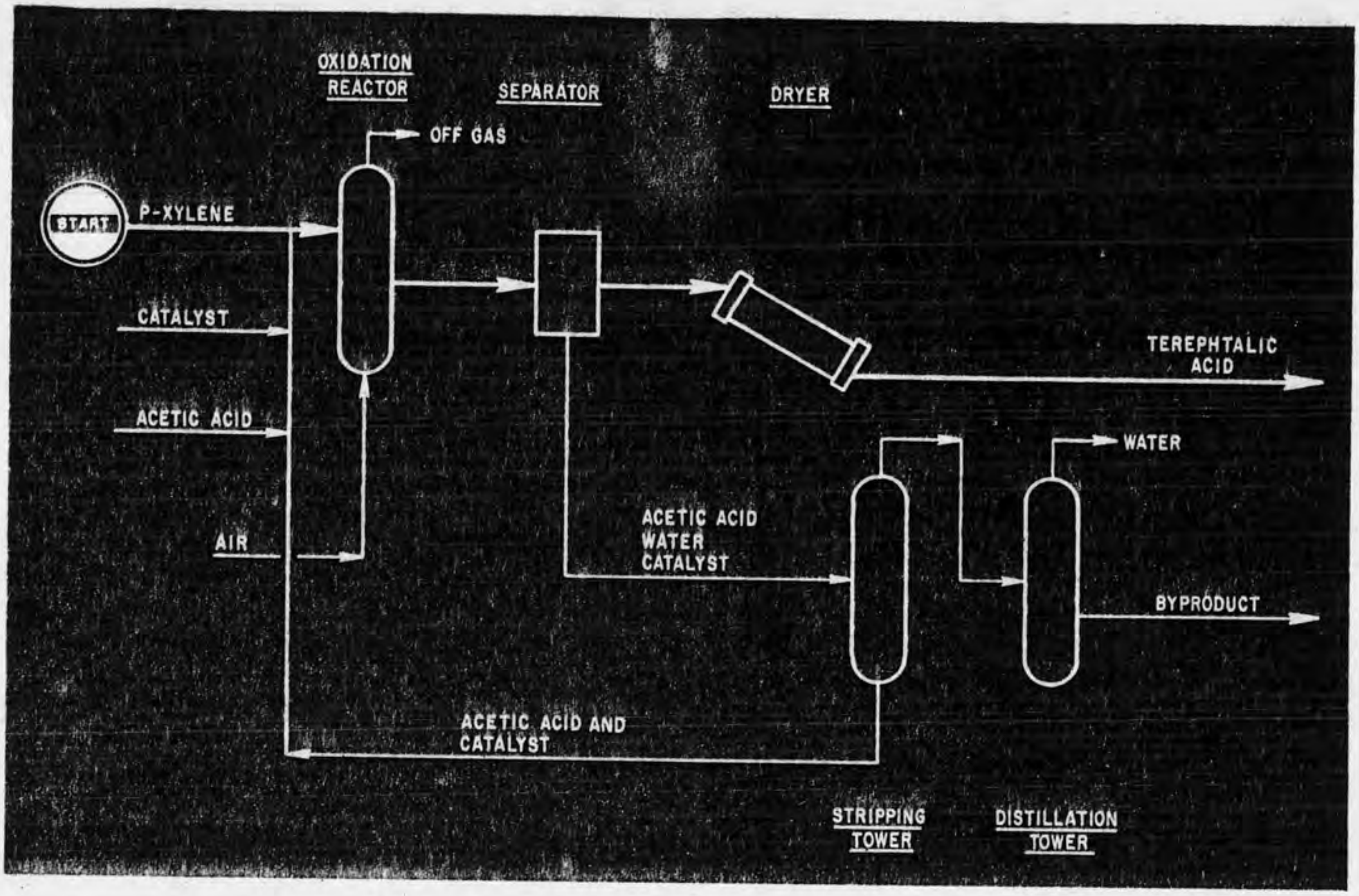
Most of the bottom products which contains acetic acid, the catalyst and the intermediate oxidates is circulated directly to the oxidation section and only a small portion of the bottom products is subjected to an effective catalyst purification for recirculation to the oxidation process. The catalyst, solvent and intermediate oxidates are recovered at a very high yield.

Consumption of Materials: Per 100 kg of HP-TPA:

para-xylene	65	kg
acetic acid	10	kg
catalyst	0.1	kg

Pilot Plant: Teijin operates a 100 kg/d plant for terephthalic acid.

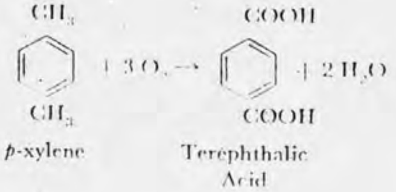
References: *European Chemical News,* Nov. 1, 32 (1968); *C&EN;* Oct. 14, 23 (1968); *Japan Chemical Quarterly,* V-1 29 (1969); *Chemical Engineering,* May 5, 78 (1969).



Terephthalic Acid— TOYO RAYON CO., LTD.

Application: A process for the manufacture of terephthalic acid by one-step liquid-phase air oxidation of *p*-xylene. The product is suitable for the manufacture of polyester fiber and film.

Description: *p*-Xylene, catalyst and solvent (acetic acid) are charged continuously to the oxidation reactor, compressed air being blown in from the bottom. Terephthalic acid is formed exothermally in accordance with the reaction:

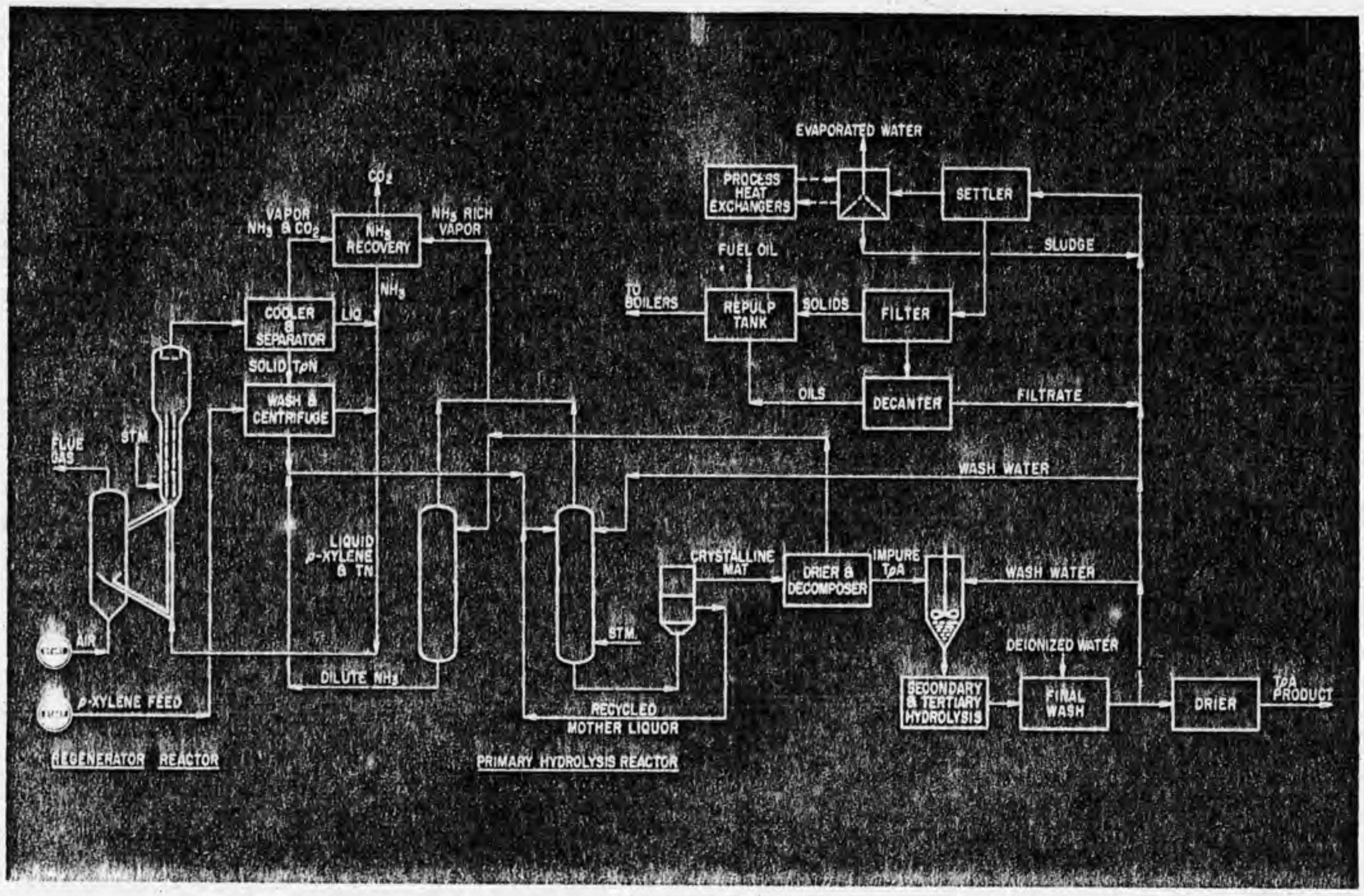


The effluent is continuously transferred to the separation section where terephthalic acid is separated. The wet cake is then washed with acetic acid and dried to give the product a purity greater than 99%. The separated solvent, containing water, catalyst and a small amount of intermediate, is passed to the stripping tower for dehydration purpose. The effluent coming out from the bottom is made up and recycled to the reactor.

Yield: The terephthalic acid yield is as high as 1.5 kg per 1 kg of *p*-xylene. In addition, this process has, as indicated in the flow chart, a byproduct which is salable with profit.

Equipment Materials: Besides the considerably low temperature required for the reaction, no corrosive halogen promoters are to be employed. Normal stainless steel can consequently be used in place of expensive material such as metallic titanium.

Commercial Installation: The first plant, which will have an annual capacity of 80 million pounds, is now under construction.



Terephthalic acid—THE LUMMUS CO.

Application: A process for the production of high purity terephthalic acid (TPA) from *p*-xylene.

Description: The process is carried out in two sections. In the first, *p*-xylene and recycle *p*-tolunitrile (TN) react with ammonia in a fluidized bed to form terephthalonitrile (TPN). A novel metal-oxide catalyst is used which provides the oxygen for the reaction in addition to catalyzing the reaction. Selectivity to TPN and TN is over 90 mole %, and no aldehyde compounds are produced.

In the second section, purified TPN is hydrolyzed and steam stripped to form mono-ammonium terephthalate (MAT). This is removed as a solid and thermally decomposed to form terephthalic acid (TPA) Mother liquor and ammonia are recycled.

Residual terephthalamic acid (TA) formed in the initial hydrolysis is further hydrolyzed and recycled.

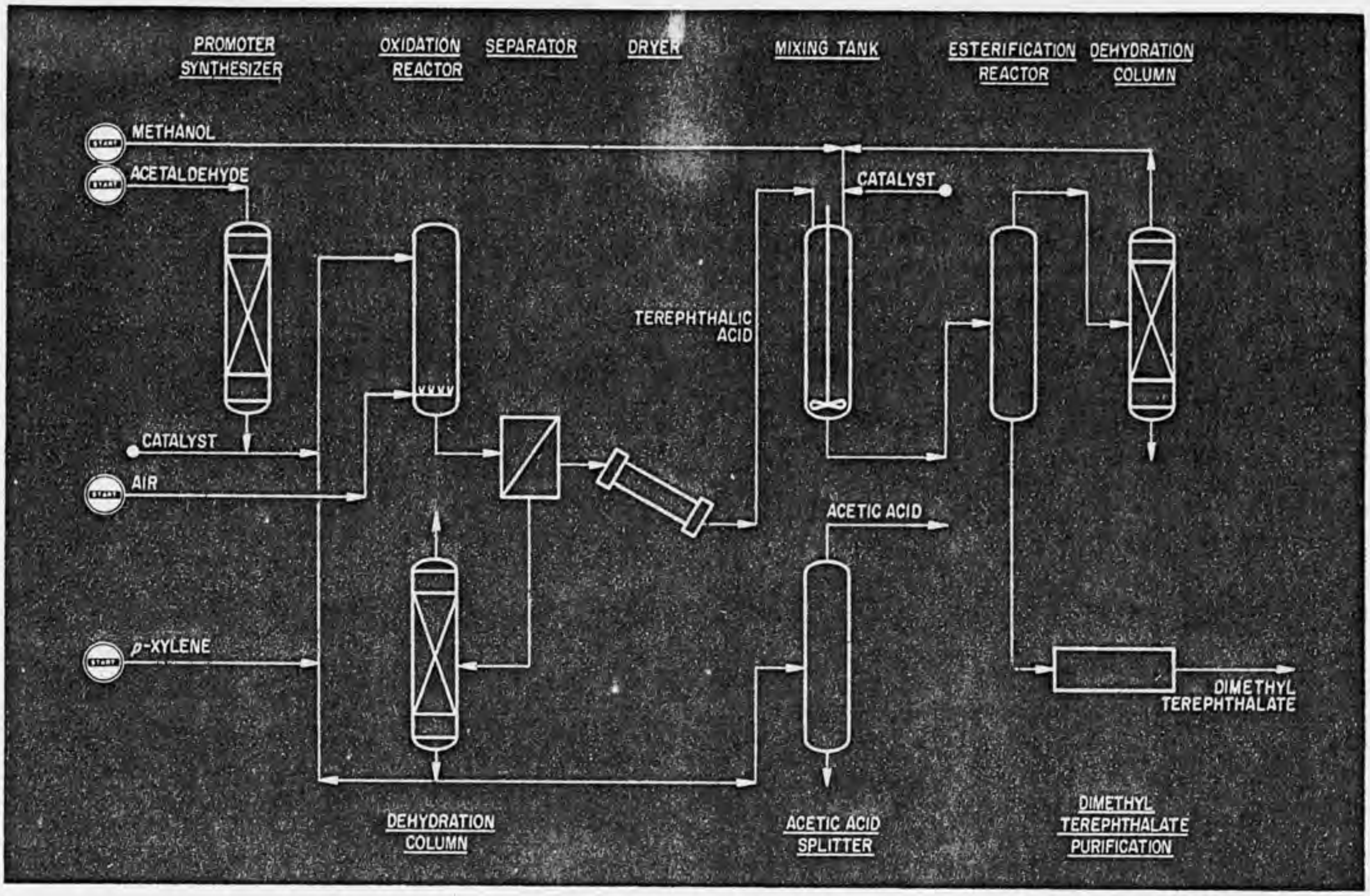
Impurities in the waste water stream are concentrated in a cooling tower and then collected and used as boiler fuel. This cooling tower provides a major part of the total plant cooling load. Aside from the small stream of CO_2, no waste streams leave the plant.

The TPA produced meets all fiber grade specifications.

Other phthalic acids can be produced by the same process.

Typical plant requirements:

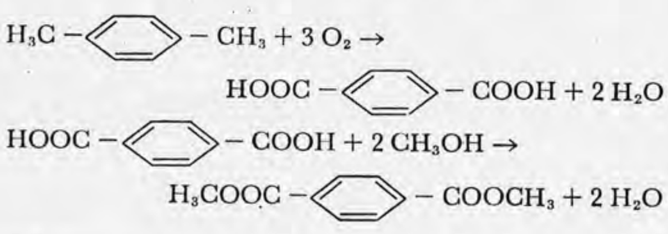
Capacity of plant	150,000 mt/yr.
ISBL investment	$17 million
Raw materials per lb. of TPA	
p-xylene	0.705 lb.
Catalyst and chemicals cost	0.29 cents
Utilities per lb. of TPA	
Steam, 1,000 psig	1.7 lbs.
650 psig	7.0 lbs.
Cooling water (including special cooling tower)	33 U.S. gallons
Deionized water	0.5 U.S. gallons
Electric power	0.055 kWh
Fuel	600 Btu's
Nitrogen	2.5 scf



Terephthalic acid & DMT — TORAY INDUSTRIES, INC.

Application: A process for production of dimethyl terephthalate (DMT) from *p*-xylene via terephthalic acid (TPA.)

Description: DMT is obtained from feedstock *p*-xylene applying the following chemical reactions:



p-Xylene in the solvent acetic acid is converted to terephthalic acid by liquid phase air oxidation in the presence of our unique reaction promoter and catalyst. The reaction promoter, synthesized from acetaldehyde, changes to acetic acid in the course of the oxidation. Granular terephthalic acid obtained in the oxidizer is washed with pure acetic acid, dried and forwarded to the esterifier. Acetic acid co-produced in the oxidizer is purified and marketed.

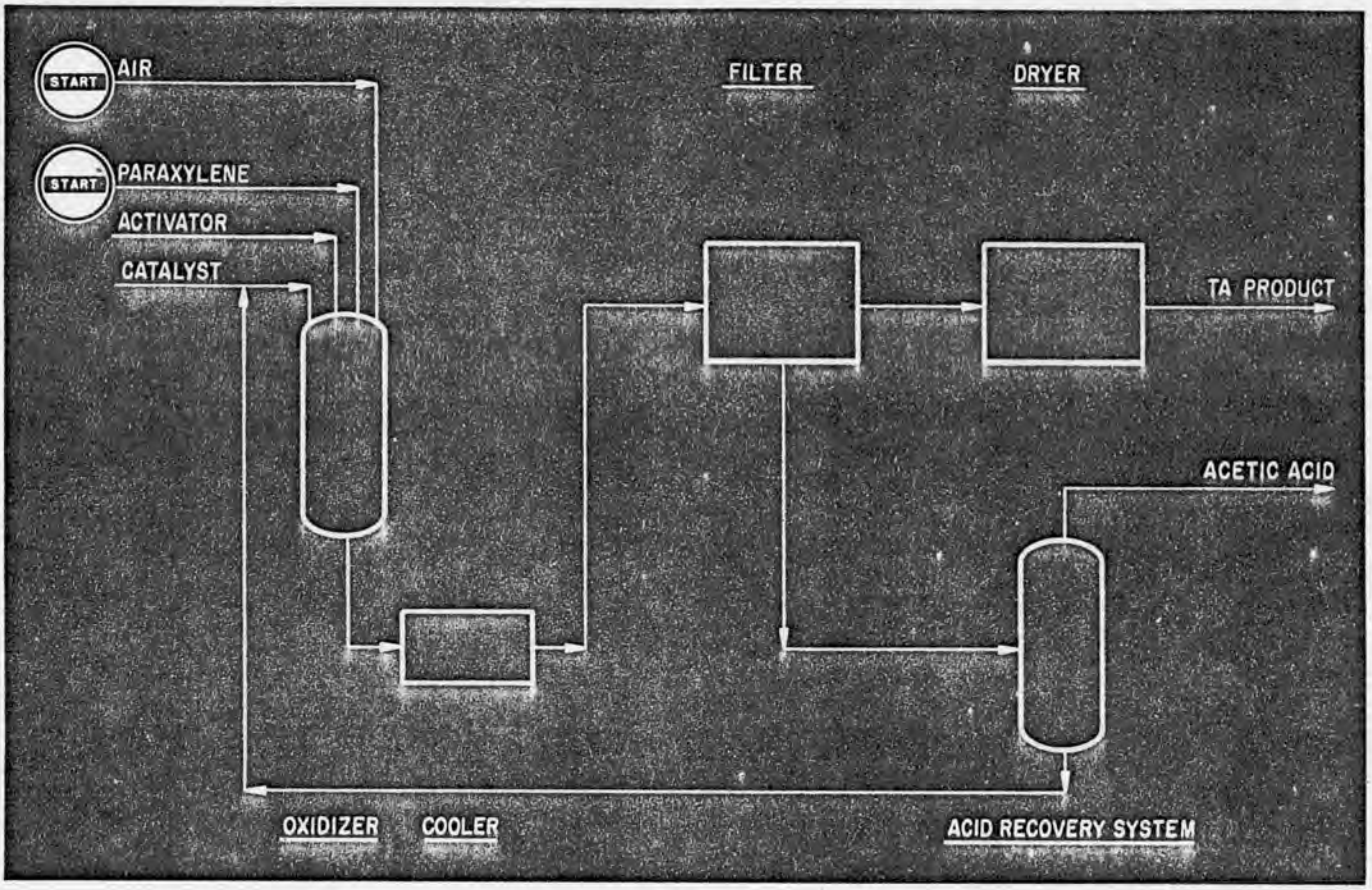
Dried terephthalic acid is fed to the esterifier with methanol to be converted to dimethyl ester. Toray developed a catalyst for the esterification. Crude ester removed from the esterifier is continuously purified to final product by special techniques.

Raw materials and utilities consumption (per Kg of DMT produced):

Consumption	
p-Xylene, kg	0.57
Acetaldehyde, kg	0.21
Methanol, kg	0.36
Steam, kg	10
Electricity, kWh	1.1
Fuel, Kcal	1800
Co-production	
Acetic acid, kg	0.21

Commercial installation: Toray operates a TPA plant having the capacity of 25,000 metric t/y which will be expanded to the total capacity of 100,000 metric t/y at Nagoya in 1973, and DMT plant of 100,000 metric t/y at Mishima. TPA-DMT plant by this process is planned at People's Republic of China.

References: *Ind. Eng. Chem. Prod. Res. Develop.* 12 (2) p 150 (1973).



Terephthalic acid — EASTMAN KODAK CO., TENNESSEE EASTMAN CO. DIVISION

Application: A process for the manufacture of terephthalic acid (TA) from para-xylene.

Description: TA is produced by an oxidation of para-xylene at low to moderate temperatures and pressures in acetic acid solvent using a cobalt catalyst and acetaldehyde as an activator. The TA produced is separated by filtration and is subsequently dried as an esterification-grade product suitable for conversion to DMT or to polymer-grade TA. The co-product acetic acid can be refined to first quality glacial acetic acid for use or sale. The amount of acetic acid co-produced can be varied from about 0.55 to 1.1 pounds per pound of TA.

The Eastman TA process offers economic advantages over other processes if the producer has an available supply of acetaldehyde and a use for the co-produced acetic acid. Conventional materials of construction are used since corrosion is of minimum concern.

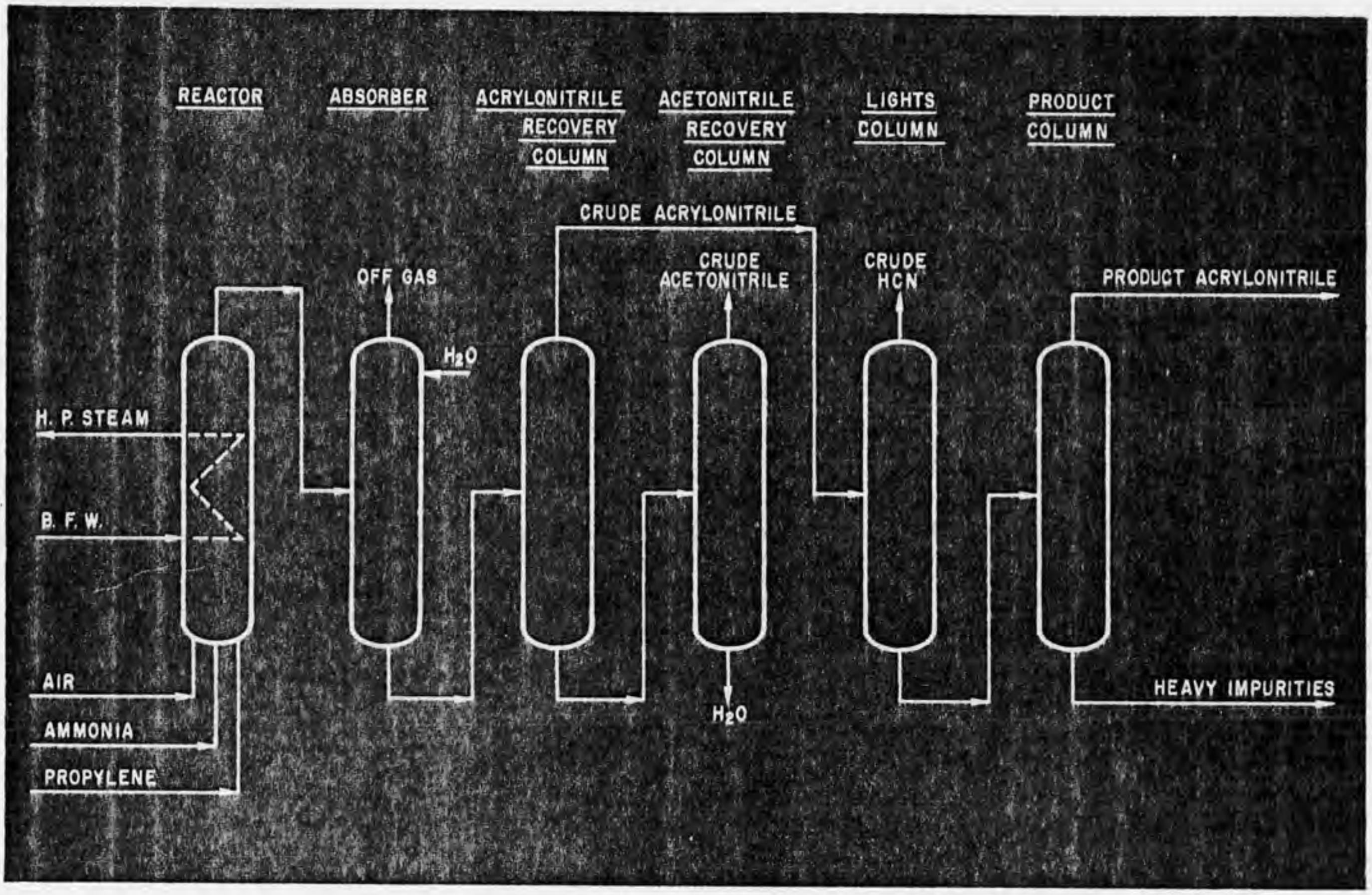
Raw material consumption: *p*-xylene—0.65 kg/kg.

Investment: Battery limits capital investment for a 100,000-metric-ton-per-year plant built in the United States in 1973 is approximately $13 million.

Utilities: Approximate heat required per kg of product—6,600 Btu.

Approximate power required per kg of product—0.1 kWh.

Commercial installation: The process is used by Eastman in its plant at Kingsport, Tenn., where hundreds of millions of pounds of esterification-grade TA are produced. Inquiries may be directed to Foster Wheeler Corp., Livingston, N.J., or Tennessee Eastman Co., Kingsport, Tenn.



Acrylonitrile (Sohio Process) — THE BADGER CO., INC.

Application: A process for the manufacture of acrylonitrile from propylene, anhydrous fertilizer grade ammonia and air. 99+% purity HCN and acetonitrile may be recovered as salable byproducts if desired.

Description: The above feeds are introduced into a fluid bed catalytic reactor operating at 5-30 psig and 750°-950° F. The reactor effluent is scrubbed in a countercurrent absorber, and the organic materials are recovered from the absorber water by distillation. Hydrogen cyanide, water, light ends, and high boiling impurities are removed from the crude acrylonitrile by fractionation to produce specification acrylonitrile product.

A feature of the process is the high conversion obtained on a once-through basis in the fluid bed reactor. Troublesome separation and recycling of unreacted raw materials is unnecessary.

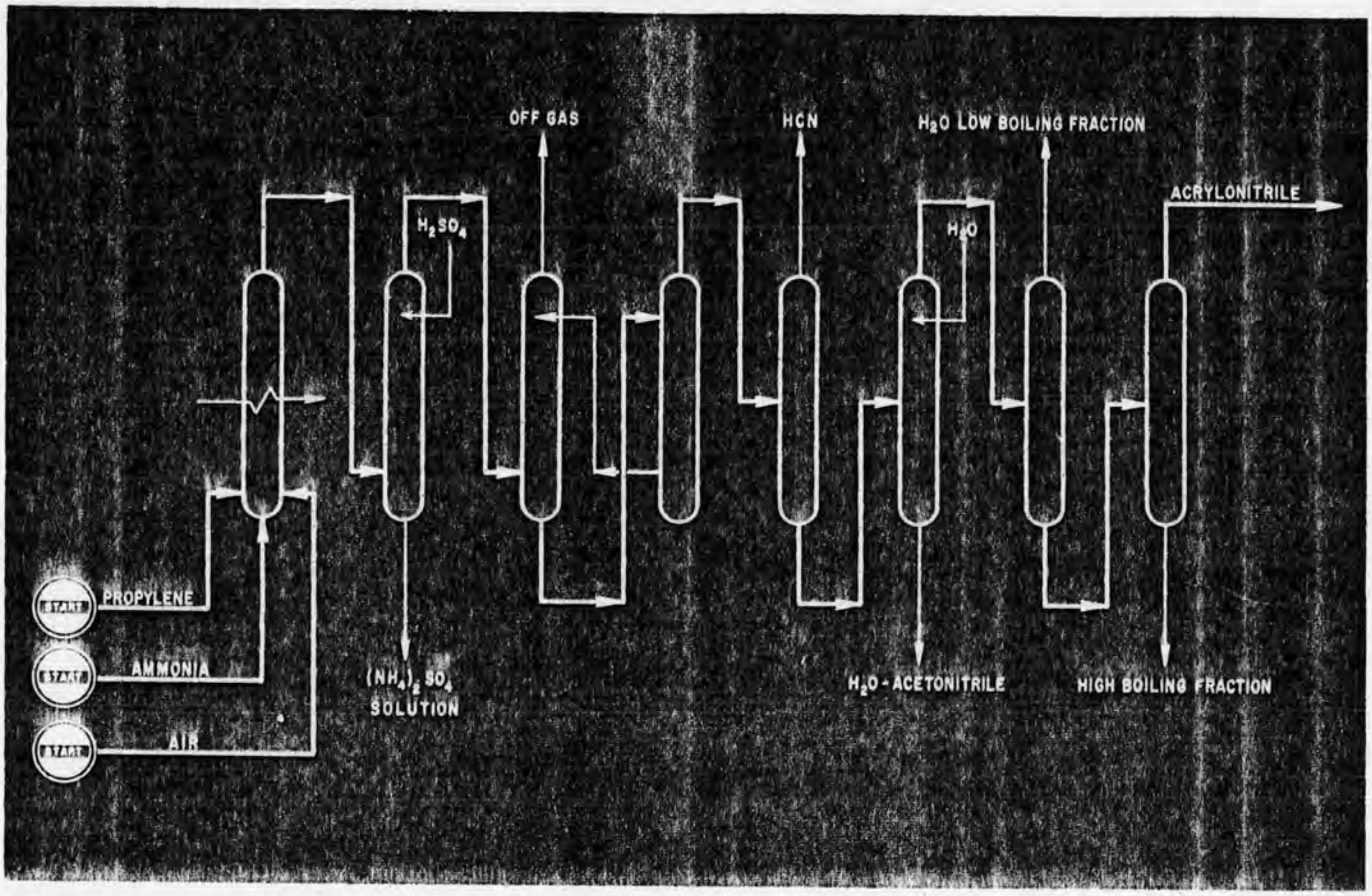
Catalyst: Two catalysts are available commercially for this fluid-bed process. The original catalyst is based principally on molybdenum and bismuth. A new catalyst produces relatively more acrylonitrile and less byproduct acetonitrile.

Operating Conditions: The reactor operating conditions are defined in the above text. Most of the fractionation is accomplished at atmospheric pressure.

Yields: Yields in excess of 0.80 pounds of acrylonitrile per pound of propylene feed are achieved. About 0.15-0.20 pounds of byproduct HCN can be recovered per pound of acrylonitrile.

Commercial Installations: The Badger Co., Inc., licenses the process and offers engineering design and construction services for plants using this process. Licenses under the process have been granted in North America, Japan and Europe.

References: *HP/PR,* Vol. 42, No. 11, Nov. 1963, p. 139; *Chemical Engineering Progress,* October 1960, p. 65; *HP/PR* Vol. 41, No. 11, Nov. 1962, p. 187; *PR,* Vol 38, No. 7, July 1959, p. 264.



Acrylonitrile — MONTECATINI EDISON SPA

Application: A process for the production of high purity acrylonitrile by propylene ammonoxidation from propylene, ammonia and air. Byproducts include: HCN, acetonitrile and ammonium sulfate.

Description: Propylene, ammonia and air are fed to a fluid bed catalytic reactor operating at 420-460° C and at about 2 kg/cm² abs. The reactor thermic control is by heat exchangers immersed in the catalytic bed. The reaction gases are washed in an ammonia removal tower by circulating ammonium sulfate solution maintained at acid pH by continuous addition of sulfuric acid. Thus unreacted ammonia is recovered as a 36% ammonium sulfate solution.

All the reaction products are water-absorbed and unreacted propylene, oxygen, reaction byproducts CO and CO_2, and nitrogen are discharged. The organic compounds are recovered by distillation, while the HCN, water, acetonitrile, and low and high-boiling products are removed from the acrylonitrile by fractionation. Fiber grade acrylonitrile is sent to the finished product store.

Catalyst: The process is based on the use of a special catalyst developed by Montecatini Edison. This catalyst is made by adding tellurium, cerium and molybdenum high oxygenated compounds to a support, e.g. silica, in the 20-30/80-70 ratio respectively. Patents covering this catalyst have been filed in many countries including the United States, Japan, the United Kingdom and Germany.

Yields: The requirements and recoveries starting with 92-93% propylene per 1,000 kg of acrylonitrile are:

Requirements

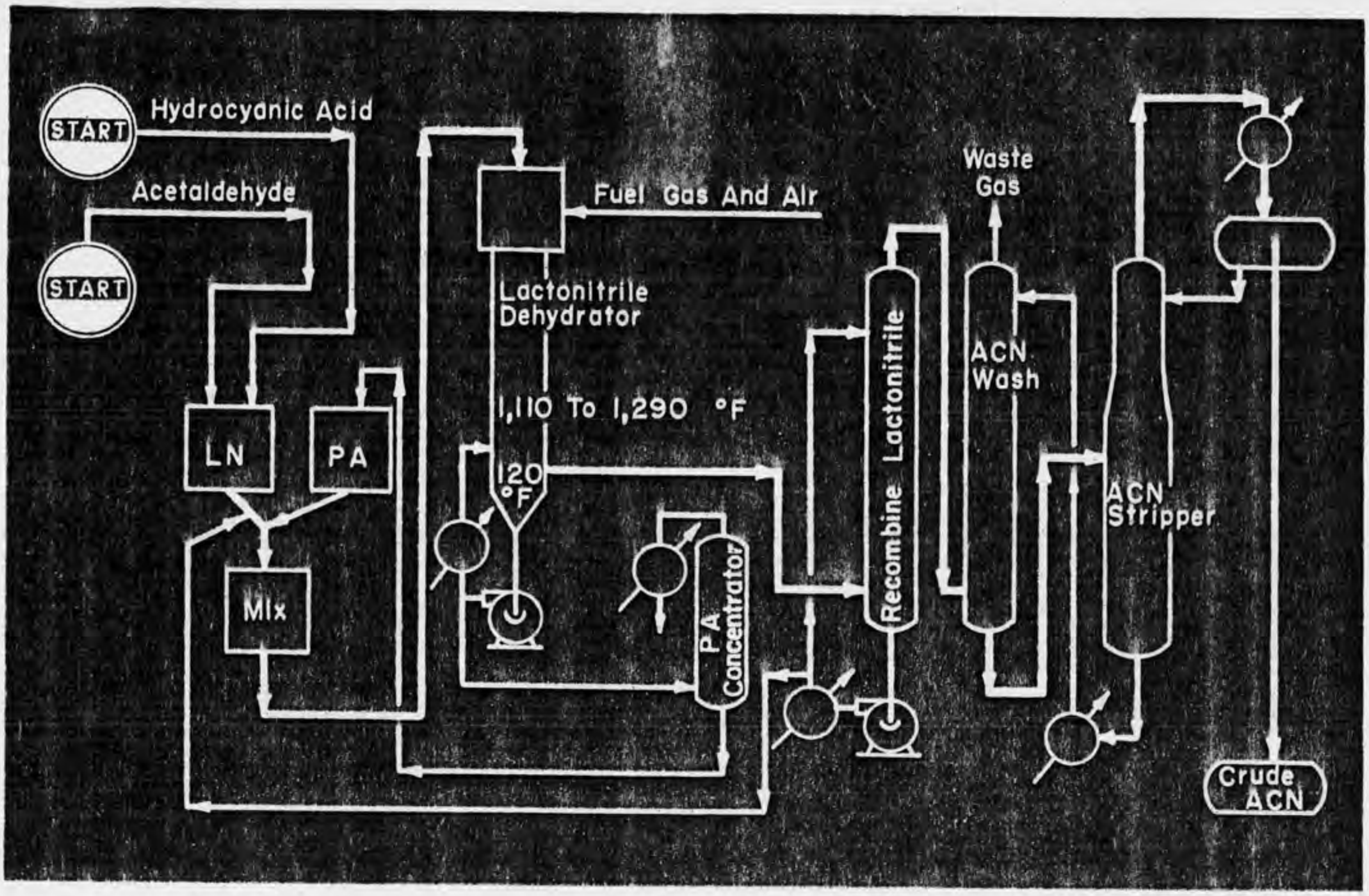
Propylene (as 100%)	1,300 kg
Ammonia	550 kg

Recoveries

Ammonium sulfate (as 100% white)	400 kg
Hydrocyanic acid	60 kg
Acetonitrile	25 kg

Commercial Installations: A 60,000 metric tons/year plant was brought onstream at Priolo, Sicily, Italy, in 1968.

References: La Chimica e l'Industria, Vol. 49, No. 8, August 1967.



Acrylonitrile (Knapsack)—HOECHST-UHDE CORPORATION

Application: A process for the manufacture of acrylonitrile from acetaldehyde and hydrocyanic acid.

Description: Lactonitrile of 97-98 percent purity is produced from acetaldehyde and hydrocyanic acid at a pH of 7.0-7.5 and a temperature of 50°-65° F, according to the following reaction:

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN + 30.4 \text{ BTU}$$

Lactonitrile is mixed with 80-85 percent aqueous phosphoric acid in a molecular ratio of 3:1 and is sprayed into a reaction furnace where the mixture is heated within a fraction of a second to 1110°-1290° F by contact with high-temperature combustion gas. The hot gas, at 1800°-2700° F, is obtained by combustion of fuel gas with 90 percent of the theoretical air requirement. The reaction gases are quenched at the furnace outlet by a recirculating stream of 30 percent aqueous phosphoric acid. Approximately 75 percent of the lactonitrile is thus converted to acrylonitrile and water. Most of the remainder splits to form acetaldehyde and hydrocyanic acid, and about 2-3 percent saponifies to ammonium phosphate and lactic acid.

The 30 percent aqueous phosphoric acid from the quenching operation is reconcentrated to 80-85 percent and is recycled to the reaction furnace. The reaction gases are directed to a venturi scrubber where the remaining phosphoric acid mist is removed.

The hydrocyanic acid and acetaldehyde contained in the reaction gases are converted to lactonitrile in a recombining tower and the lactonitrile is pumped to the reaction furnace. The acrylonitrile content of the reaction gases is removed by absorption in water at 68° F. Recovery of crude acrylonitrile from the 2-3 percent aqueous solution is accomplished in a stripper by direct heating with steam.

The crude acrylonitrile is finally directed to a distillation section comprising two columns in a series. The water content is removed in the first column, as well as small quantities of lactonitrile, acetaldehyde, and hydrocyanic acid. Pure acrylonitrile is the overhead product from the second column. A residue of high-boiling nitriles, equivalent to 2.5-3 percent of the acrylonitrile production, is obtained from the bottom of the second column.

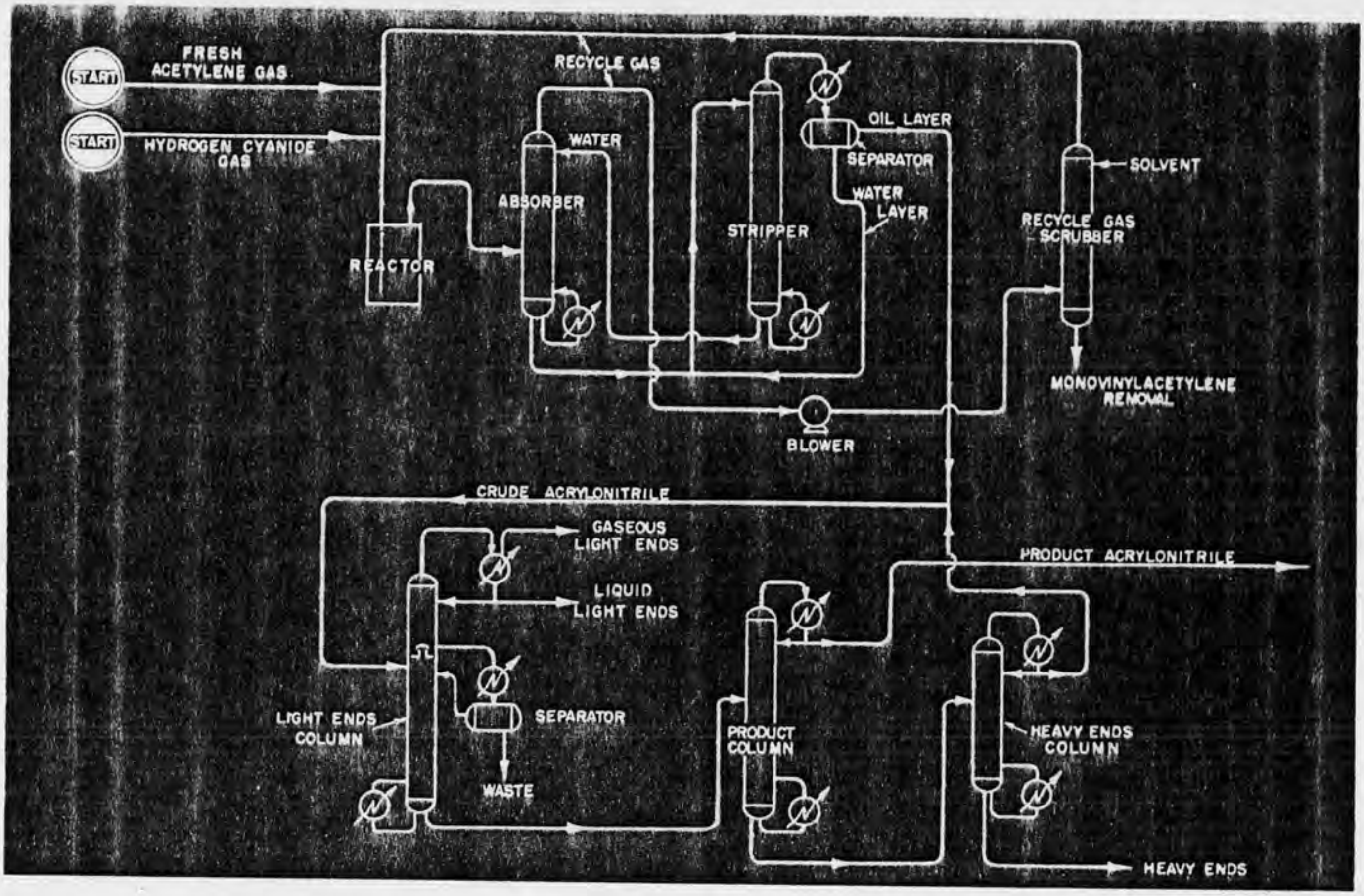
The problem of phosphoric acid corrosion at the high temperatures involved has been met through use of suitable materials. The ammonium phosphate produced by the 2-3 percent saponification of lactonitrile is concentrated in the recycle acid and crystallizes at a concentration of 15-20 percent in the lactonitrile mixture. It is removed by filtration. The ammonium phosphate production is approximately 7-8 pounds per 100 pounds of acrylonitrile produced. This material is at least as valuable as the equivalent phosphoric acid.

The acrylonitrile produced by the Knapsack Process is particularly suitable for the manufacture of high-quality polymers.

A pilot plant of 30 tons/month acrylonitrile capacity has been operated in the plant of Knapsack-Griesheim AG, near Cologne, Germany.

Yields: The yields of acrylonitrile based on the quantities of acetaldehyde and hydrocyanic acid reacted are 90 and 92 percent respectively, and may be improved as the development of the process is advanced.

References: Sennewald, K., Steil, K. H., *Chemie-Ingenieur Technik* No. 7, 440-446 (1958); Sennewald, K., "Acetaldehyde as Raw Material for Acrylonitrile." Paper presented at Fifth World Petroleum Congress, New York, 1959.



Acrylonitrile—AMERICAN CYANAMID COMPANY

Application: A process for manufacturing acrylonitrile from acetylene and hydrogen cyanide.

Charge: Acetylene gas (99 percent purity); hydrogen cyanide gas (99+ percent purity).

Product: Acrylonitrile liquid of 99.5 percent purity.

Description: Acrylonitrile may be produced either by the dehydration of ethylene cyanohydrin or by the direct combination of acetylene and hydrogen cyanide. The latter method is known as the "natural gas process." It is the more important method today, commercially, and accordingly will be described here.

Acetylene and hydrogen cyanide in a ratio of 6:1 form the reactor charge. The reactor is a rubber-lined cylindrical vessel containing liquid catalyst to a depth of several feet. The reactants are injected separately under the liquid surface. About 15 percent of the acetylene is converted, and this consumes practically all of the hydrogen cyanide.

The aqueous catalyst consists of cuprous chloride, hydrogen chloride, and alkali chlorides in 36 weight percent water. All salts are in solution at 175° F which is also the reaction temperature. Yields of 1.5 pounds of acrylonitrile per hour-foot^3 of solution are obtained. The catalyst must be regenerated to prevent deactivation.

The reaction pressure is 2-5 pounds above atmospheric.

The reaction products pass to an absorber, the lean gas from which contains acetylene and divinylacetylene. The latter constituent is removed in a separate scrubbing operation. The residual acetylene is recycled through a blower to the reactor charge.

The absorber is operated at a water rate such that a three percent acrylonitrile solution is withdrawn as bottoms. This stream is sent to the stripper, from which a crude acrylonitrile-water azeotrope is recycled to the stripper feed. The oil layer, or "crude acrylonitrile," is sent to a distillation train for separation and purification.

The concentration of acrylonitrile in the crude solution is about 75 weight percent; that of the materials other than water is about 15 weight percent.

The first tower in the distillation train (light ends column) enables the overhead removal of materials boiling below acrylonitrile. Acetylene and monovinylacetylene pass off as gases.

Product acrylonitrile, having a purity of about 99.5 percent on a dry basis, is removed as overhead from the second column. The operating head pressure is about 140 mm Hg abs. The bottoms stream contains heavy ends plus a significant amount of acrylonitrile.

The third tower in the train, the heavy ends column, serves to recover acrylonitrile from the product column bottoms. The heavy ends column operates at a head pressure of 120-150 mm Hg abs. The recovered acrylonitrile is not specification-grade and must be recycled to the light ends column.

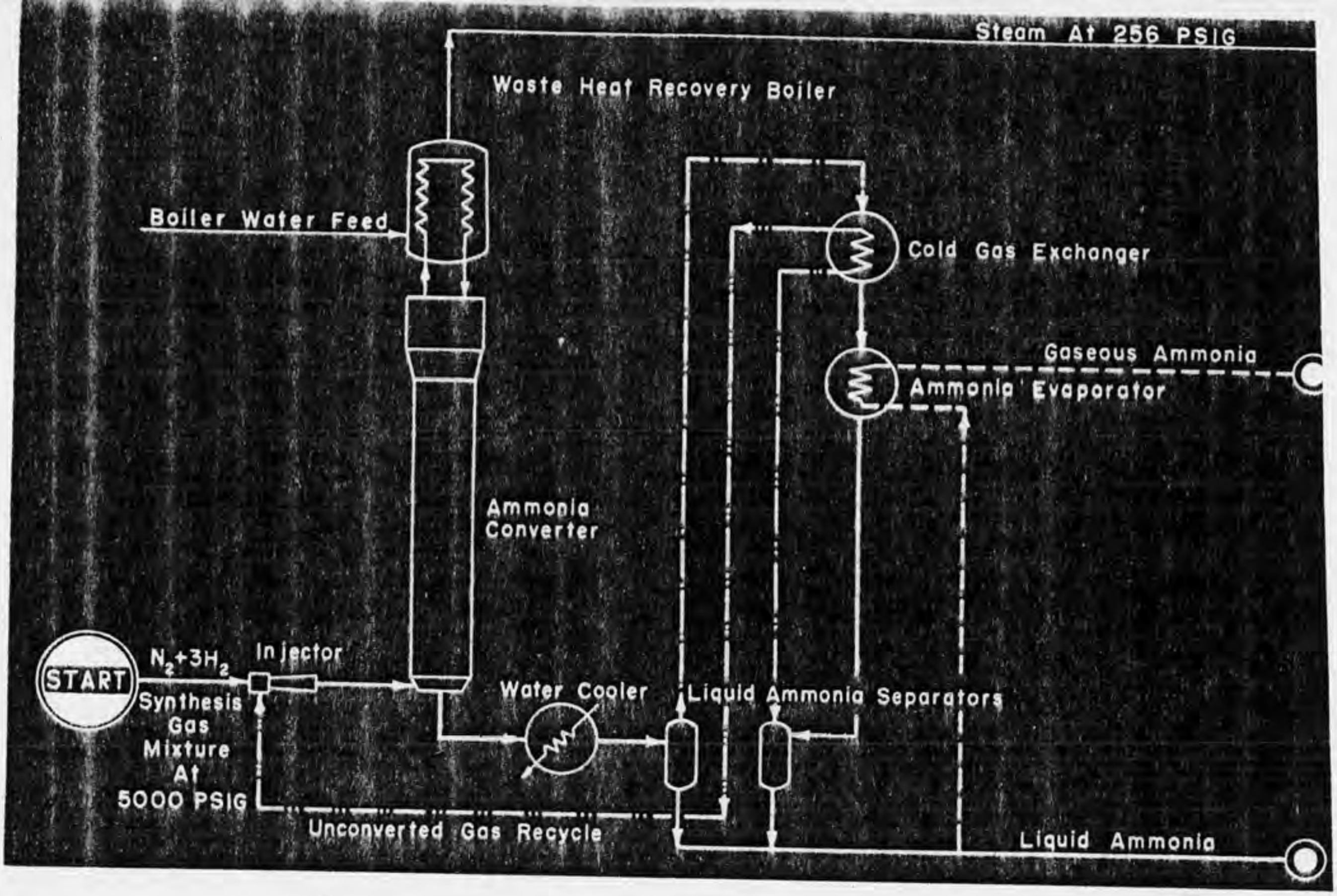
The product acrylonitrile has a boiling range of 169°-173° F

Operating Conditions: The important operating conditions are those in the reactor. They are defined in the above text

Yields: Typical over-all process yields are:
Acrylonitrile from HCN, 85 percent.
Acrylonitrile from C_2H_2, 75 percent.

Commercial Installations: Plants utilizing the methane process are: Monsanto Chemical Company, Texas City, Texas; American Cyanamid Company, Fortier, La.: The B. F. Goodrich Company, Calvert City, Ky.

References: "The Manufacture of Acrylonitrile From Natural Gas," J. T. Thurston, E. L. Carpenter, and F. Derbenwick of American Cyanamid Co., Fourth World Petroleum Congress, Rome, Italy.



Ammonia—MONTECATINI

Application: Synthesis of ammonia by the Fauser-Montecatini processing technique.

Charge: It is essential to have a pure $N_2 + 3H_2$ synthesis gas mixture, compressed at about 5000 psig. Hydrogen contained in said mixture can be obtained by several methods and should be chosen according to the most favorable local conditions.

Product: Pure ammonia, partially available in the liquid form and partially in gaseous form. High-pressure steam is also obtained.

Description: Fresh synthesis gas mixture, before entering the converter, acts as a mechanical compelling medium for recycling the unreacted gases in a special, highly efficient injector. The converter, designed according to the up-to-date Fauser-Montecatini patented type, operates at a pressure of 4,260 psig and is equipped with a highly effective system for recovering the reaction heat.

The temperature of the different catalyst sections can be carefully controlled so as to obtain from the catalyst itself the best performance, thus increasing conversion efficiency and preventing dangerous super-heating.

The catalyst temperature control is achieved by circulating distilled water in a set of various heat exchangers placed at different levels in the catalytic mass. The waste heat recovery produces steam having the remarkable pressure of 250 psig.

As a result of such careful temperature control, gases leaving the converter have an average ammonia content of 20 percent. This is exceptionally high considering the rather low synthesis pressure.

Ammonia is condensed down at approx. —5° F in three stages: first in a water cooler, then in a cold gas exchanger and finally in an ammonia evaporating cool

The condensed ammonia is removed from the cyc and expanded in a let down tank. A fraction of t ammonia collected in this tank feeds the ammonia cool where it vaporizes at about 30 psig giving the requir amount of refrigeration.

After removal of the condensed ammonia the unreacte cold gases flow through the exchanger and are then r cycled to the converter by means of the injector.

Several main advantages are offered by this improve process and can be summarized as follows:

The synthesis pressure chosen for this process permits sa and efficient operation of the unit together with low maintenanc and operative costs.

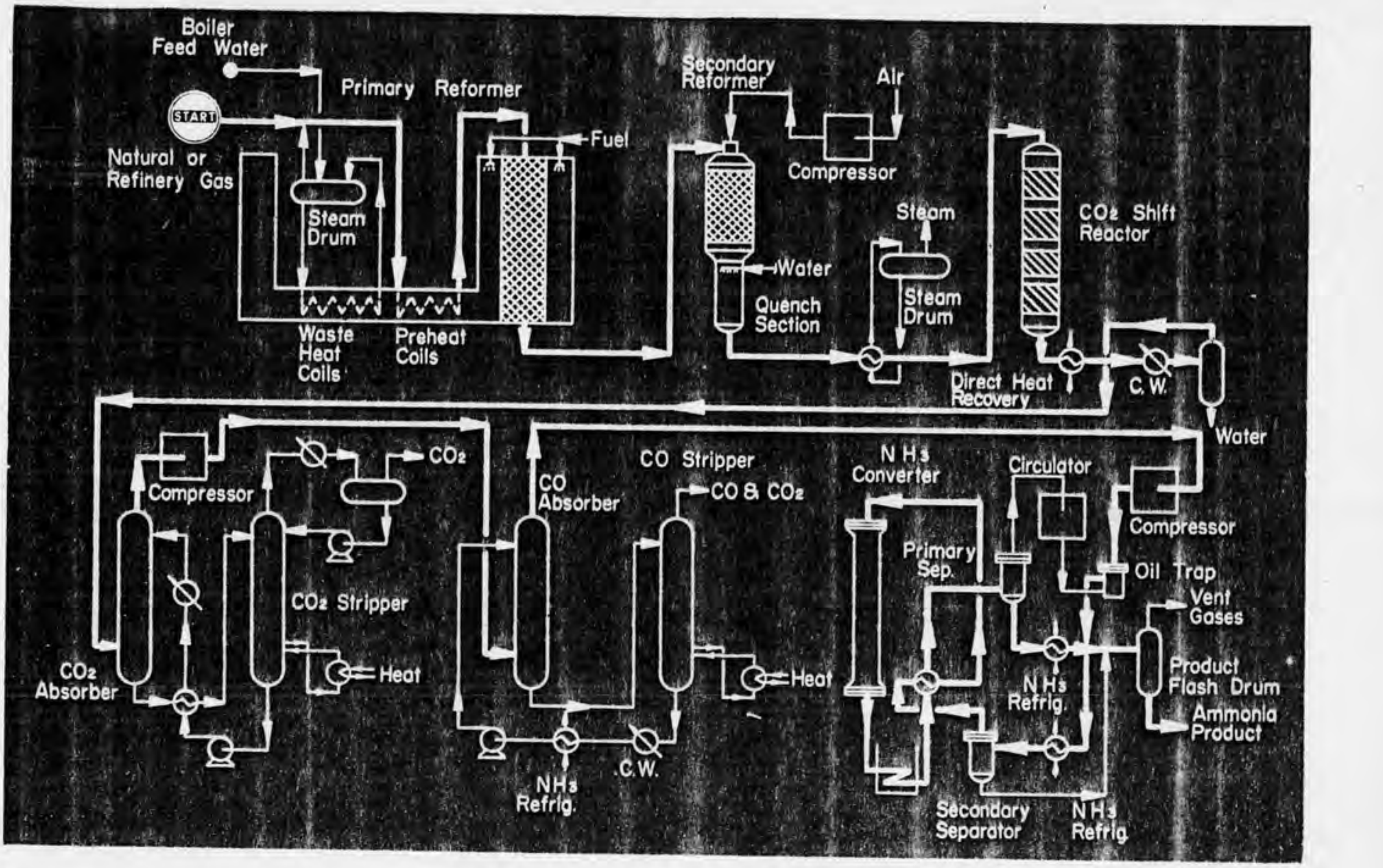
The temperature control in the catalyst layers permits hig conversion, long catalyst life and makes possible the recovery c 0.85 ton of steam per ton of ammonia produced. This is an impor tant economic factor.

The high efficiency of the injector adopted offers, in com parison with a mechanical circulator, several advantages includ ing low cost, no maintenance, no oil entrainments (this mean best operating conditions for the catalyst), power consumptio comparable to that of mechanical circulators.

Operating Conditions: The main operative conditions are give in the above description. The temperature in the converter i kept at about 900° F.

Yields: For the production of 1,000 kg of ammonia, 2,750 N cu. meters of N_2+3H_2 synthesis gas mixture, compressed at 5,000 psig are required. For the same amount of produced ammonia, 850 kg of high-pressure steam are recovered.

Commercial Installations: 63 ammonia plants have been erected in 20 countries throughout the world, utilizing the Fauser-Montecatini process and accounting for more than 2,700,000 metric tons per year of ammonia capacity.



Ammonia — THE M. W. KELLOGG COMPANY

Application: A high pressure steam methane reforming process for ammonia production.

Charge: Natural gas, refinery gas, coke oven gas or light hydrocarbons and air.

Product: High purity ammonia.

Description: The steam methane reforming process produces ammonia by steam reforming natural or refinery gas under pressure, followed by carbon monoxide shift, purification of raw synthesis gas, and ammonia synthesis.

In the process, saturated and unsaturated hydrocarbons are decomposed by steam according to the basic equation:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

Feed streams high in olefins or sulfur require pretreatment.

The primary reformer converts about 70 percent of a natural gas feed into raw synthesis gas, in the presence of steam using a nickel catalyst.

In the secondary reformer, air is introduced to supply the nitrogen required for ammonia. The heat of combustion of the partially reformed gas supplies the energy to reform the remainder of the gas after reacting with the oxygen in the air.

High pressure reforming conserves 30-40 percent in compressor horsepower over usual practices giving low pressure synthesis gases.

Next, the mixture is quenched and sent to the shift converter. Here CO is converted to CO_2 and H_2. When heat is still available after satisfying the water requirement for the shift reaction, a waste-heat boiler may be installed.

Shift reactor effluent, after heat recovery, is cooled and compressed, then goes to the gas purification section. CO_2 is removed from the synthesis gas in a regenerative MEA (monoethanolamine) or other standard recovery system.

After CO_2 removal, CO traces left in the gas stream are removed by scrubbing with a regenerative cuprous ammonium acetate solution. Flowsheets using methanation rather than copper solution for final purification are also available.

The resulting pure synthesis gas passes to the oil separator, is mixed with a recycle stream, cooled with ammonia refrigeration, and goes to the secondary separator where anhydrous ammonia (contained in the recycle stream) drops out.

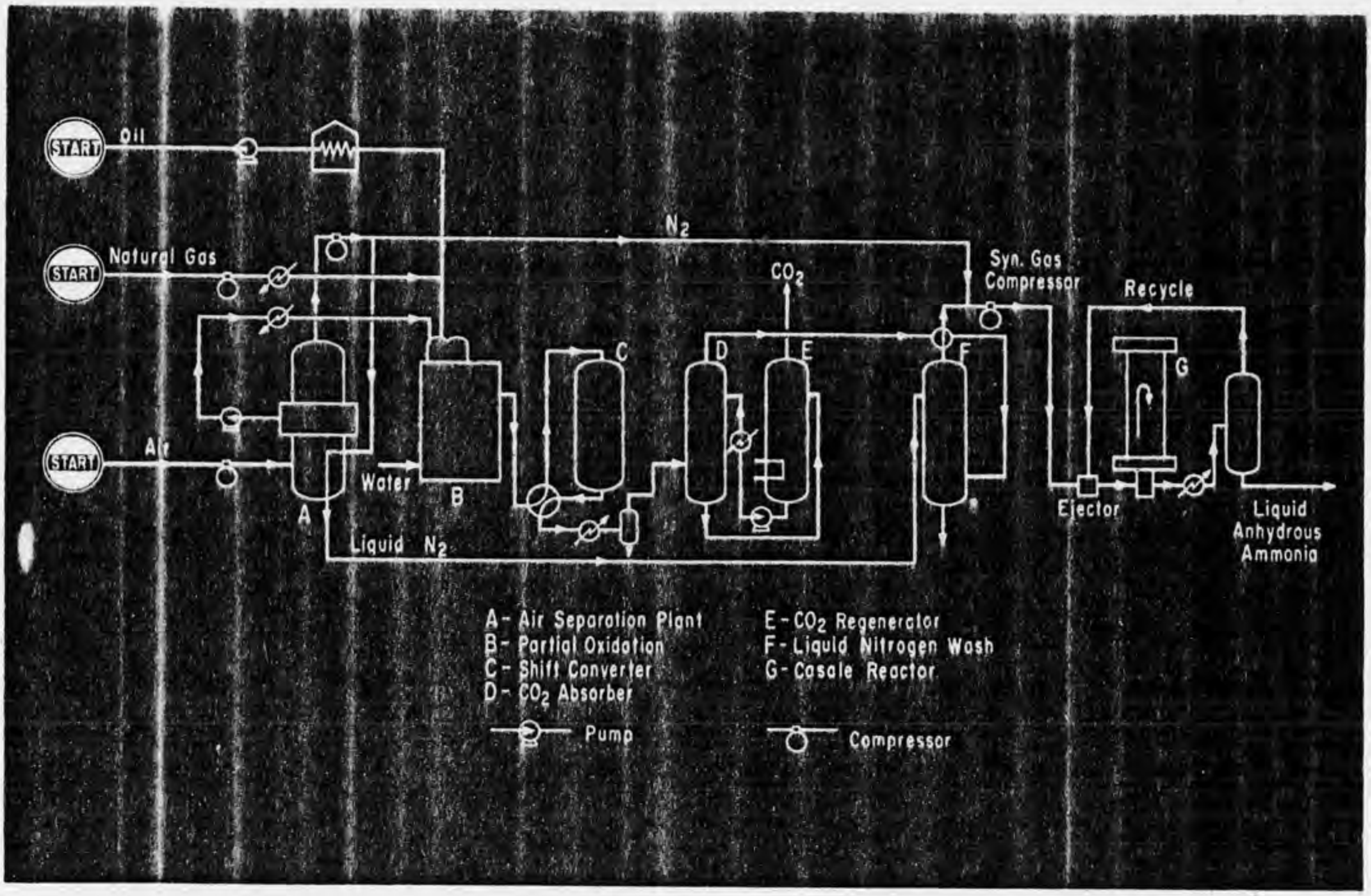
Synthesis gas is then passed through heat exchange and charged to the catalytic ammonia converter. Product gas from the converter is cooled and exchanged against converter feed gas.

Anhydrous liquid ammonia then separates out in the primary separator and, after further cooling, goes to the anhydrous ammonia product flash drum.

Operating Conditions: The feed to the reforming section is normally in the order of 500 psig. The pressure, however, is not fixed and may be varied to provide optimum design for specific local conditions. Temperatures in primary and secondary reformers are 1,400-1,800° F., while shift reaction temperatures are 700-850° F.

Ammonia synthesis is normally at 4,700 psig. The "quench-type" ammonia converter was developed by Kellogg. Temperature is accurately and flexibly controlled inside the catalyst mass to allow a catalyst basket temperature gradient giving a maximum yield of ammonia per pass, regardless of production rate.

Commercial Installations: This process is in production at eight plants with three more in construction. Total ammonia production is rated at over 2,400 tons per day. Additional installations of gasification and purification sections are rated at more than 160 MM SCFD of hydrogen and synthesis gas.



Ammonia—FOSTER WHEELER CORPORATION

Application: A process for manufacturing ammonia.

Charge: Hydrocarbon oil and/or gas, water and air.

Product: Liquid Anhydrous Ammonia.

Description: The processing sequence for the synthesis of ammonia comprises six steps: air fractionation, partial oxidation, shift conversion, carbon dioxide removal, liquid nitrogen wash and ammonia synthesis.

An alternate processing sequence would involve catalytic reaction of steam with hydrocarbon gases (the steam-methane reaction) in place of partial oxidation.

Air, filtered and caustic scrubbed, is compressed to approximately 600 psig, liquefied and separated into nitrogen and oxygen in the air separation plant. The nitrogen is compressed and the bulk of it is used for blending into the purified synthesis gas. A slip stream of this nitrogen re-enters the air plant and is liquefied for use in the liquid nitrogen wash tower. Liquid oxygen is pumped thru a preheater to the Texaco generator.

Preheated hydrocarbon oil/water mixture (or hydrocarbon gas) also enters the generator, mixes with the oxygen and the highly exothermic reaction takes place. The products, mainly carbon monoxide and hydrogen, are quenched with water and enter the shift converter where in the presence of a catalyst, carbon monoxide reacts with steam to form additional hydrogen and carbon dioxide. The effluent from the shift converter passes through a heat exchanger for recovery of process heat, is cooled, flows through a liquid knockout drum and then to the carbon dioxide removal system.

Carbon dioxide is removed by absorption in a suitable medium such as monoethanolamine which is then reactivated by heat, releasing the carbon dioxide to battery limits.

The hydrogen stream then enters the liquid nitrogen wash tower where residual carbon monoxide, methane and argon are removed. The purified hydrogen is blended in specified proportions with nitrogen, produced at the air separation plant, and enters the Casale synthesis system.

The gaseous mixture of hydrogen and nitrogen is compressed to approximately 9,000 psig and enters the reactor, via the jet ejector system which serves to return the uncoverted recycle gases to the reactor. The ammonia synthesis is completed in the presence of a special catalyst.

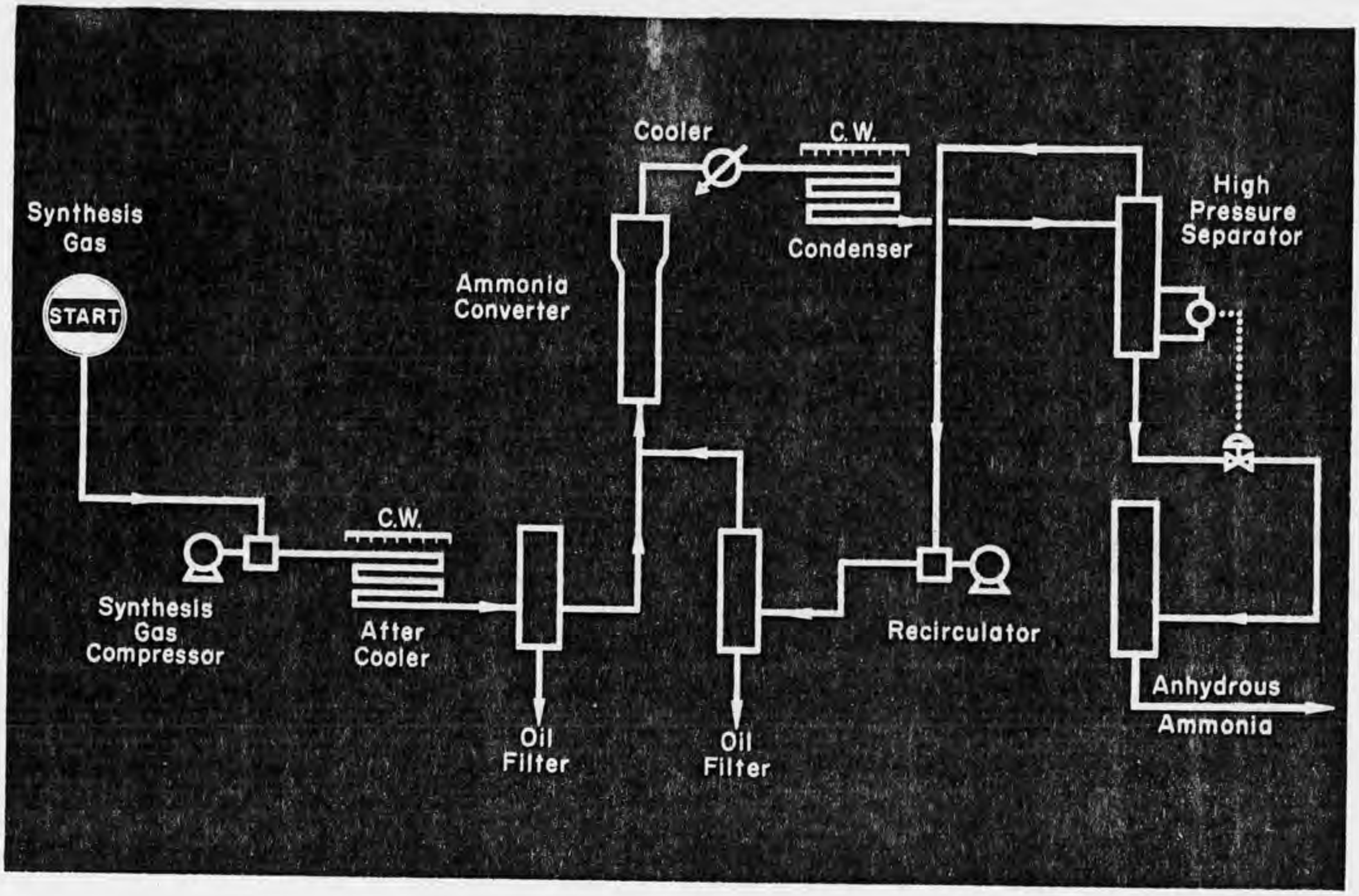
The effluent gases are cooled, the anhydrous ammonia is condensed and separated from the unconverted gases which are returned to the reactor via the ejector system. The liquid anhydrous ammonia flows to storage.

The ejector system eliminates the necessity for a recirculating compressor for the unconverted gases.

Operating Conditions: Important operating conditions are mentioned in the above description.

Commercial Installations: Over 2000 tons per day of installed capacity.

References: PETROLEUM REFINER, Sept.'53,p178; CHEMICAL ENGINEERING, May'54,p332.



Ammonia (Claude Process)—THE FLUOR CORPORATION, LIMITED

Application: A process for the manufacture of anhydrous ammonia.

Charge: Feed to the ammonia synthesis unit is gas containing 75 percent hydrogen and 25 percent nitrogen. Such synthesis gas may be produced from catalytic reformer off-gas, butadiene off-gas, coke oven gas, electrolytic cell hydrogen, or other sources by nitrogen scrubbing. It may also be produced by steam methane reforming or partial oxidation of natural gas or other hydrocarbons.

Product: Liquid anhydrous ammonia of 99.9 percent purity.

Description: Synthesis gas containing 75 percent hydrogen and 25 percent nitrogen flows to the synthesis gas compressors for compression to about 400-600 atmospheres, cooled, passed through a lube oil removal unit, blended with recycle gas, and fed into the Claude Converter. The gases enter the Claude Converter at about 100° F and internal heat exchange increases this temperature to a suitable level for rapid conversion to ammonia. The exothermic reaction raises the temperature level within the converter to about 1100° F, but this heat is transferred to the incoming feed gas so that the gases leave the converter at about 480°-510° F. The effluent gases pass through the tubes of a water-cooled condenser which condenses most of the ammonia produced, allowing a very small fraction to recycle with the unconverted gases. The anhydrous ammonia produced is passed to storage through an automatic let-down valve. Unconverted gases are recompressed and passed through a filter for lube oil removal before passing back to the converter inlet.

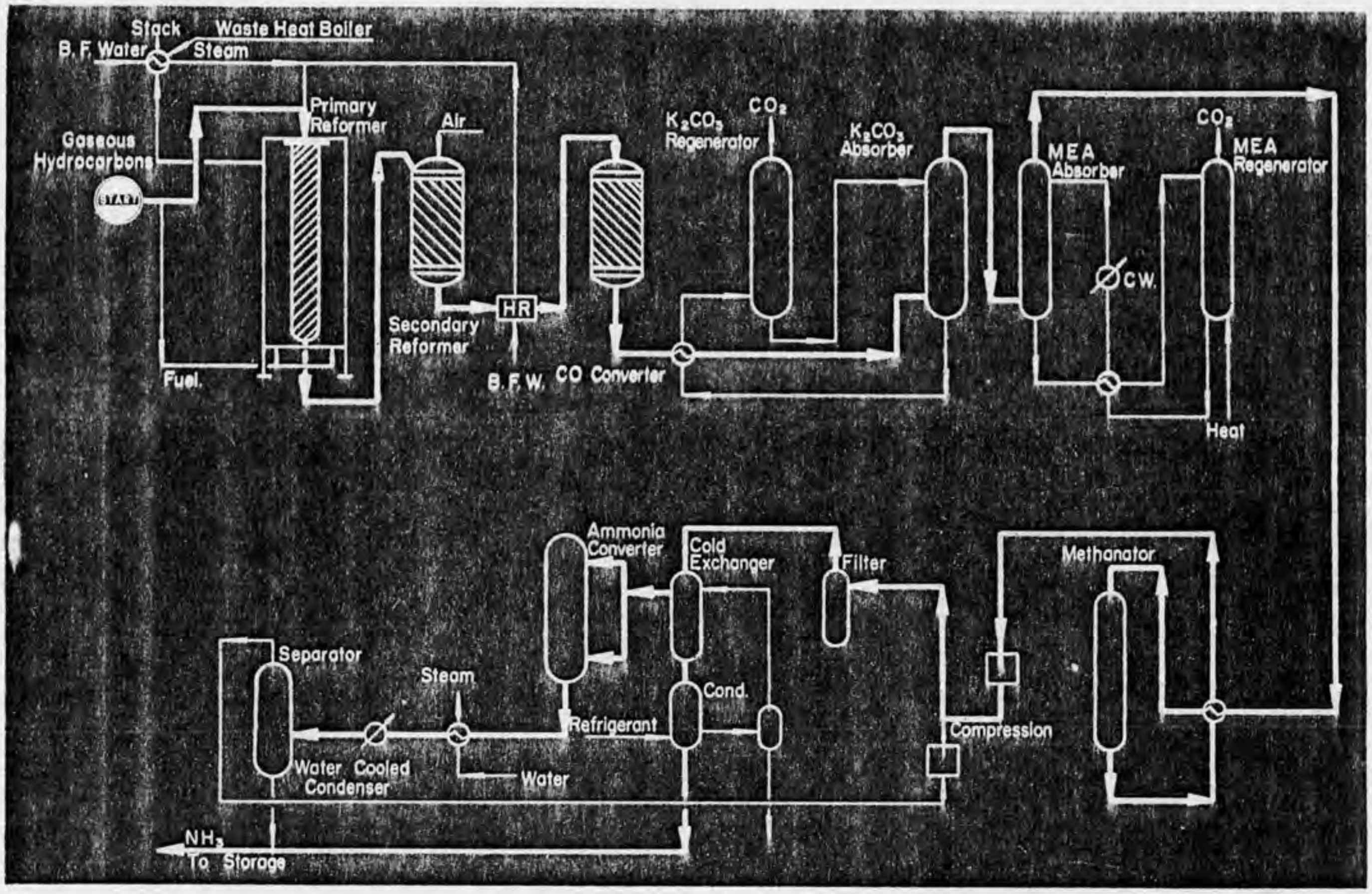
Synthesis gases purified in a liquid nitrogen scrubbing unit are so pure that no vapor purge from the loop is necessary. An equilibrium is established wherein the small quantity of inerts introduced with the syn gas passes from the high pressure separator dissolved in the liquid ammonia as long as inerts in fresh synthesis gas are less than 250 ppm.

Operating Conditions: The synthesis converter starts producing at about 400 atmospheres, and most of the ammonia production is made near that level. The converter is designed to permit operation as high as 600 atmospheres, which will occur after the catalyst has aged.

Yield: About 97 percent based on nitrogen and hydrogen.

Commercial Installations: The Claude converter is in use at Mississippi River Chemical Company, Selma, Missouri; Hercules Powder Company, Pinole, California; Mississippi Chemical Corporation, Yazoo City, Mississippi; San Jacinto Chemical Company, Houston, Texas; Ketona Chemical Company, Ketona, Alabama; and Calumet Nitrogen Products Company at Whiting, Indiana. A plant incorporating the Claude Converter is under construction for Petroleos Mexicanos at Minatitlán, Mexico.

Reference: *Chem. Eng. Progress,* 48, 468 (1952).



Ammonia — CHEMICAL CONSTRUCTION CORPORATION

Application: This is a process for the production of ammonia.

Charge: The feed to the process may be any mixture of lower molecular weight gaseous hydrocarbons consisting primarily of saturates, acetylene off-gas, or a mixture of hydrocarbons and off-gas.

Description: The feed gases are reformed by reaction with steam at any pressure up to 300 psig. Optimum pressure is selected for the particular gas to be processed. Process steam requirements are generated in waste heat boilers.

Most of the hydrocarbons are reformed to hydrogen, carbon monoxide and carbon dioxide in the primary reformer. Heat for the reaction is supplied by liquid or gaseous fuels.

The reactions are completed in the secondary reformer where the correct amount of nitrogen to form a 3:1 hydrogen-nitrogen ratio enters with the air. Necessary heat is supplied by reaction of combustible products with oxygen in air.

Heat in gases exit the secondary reformer and is recovered as steam for use in the process. Most of the carbon monoxide formed by reforming is converted to carbon dioxide in the CO converter by reaction with steam to form hydrogen and carbon dioxide.

The gas stream is cooled in a reboiler, supplying heat for CO_2 removal solution regeneration.

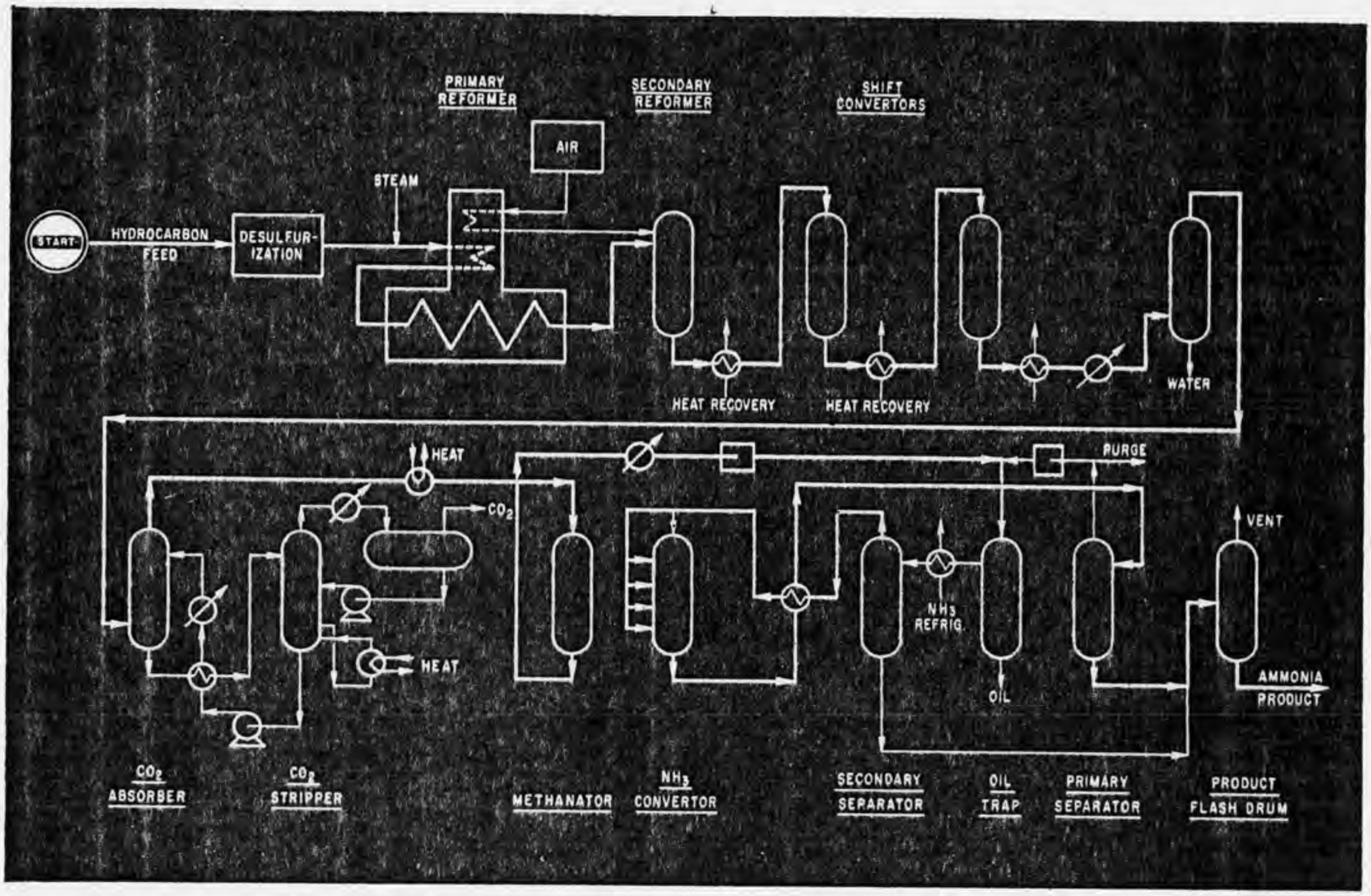
The bulk of CO_2 is removed from the synthesis gas stream by regenerative liquid absorption, using either a combination of hot potassium carbonate and monoethanolamine (MEA) in successive stages or two stages of MEA. Final cleanup is accomplished by methanation, reducing oxides to 10 ppm. or less.

After purification the gas is compressed to 5,200 psig and synthesized to ammonia as illustrated in the flow diagram. Production of steam in the synthesis loop is optional depending on economic considerations for a particular plant.

Products: Anhydrous liquid ammonia with a minimum purity of 99.9 percent.

The carbon dioxide produced is of sufficient purity to be reused for the production of dry ice or urea especially where K_2CO_3 scrubbing is used.

Commercial Installations: There are seventy-six Chemico designed ammonia synthesis plants ranging in size up to 450 T/D in operation all over the world.



Ammonia

Application: A process for the manufacture of ammonia from various hydrocarbons, i.e., natural gas, naphtha, refinery gas, residual oil by high-pressure steam hydrocarbon reforming.

Description: Synthetic ammonia manufacturing processes can be divided into four steps—synthesis gas production (reforming), carbon monoxide shifting, carbon dioxide removal (clean-up), and compression and conversion.

Reforming: The hydrocarbon feedstock is first desulfurized and vaporized if required. It is then mixed with steam, further preheated, and fed to the primary reformer where the hydrocarbon and steam react over a nickel catalyst to form hydrogen and carbon oxides. Primary reforming normally takes place between 350-550 psig and between 1,350° F to 1,500° F. Normal conversion in the primary reformer of hydrocarbon to synthesis gas is about 70%.

Reforming is completed in the secondary reformer where the hot synthesis gas is reacted with preheated secondary air up to temperatures of 1,850° F to achieve a very low residual methane content. Here the desired proportion of nitrogen which is ultimately required for ammonia synthesis is accomplished. Heat for the secondary reforming is supplied by combustion of some of the hydrogen formed in the primary reformer with oxygen in the added air to the secondary reformer.

Carbon Monoxide Shift: The secondary reformer effluent gas is cooled for heat recovery and passed to the CO shift converter. Normally shift conversion is conducted with two catalyst charges: (1) conventional high temperature catalyst in the first shift stage, and (2) low temperature shift catalyst in the second stage. Gas mixed with steam enters the first shift converter at 650-750° F and the bulk of the carbon monoxide is converted to carbon dioxide. Some of the steam reacts to form more hydrogen. Effluent from the first stage shift conversion is cooled to 400-475° F and passed over the second shift conversion catalyst which further reduces the carbon monoxide content to below 0.5%. Excess heat in the combined shift gas is used to regenerate the carbon dioxide removal system.

Carbon Dioxide Removal: Various solvents are used for removal of the carbon dioxide from the synthesis gas. Potassium carbonate—with and without activators—aqueous monomethanol amine, or other organic solvents. With each solvent, the heat in the shift gas effluent is used to regenerate the rich solvent to conserve heat. Essentially all the carbon dioxide is removed by these systems but residual carbon dioxide and carbon monoxide which was not converted in the upstream shift reaction are eliminated by catalytic reaction to form methane in the methanator. Since the methanator usually operates at about 600° F, the purified synthesis gas must be cooled and dried (particularly if cryogenic purification is to be used) before being sent to compression.

Compression and Conversion: The synthesis gas has been compressed to synthesis pressure before reaching the conversion section of the plant. This pressure ranges from as low as 2,000 psig for very large capacity ammonia plants using centrifugal compressors to as high as 9,000 psig for smaller capacity plants using reciprocating compressors. Also, some processes, i.e., the Casale process as used by Foster Wheeler requires high initial pressure to operate the jet powered synthesis gas recycle system. The resulting pure synthesis gas is mixed with a recycle stream, cooled with ammonia refrigeration, and goes to the secondary separator where anhydrous ammonia (contained in the recycle stream) drops out.

The cooled synthesis gas from the secondary reformer is next exchanged with convertor effluent and feed to the ammonia converter. The converter product goes to the primary separator where anhydrous ammonia separates and then to the product flash drum. Primary separator overhead is recycled back to the catalytic convertor by the circulator compressor.

Temperature control in the ammonia catalytic convertor is controlled by introducing unreacted feed at various levels in the catalyst bed of the convertor. Various companies offering ammonia synthesis processes specify convertor conditions to meet the needs of the ammonia plant operator.

With the advent of the 1,500-t/d ammonia plant, and even more recently, interest in the 2,000-t/d plant, consideration is being given again to the proper selection of synthesis pressure. Factors such as converter design limitations and proven commercial centrifugal compressors, which dictate discharge pressure selection four years ago, do not apply today. Compressors are available for 1,500-ton ammonia plants, to compress synthesis gas to much higher pressures. Similarly, vendors of high pressure vessels have demonstrated ability for fabricating heavier, larger diameter, full closure converters capable of handling greater catalyst volumes at higher pressure levels. Therefore, selection of synthesis pressure for a new 1,500-t/d plant must involve other factors such as power for synthesis gas, recycle gas, and refrigeration compression; shaft horsepower, efficiency, and rotative speed for the synthesis gas compressor; and the usual process considerations involving reaction kinetics, conversion efficiency, and ease of product condensation.

Three synthesis loop designs will be considered: (1) Single product condensation featuring chilling the mixture of fresh feed synthesis gas and converter effluent at the discharge of the recycle compressor using several levels of ammonia refrigeration. Ammonia is withdrawn at a single location at low temperature. After separation of liquid product, vapor is recycled to the ammonia converter, a quench type vessel having three or more beds of catalyst.

Following conversion to ammonia, the effluent from the converter flows, after heat removal, to the recycle compressor for combination with makeup synthesis gas. A purge stream is withdrawn from the circuit to rid the system of excess inert methane and argon. A chiller and separator are generally provided in the purge circuit to recover small amounts of ammonia contained in the purge gas.

(2) Product recovery before recycle compression is the same as (1) except that converter effluent is cooled for product recovery before recycle compression. The converter effluent joins makeup gas at a slightly lower pressure after which the mixture is chilled for product recovery. Disengaged vapor then flows to the recycle portion of the compressor. It is then fed to the ammonia converter.

(3) Two-stage product condensation is generally applied to synthesis loops designs based on synthesis at much higher pressures. Recovery of ammonia product is made at two locations using a combination of water cooling and refrigeration. Briefly, the sequence consists of chilling converter effluent to an intermediate level for condensation of the bulk of the ammonia contained in the effluent. Condensed ammonia is recovered in a primary separator. Disengaged gas from this separation step flows to the recycle compressor where it is combined with make-up gas and further compressed. The combined gas is then water-cooled and chilled for recovery of the remaning product in a secondary separator. The two product streams are joined and delivered to a flash drum for removal of dissolved gases. The stream is then run down through the plant refrigeration system. This system is used for loop design operating at 4,000-5,000 psia. Feed gas to the converter with this process sequence is always in a high state of purity because of the purifying function of the secondary product condensation stage.

In order to compare various synthesis loop systems, certain assumption must be made. Using these simplyfying assumptions, best synthesis loop arrangement depends upon compressor efficiency for best loop pressure. An example to show major equipment costs when comparing 2,100 psia and 2,800 psia synthesis loop pressures for a 1,500 t/d plant delivering product at −28° F with a single product condensation system shows the following:

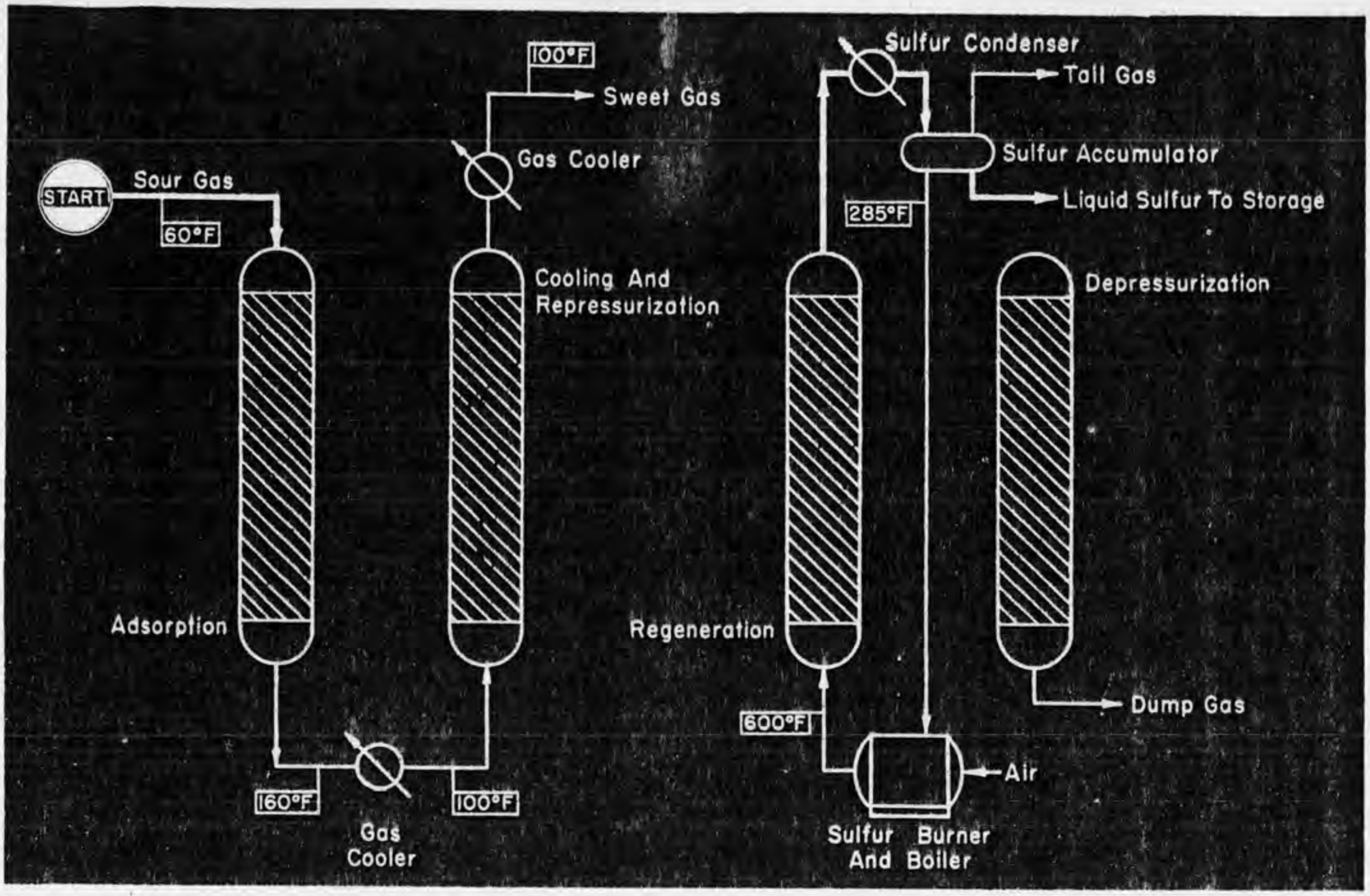
	Major Equipment Costs	
	2,100 psia Synthesis	**2,800 psia Synthesis**
Startup heaters, exchangers, converter, drums	$1,833,000	$1,661,000
Refrigerant systems exchangers, drums, etc.	137,000	130,000
Compressors, interstage equipment and associated items	1,363,000	1,405,000
Total	$3,333,000	$3,196,000
Catalyst Cost (Diff.)	85,000	–
Total	$3,418,000	$3,196,000
Net Difference	$222,000 (favor 2,800 psia)	

It should be noted however, that synthesis pressure levels, equipment and fuel costs, and brake horsepower figures are a function of the specific design and equipment employed in the analyses. The suppliers of ammonia plants listed below are best able to answer specific questions for prospective purchasers.

Economics: The economics of ammonia production are highly specialized and the companies listed below are well known in this field. The reader is advised to consult with any of these companies directly for specific details concerning the processes offered.

Commercial Installations: The following companies offer design, engineering and/or construction services for ammonia plants: C F Braun & Co., Alhambra, California 91802; Chemical Construction Corp., 320 Park Avenue, New York, New York 10022; The Fluor Corporation, Ltd., 2500 South Atlantic Blvd., Los Angeles, California 90022; Foster Wheeler Corp., 666 Fifth Avenue, New York, New York 10019; Humphreys & Glasgow Ltd., 22 Carlisle Place, London S. W. 1, England; The M. W. Kellogg Co., 711 Third Avenue, New York, New York 10017, and Montecatini Edison S.p.A., 20100 Milano, Italy.

References: *Hydrocarbon Processing*, Vol. 46, No. 4, April (1967) p. 197-202; Strelzoff, S., "A Description of Some of the Recent Advances in Petrochemical Technology in the United States", 60th National Meeting AIChE, New York Nov. 1967; Allen, J.B., "Ammonia Manufacture," *Chemical & Process Engineering*, Sept. 1965. Nitrogen, Sept./Oct. 1968; "Best Pressure for NH$_3$ Plants?", *Hydrocarbon Processing*, Nov. 1968, p. 153-161.



Sulfur Recovery (Haines Process) — KRELL AND ASSOCIATES, INCORPORATED

Application: A process for the desulfurization of natural gas.
Charge: Sour natural gas.
Product: Sulfur of 99.9 percent purity.
Description of Process: Hydrogen sulfide is removed from the raw gas stream by adsorption on synthetic crystalline zeolities. The adsorbent, which also functions as a Claus catalyst, is then regenerated with hot sulfur-burner gases for production of elemental sulfur:

$$H_2S + \frac{1}{2} SO_2 = H_2O + \frac{3}{2} S$$

Sulfur-burner gases, in turn, are generated by combusting a portion of the condensed sulfur output. Normally, the process is carried out continuously in a four-tower system.

Raw gas is fed downward through the adsorption tower; sweet gas leaving this tower will contain considerably less than ¼ grain of hydrogen sulfide per 100 standard cubic feet. At the conclusion of the adsorption period the flow of raw gas is automatically switched to a second tower containing synthetic crystalline zeolites, which, after regeneration, has previously been cooled by series flow of the sweet gas or by closed-cycle vaporization of a liquid hydrocarbon.

During the adsorption period, the third tower in the system is being regenerated upflow with hot sulfur-burner gases at essentially atmospheric pressure. Sulfur vapor leaving the tower is condensed by a water-cooled or air-cooled condenser; a portion of the liquid make is recycled to the sulfur burner for production of the sulfur dioxide containing regeneration gas.

Prior to regeneration, the fourth tower is depressurized. "Dump" gas from this tower may be fed to the plant stack for incineration of unconverted hydrogen sulfide in the tail gas, or to the air intake of the sulfur burner for production of additional sulfur dioxide. After regeneration and prior to cooling, the second tower is purged and repressurized with a bleed stream of raw gas.

When low pressure gases are to be purified, the fourth tower may be omitted from the system. In situations where the raw gas contains very low concentrations of hydrogen sulfide, such that the daily sulfur production does not justify operation of a sulfur burner, the system may be regenerated with air:

$$H_2S + 3/2\ O_2 = H_2O + SO_2$$

This type of desulfurization plant does not manufacture elemental sulfur and sulfur dioxide must be vented to the atmosphere.

Operating Conditions: When gases containing high concentrations of hydrogen sulfide are processed the heat of adsorption may cause a temperature rise of 100° F across the adsorption tower. Hence, a cooler is provided for lowering the temperature of the sweet gas flowing to the cooling tower.

Sulfur-burner gases enter the regeneration tower above the sulfur dew point (500 to 550° F) and the product gases leave at substantially the same temperature. Liquid sulfur is condensed from these gases at 285 to 300° F.

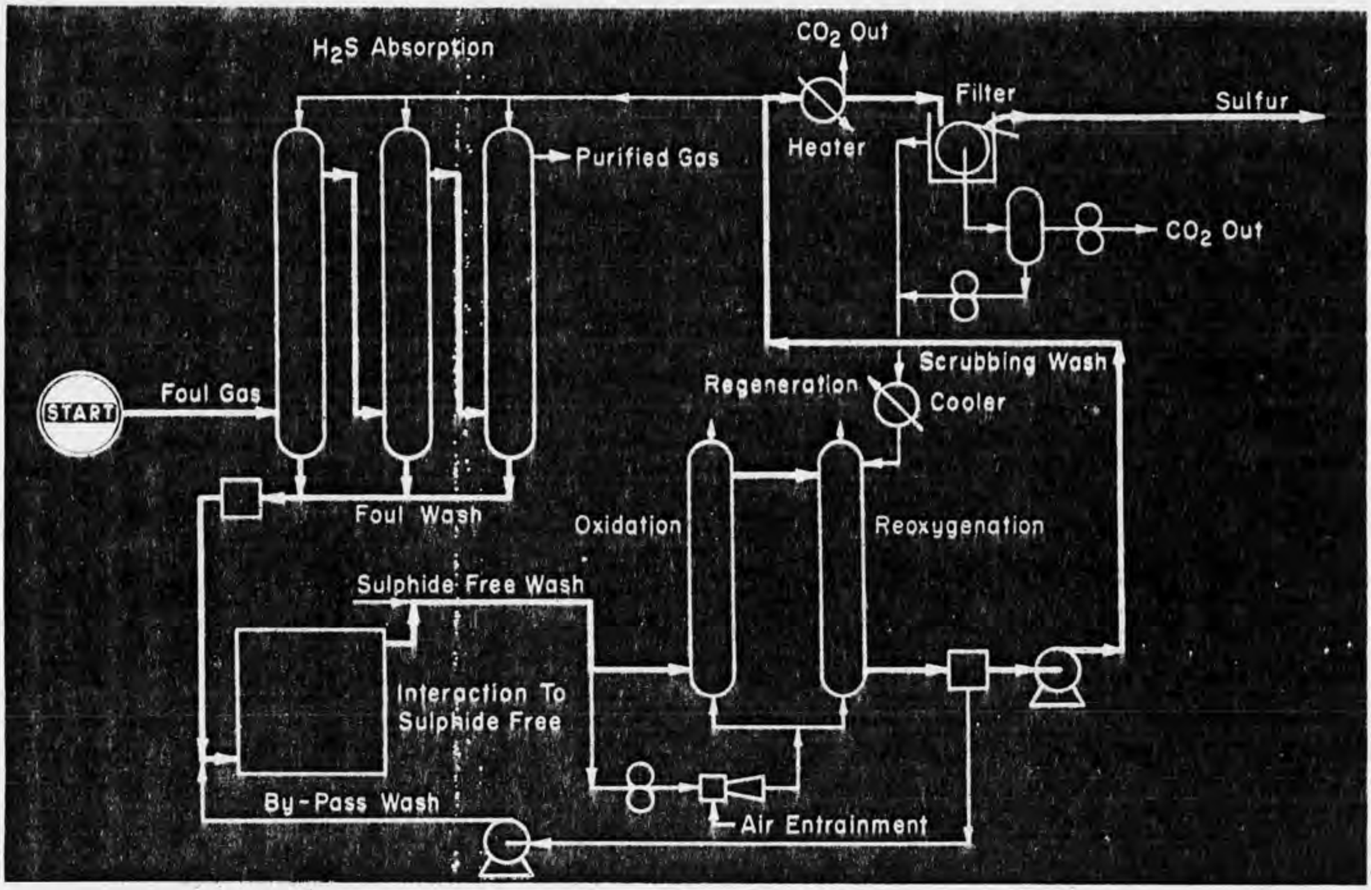
Depending upon inlet hydrogen sulfide concentrations, the adsorption period may vary from about 30 minutes to 1½ hours. Under normal operating conditions, mass velocities of gases flowing through the system will fall in the range of 800 to 8,000 pounds per hour per square foot.

Yields: Sulfur yields of 85 to 88 percent may be obtained in a single-stage unit, based on hydrogen sulfide fed to the adsorption tower. Where higher recoveries are required (up to 95 percent) a conventional Claus catalyst chamber may be placed offsite in series with the tail gas leaving the sulfur accumulator.

Commercial Installations: Bench-scale tests have been concluded and a semi-works pilot plant is under construction in Alberta, Canada.

References: Petroleum Refiner, Vol. 40, No. 4, April 1961 pp. 123; The Oil and Gas Journal, May 22, 1961, pp. 78.

Licensor: United States—Sulfur Recovery, Inc.; Canada—Western Sulfur Recovery Ltd.; Foreign—Krell & Associates, Inc.



Sulfur Recovery (Stretford Process)—THE CLAYTON ANILINE COMPANY, LTD.

Application: A continuous liquid oxidation process for the removal of hydrogen sulfide from gaseous mixtures and liquid hydrocarbons.

Principle: The gaseous mixture is washed with an aqueous alkaline solution of anthraquinone disulfonic acids which react with the SH$^-$ ion, giving an intermediate compound which, in the presence of oxygen, liberates sulfur and is itself oxidised back to its original state. The process can be accelerated by the addition of vanadates.

End-product: Gaseous mixtures with a hydrogen sulfide content of less than 1 p.p.m. and sulfur of saleable quality.

Description: Gaseous mixtures containing hydrogen sulfide are scrubbed continuously in counter-current flow in packed towers, the gas being fed through the towers in series flow while the washing medium passes down the towers in parallel flow. The number and size of towers required depends on the volume of gas to be treated, concentration of hydrogen sulfide in the gas, and the degree of removal required.

The washing solution from the scrubbing towers is passed through a reaction tank where the SH ion in solution reacts with the anthraquinone disulfonic acid and dissolved oxygen, resulting in the precipitation of sulfur.

The washing solution, which is then substantially free of SH ion, is passed to an oxidiser, preferably in co-current flow with a stream of air, whereby the reduced form of anthraquinone disulfonic acid is oxidised to its original state and the washing solution is reoxygenated.

The whole or a portion of the washing solution is passed through a filtration system for sulfur removal. The sulfur so obtained can be directly dried to a product of 95 percent purity, or if suitably treated to yield sulfur of 99.9 percent purity. The washing solution is then returned after filtration to the scrubbing towers.

The washing solution is generally buffered in the required pH range of 8.5 to 9.5 with sodium carbonate/bicarbonate and when the gas being scrubbed contains carbon dioxide, some form of decarbonification is necessary to prevent reduction of the pH value below optimum range. This is achieved by by-passing a portion of the washing liquor, after oxidation, through a heating chamber where carbon dioxide is expelled.

The addition of vanadates to the anthraquinone disulfonic acid solution has the following advantages:

1. Increase in speed of reaction, resulting in the use of smaller amounts of washing liquor and therefore a decrease in capital outlay for the plant.
2. The lower pH, 8.0 to 8.5, at which the Vanadate/anthraquinone disulfonic acid process operates, obviates the necessity for decarbonification thus reducing operational costs.
3. Side reactions, e.g. formation of thiosulfate, are reduced.

The process can be carried out at, or above, atmospheric pressure and requires very little supervision.

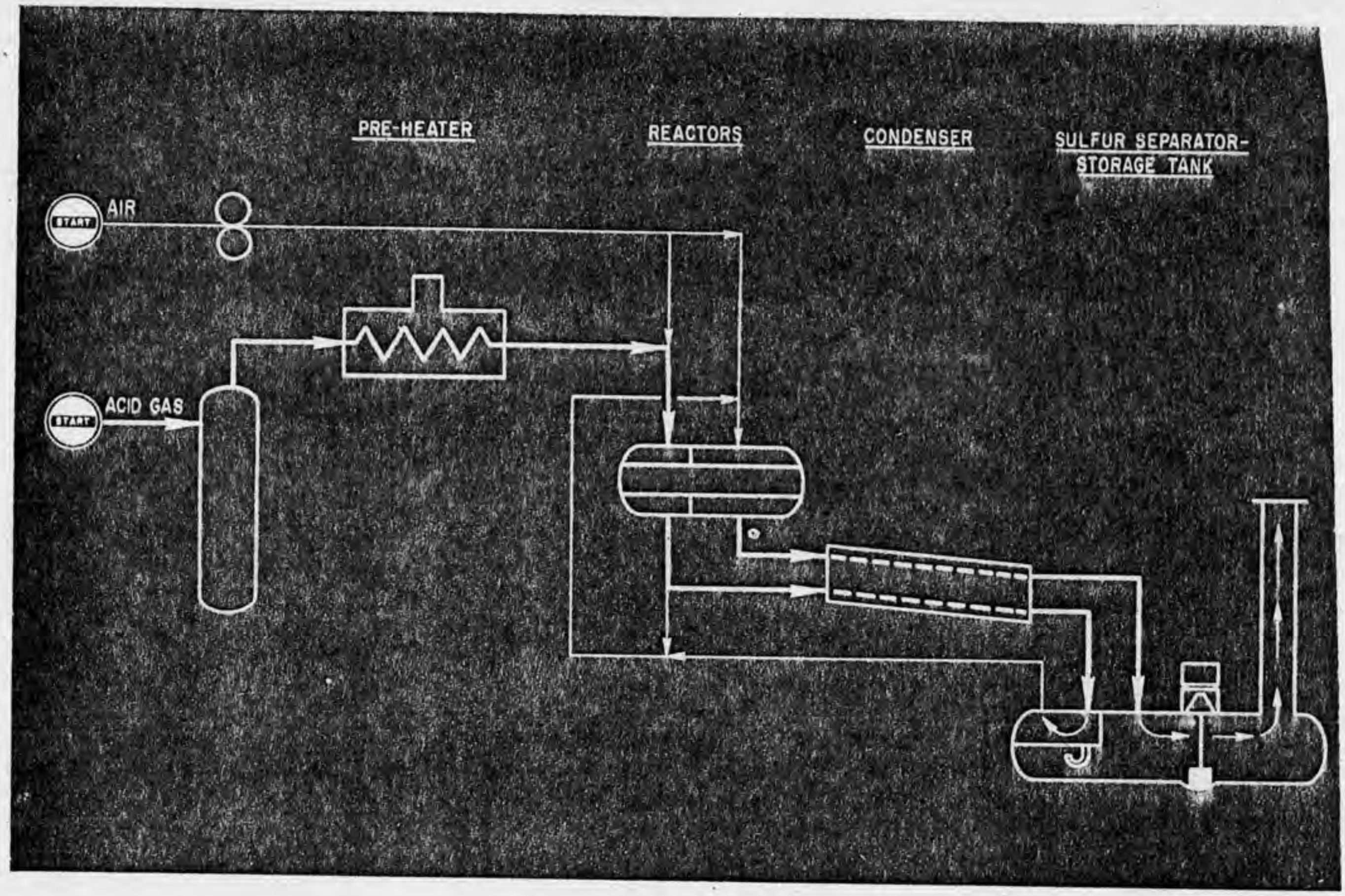
Further advantages over known liquid purification processes are:

a) The stability of the reactants to conditions other than process requirements.
b) The ability to limit side reactions, e.g. thiosulfate formation, to 2-3 percent of the sulfur input thus ensuring long life of the initial charge.
c) Sulfur can be recovered in a high state of purity.
d) Low power costs for operation.

Commercial Installations: The North Western Gas Board have successfully operated a small scale plant, purifying coal gas, at Whitchurch, Shropshire for two years and a large scale plant at Linacre Gas Works, Liverpool, for 10 months. The South Western Gas Board have also operated a large scale plant at Bristol for eight months.

Orders for further installations, both in Great Britain and on the Continent, have been received and these are now under construction.

The licencees of the process are: W. C. Holmes & Co. Ltd., Newton Chambers & Co. Ltd., R. & J. Dempster Ltd., Simon-Carves Ltd., Humphreys & Glasgow Ltd., and Woodall-Duckham Construction Co. Ltd.



Sulfur Recovery (Direct Oxidation Process)—PAN AMERICAN PETROLEUM CORP.

Application: This process is used to recover sulfur from acid gas streams which are too low in H_2S content to support noncatalytic combustion. It is also used to recover sulfur directly from sour natural gas streams, from which it is sometimes uneconomical to produce sulfur by the two-step process of sweetening and Claus conversion.

Gas streams containing about 2-15 mole % H_2S which may also contain carbon dioxide, light hydrocarbons, nitrogen, etc., may be used.

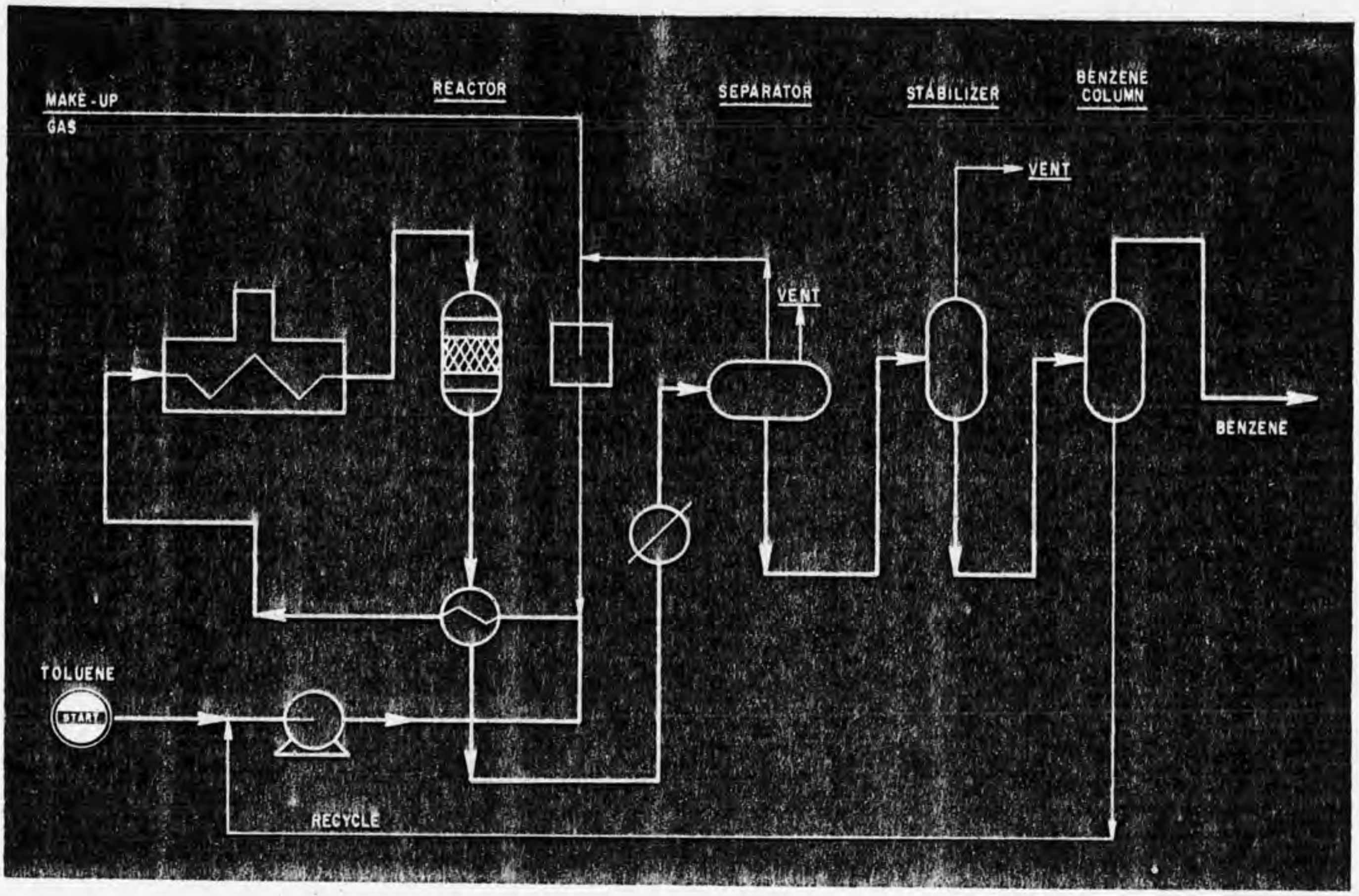
Description: The preheated feed stream, with air, is sent to the direct oxidation reactor in which oxygen reacts with H_2S over a bauxite catalyst. Products of the direct oxidation reaction are sulfur and SO_2. Since the reaction is exothermic, the temperature rise is sometimes moderated by using two or more direct oxidation reactors, cooling the gas between reactors and then feeding it to the next direct oxidation reactor along with additional air. The effluent gas from the final direct oxidation reactor i cooled to condense sulfur. The cool effluent may be dis charged from a stack or may be fed to a Claus-typ reactor to obtain additional reaction of H_2S with SO_2 t increase the sulfur yield.

Yield: Percent sulfur recovery depends principally on th H_2S concentration in the inlet gas. Usually this process can be used to obtain 70-85% sulfur recovery from a gas which could not be processed economically from any other method.

Commercial Installations: Six installations have been completed.

Licensees: A list of licensees can be obtained from Pan American Petroleum Corp., Tulsa, Okla.

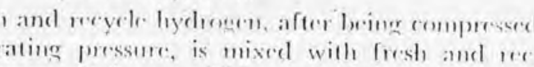
References: Gas Conditioning Conference, University of Oklahoma, April 4-5, 1967.



Benzene (Hydrodealkylation)

Application: A process for the hydrodealkylation of toluene or other alkyl aromatics, mixtures of alkyl aromatics and non-aromatics to produce benzene and/or naphthalene. The process can be catalytic or thermal and uses hydrogen or hydrogen rich gas. Benzene is normally produced from toluene or toluene/xylene mixtures. Naphthalene can be produced from alkyl-naphthalenes. The benzene product is high purity ASTM nitration grade generally from 99.95 to 99.99 weight percent. Naphthalene product has a melting point higher than 79.6° C.

Description: The process involves the hydrodealkylation of alkyl aromatics to simple aromatics and gas. Using toluene or methyl naphthalene as feedstocks, the principal reactions are:



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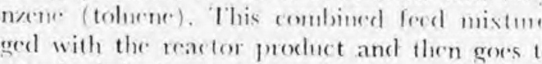


(2)

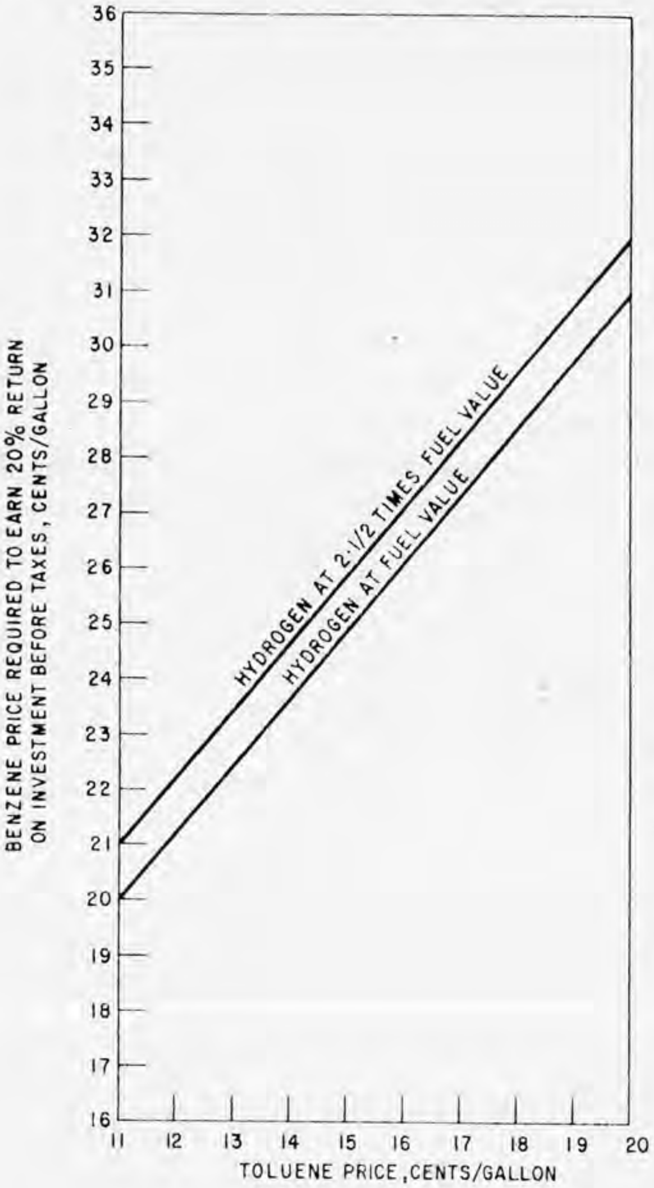
The flow sheet shown above is for the production of benzene from toluene. It is greatly simplified and makes no distinction between a catalytic process and a thermal process of hydrodealkylation.

Fresh and recycle hydrogen, after being compressed up to operating pressure, is mixed with fresh and recycle alkylbenzene (toluene). This combined feed mixture is exchanged with the reactor product and then goes to a fired heater for bringing up to reaction temperature. Some reaction systems require quench injection to control the exothermic heat of reaction when necessary. The reactor effluent is exchanged with combined feed mixture, further cooled by heat exchange and sent to a separator drum. In the separator drum, unreacted hydrogen is taken off and some gases vented to the fuel system of the plant.

Separated product is sent to a stabilizer tower where further gases are vented and the product prepared for further purification. Where high purity benzene is the desired product, addition distillation is used and in some cases clay treatment is used. Bottoms from the final distillation column are recycled to the reaction system to be combined with fresh feed. Bottoms consist primarily of toluene in the case being described and also diphenyls. In some cases there is a tar rejection step in one of the finishing distillation columns.

Hydrogen may be obtained from off-gas from reforming units or may be manufactured in a separate hydrogen plant. Some thermal hydrodealkylation processes utilize the hot reactor effluent to generate steam for process use in the unit or for the plant system.

Some thermal hydrodealkylation processes have the ability to treat feedstocks containing up to 30 weight percent of non-aromatics directly which enables the elimination of conventional aromatics extraction step. Other processes feature the use of reduced requirements of make-up hydrogen and the use of low purity hydrogen. Long continuous operation without shutdown for catalyst regeneration or decoking distinguish thermal processes.



Both catalytic and thermal processes make claims to ease of operation and low maintenance cost.

In catalytic hydrodealkylation processes, the catalyst is usually in the form of cylindrical pellets and is rugged and poison resistant. Occasional regeneration is easily accomplished in situ by burning off the coke with preheated inert gas containing controlled quantities of air. Catalyst life in commercial operation has been over four years with original catalyst charge. During these long periods of commercial operation, catalyst activity and selectivity has been maintained with infrequent regenerations.

Operation Conditions: Usual operating conditions range from 1,110 to 1,400° F and pressures from 500 to 1,000 psig.

Yields: Commercial operations have reached 99% of theoretical yield of benzene from toluene. Yields of naphthalene from methyl naphthalene have reached 95% of theoretical. Where feed streams have not been pure materials these yields have held based on the precursors in the charge stocks. The benzene product has an acid wash color of 1−, bromine index of < 1, freeze point of at least 5.4° C, and thiophene and sulfur of < 0.1 ppm.

Economics: When hydrodealkylating toluene to produce benzene, the economics can be approached in the usual manner of starting with a raw material cost and adding conversion costs and profit.

Sales values required to meet various financial objectives for a 15 million gallon per-year benzene plant located on the Gulf Coast are:

Investment (Battery Limits)	$1.5 million
Offsite Investment (⅓ of B.L.)	0.5
Total Capital	$2.0 million
Direct Operating Costs	2.3 cents/gallon
Return on Investment @ 20 percent before tax	
Sales and Administration Overhead @	1 cent/gallon

The effect of toluene value on required benzene sales prices can be seen from the following tabulation:

	All Figures in Cents/Gallon				
Toluene value	14	15	16	17	18
Raw material cost of benzene	17.5	18.8	20	21.2	22.5
Direct operating costs	2.3	2.3	2.3	2.3	2.3
Subtotal—Out of pocket costs	19.8	21.1	22.3	23.5	24.8
Depreciation at 10% of B.L. plant	1.0	1.0	1.0	1.0	1.0
Subtotal—Breakeven costs	20.8	22.1	23.3	24.5	25.8
Return on investment at 20%	2.7	2.7	2.7	2.7	2.7
Subtotal without sales % admin.	23.5	24.8	26.0	27.2	28.5
Sales & admin. overhead	1.0	1.0	1.0	1.0	1.0
Grand Total	24.5	25.8	27.0	28.2	29.5

The above figures assume hydrogen is valued at about 2½ times fuel value. Although some refiners have hydrogen at fuel value now, the large amounts of hydrogen to be required in the future in refineries for hydrocracking will result in hydrogen values higher than fuel value. Hydrogen taken at fuel value would decrease required benzine price by 0.8 cents per gallon.

The sales value (grand total) in the above tabulation represent the value required to justify a new plant; the out-of-pocket costs represent the sales value required to keep from shutting down an existing plant. Also, notice the large effect toluene value has on the required sales price.

Commercial Installations: The following companies offer design, engineering and/or construction services for hydrodealkylation plants:

Thermal Hydrodealkylation Processes: Hydrocarbon Research, Inc., 115 Broadway, New York, New York 10006; Gulf Research & Development Co., P. O. Drawer 2038, Pittsburgh, Pa. 15230; Mitsubishi Petrochemical Company, Ltd., Mitsubishi Main Building, No. 4, 2-chome, Marunouchi, Chiyoda-Ku, Tokyo, Japan.

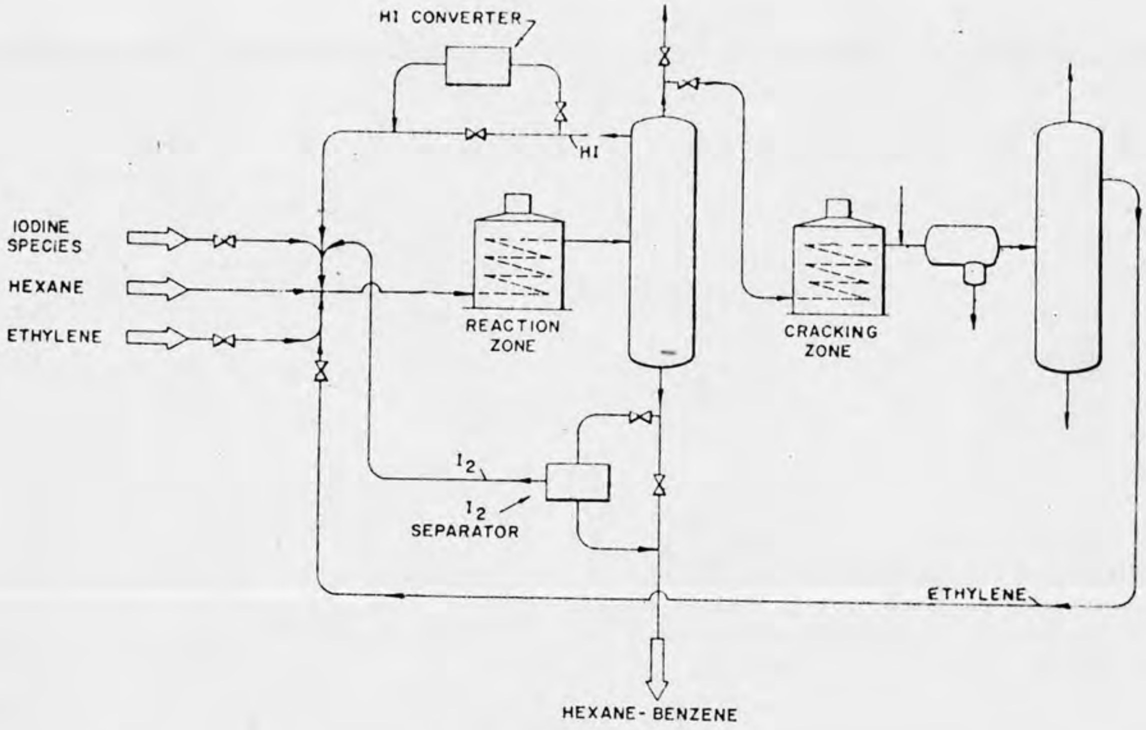
Catalytic Hydrodealkylation Processes: Universal Oil Products Co., 30 Algonquin Road, Des Plaines, Illinois 60016; Houdry Process & Chemical Co., Division of Air Products and Chemicals, Inc., P. O. Box 538, Allentown, Pa. 18105.

References: Hydrocarbon Processing, Feb. 1967 p. 155; Hydrocarbon Processing May 1966 p. 140-144; Chemical Engineering Progress, April 1962 p. 47-52; Chemical Engineering, July 22, 1963 p. 112-114; Petroleum Refiner, June 1961 p. 228.

BENZENE FROM HEXANE AND IODINE

Reaction:

$$\begin{array}{l} C_6H_{12} + 3I_2 \longrightarrow C_6H_6 + 6HI \\ 6HI + 3/2\,O_2 \longrightarrow 3H_2O + 3I_2 \\ \hline C_6H_{12} + 3/2\,O_2 \longrightarrow C_6H_6 + 3H_2O \end{array}$$



Feed Materials:
- Benzene
- Iodine
- Ethylene

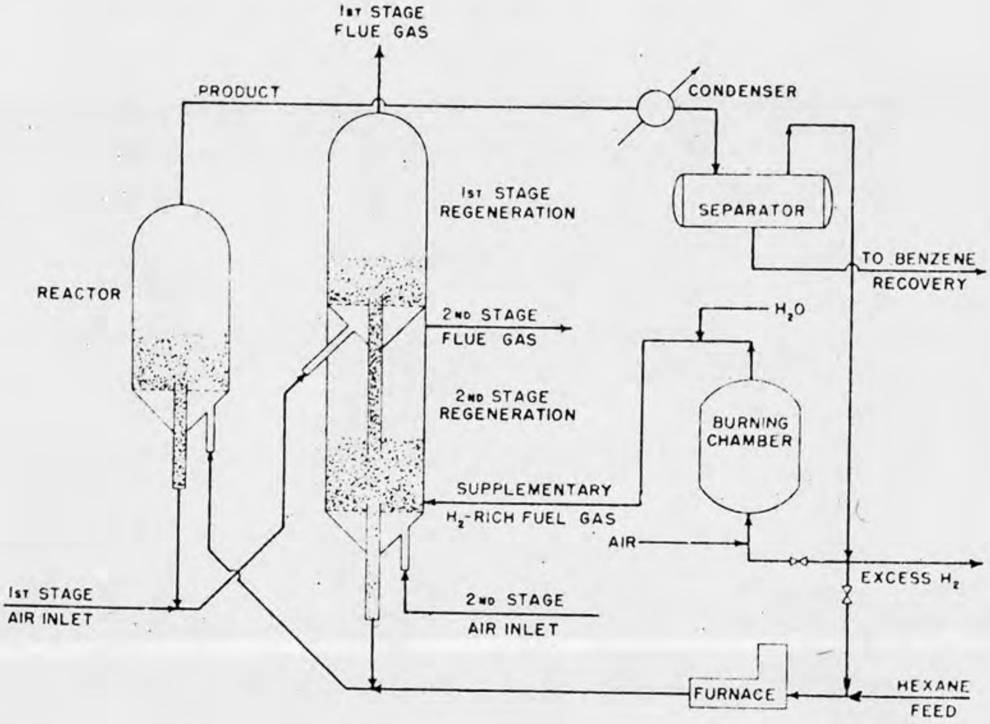
Coproducts:
- Hydrogen Iodide
- Water

Catalyst: None
Phase: Vapor
Reactor type: Fired Heater Coil
Solvent used: None
Temperature, °C: 400-600
Pressure psi: 15-150
Reaction time: 0.1 to 10.0 seconds
Heat Required: Yes
Heat evolved: -
Product yield:
Product purity:
Materials of Construction:

Major Product Uses: As solvent and as raw material for a wide variety of industrial organic chemicals (aniline, phenol, etc.).
Reference: U.S. Patent 2,880,249 by J.H. Raley et al (to Shell Development Co.) (March 31, 1959)

BENZENE FROM HEXANE

Reaction:



Feed Materials:

- Hexane
- Hydrogen Recycle

Coproducts:

- Hydrogen

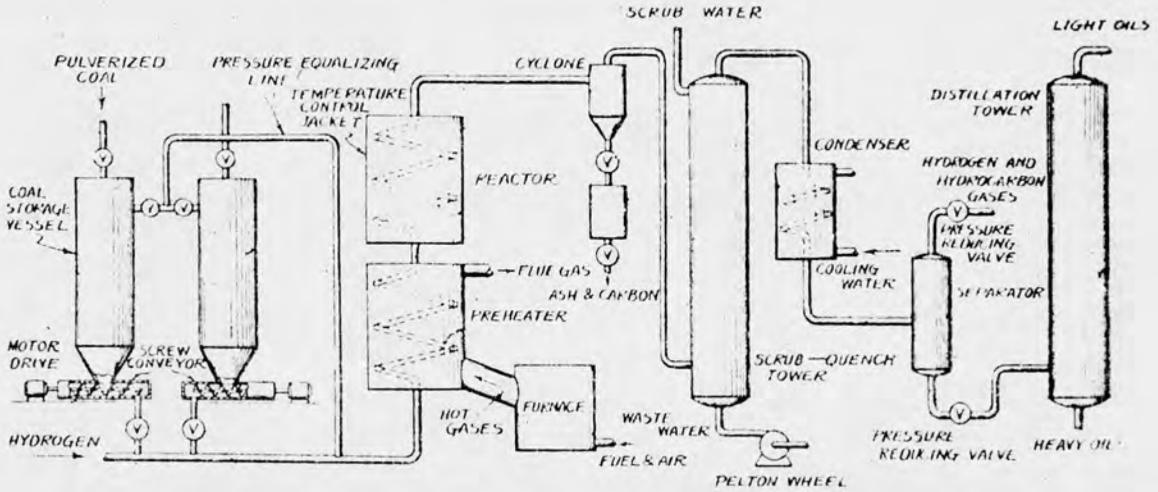
Catalyst:	Chromia on Alumina
Phase:	Vapor
Reactor type:	Fluidized-Bed
Solvent used:	None
Temperature, °C:	500-600
Pressure psi:	Atmospheric
Reaction time:	LHSV 0.3 to 0.7
Heat Required:	Yes
Heat evolved:	-
Product yield:	40%
Product purity:	
Materials of Construction:	Steel

Major Product Uses: As solvent and as raw material for a wide variety of industrial organic chemicals (aniline, phenol, etc.).

Reference: U.S. Patent 3,033,906 by R.G. Hay et al (to Gulf Research & Dev. Co.) (May 8, 1962)

BENZENE FROM COAL BY HYDROGENATION

Reaction: $3(C_3H_4)_n + 3nH_2 \longrightarrow nC_6H_6 + 3nCH_4$



Feed Materials:
- Coal
- Hydrogen

Coproducts:
- Methane

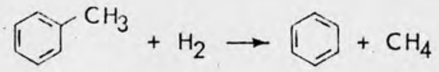
Catalyst:	None
Phase:	Mixed
Reactor type:	Tubular
Solvent used:	None
Temperature, °C:	475-525
Pressure psi:	500-3000
Reaction time:	1-2 minutes
Heat Required:	-
Heat evolved:	-
Product yield:	30% Mixed Liquid Products
Product purity:	
Materials of Construction:	Steel

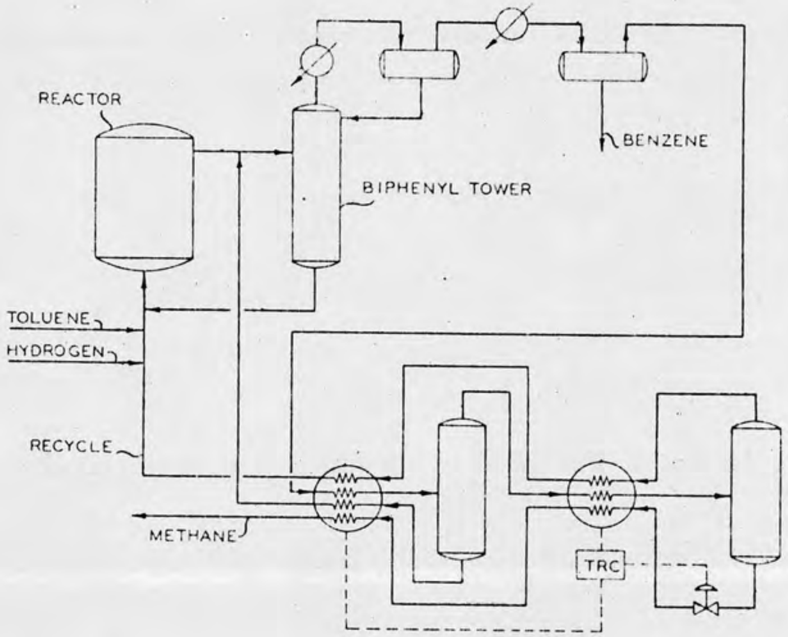
Major Product Uses: As solvent and as raw material for a wide variety of industrial organic chemicals (aniline, phenol, etc.).

Reference: U.S. Patent 3,030,297 by W.C. Schroeder (to Fossil Fuels, Inc.) (April 17, 1962)

BENZENE FROM TOLUENE

Reaction:





Feed Materials:
- Toluene
- Hydrogen

Coproducts:
- Methane

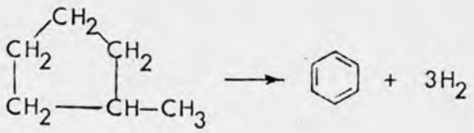
Catalyst:	None (Optical)
Phase:	Vapor
Reactor type:	Multi-Tubular
Solvent used:	None
Temperature, °C:	650-750
Pressure psi:	500-600
Reaction time:	100 seconds
Heat Required:	-
Heat evolved:	Yes
Product yield:	Over 90%
Product purity:	
Materials of Construction:	Ceramic-Lined Steel Reactor

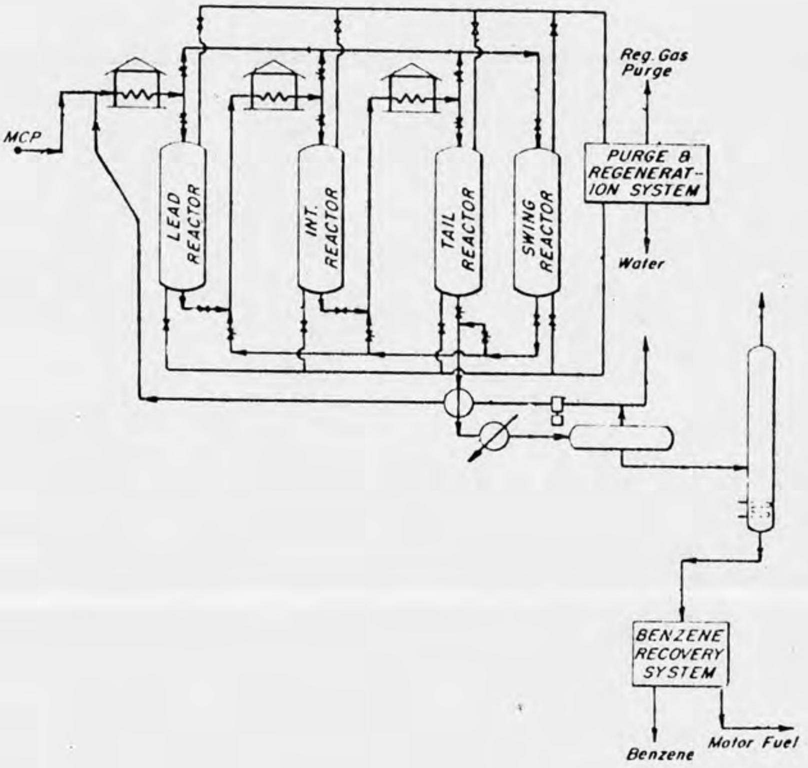
Major Product Uses: As solvent and as raw material for a wide variety of industrial organic chemicals (aniline, phenol, etc.).

Reference: U.S. Patent 3,223,745 by J.W. Davison (to Phillips Petroleum Co.) (Dec. 14, 1965)

BENZENE FROM METHYLCYCLOPENTANE

Reaction:





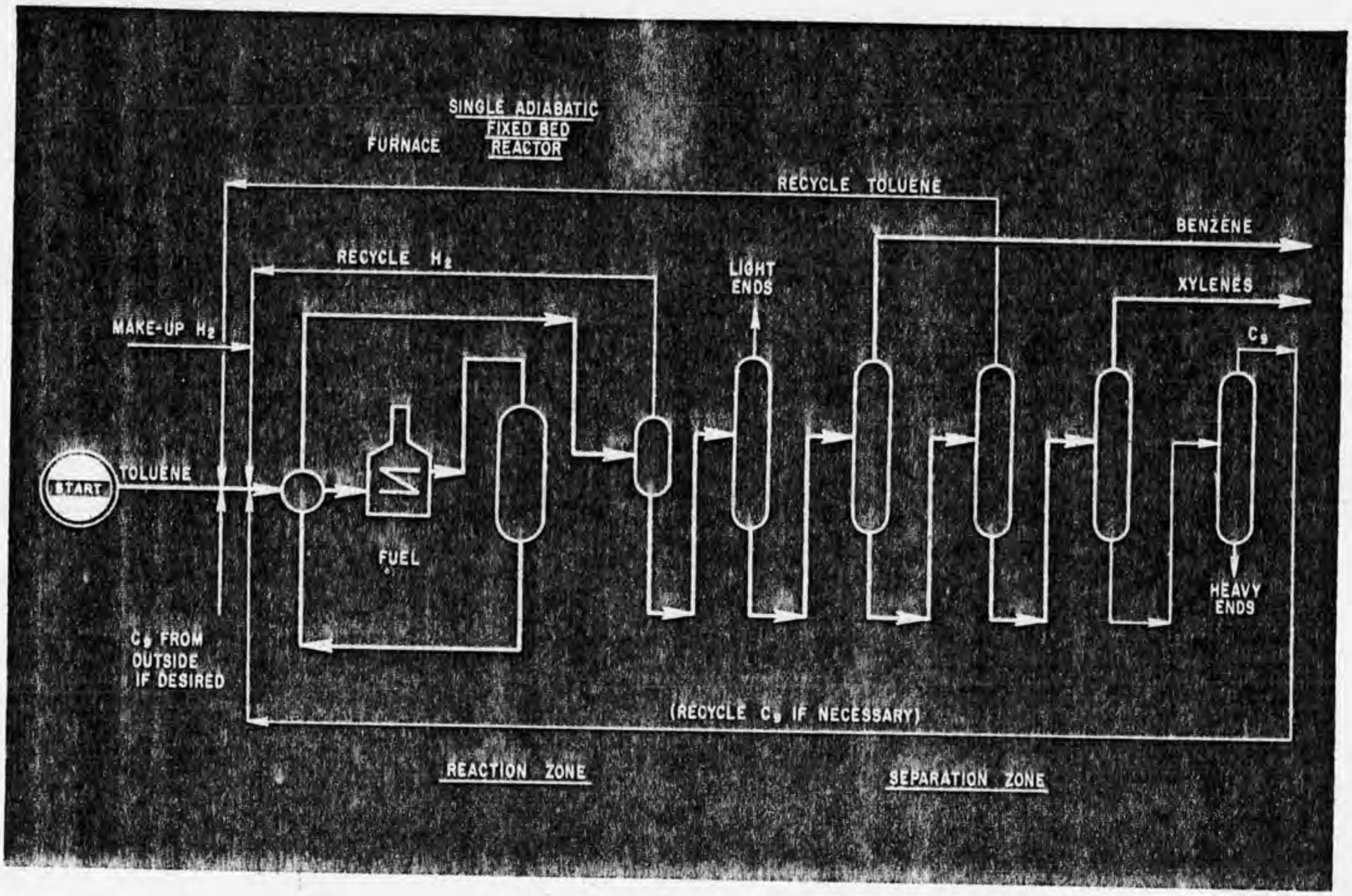
Feed Materials:
Methylcyclopentane
Hydrogen Recycle

Coproducts:
Hydrogen
High Octane Motor Fuel

Catalyst:	Platinum on Alumina
Phase:	Vapor
Reactor type:	Fixed-Bed
Solvent used:	None
Temperature, °C:	485-525
Pressure psi:	50-150
Reaction time:	3-4 seconds
Heat Required:	Yes
Heat evolved:	-
Product yield:	
Product purity:	
Materials of Construction:	Aluminized Steel or Refractory-Lined Reactors

Major Product Uses: As solvent and as raw material for a wide variety of industrial organic chemicals (aniline, phenol, etc.).

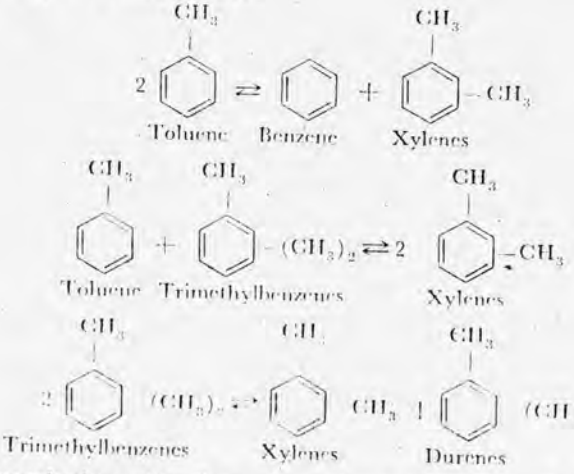
Reference: U.S. Patent 2,861,944 by J.R. Coley et al (to Standard Oil Co., Indiana) (Nov. 25, 1958)



Benzene & Xylenes — TOYO RAYON CO., LTD.

Application: A process for the transalkylation of alkylaromatics—typically toluene and/or C_9 aromatics, particularly trimethylbenzenes—to produce benzene and xylenes.

Typical reactions are:



Description: The flow scheme for toluene transalkylation is shown. The reactor contains a single adiabatic fixed bed of catalyst. This catalyst system permits high conversion per pass, has stable activity, is totally regenerable and is expected to have a total life of over 18 months. With an optimized operation, over-all selectivity of over 97% of theoretical is easily attained with H_2 consumption of less than 4 Kg/1000 Kg (230 standard cu. ft./bbl. of fresh feed.

Process features are: (1) The product mole ratio of xylene to benzene is adjustable from 0.7 to over 10 by varying feedstock composition, (2) Operating conditions are much milder than in conventional hydrodealkylation processes. Investment and utilities requirements are moderate, (3) Consumption of hydrogen is very low, (4) The products are essentially free of non-aromatics.

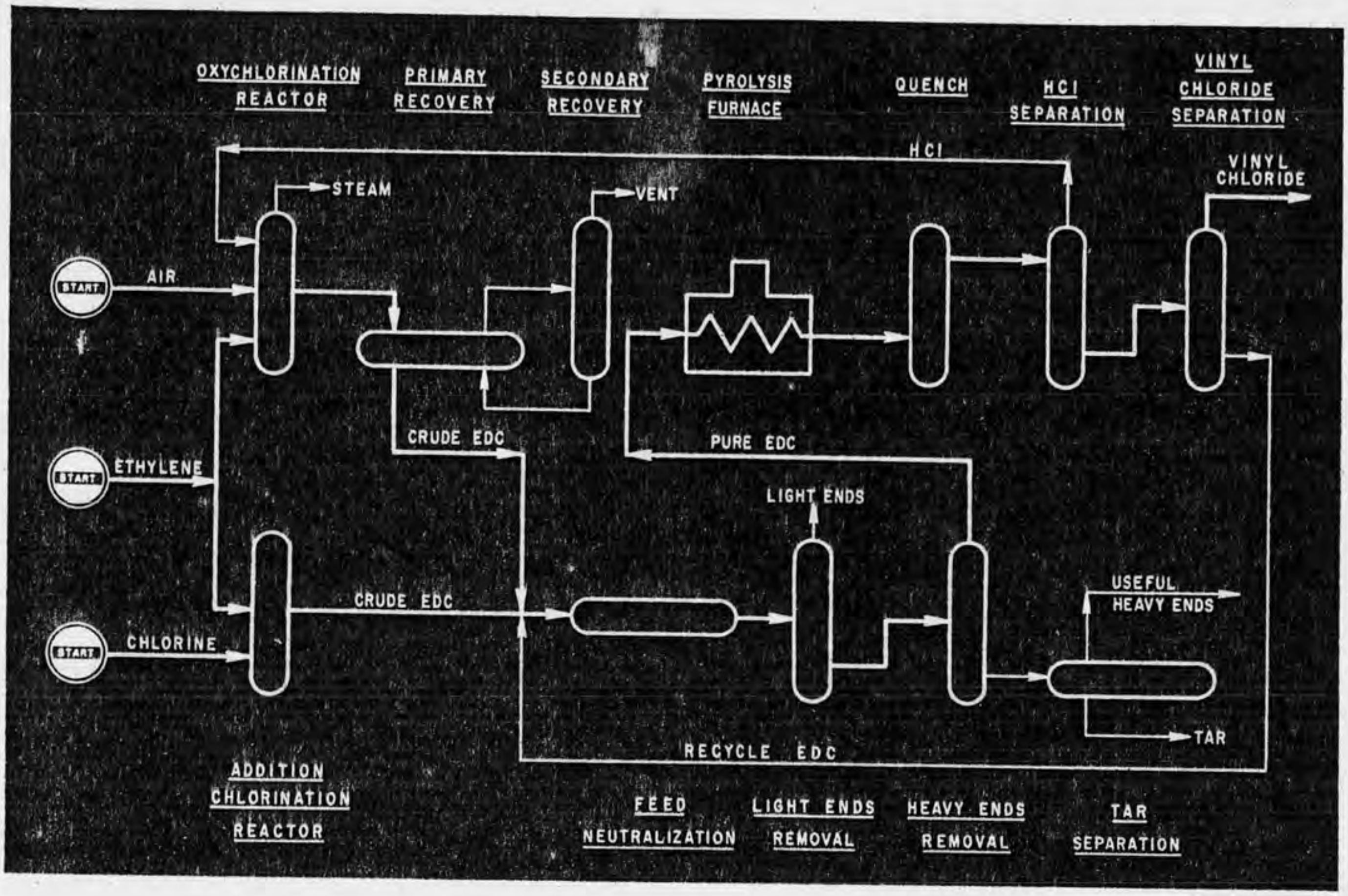
Commercial Installation: The first commercial plant is under construction for Toyo Rayon, Japan, with design annual capacity of 70,000 metric tons of fresh toluene feed.

Reference: S. Otani, S. Matsuoka and M. Sato, *Japan Chemical Quarterly*, 4, No. 4, 16 (1968).

Economics: 100,000 MT/yr. toluene feed. $2 million (U.S.) Japanese location, less engineering and royalty fees. X/B = 1.0 with C_9 recycle per 1,000 Kg. toluene feed.

Feed	
Toluene	1,000 kg
Make-up H_2	4 kg
Products	
Benzene	411 kg
Xylenes	561 kg
C_{10}^{+}	10 kg
Off-gas	19 kg
Utilities/metric tons of feed	
Electric power	73 kwh
Steam	1.5 Ton
Cooling water (Δt = 10°C)	2.6 Ton
Fuel	0.7×10^6 kcal
Labor	
1 man/shift	

Catalyst Costs: Approximately $80,000 (U.S.) per year.



Vinyl Chloride— STAUFFER CHEMICAL CO.

Application: A process to produce vinyl chloride monomer from ethylene, chlorine and air.

Description: Ethylene dichloride (EDC) is produced in both addition (direct) chlorination and oxychlorination units.

In the addition chlorination unit ethylene and chlorine are combined to produce EDC in a liquid phase reactor per equation:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \text{ (EDC)}$$

In the oxychlorination unit ethylene, air and byproduct HCl from the EDC cracking unit are reacted to produce EDC per equation:

$$C_2H_4 + 2HCl + 1/2O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

An efficient catalyst in the vapor phase oxychlorination reactor is used to promote high yields. High pressure steam generated in the oxy reactor removes reaction heat and is used as heat medium in other points in the process. EDC is separated from vent gas by condensation in two recovery units. There are no moving parts in the entire oxy process except in the air compressor and refrigeration units.

Crude EDC from the addition and the oxychlorination units is combined with recycle EDC from the cracking unit and purified by removal of small quantities of light and heavy materials. Both light and heavy ends may be treated for further use as feed to other chlorination processes.

Vinyl chloride monomer (VCM) is produced by cracking purified EDC in a pyrolysis furnace per equation:

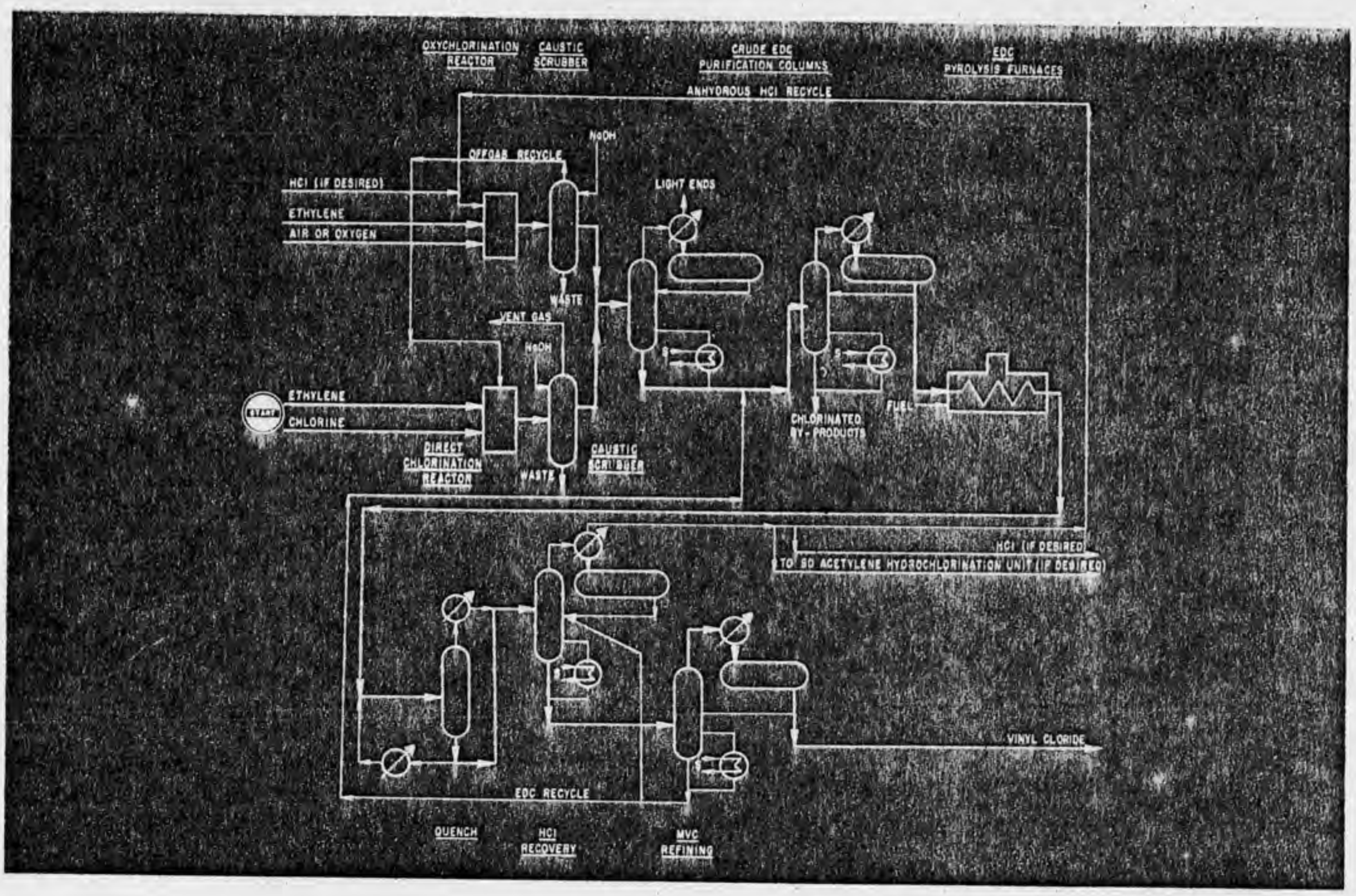
$$C_2H_4Cl_2 \xrightarrow{\Delta} C_2H_3Cl + HCl$$

After quenching, the furnace products are separated into HCl, which is recycled to the oxy unit, and high purity VCM. Unreacted EDC is recycled through the EDC purification system.

The over-all process is balanced so that only VCM is produced without byproduct HCl. Design is easily adapted to produce HCl for other uses, to use HCl from other sources, or to make EDC as a separate product.

The process is highly automated for stable, fail-safe operation at high yields over a wide turn-down range. Startup is easy and rapid. Units combine simplicity of operation with low manpower, capital, operating and maintenance costs.

Commercial Installations: Stauffer Chemical Co. offers licenses for plants based on the Balanced Process shown. The three units of the process are available separately or in any combination. There are 17 major units in operation, construction or design phase. Combined capacity of these plants is 3.7 billion pounds per year of VCM and 6.3 billion pounds per year of EDC by oxy or addition chlorination.



Vinyl Chloride (Monsanto Co.)— SCIENTIFIC DESIGN CO., INC.

Application: Processes for the manufacture of vinyl chloride monomer from ethylene, chlorine, air or oxygen. Externally produced hydrogen chloride may also be fed.

Description: The flowsheet presented represents a "balanced" vinyl chloride plant, wherein all hydrogen chloride produced as a co-product of the cracking of ethylene dichloride to monovinyl chloride is recycled to the oxychlorination reactor. The latter may also receive externally produced hydrogen chloride as a feed.

Reactions:

$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$ (Direct Chlorination)

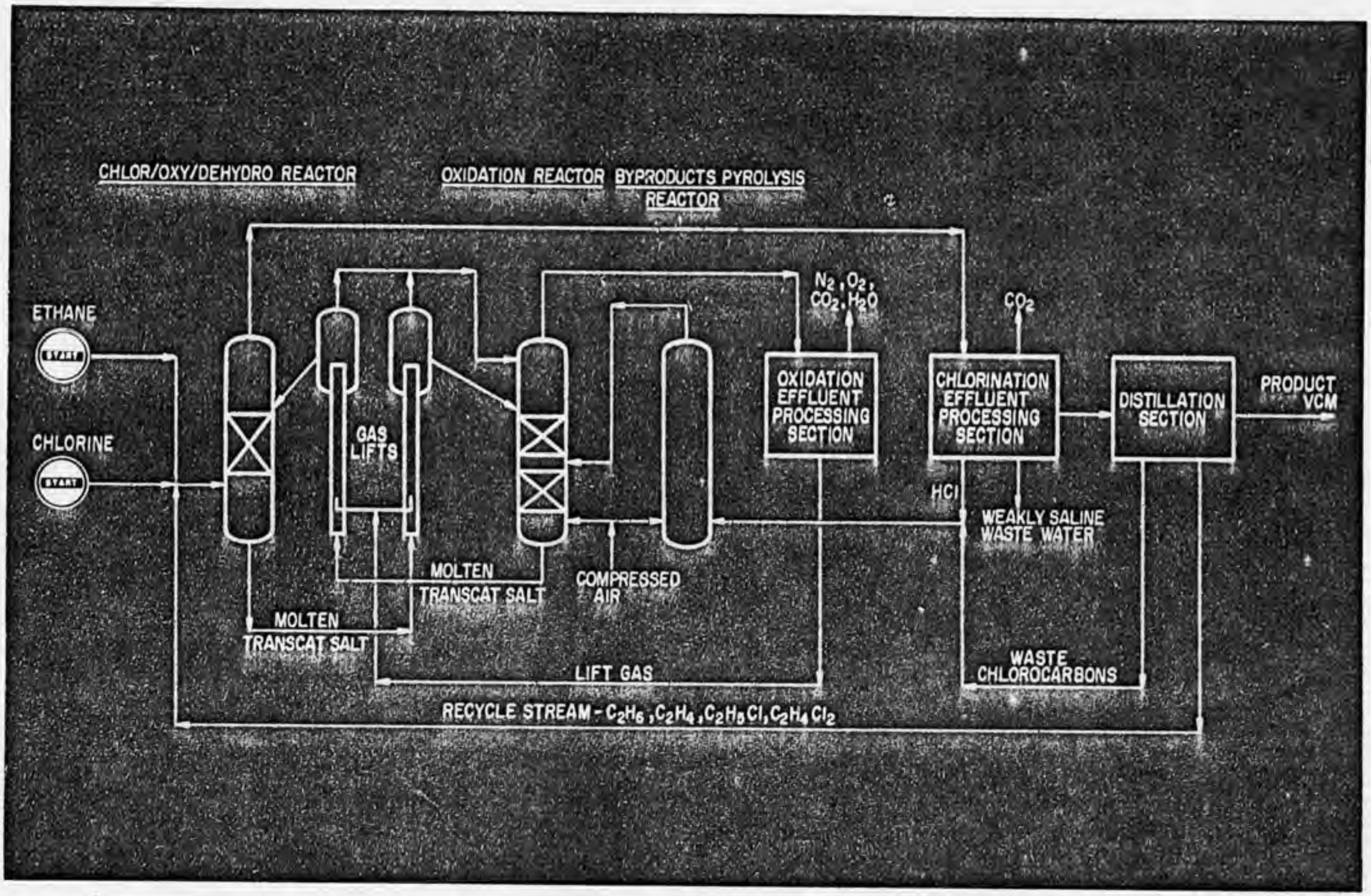
$2C_2H_4 + 4HCl + O_2 \rightarrow 2C_2H_4Cl_2 + 2H_2O$ (Oxychlorination)

$C_2H_4Cl_2 \rightarrow CH_2 = CHCl + HCl$ (Cracking)

The oxychlorination process is a vapor-phase reaction carried out in a carbon steel reactor operating at moderate pressures. In direct chlorination, ethylene and chlorine gases are charged to a reactor system containing liquid EDC as reaction medium and coolant. The EDC produced in the reaction system is then treated for removal of chlorine and HCl.

The crude EDC is purified by distillation and fed to direct-fired furnaces where it is cracked to yield vinyl chloride and HCl. The anhydrous hydrogen chloride is recycled to the oxychlorination reactor. Vinyl chloride is refined to product meeting the highest industrial specifications.

Commercial Installations: Monsanto Co., Texas City, Texas; Electrochemical Industries (Frutarom) Ltd., Haifa, Israel; Mitsubishi Chemical Industries, Ltd., Mizushima, Japan. Under construction: Petroleos Mexicanos, Pajaritos, Vera Cruz, Mexico; Chinese Petroleum Corp., Kaohsuing, Formosa.



Vinyl chloride monomer (Transcat)—THE LUMMUS CO.

Application: A process to produce vinyl chloride monomer from ethane and chlorine. When desirable, feedstocks can be partially or completely replaced by ethylene and hydrogen chloride, or by chlorohydrocarbon wastes and byproducts. The process can also be used to produce chlorinated hydrocarbons, e.g., tri- and perchloroethylene and chloromethanes.

Description: Fresh ethane and chlorine (in the simplest case) are fed to the chlorination/oxychlorination/dehydrochlorination reactor. In the presence of a molten salt containing copper oxychloride they form vinyl chloride. Impure vinyl chloride reactor effluent flows to a processing section where reaction water and waste carbon dioxide are removed and the small amount of hydrogen chloride present is recovered and recycled. The main stream goes to the distillation where viny chloride monomer is purified.

Ethane, ethylene, ethyl chloride and dichloroethane are recycled to the main reactor, while other unwanted chlorohydrocarbon byproducts are burned in the byproduct pyrolysis reactor to form CO_2, HCl, Cl_2 and H_2O.

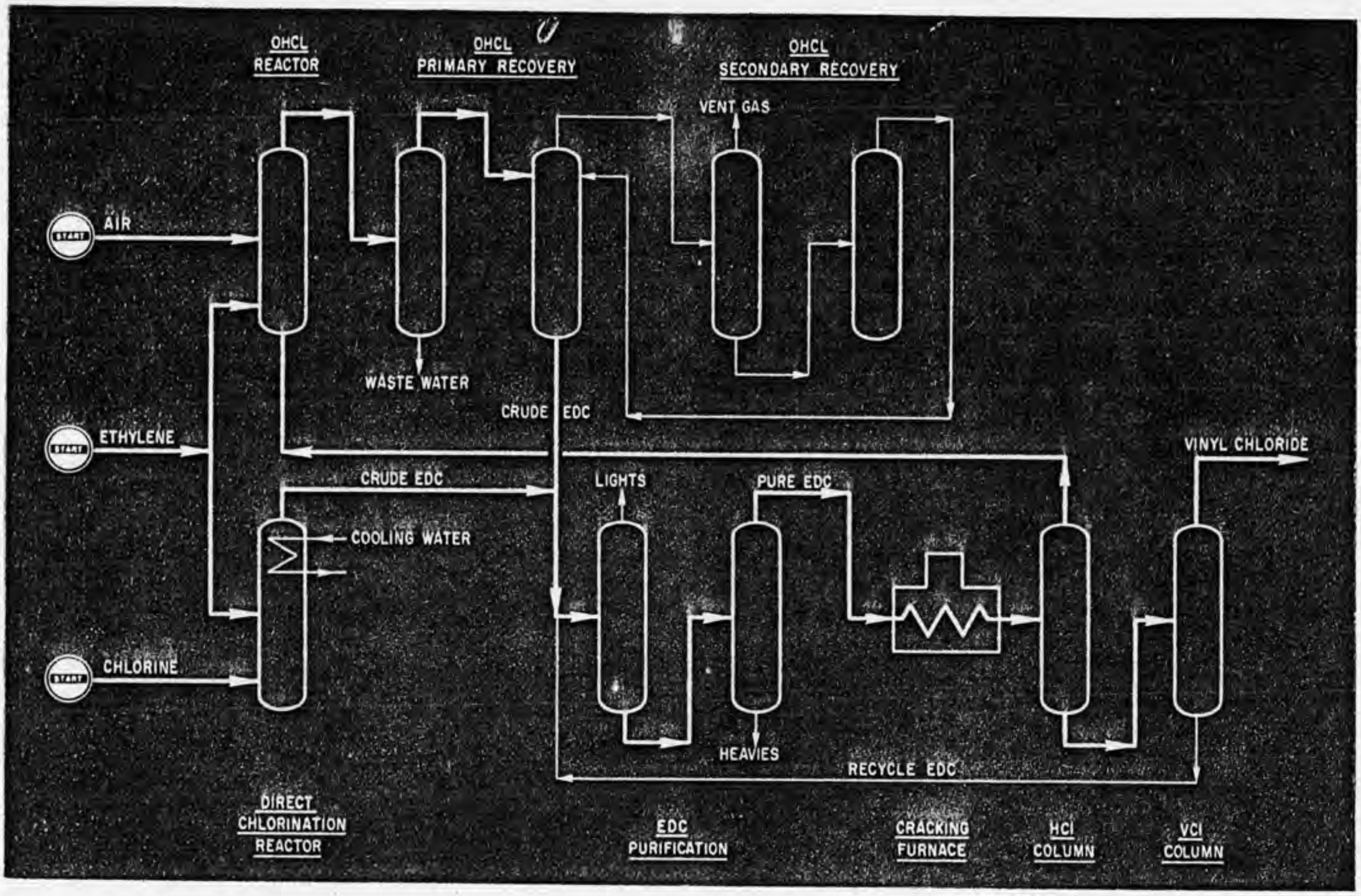
During the reaction in the chlor/oxy/dehydro reactor, the copper oxychloride is converted to cuprous and cupric chloride. The molten salt flows to the oxidation reactor, where it is oxidized with air to reform copper oxychloride. At the same time, HCl and Cl_2 in the combustion effluent from the byproduct pyrolysis reactor combine with the molten salt stream to form $CuCl_2$.

The gas from the oxidation reactor goes to the oxidation effluent processing section. Part of the gas is recycled as lift gas and the remainder is treated so it can be vented to the atmosphere, free of objectionable pollutants.

Typical plant requirements: For 500-million-pound/year vinyl chloride production—

ISBL investment	$15.7 MM
	Per pound of VCM
Ethane, 100%, lbs.	0.603
Chlorine, 100%, lbs.	0.574
Steam, 600 psig/750° F, lbs.	3.72
Condensate return, 300° F, lbs.	3.54
Cooling water, $\Delta T = 23°$ F, gal.	45.4
Electric power, kwh	0.149
Fuel, Btu	36 .
Catalyst and chemicals, cents	0.02

Yields: About 80% based on ethane and 99% based on chlorine.



Vinyl chloride — B. F. GOODRICH CHEMICAL CO.

Application: A process to produce vinyl chloride monomer and ethylene dichloride (EDC) from ethylene, chlorine and air.

Description: Vinyl chloride monomer is produced by thermal cracking of EDC according to the following equation:

$$C_2H_4Cl_2 \text{ (EDC)} \xrightarrow{\Delta} HCl + C_2H_3\,Cl$$

The feed EDC for this operation is supplied from two sources. In the first source, ethylene and chlorine are reacted in essentially stoichiometric proportions to produce EDC by direct addition thusly:

$$Cl_2 + C_2H_4 \rightarrow C_2H_4Cl_2$$

In the second source ethylene is reacted with the HCl produced from the thermal cracking operation to produce EDC by oxyhydrochlorination as follows:

$$C_2H_4 + 2\,HCl + 1/2O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

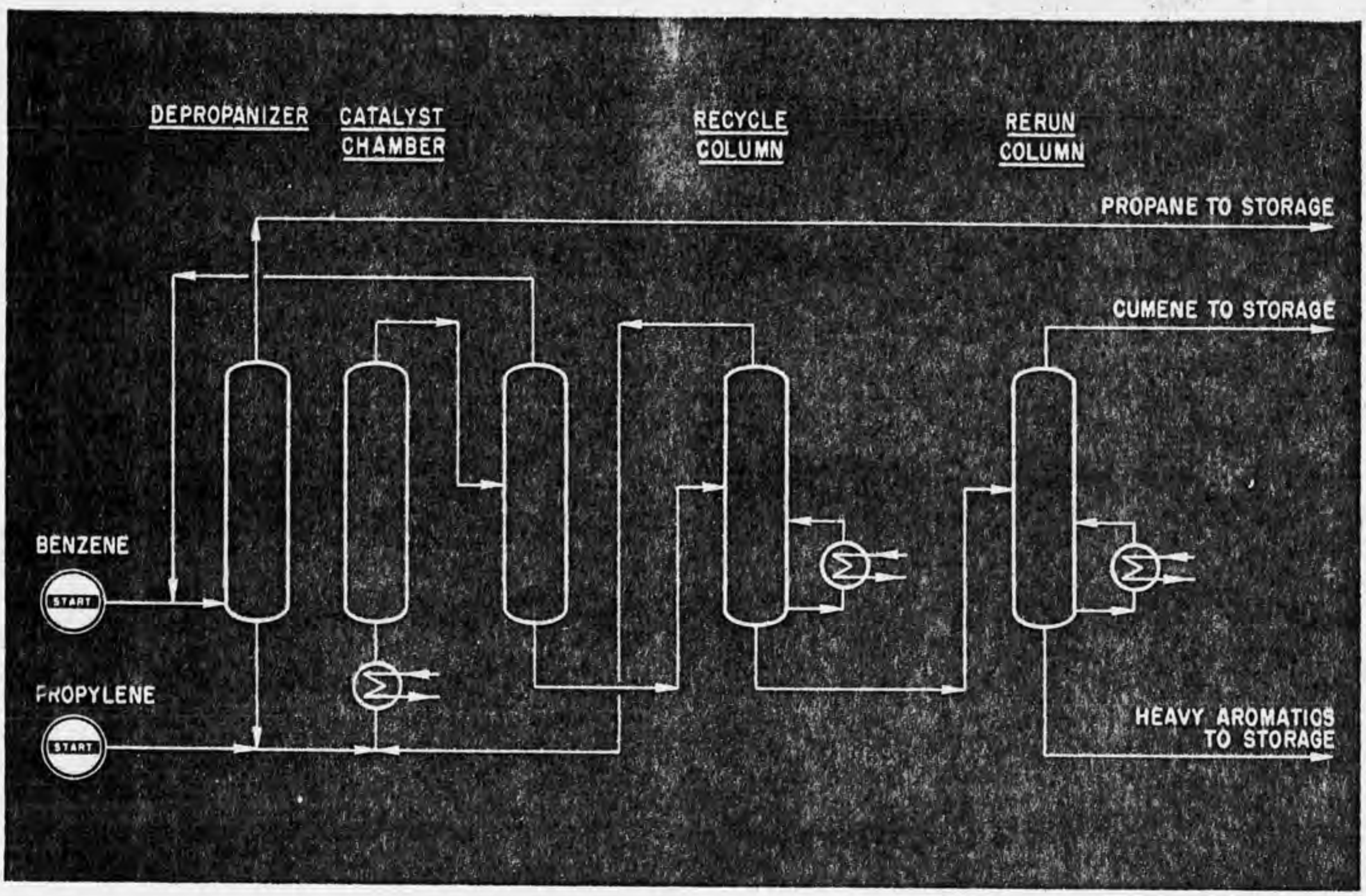
The oxyhydrochlorination reaction takes place in a fluid bed of copper chloride impregnated catalyst. Special reactor design and process conditions allow use of an all-carbon-steel reactor without risk of corrosion. The reaction products are efficiently recovered by condensation in the primary recovery unit and absorption in the secondary recovery unit. Unreacted HCl is discharged with the water of reaction as a dilute (less than 1%) hydrochloric acid stream which is easily neutralized and disposed of. The heat of reaction is removed by the generation of steam.

In the direct chlorination unit, the heat of reaction is removed with cooling water. The resultant crude EDC is combined with the crude EDC from the OHCl unit and recycle EDC from the cracking unit. The mixed stream is then fractionated to remove the small quantities of low boiling and high boiling contaminants.

The purified EDC is cracked in a furnace at elevated temperature and pressure. The hot effluent gases are rapidly quenched and distilled to remove first HCl and then VCl. Unconverted EDC is returned to the EDC purification train to remove small quantities of contaminants which would otherwise build up in the system.

Commercial installations: The Badger Co., Inc., offers engineering design and construction services for plants using this combined process scheme. B.F. Goodrich Chemical Co. processes are in operation or construction at 26 locations throughout the world. Aggregate capacity of the plants exceeds 9 billion pounds per year of total EDC by oxyhydrochlorination and direct chlorination, and 6.5 billion pounds per year of vinyl chloride monomer.

Reference: U.S. patent 2,724,006 F. Hoechst; U.S. Patent 3,488,398 B. F. Goodrich; *Chemical Week,* Aug. 29, 1964, pp. 101-108; U.S. and foreign patents applied for.



Cumene— UNIVERSAL OIL PRODUCTS CO.

Application: For the production of alkyl aromatics via the alkylation of olefins with benzene or other aromatics. Specifically used for the production of high-purity cumene (isopropylbenzene) from propylene and benzene, utilizing solid phosphoric acid catalyst. Products also include sec- and tert-butylbenzene and other alkyl aromatics.

Description: The olefin- and aromatic-containing feed stream is brought in contact with the catalyst at 350 to 435° F and 400-600 psig. An excess of aromatic is maintained to suppress dialkylation, oligomerization and other side-reactions. The catalyst is solid phosphoric acid, a pelletized and calcined mixture of phosphoric acid with kieselguhr. Chamber-type reactors are used.

The process flow is that for cumene. As illustrated in the diagram, the reactants after passing through the catalyst chamber are flashed with the vapors being charged to a depropanizer where the net propane, included with the olefin charge, is removed. The column bottoms product containing benzene is returned to the reactor. The liquid product from the flash drum is sent to the recycle column where the residual benzene is removed from the cumene product and returned to the reactor. The recycle column bottoms, containing predominately cumene product, is then sent to the rerun column where heavy aromatic byproducts are removed as a bottoms product. The overhead product cumene is of high purity, generally having less than 1000 ppm of total impurities and a bromine index of less than 100.

Yields: Yields from a modern cumene unit are approximately 96% of stoichiometry based on benzene, and 90% on propylene. The propane product is virtually free of attendent propylene and can be easily processed to make LPG specs.

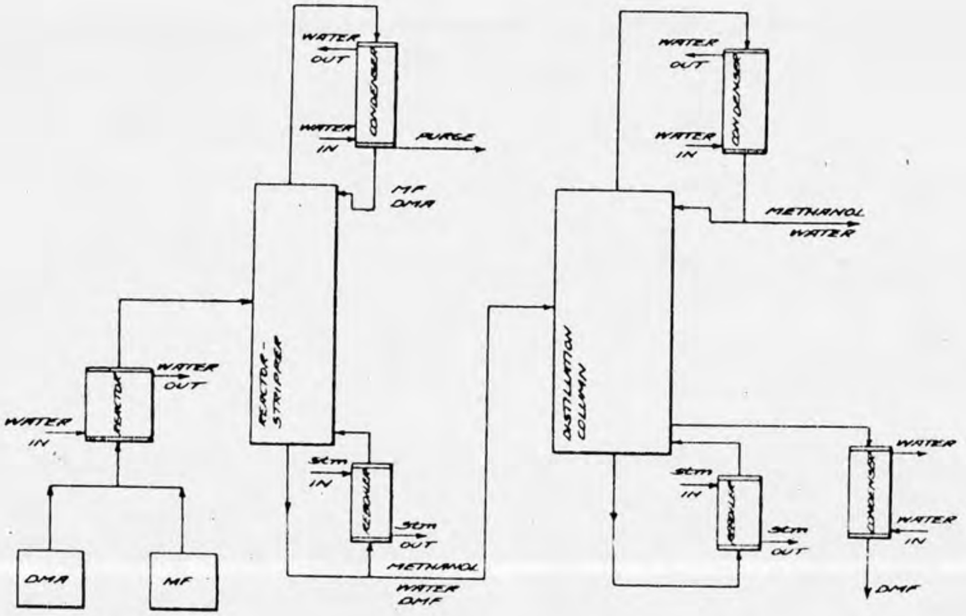
PROPERTIES OF PRODUCT CUMENE

RVP, psi	0.2
Gravity, API	31.8
Acid Wash Color	2 (max)
Total Impurities, wt-ppm	1000 (max)

Commercial Operations: The majority of the Free World's supply of cumene is made via this process in over 18 units in operation. Several others are in design or construction stages.

DIMETHYL FORMAMIDE

Reaction: $(CH_3)_2NH + HCOOCH_3 \longrightarrow HCON(CH_3)_2 + CH_3OH$



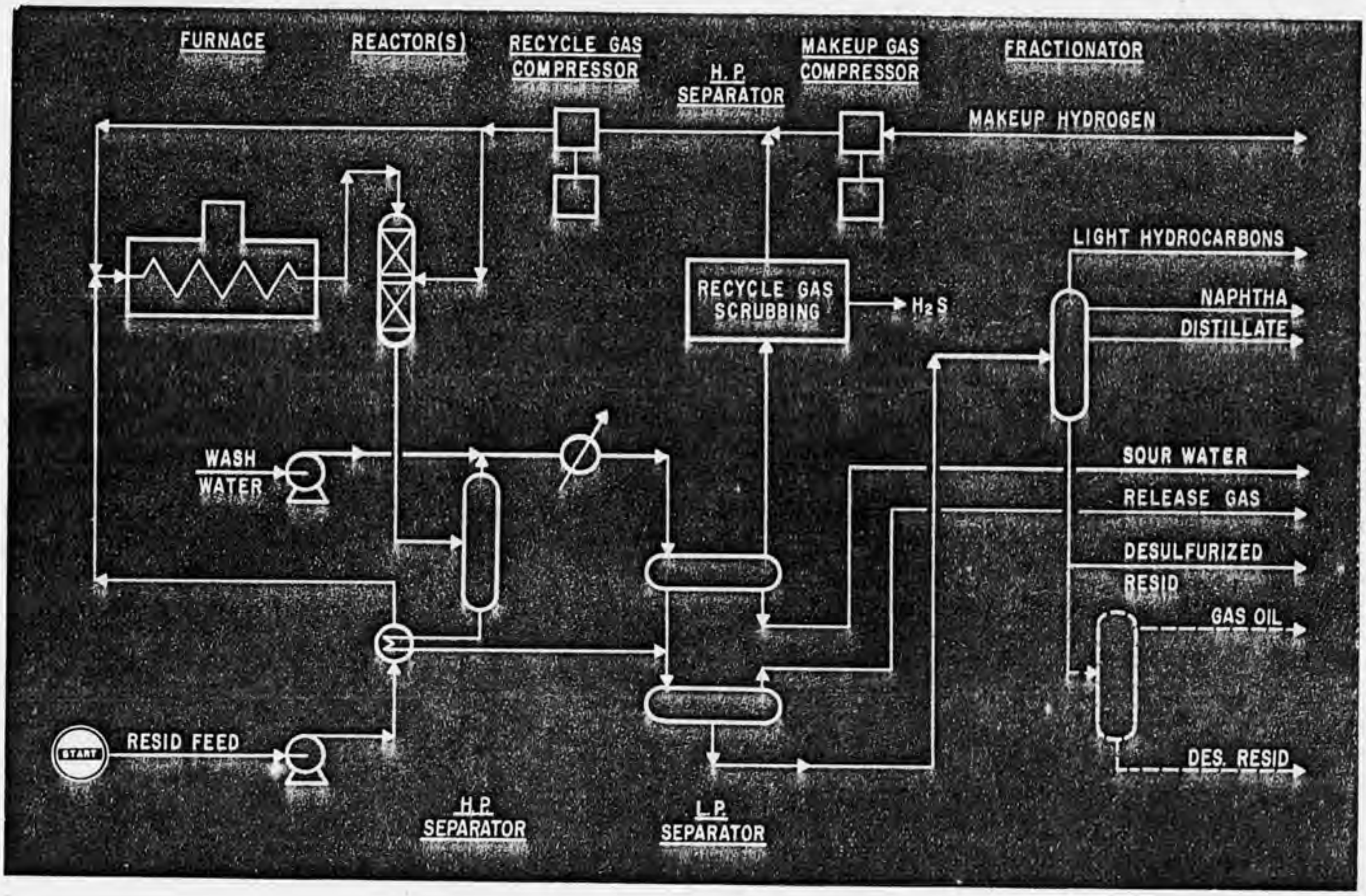
Feed Materials:
Dimethyl Amine
Methyl Formate

Coproducts:
Methanol

Catalyst:	None
Phase:	Liquid
Reactor type:	Shell and Tube Heat Exchanger
Solvent used:	None
Temperature, °C:	110–120
Pressure psi:	50
Reaction time:	
Heat Required:	–
Heat evolved:	Yes
Product yield:	
Product purity:	
Materials of Construction:	

Major Product Uses: Solvent with high solvent power for wide variety of difficultly soluble materials.

Reference: U.S. Patent 3,072,725 by R.C. Surman (to Du Pont) (Jan. 8, 1963)



Resid hydroprocessing

Applications: Desulfurization of high sulfur resids or to improve catalytic cracking unit feed.

Charge: Typical feedstocks consist of atmospheric and vacuum resids from Khafji, Gach Saran, Cyrus, Jobo, Darius, El Morgan, Kuwait, West Texas and Mid-Continent crudes.

Products: Low sulfur fuels ranging upward from about 0.3 wt% sulfur depending upon feedstock and refiners needs. The fuels are stable and low in viscosity and metal contaminant content. Significant conversion of resid to a low sulfur gas oil is an alternate operation.

Description: A fixed-bed process for direct desulfurization or partial conversion of atmospheric or vacuum resids. The catalyst utilized in the process is unique and highly effective. It has high activity so that desulfurization of resid can be carried out at attractive hydrogen partial pressures and catalyst loadings. The catalyst is highly tolerant to metal contaminants and is specifically designed to overcome pressure drop problems. The process includes several design features which insure a low cost operation, including a catalyst replacement technique which has been highly developed for rapid change out of catalyst.

The process flow is as follows: Makeup and recycle H_2 gas streams are combined with resid and desulfurized in a multibed reactor. A vapor-liquid separation is made at reactor effluent. Vapor flows through heat exchange to a low temperature separator where recycle gas is separated from liquid. The recycle gas is scrubbed for H_2S removal. Hydrocarbon liquid from the two separators is fractionated into a desulfurized resid and lighter products. The desulfurized resid can be blended to fuel or be further processed, for example, to recover gas oil. Off gases are scrubbed for H_2S removal. The rich solvent is regenerated for further use. Sour water is stripped for H_2S and NH_3 removal.

Yields:

Charge (Atm. Resids)	Kuwait		Sour W. Texas		Khafji	Gach Saran
°API	15.1		15.4		12.3	14.6
Sulfur, wt. %	4.02		3.65		4.47	2.55
Ni + V, ppm	69		41		141	258
Viscosity, cs at 122° F.	400		300		3,000	650
Pour Point, °F	55		80		70	75
Vol. % 650° F−	0		13.3		0	0
Yields (average)						
H_2 consumption, SCFB	560	660	700		780	400
C_1-C_4, wt. %	.46	.87	1.4		.70	.80
C_5-360° F, vol. %	1.4	1.9	3.0		2.2	2.4
360-650° F, vol. %	8.7	11.7	26.8		10.9	11.8
650° F+, vol. %	91.0	88.0	72.1		89.5	88.0
Gas Oil, vol. %	......	......	57.1		.....	.....
Residuum, vol. %	......	......	15		.....	.....
Product Quality, 650° F.+			Gas Oil	DeS. Resid		
Sulfur, wt. %	1.0	0.5	0.23	0.7	.65	.40
°API	19.9	21.4	24.8	9.8	20.5	20.5
Ni + V, ppm	16	9	0.1	31	57	67
Viscosity, cs at 122° F.	270	140	72	80*	270	260
Pour Point, °F	25	25	100	155**	60	65
Ramscarbon, wt. %	......	......	1.0	16	.....	.....

* At 250° F.
** Softening point.

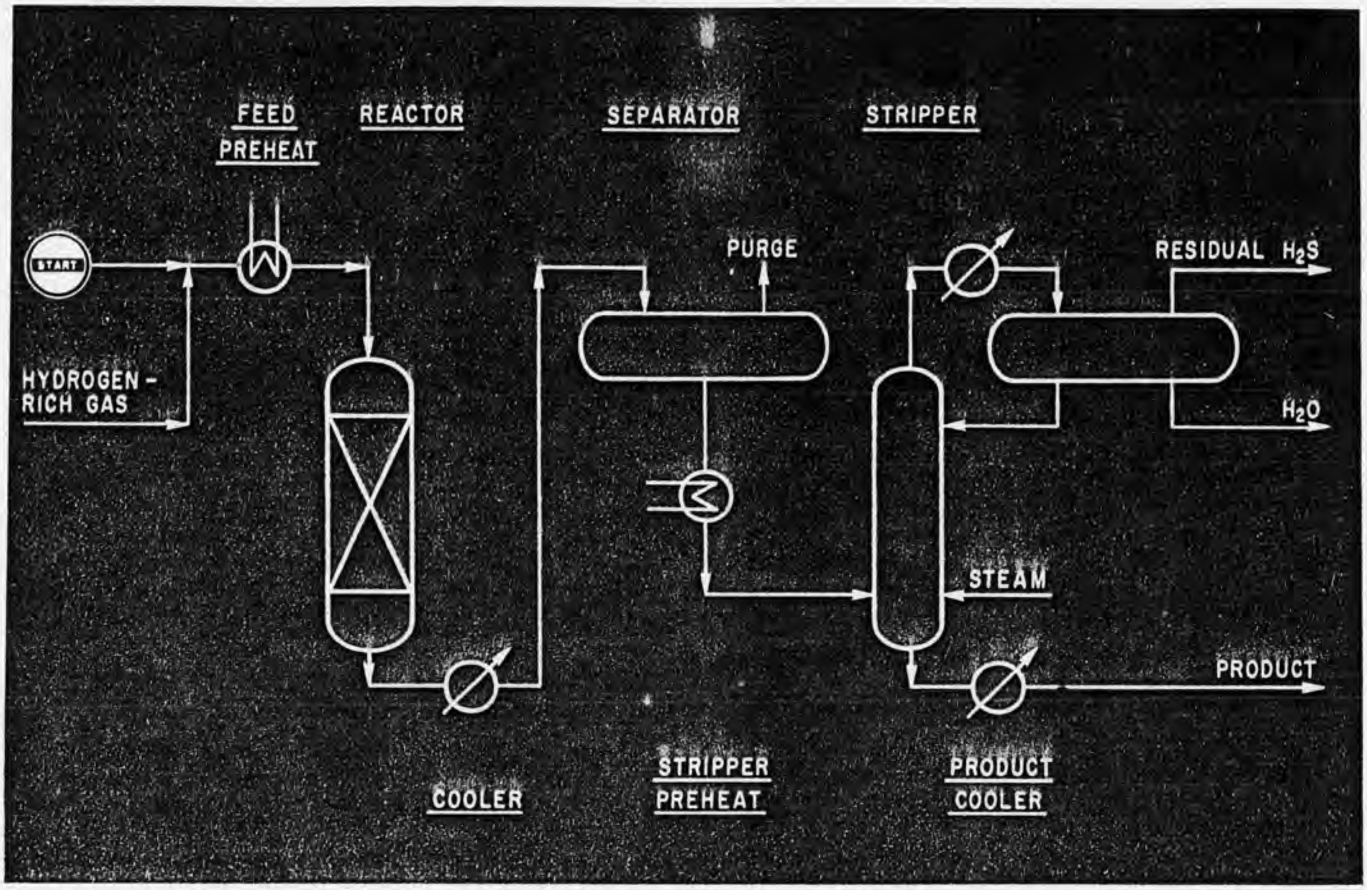
Economics:***

Investment, (Basis: desulfurizing 20,000 to 40,000 bpsd of Kuwait atmos. resid to 1.0 wt% sulfur in 650° F+ product, Jan. 1973, Gulf Coast), $ per bpsd capacity	560-620
Typical requirement, unit per bbl feed	
Electricity, kwh	4.4
Steam, lb	2.6
Fuel, M Btu	86
Water, cooling, gal.	160
Water, process gal.	4.2
Catalyst $	0.08
Average hydrogen consumption scf	560

*** Includes amine recovery and regeneration

Reference: *Hydrocarbon Processing*, Vol. 49, No. 11, Nov. 1970, pp. 187-191.

Licensor: Standard Oil Co. (Indiana).



Hydrofining

Application: Hydrofining improves the quality of a wide variety of petroleum feedstocks and products by catalytic treatment with hydrogen. This process is extremely versatile and with the proper choice of catalyst and conditions has been successfully used to remove impurities such as sulfur and nitrogen as well as to improve the odor, color, stability, and burning characteristics of virgin and cracked materials ranging from light ends to heavy distillate gas oil and lube stocks.

Hydrofining will reduce the sulfur content of naphthas to the low ppm levels required in bimetallic reforming catalysts or the active SNG catalysts. It may also be used to upgrade highly unsaturated materials such as cat cracker or coker naphthas. These feeds can be partially treated to form stable desulfurized fuels or completely hydrofined to remove essentially all sulfur, nitrogen and olefinic impurities. The latter operation will yield feedstock suitable for catalytic reforming or for petrochemical grade naphtha.

Hydrofining is used to sweeten and improve the color, stability and burning qualities of kerosine and jet fuels. High quality diesel fuels can be made from sour crudes. When applied to cracked heating oils, Hydrofining upgrades the color and stability to make these stocks compatible with virgin heating oils. Light coker gas oils can similarly be treated to produce a desulfurized fuel oil comparable in quality to a straight run gasoline. Hydrofining also improves the color, odor, stability, demulsibility and other properties of lubricating oils and waxes.

High activity catalysts are available which can be applied in a number of situations to reduce overall catalyst requirements and improve cycle lengths. These catalysts can also be applied for debottlenecking of existing hydrotreaters to permit increased desulfurization capabilities.

Description: The oil feed is preheated to a temperature usually between 400 and 700° F. It then passes to a fixed bed reactor vessel together with hydrogen-rich gas. In the reactor, the feed is treated in the presence of the hydrogen and a regenerable metal oxide catalyst at pressures usually between 200 and 500 psi. After leaving the reactor, the product stream is cooled before entering a separator where hydrogen-rich gas is separated for use in other operations. After separation, the product is stripped for removal of any residual hydrogen sulfide.

Economics:

Investment (Basis: direct material and labor, 2nd quarter 1973, U.S. Gulf Coast), $ per bpsd capacity	50-200*
Typical requirement, unit per bbl. feed	
Electricity, kwh	0.3-0.5
Steam (125 psig), lb.	5-12
Fuel, M Btu	0-25
Water, cooling (25° rise), gal.	0-50
Maintenance, per yr. as % of investment	3

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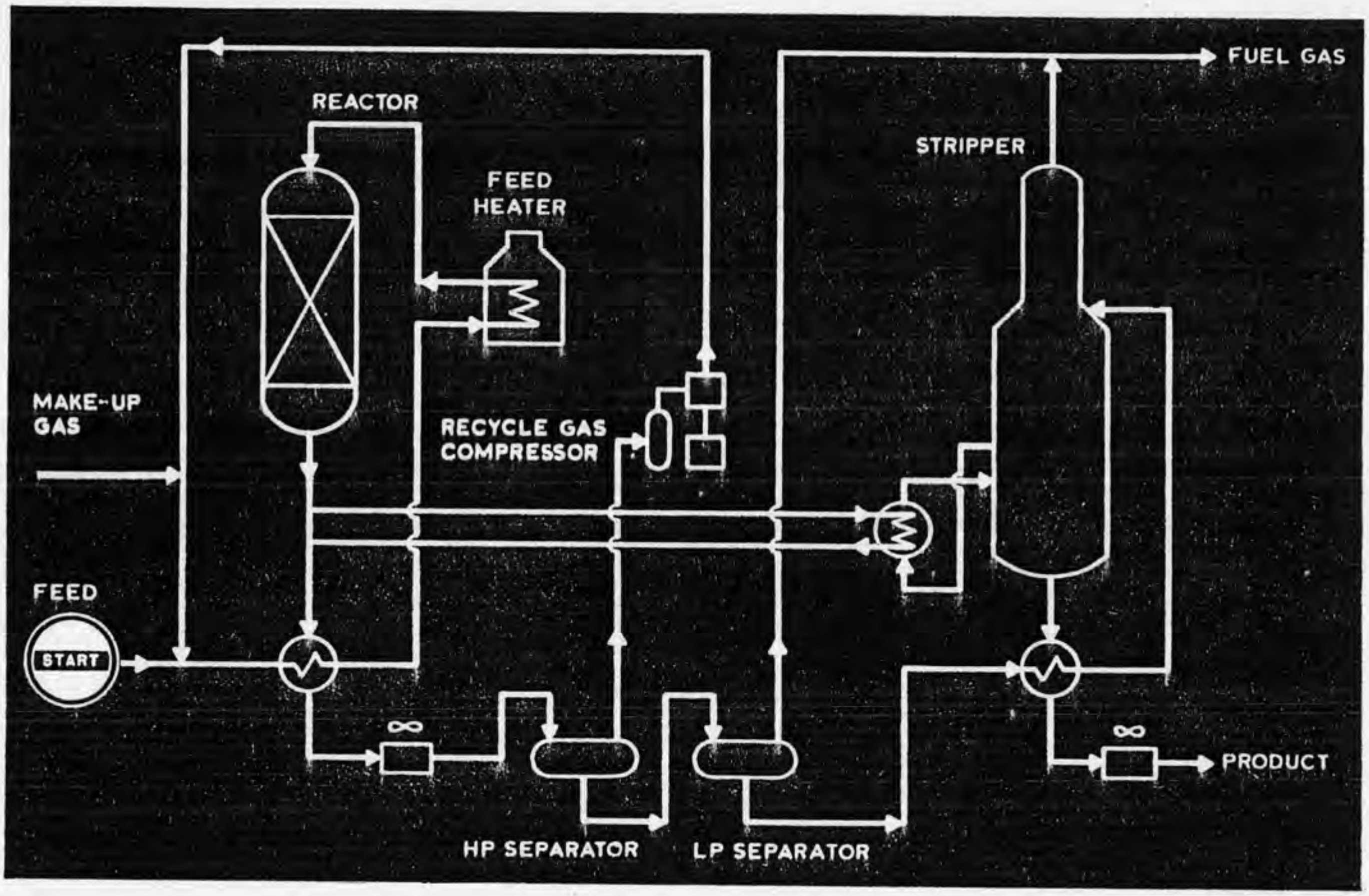
* As an approximation, the mid 1974 total erected cost can be obtained by multiplying the direct material and labor cost by a factor of 1.5. Wide range of investments due to variety of applications; large virgin feed units tend to be at lower cost range while small cracked stock feed units are covered by upper cost range.

Commercial installations: Approximately 200 units are in operation or being designed with a total capacity of about 3 million bpsd.

Reference: *Petroleum Refiner,* Vol. 36, No. 9, Sept. 1957, pp. 233-235.

Licensor: Exxon Research and Engineering Co.



Hydrofining

Application: To remove the sulfur from a wide range of distillate feedstocks by catalytic hydrogenation. The desulfurized products are also improved in odor, color and stability and in addition meet the feedstock requirements of other processes.

Charge: Distillates ranging from light gasolines to vacuum gas oils of up to 1020° F end point, including catalytic cracker cycle oil or coker gas oil components.

Description: Feedstock is mixed with hydrogen rich gas, heated to treatment temperature and passed through a reactor containing a fixed bed of desulfurization catalyst. The hot reactor effluent exchanges heat with the incoming feed mixture, is cooled and separated into gaseous and liquid streams at high pressure. The separated gas stream is then recycled to the process to minimize make-up gas hydrogen requirements.

The liquid product stream is passed to a low pressure separator which allows the removal of dissolved gases before the next stage, a stripper column, where the product is freed from hydrogen sulfide and any light ends. Part of the reactor effluent stream may be used to supply heat to the product stripper reboiler or alternatively steam can be used if available.

The catalyst used in the process is robust and easily regenerable.

Economics:

Type of feedstock	Naphtha	Kerosine	Gas oil	Vacuum gas oil
Plant capacity, bpsd	6,000	20,000	20,000	20,000
Investment, $ per bpsd*	145	140	160	170
Utilities, per bbl feed				
Electricity, kwh	0.54	1.2	2.0	2.4
Steam, reboiling (450 psig), lb.	50	—	—	—
Steam, atomizing (175 psig), lb.	—	—	1	—
Steam, stripping (25 psig), lb.	—	—	—	8
Cooling water (30° F rise), USG	144	168	7***	7***
Fuel, M Btu	42	65	71	74
Catalyst replacement cost, cents**	0.2	0.3	0.3	0.7

* Estimated erected cost—materials and direct labor—mid 1973, U.K. location, excluding initial catalyst charge.

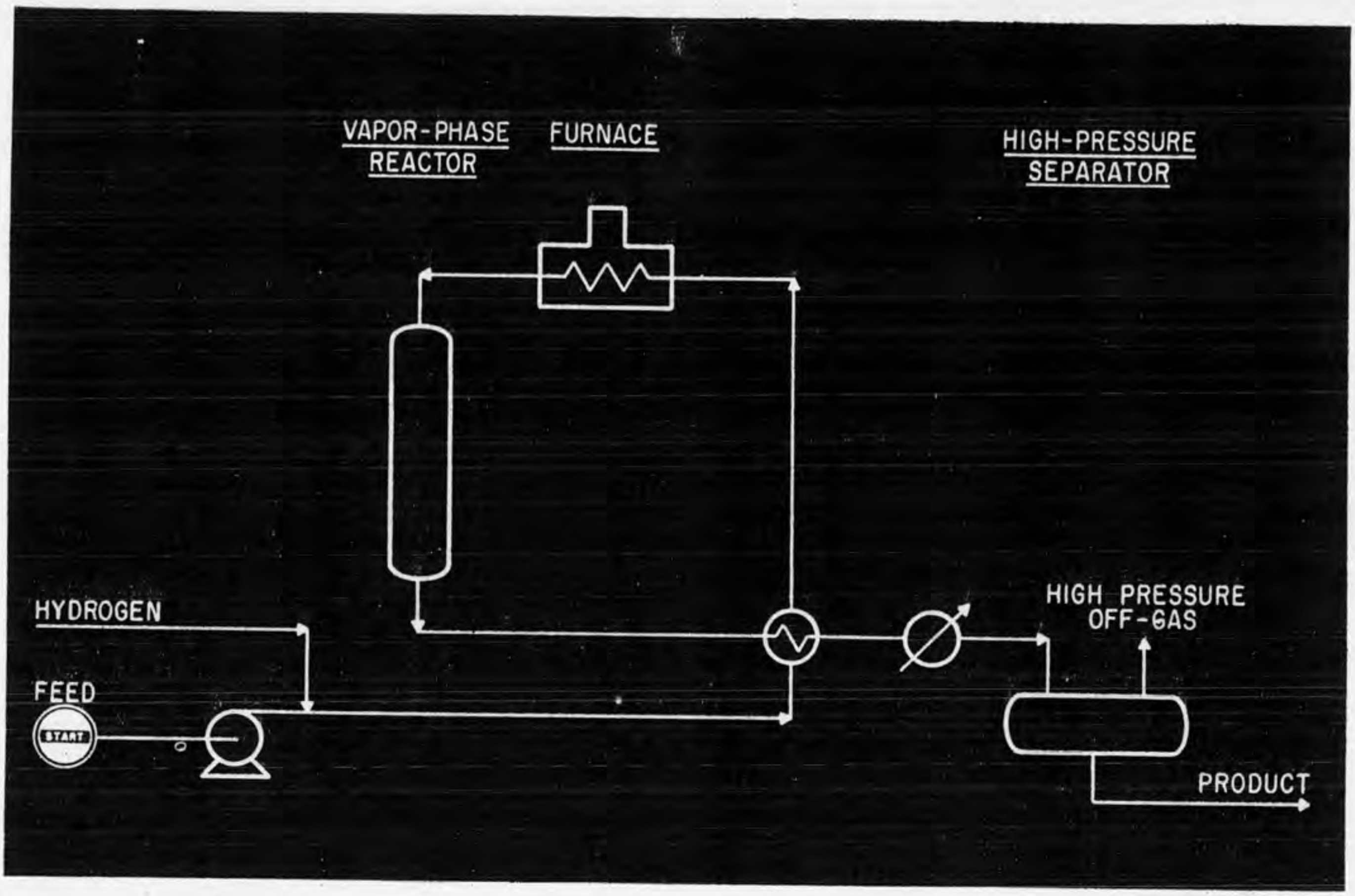
** Based on minimum life of 3 years.

*** Maximum air cooling.

Commercial installations: 48 units are in operation, or under construction, with a total capacity of 720,000 bpsd.

Reference: *Petroleum Engineer,* Vol. 28, No. 3, March 1956, pp. C37-C44.

Licensor: BP Trading Ltd.



Hydrodesulfurization, vapor phase

Application: To improve the quality of light petroleum fractions by the removal of sulfur and nitrogen compounds.

Charge: A naphtha fraction (up to 400° F) or a naphtha-plus-kerosine fraction (up to 480° F), either stabilized or non-stabilized, which may include a certain proportion of cracked material.

Products: A sweet product, yielding a stabilized naphtha with a sulfur content below 5 ppm, suitable for use as catalytic reformer feedstock, and, if applicable, a kerosine fraction with a sulfur content below 100 ppm wt.

Description: The feedstock is combined with hydrogen-rich make-up gas and passed through feed/effluent exchangers and a furnace, where it is heated to a maximum temperature of 715° F. The combined reactor charge passes through the reactor essentially in the vapor phase, exchanges heat with reactor charge, is cooled down to 100-120° F and flashed in a high-pressure separator. The liquid product leaving the high-pressure separator is sent to a work-up section for the removal of all the H_2S and dissolved gases.

The gas from the high-pressure separator may be recycled or applied as hydrogen-rich make-up gas for other desulfurization units.

Operating conditions:

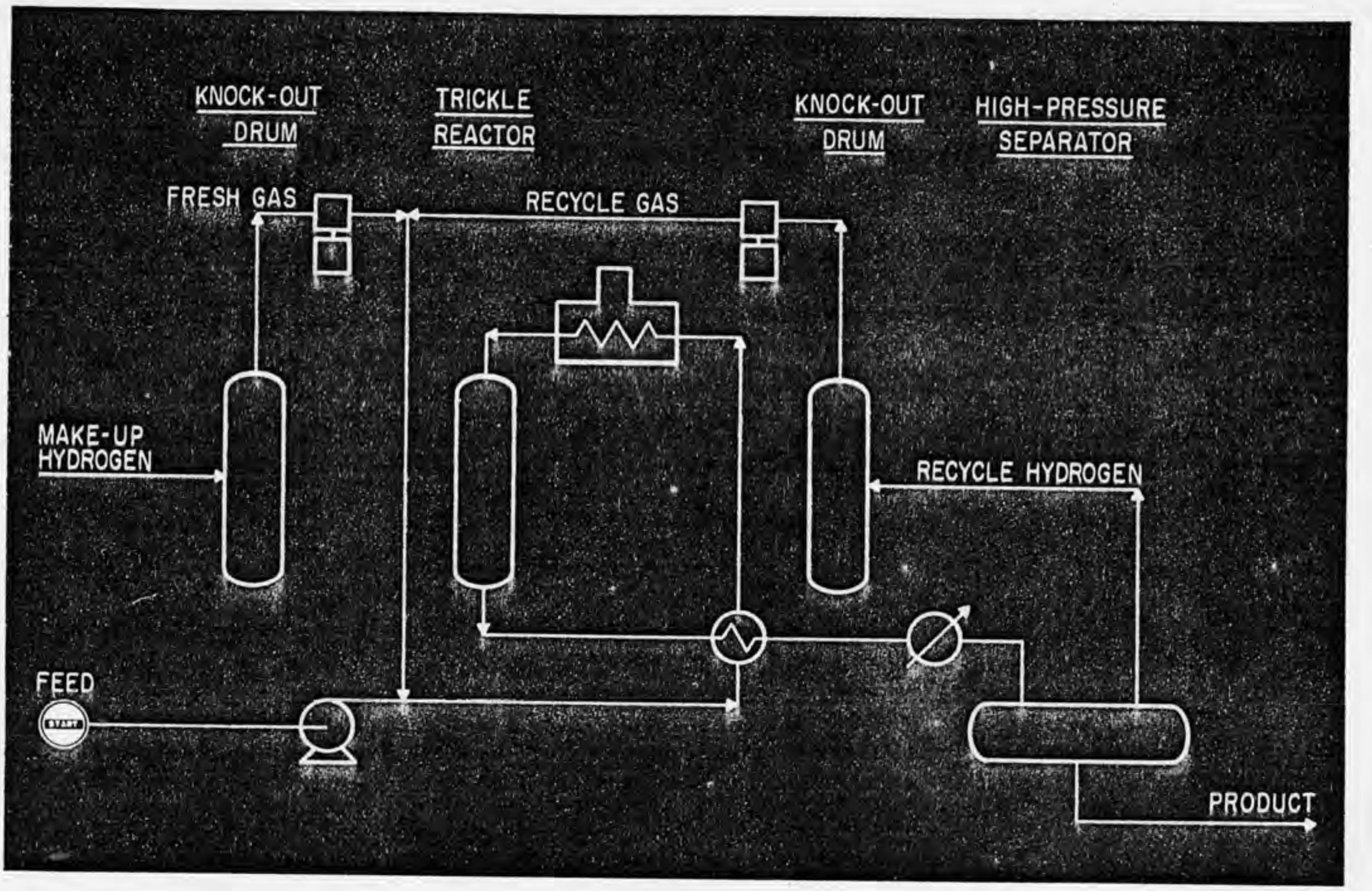
Temperature, ° F	600 - 715
Total pressure, psig	300 - 600
Space velocity, vol/hr/vol	5 - 8
Gas rate, scf/bbl	400 - 800

For feedstocks with high nitrogen contents somewhat more severe conditions may have to be applied.

Commercial installations: The total number of units operating at the end of 1973 is 62 with a total capacity of 1,250,000 bpsd.

Reference: *Petroleum Refiner,* Vol. 34, No. 6, June 1955, pp. 118-122.

Contributor: Shell Internationale Research Maatschappij N.V. or Shell Development Co.



Hydrodesulfurization, trickle flow

Application: Improves the quality of petroleum fractions ranging from kerosine to heavy gas oil (straight-run and cracked material) as well as vacuum flashed distillate by the removal of sulfur and by the hydrogenation of unsaturated components.

Description: Feedstock, combined with hydrogen-rich make-up and recycle gas, is passed through feed/effluent exchangers and a furnace, where the temperature is raised to operating temperature. The combined reactor charge then passes through the reactor in trickle flow, exchanges heat with the reactor charge, is further cooled and then is flashed in a high-pressure separator at a temperature of 100-120° F or for extra heavy gas oils at 300-350° F. The liquid product is routed to a work-up section where H_2S and dissolved gases are removed. The gas leaving the high-pressure separator is used as a recycle gas. If a "hot" high-pressure separator is used, the gas is further cooled to 100-120° F and washed with a solvent.

Operating conditions:

Temperature, °F	630-750
Pressure, psig	600-1200
Space velocity, vol/hr/vol	1-3.5
Gas rate, scf/bbl.	750-1500

Yields: Typical results from hydrodesulfurization of thermal cracker gas oil (380-650° F fraction) are as follows:

	Feedstock	Product
Specific gravity 20°/4° C	0.8469	0.8326
Sulfur content, % wt.	1.33	0.16
Bromine number, g/100 g	23	< 1
Maleic anhydride value, mg/g	5.2	--
Pour point, °C	−13	−16
Cloud point, °C	−9	−9
Desulfurization, %		88.0
Chemical H_2 consumption, scf/bbl		315

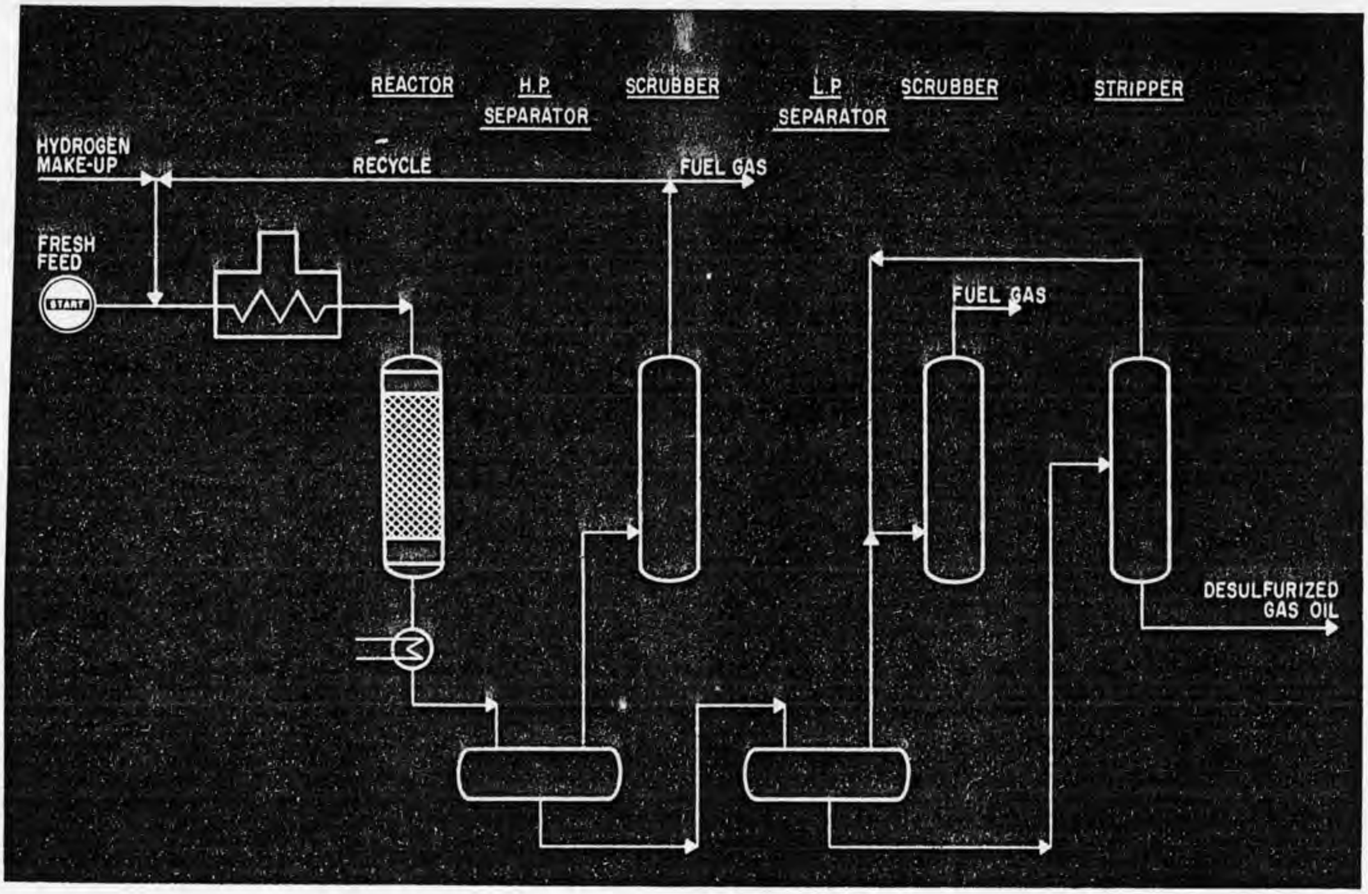
Economics:

Typical requirement, unit per bbl. middle distillate	
Electricity, kwh	1.2
Steam (200 psig), lb	9.6
Fuel, M Btu	52.8
Water, cooling (30° F rise), gal	260
Catalyst consumption, lb.	< 0.01

Commercial installations: 82 units operating at end of 1973 with a total capacity of 1,050,000 bpsd.

Reference: *Petroleum Refiner,* Vol. 34, No. 9, September 1955, pp. 152-154.

Contributor: Shell Internationale Research Maatschappij N.V. or Shell Development Co.



Gulfining

Application: Hydrodesulfurization of heavy distillate gas oils.

Charge: Distillate gas oils including vacuum distillate.

Products: Low sulfur fuel oil or catalytic cracking unit charge stock.

Description: The gas oil including heavy vacuum gas oil is mixed with fresh and recirculating hydrogen, and heated before being passed into the Gulfining reactor. Sulfur compounds are converted to hydrogen sulfide.

Reactor effluent is cooled, and sent to a flash drum from which the liquid oil is withdrawn from the bottom. High pressure flash drum liquid goes to the low pressure flash drum where hydrogen sulfide and additional fuel gas is flashed off.

Liquid from the low pressure separator is fed to the stripper tower where the desulfurized gas oil product is stabilized.

Yields: For Gulfining processing Middle East vacuum gas oil at 90% desulfurization:

Typical yield	
Product (heavier than gasoline), vol. % change	99.3
Chemical hydrogen consumption, scf/bbl. change	350

Inspections	Charge	Product
Gravity, °API	24.0	29.0
ASTM distillation, °F		
IBP	410	
10%	622	
50%	870	
90%	1020	
EP	1090	
Sulfur, wt. %	2.20	0.2
Carbon residue, wt. %	0.7	0.2
Nickel + vanadium, ppm	2	—
Viscosity, cs at 122° F	20	16

Economics:

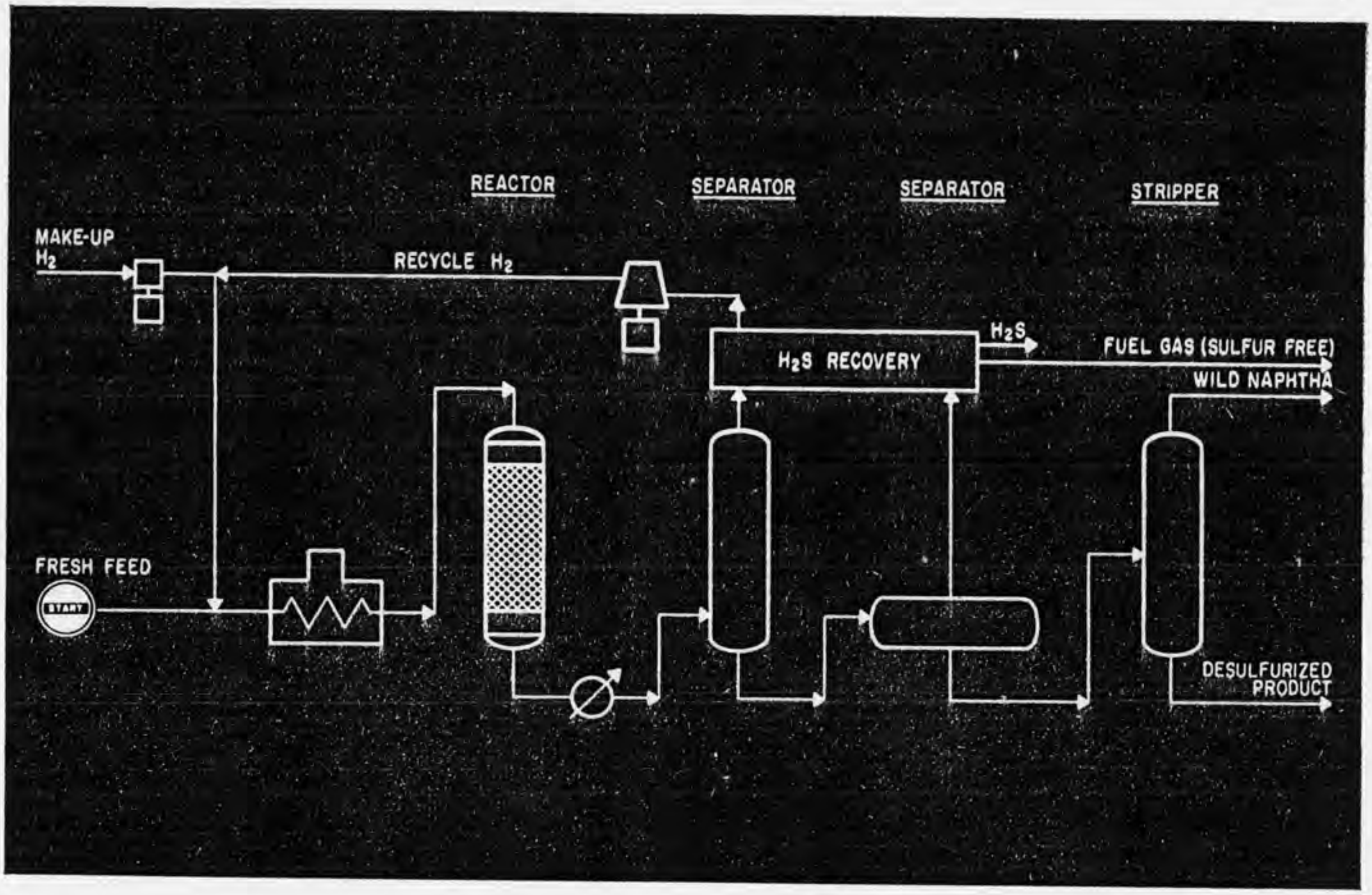
Investment: Varies with feedstock, but on the basis of a 35,000 bpsd plant with a feed and desulfurization level similar to that shown above, $ per bpsd	275
Typical utility requirements, units per bbl. feed	
Electricity, kwh	1.7
Fuel, M Btu	55
Steam, lbs.	6
Water, cooling, gal.	160

Note: Above include H_2S scrubbing from gas; exclude fresh H_2 compression.

Commercial installations: Six plants are currently in operation with feed capacities ranging between 7,000 to 18,000 bpsd. Additional facilities are under study.

Reference: *Hydrocarbon Processing,* Vol. 52, No. 9, September 1973, pp. 131-133.

Licensor: Gulf Research and Development Co. and Houdry Div. of Air Products and Chemicals, Inc.



GO-fining and RESIDfining

Application: GO-fining usually serves as an initial desulfurization step in the production of low sulfur fuel oils to reduce the sulfur content of the total fuel oil pool by about 50%. High boiling distillate products such as virgin vacuum gas oils, visbroken gas oils, thermal and cat cycle oils, along with coker gas oils can be more than 90% desulfurized via GO-fining. From 60 to 90% reductions in the sulfur content of the fuel oil pool can be achieved via RESIDfining. RESIDfining offers the refiner the opportunity to achieve up to 90% desulfurization on residuum feedstocks.

Description: GO-fining and RESIDfining have essentially the same basic flow plan. RESIDfining, however, incorporates a reactor plugging protection system to compensate for the fouling and coking tendency of the more difficult feeds. In both processes, the feed and hydrogen rich treat gas are mixed and preheated prior to entering the fixed bed reactor. The treat gas comes from recycle of unreacted gas and the hydrogen makeup stream.

The reactor effluent is cooled and the desulfurized product is separated from the unreacted hydrogen and light ends. This hydrogen rich stream from the separator is scrubbed to remove H_2S and NH_3, then combined with makeup hydrogen to provide the required treat gas for the process. The bottom stream from the separator is subsequently stripped or fractionated to remove gases and a small quantity of naphtha from the desulfurized product.

The fixed bed reactor utilizes a proprietary low cost catalyst with high activity and activity maintenance. The catalyst enables both processes to operate at reduced pressures. The moderate pressure requirements results in significant economic advantages in both investment (reduced pressure ratings for major equipment) and operating costs (lower hydrogen consumptions).

Yields:

Feed Properties	GO-fining		RESIDfining	
Source	Arab Heavy	Athabasca Tar Sands	Gach Saran	Arab Heavy
Cut Range, °F	700/1050	380+	650+	650+
Gravity, °API	21.1	14.5	15.0	12.3
Sulfur, Wt.%	2.96	3.97	2.50	4.19
V + Ni, wppm	—	—	220	120
Conradson Carbon, wt.%	—	—	9.5	13.3
Average Yields				
Light Ends, wt.% on FF	0.38	0.75	0.83	1.46
C_5/400° F, LV% on FF	0.9	8.0	3.4	6.0
400° F+, LV% on FF	100.6	95.0	98.1	96.4
Gravity, °API	27.5	22.8	19.6	20.7
Sulfur, Wt.%	0.10	0.11	0.3	0.3
Chemical H_2 Cons., scf/bbl	410	975	625	915

Economics:

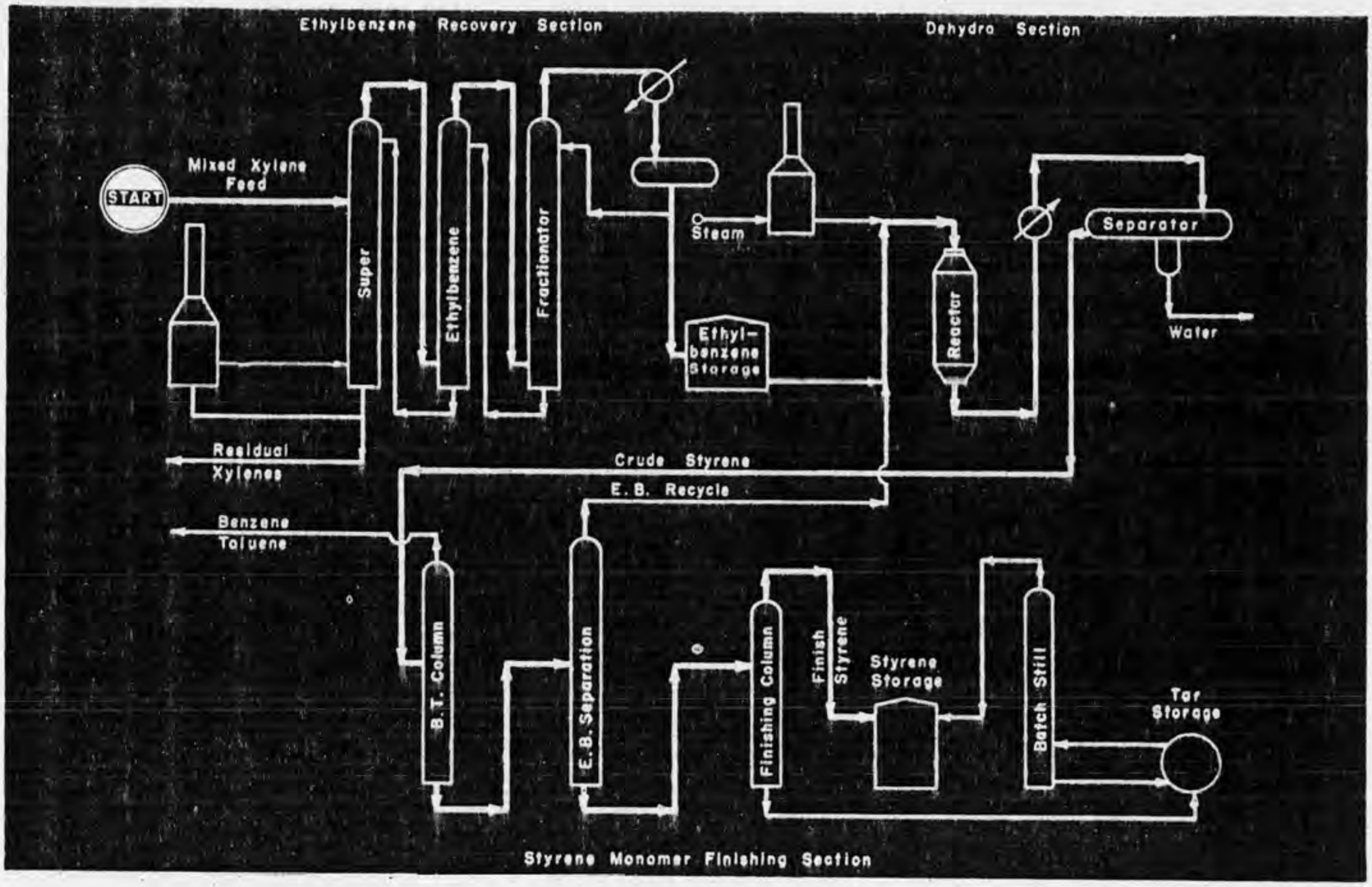
	GO-fining	RESIDfining
Investment (Battery limit onsite, direct materials and labor, second quarter 1973, U.S. Gulf Coast), $ per bpsd capacity*	80-150	300-750
Typical requirements, units per bbl feed.		
Fuel fired, M Btu	10-50	50-100
Power, kwh	0.7-1.0	2-4
Water, cooling, gal	30-50	150-300

* As an approximation, the mid 1974 total erected cost can be obtained by multiplying direct materials and labor cost by a factor of 1.5.

Commercial installations: Fourteen GO-finer units with feed capacities ranging between 18,000 and 95,000 bpsd are currently in operation. There are about 615,000 bpsd of GO-fining capacity onstream with an additional 470,000 bpsd expected onstream by 1977. Six RESIDfining units totaling 330 M bpsd of capacity are under construction or in the design stages.

Reference: Rionda et al, "Recent advances in residua processing," National Petroleum Refiners Association, Miami, Florida, April 2, 1974.

Licensors: Exxon Research and Engineering Co. and Union Oil Co. of California.



Styrene— COSDEN PETROLEUM CORPORATION

Application: Process for manufacturing styrene monomer by recovery of ethylbenzene in petroleum stocks.

Charge: Mixed xylenes from aromatic purification unit.

Product: Plastic or rubber grade styrene monomer.

Color	10 Max.	(APHA)
Assay		99.6% Min.
Polymer		Nil
Sulfur		0.003% Max.
Aldehydes		0.02% Max.
Peroxides		0.01% Max.

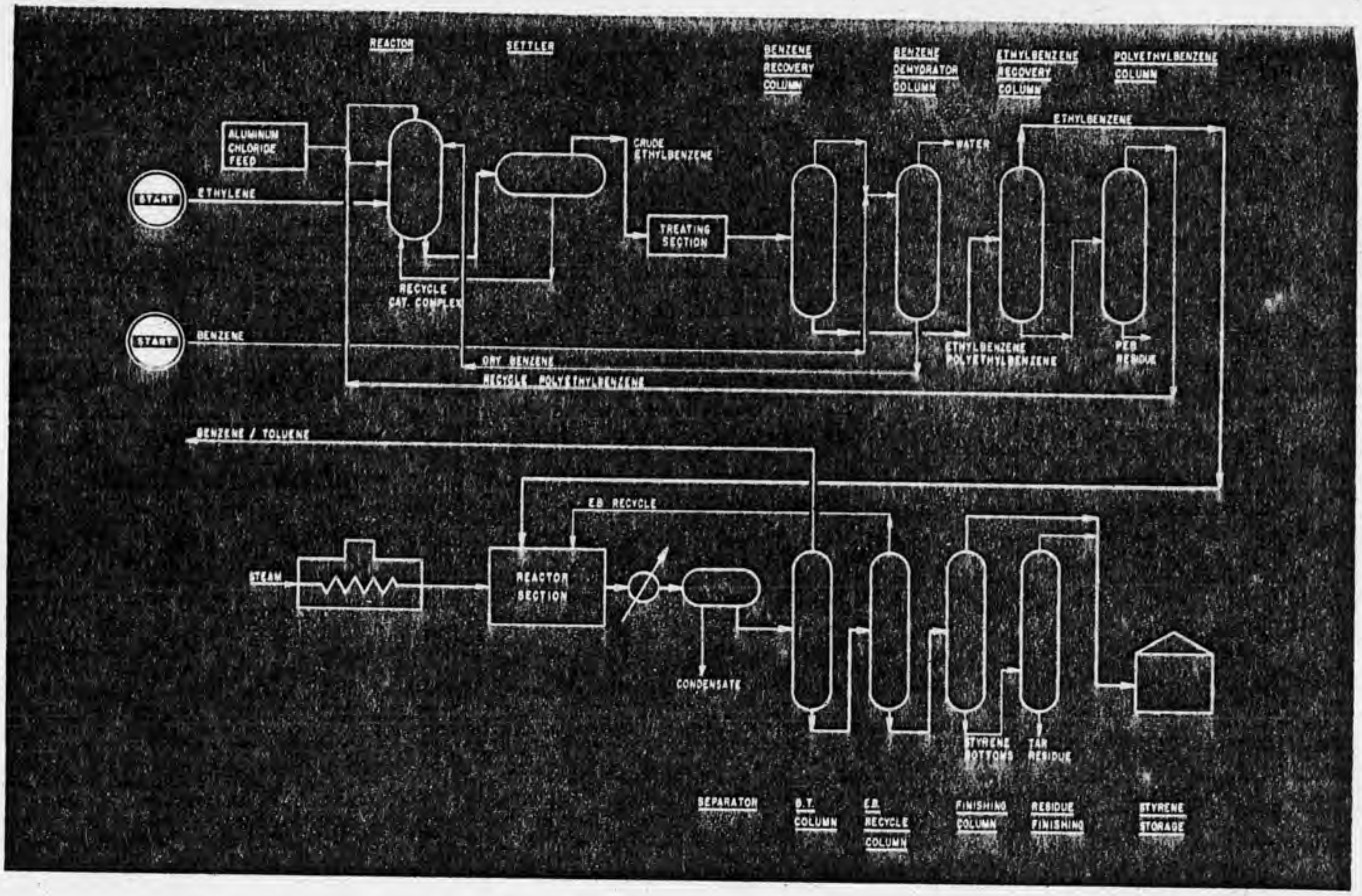
Description: The feed stock to the super fractionating column is mixed xylene isomers containing essentially no non-aromatic hydrocarbons boiling in the xylene range. In this column, ethylbenzene which boils at 3.9° F lower than its nearest xylene isomer, (paraxylene), is separated in sufficient purity to make at least 99.6 percent styrene monomer. To affect this separation, three 200-foot columns are used in series and operated at high reflux rates. The ethylbenzene product from the recovery section has to be maintained essentially free from any other hydrocarbons boiling in the range of ethylbenzene and styrene monomer as purity produced here will govern the maximum purity of finished styrene monomer.

Fresh ethylbenzene is combined with recycle and charged to the dehydrogenation reactor after mixing with super heated steam. The dehydrogenation takes place at low pressure and a high mole ratio of steam to ethylbenzene is maintained. The reactor effluent is condensed and collected in a separator where the steam condensate is withdrawn. Reactor pressure and temperature are major control points for maintaining conversion in the optimum range of 35 to 40 percent per pass. Ethylbenzene conversion to styrene monomer will approximate 90 weight percent.

In the styrene monomer finishing section, the small amount of benzene and toluene produced by cracking in the reactor is first removed by fractionation in a small vacuum column. In the next column, ethylbenzene, for recycle back to the reactor, is separated from the styrene. This separation is accomplished in one column operating at an extremely low pressure. This effects substantial savings in investment and operating cost over the conventional two-column system. Inhibitors are added and high temperatures avoided in order to minimize polymer formation. Another small column is required to separate the finished styrene monomer from small amounts of tar and polymer formed during the operation. The tars and polymers are collected in a batch pot and periodically the remaining monomer in this material is recovered.

Very high recovery of ethylbenzene is realized by this process. It avoids the corrosion and purification problems associated with aluminum chloride alkylation of benzene and ethylene. Furthermore, no impurities of the type normally found in synthetic ethylbenzene are present which produce unstable monomers that complicate styrene monomer recovery and finishing operations. The entire unit is essentially free of corrosion and fouling problems and can be operated for long periods without downtime.

Reference: Industrial & Engineering Chemistry, Vol. 52, July 1960 p 550.



Styrene (Union Carbide-Cosden-Badger)—THE BADGER CO., INC.

Application: Process for manufacturing styrene monomer by the alkylation of benzene and ethylene to ethyl-benzene and subsequent dehydrogenation of the ethylbenzene to styrene.

Description: Benzene is contacted with ethylene gas in the presence of aluminum chloride and recycle polyethylbenzene. The reactor effluent is decanted in a settler, and the heavy catalyst complex layer is recycled to the reactor.

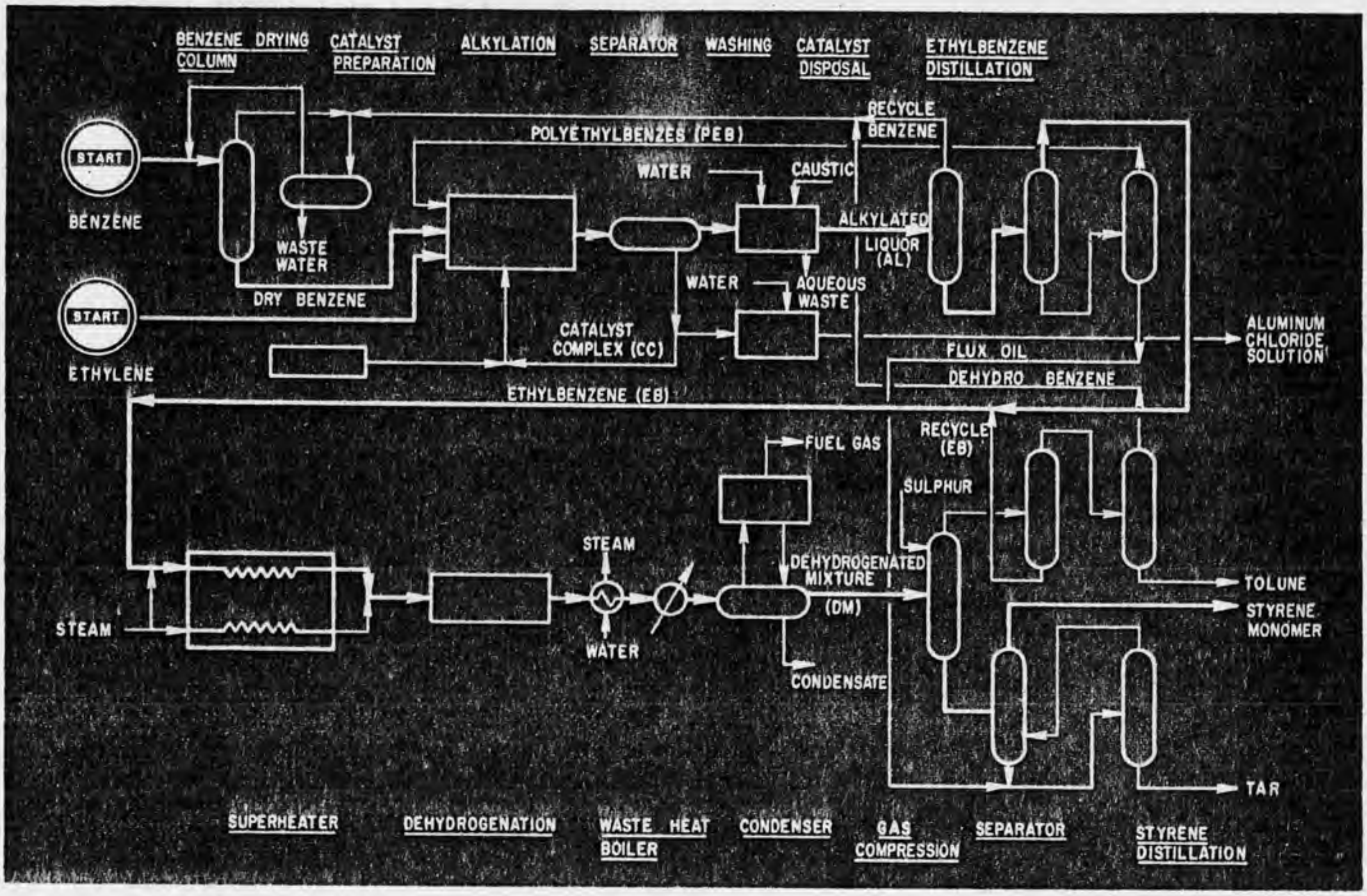
Crude ethylbenzene from the settler is treated to remove traces of chlorides and charged to the distillation system. Here, recycle benzene is first separated from the crude ethylbenzene, and the product ethylbenzene is separated from the heavy components. The heavy components are finally distilled to separate polyethylbenzene for recycle to the reactor.

Ethylbenzene purity is consistent with the manufacture of polymer grade styrene.

In the styrene section, fresh ethylbenzene is combined with recycle ethylbenzene and charged to the dehydrogenation reaction section in admixture with superheated steam. Reaction pressure and temperature are major control variables for maintaining a high conversion per pass.

The styrene monomer recovery section consists of three columns. The small amount of benzene and toluene produced by cracking in the dehydrogenation reaction is removed in the first column and returned to the ethylbenzene system. Ethylbenzene for recycle is separated from the styrene monomer in the second column. The separation is accomplished in a single high efficiency column which results in savings in investment and operating costs as compared with the conventional two-column system. Inhibitors are added to minimize polymer formation. The styrene monomer is separated in the third column from small amounts of tar and polymer formed during the operation.

Commercial Installations: **Ethylbenzene Units:** A total of 11 licensees have 13 units in service, under construction or in the engineering phase; capacity exceeds 5.2 billion pounds per year. **Styrene Units:** A total of 14 licensees have 16 units in service, under construction or in the engineering phase; capacity exceeds 4 billion pounds per year.



Styrene (Monsanto Co.) — THE LUMMUS CO.

Application: A process for the production of styrene by alkylation of ethylene and benzene and the dehydrogenation of ethylbenzene.

Description: The primary reactions of the process are:

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethylene}}{C_2H_4} \xrightarrow{\text{Catalyst}} \underset{\text{Ethylbenzene}}{C_6H_5C_2H_5}$$

$$\underset{\text{Ethylbenzene}}{C_6H_5C_2H_5} \xrightarrow{\text{Catalyst \& heat}} \underset{\text{Styrene}}{C_6H_5C_2H_3} + \underset{\text{Hydrogen}}{H_2}$$

Ethylbenzene (EB) is produced by alkylating benzene with ethylene in the presence of an anhydrous organic aluminum chloride catalyst complex (CC).

The reactor effluent is cooled and then phase separated, with the alkylated liquor (AL) being fed forward to washing and EB distillation, while the CC is recycled to the alkylation reactors.

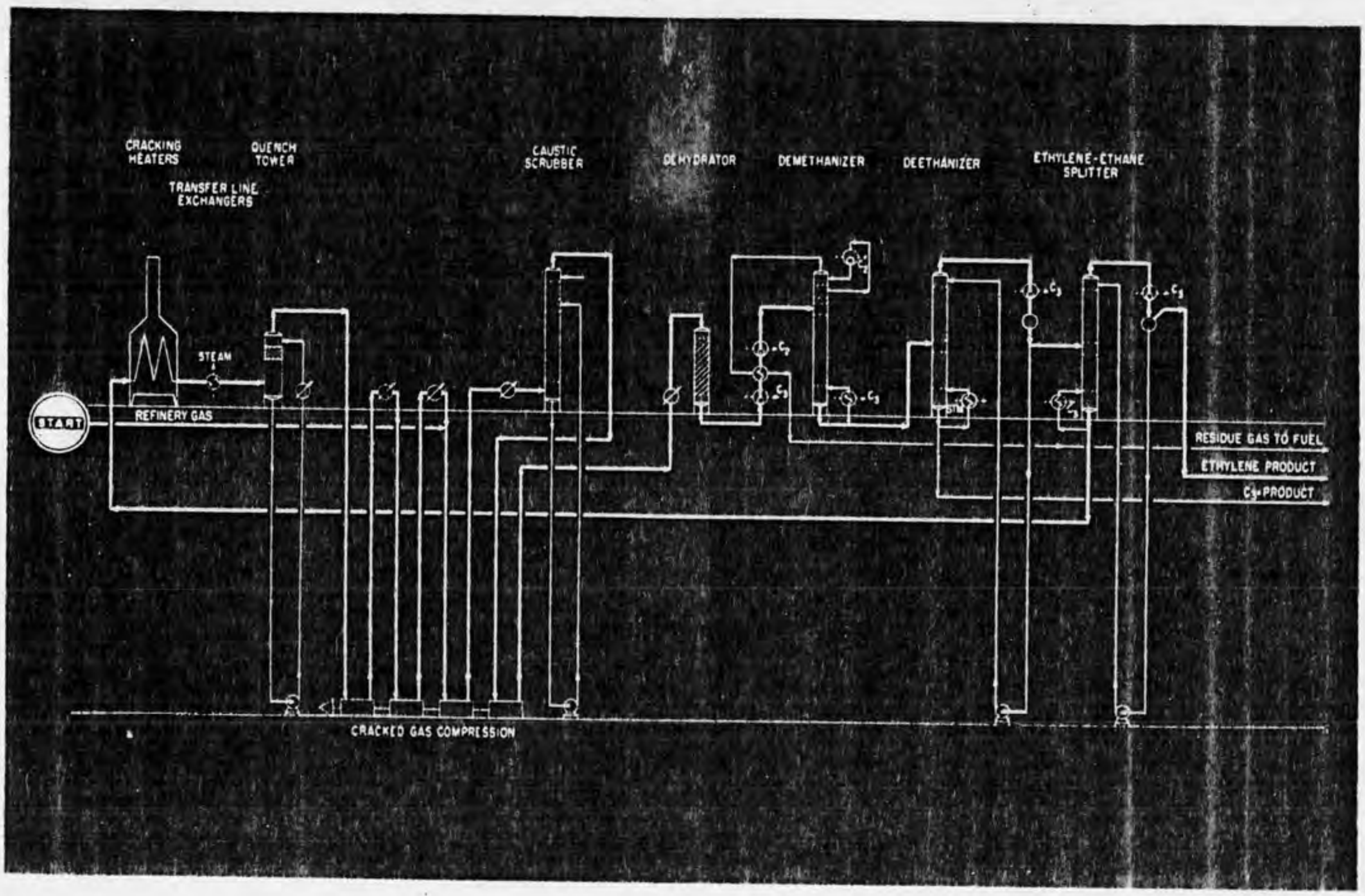
EB (fresh from EB distillation and recycle from styrene distillation) is vaporized, mixed with primary steam and is superheated in the convection section of the steam superheater. The EB-primary steam mixture is combined with superheated secondary steam and is dehydrogenated in the catalytic reactor. The hot reactor effluent is cooled in a waste heat boiler and condensed. The non-condensible gases are compressed to the fuel gas system. The liquid is separated into an aqueous condensate layer and the organic dehydrogenated mixture (DM).

Product styrene monomer (SM) is separated from DM by fractionation. The DM (styrene, unreacted EB, benzene, toluene and higher boilers) is first distilled in the EB/SM splitter to take EB and lighter components overhead. Sulfur is dissolved in hot EB and injected into the top of the EB/SM splitter as a polymerization inhibitor.

The EB/SM splitter overhead is separated into benzene byproduct, toluene and EB. The benzene is fed to the benzene drying column, while the EB bottoms are fed to the dehydrogenation reactor together with fresh EB.

A major advantage of the process is its low consumption of steam which was achieved through a number of engineering improvements in the reaction and distillation systems.

Commercial Installations: Monsanto's Texas City, Texas, facility has an installed capacity of 800 million pounds a year of styrene monomer. Other commercial installations are at: Forth Chemicals (Grangemouth and Baglan Bay, U. K.) with a new plant under construction, Australian Petrochemicals, and Montecatini-Edison.



Ethylene — STONE & WEBSTER ENGINEERING CORPORATION

Application: A process for the production of ethylene and propylene from various distillate or light hydrocarbon feed stocks.

Charge: Designs are available for charging hydrocarbon feed stocks ranging from ethane to gas oil, including refinery gas.

Products: The primary products are high purity ethylene and propylene. Principal byproducts are residue gas, substantially hydrogen and methane, and a C_4's plus stream from which may be recovered butylenes and butadiene, and B-T-X aromatics.

Description: The flowsheet shows the processing scheme employed with refinery gas feed. The feed gas is combined with the gas from the cracking furnaces, compressed to about 500 psig and thoroughly dried. An aromatic rich condensate is separated in the compression system and combined with the depropanizer bottoms. The dried mixture of feed gas and cracked gas is cooled and demethanized at 475 psig utilizing ethylene refrigerant at −150° F. Hydrogen and methane are taken overhead. The bottoms, essentially free of methane, pass to a deethanizer where ethylene and ethane are taken overhead. Propylene and heavier are discharged as a bottoms stream which is sent to a depropanizer (not shown). The ethylene is separated in an ethylene-ethane splitter, operating at 225 psig.

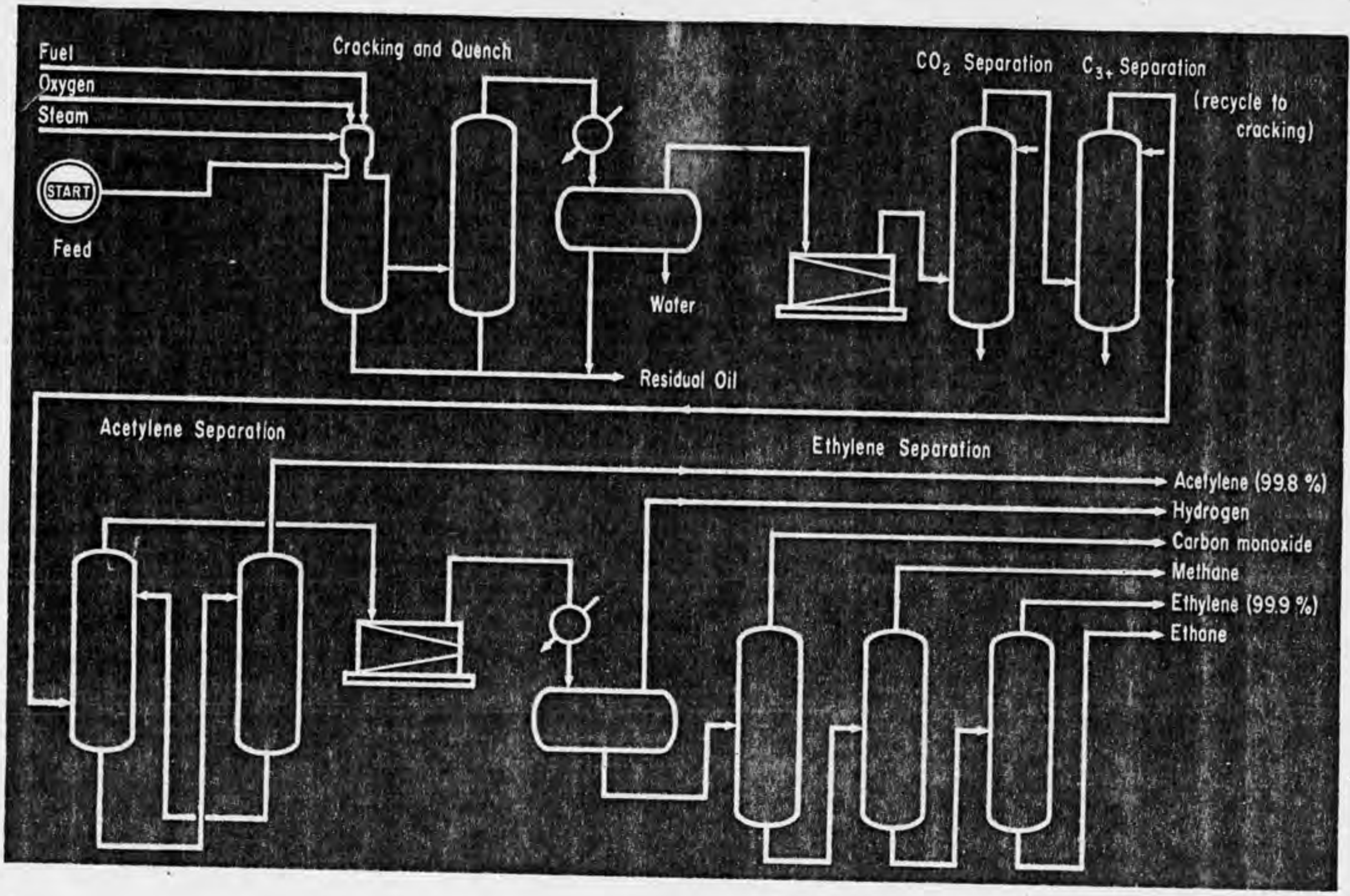
For polyethylene grade ethylene it is necessary to provide additional rectifying trays in the splitter, and to include acetylene removal facilities. This is accomplished by catalytic hydrogenation over highly selective catalysts, located either in the cracked gas compression system or in the deethanizer overhead.

Ethane separated in the fractionation section, and C_3's if not desired as a product, are recycled to tubular cracking furnaces where they are cracked in mixture with dilution steam. If the feed stock is ethane, propane or butane, the vaporized feed is charged directly to the cracking furnace. Naphtha and other distillate feed stocks are processed in similar fashion, but the substantial amount of aromatic distillate and fuel oil in the coil effluent requires additional facilities for separating and stabilizing these streams. Refrigeration is by an ethylene-propane cascade system. Ethylene losses in the residue gas are kept to a low value by supplemental cooling with an expansion system.

Yields: Yields of ethylene from cracking ethane and propane are approximately 80 and 48 weight percent respectively. Ethylene yields from naphtha range from 20 to 28 weight percent depending on the feed stock characteristics.

Commercial Installations: Thirty-seven plants with a combined production of 10 million pounds per day.

Reference: Petroleum Refiner, July '51, p 135.



Acetylene and Ethylene—FARBWERKE HOECHST AG

Application: The Hoechst high temperature pyrolysis process for manufacturing acetylene and ethylene from hydrocarbons.

Charge: Feed stocks ranging from methane through middle distillates.

Products: Acetylene of 99.8 percent purity and ethylene of 99.9 percent purity.

Description: Farbwerke Hoechst AG, Frankfurt/Main-Hoechst, Germany, has developed a process which produces a high yield of acetylene and ethylene from hydrocarbon feed stocks. The large amount of high-temperature heat required for the cracking of hydrocarbons into acetylene and ethylene is obtained by combustion of gaseous or liquid fuels with oxygen in a newly developed burner. Combustion with oxygen minimizes the gas volume and permits the use of tail gas as burner fuel. The burner heat release exceeds 10^8 Btu/ft^{3}hr. Its high capacity and all-metal construction minimizes size and weight of the burner. The absence of ceramic parts permits rapid start-up and shut-down. The burner is water cooled and has a very low heat loss.

The feed stock is injected into the hot combustion gas. The mixture enters a reaction zone where the heat necessary to form acetylene and ethylene is transferred by direct contact, with a reaction time of about 0.001 second. An economical and reliable quench method prevents coke formation. The reactor-effluent gas is cooled in steam-generating equipment.

Condensed hydrocarbons are separated and the raw gas is compressed to moderate pressure. Its carbon dioxide and hydrogen sulfide contents are removed by contact with a newly developed absorption agent which is chemically stable, easily regenerated with low-temperature heat, and is noncorrosive. The gas is then cooled and dried, and the C_3 and heavier hydrocarbons are separated. Higher acetylenes, which tend to polymerize, are removed completely and recycled to the reactor.

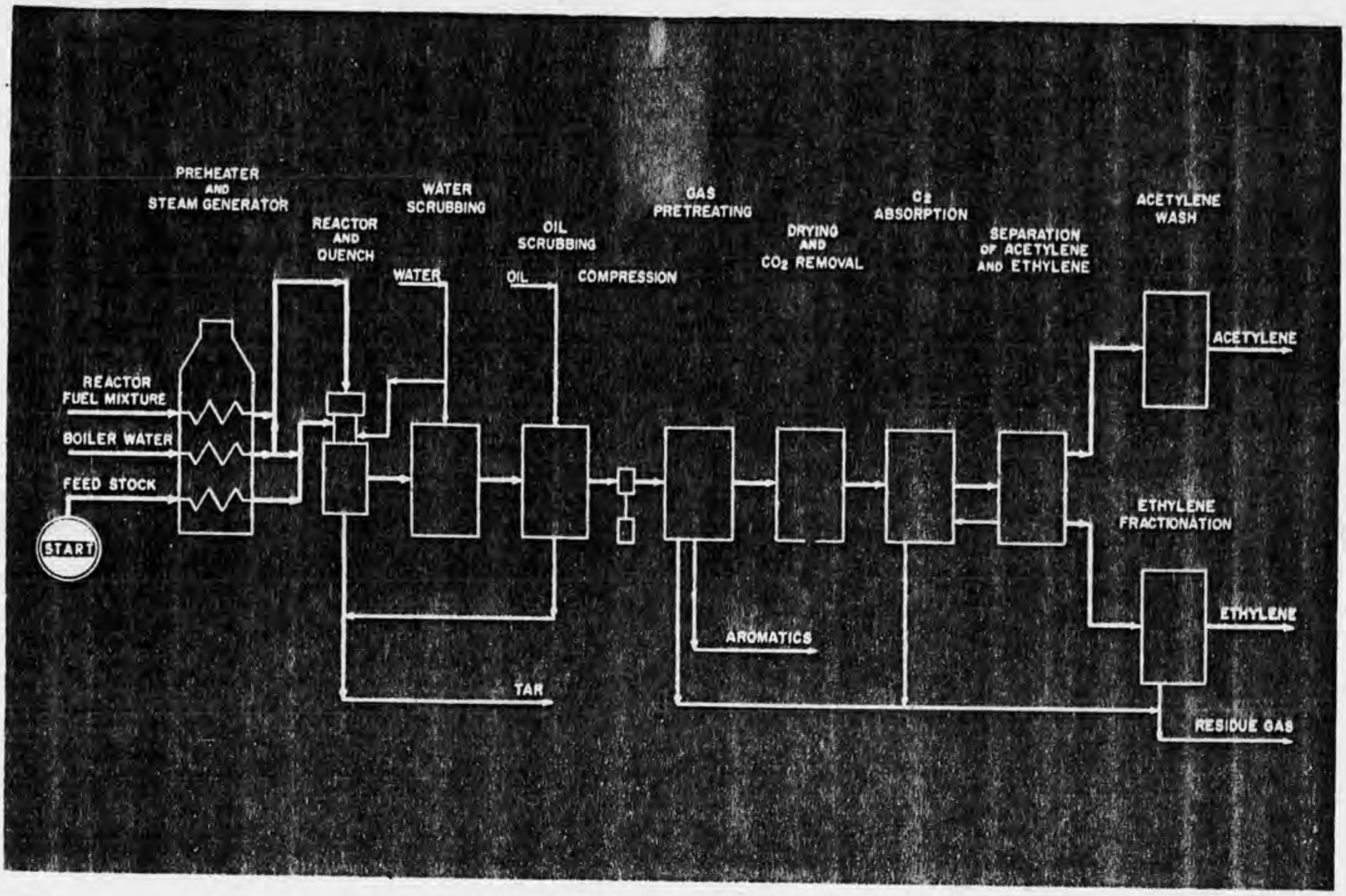
In the next step, a solvent is used to absorb the acetylene, which is recovered as a product of 99.8 percent purity, and higher. A solvent of high selectivity and absorptive power is utilized. This solvent is inexpensive, readily available, and non-corrosive. Regeneration is simple and economical, and solvent losses are low.

High-purity ethylene is separated from the remaining gas by a low-temperature process. The residual gas is rich in hydrogen and may be used as burner fuel. However, if burner fuel is available from other sources, the tail gas may be used for ammonia or methanol synthesis.

Yields: Yields of 50 to 54 wt. percent of acetylene plus ethylene are obtained from light virgin naphtha. A 40 wt. percent yield of acetylene is obtained from methane. These yields are net and after process losses. The ratio of acetylene to ethylene obtained from the burner may be varied from 80:20 to lower than 30:70 by changing operating conditions.

Commercial Installation: A plant designed to produce 100,000,000 lb/yr of acetylene plus ethylene went into operation in 1960 at the Hoechst plant of Farbwerke Hoechst AG in Germany.

References: Further information is available from Hoechst-Uhde Corporation, Empire State Building, Suite 8204, New York 1, N.Y.



Acetylene and Ethylene (EASTMAN PROCESS)—STONE & WEBSTER ENGINEERING CORP.

Application: A process for the simultaneous production of acetylene and ethylene.

Charge: Ethane, propane, butane, light naphtha.

Products: Acetylene, ethylene, synthesis gas.

Description: The hydrocarbon feed is converted into acetylene, ethylene and byproduct gas by short time pyrolysis in a stream of hot combustion products in a reactor of special design. The reactor consists of five elements in series: a fuel burner, a combustion chamber, a feed injection zone, a reaction zone and a quenching section.

Fuel gas and air, or oxygen, are burned in the combustion chamber, and the hot gases enter the mixing duct at high velocity. The hydrocarbon to be pyrolyzed is injected into the turbulent combustion gas stream where rapid and uniform mixing is attained. The reaction section provides the additional small residence time required for completing the pyrolysis to maximum yields of acetylene and ethylene, after which the gas mixture is rapidly quenched by water sprays to relatively low temperatures.

Steam is introduced with the fuel and oxygen, to temper the combustion temperature and to serve as a heat carrier. Steam is also admitted with the feed stock as a diluent, producing a partial pressure favorable to the desired pyrolysis reaction. The proportion of acetylene to ethylene is governed principally by the reaction temperature-level, which may be varied easily by changing the quantity of combustion gas used, or the quantity of feed injected. Acetylene to ethylene ratios of 0.3/1 up to 4/1 have been demonstrated.

A water quench spray is located at the outlet of the reaction zone, and the effluent passes into a tar knockout drum where most of the small amount of tar made settles out and is drawn off. The gases then pass into a water scrubbing tower where they are cooled to about 100° F, and the steam in the gases is condensed. In the oil scrubber which follows, a circulated stream of oil removes fine particles of tar and heavy oils from the gas. Cleanup of the circulating oil is effected by steam in a stripping column. The residue tarry oil from this stripper is mixed with the tar from the quench drum, so that a freely flowing material results.

The scrubbed gas is compressed and sent to a pretreating section, where oil absorption removes material heavier than acetylene and ethylene.

Conventional carbon dioxide removal and dehydration treatment are the final steps in preparing the gas for entry into the recovery system.

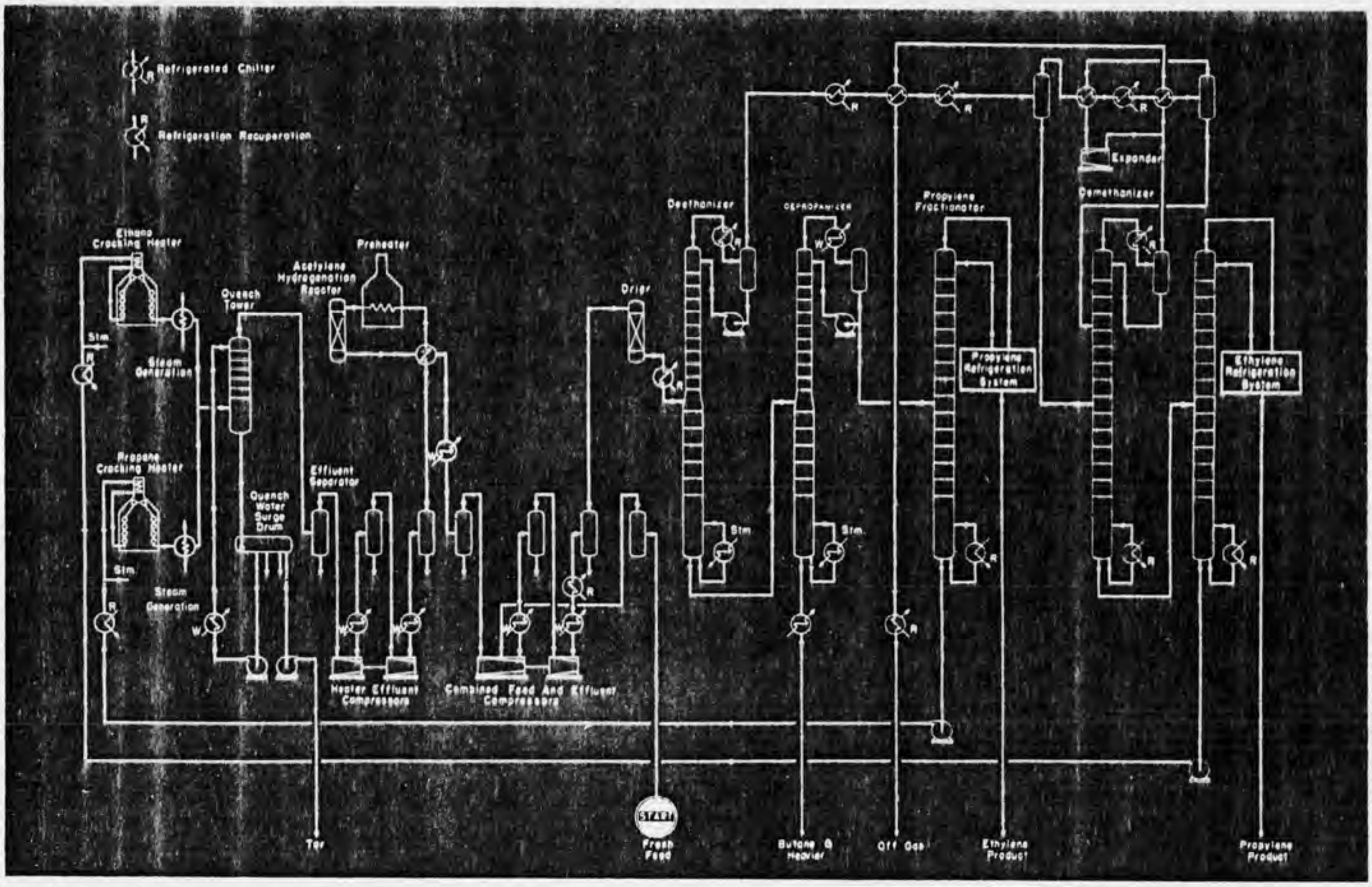
The recovery system employs a combination of absorption and extraction steps with hydrocarbon and organic solvents to recover acetylene and ethylene from the gas. Suitable purification steps are included to produce acetylene and ethylene at high purities.

Operating Conditions: The reactor operates substantially at atmospheric pressure and at a flame temperature of about 2,000° C.

Yields: A combined yield of acetylene and ethylene of over 50 weight percent on the charge is obtained.

Commercial Installations: Reactor in commercial operation at Chemische Werke Hüls, Germany, demonstrated a combustion chamber refractory life of more than two years.

Reference: *Chem. Engr. Progress*, Vol.54, No.1, '58, p41-48.



Ethylene and Propylene—THE LUMMUS COMPANY

Application: A process for the production, recovery and purification of ethylene and propylene.

Charge Stock: Refinery gases, ethane or propane.

Products: Ethylene and/or propylene at the desired purity up to 99.9-mole percent.

Description: The flow diagram illustrates a plant to produce ethylene and propylene from ethane and propane, and to recover these olefins.

Ethane and propane entering as fresh feed plus unconverted ethane and propane are recovered to provide the feed to the cracking heaters.

Separate furnaces are used for cracking ethane and propane in order that each be cracked at the optimum conditions for maximum yield and on-stream time. The effluents from the furnaces pass through transfer line exchangers and are combined and further cooled in water scrubbing tower before introduction to the compression system. Polymer and aromatic distillate are collected in the quench water surge drum and decanted there.

When the ethylene must be acetylene-free, the acetylene is selectively hydrogenated by passing the cracking heater effluent over a catalyst, generally after the second compression stage.

The combined heater effluent and fresh feed is compressed to approximately 500 psig, chilled, and dried over soild desiccants such as activated alumina or bauxite. The dryers consist of multiple desiccant chambers which are regenerated on a predetermined cycle.

The dried feed gas is further chilled and introduced into the deethanizer operating at 450 psig. Hydrogen, methane, ethane and ethylene are taken overhead and proplene, propane, and C_4 and heavier bottoms are charged to the depropanizer. The deethanizer overhead is then chilled by exchange and ethylene refrigeration to —130° F. The remaining vapor is further chilled to about —195° F. The condensed liquids are charged to the demethanizer. The residual vapor is expanded in a centrifugal expander to the fuel gas system pressure. The low temperature produced in the expander is used to produce the final cooling of the feed gas to —195° F.

The demethanizer overhead goes to fuel and the bottoms (recovered ethane and ethylene), is charged to the ethylene fractionator operating at about 60 psig. The ethylene fractionator is integrated with the ethylene refrigeration system for reflux and reboil heat. The ethylene product is taken overhead and the ethane bottoms are recycled to the ethane heater.

The depropanizer takes propylene-propane overhead and C_4 and heavier as bottoms. The propylene-propane is charged to the propylene fractionator operating at about 20 psig. Propylene products is taken overhead and propane bottoms are recycled to the cracking heater or withdrawn as LPG.

Refrigeration for the unit is supplied by centrifugal compressors operating in a cascade system.

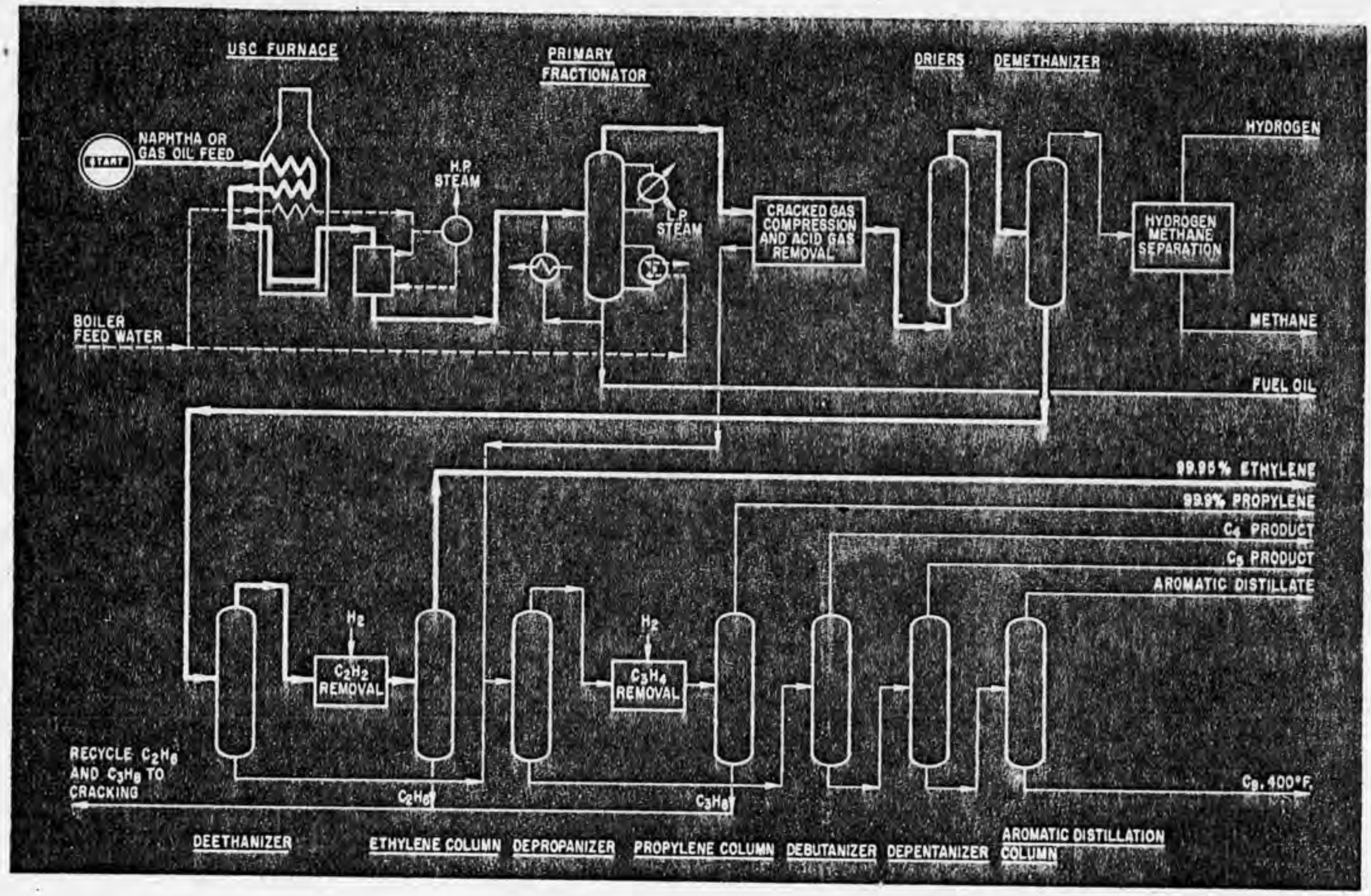
Yield: One million SCF of refinery feed gas gives yields as follows:

Refinery Gas	Volume Percent	Product Pounds
Hydrogen plus inert	7.4	———
Methane	28.5	———
Ethylene	9.9	32,200
Ethane	33.9	———
Propylene	3.3	7,800
Propane	13.4	———
C_4 and heavier	3.6	8,900
Fuel Gas	———	855,000 SCF

A modification of the fractionation system shown above permits the manufacture of ethylene and propylene from naphtha charge stocks. Ethylene of purities to 99.9+ volume percent may be produced with this system.

Commercial Installations: The Lummus Company has designed and constructed 24 units producing ethylene and/or propylene from various feed stocks.

Reference: PETROLEUM REFINER, Vol. 33, No. 7, July 1954, p 135.



Ethylene

Application: A process for the production of ethylene. Propylene and butadiene is also produced depending on the charge stock. The process can also produce benzene and pyrolysis gasoline. Ethylene product purity is greater than 99.9 percent by volume.

Description: The schematic flow diagram shown is typical only, and is frequently varied to accommodate the requirements of specific installations as well as feedstocks and product specifications.

Pyrolysis Section: Feedstocks are cracked in the presence of steam in tubular pyrolysis furnaces. The feedstock is preheated, diluted with steam and the mixture heated to 1,550-1,650° F. The effluent from the furnace is quenched rapidly by direct means or in exchangers which are used to raise steam for process use. The selection of cracking conditions and the rapid quenching achieve high yields of valuable products with a concurrent reduction in the make of undesirable co-products such as methane. High thermal efficiency is achieved by generating steam at 400-2,000 psi gage, by heat recovery from the furnace flue gas, cracking coil effluent and quench oil (if used). Depending on economic factors and coordination with offplot facilities, the heat recovered is used as an energy source. It permits steam balancing, or enters into selection of the optimum combination of steam turbines, gas turbines, and electric motors for driving equipment.

Where the cooled cracked gases are quenched with a circulating oil, the removal of heavy oil fractions is accomplished here and these can be recovered for fuel. Final cooling is usually done in a direct water quench tower at low pressure. Since gasoline-range materials are condensed in this water quench step, this is followed by a fractionation or stabilizer tower before going to raw gas compression.

Compression, Treating and Purification: Raw gas from the quenching section and primary fractionator is compressed in a multistage centrifugal compressor to about 500 psi gage. Hydrocarbons condensed during the various stages of compression are separated and sent to the fractionation system. Also, during and after the compression stages, the raw gas is treated to remove acid gases, usually by caustic washing. The treated and compressed gas is then dried and cooled before being sent to the low temperature fractionation system.

The gas then passes to a demethanizer where residual hydrogen is taken overhead along with the methane. In some plants a hydrogen-methane separation system is used to further treat the demethanizer overhead gases to provide hydrogen for acetylene removal. Demethanizer bottoms flow to the deethanizer with the bottoms going to the depropanizer column. Overhead from the deethanizer is catalytically treated with hydrogen to remove acetylenes. C_2's taken overhead from the deethanizer are fed to the ethylene column, or C_2 splitter. Overhead product is pure ethylene and the ethane bottoms are returned as recycle to the pyrolysis furnace. Bottoms from the deethanizer go to the depropanizer with the C_3's going overhead and the heavier bottoms going to the debutanizer column. C_3's are hydrogen treated before going to the propylene column. Overhead from the propylene column is high purity propylene and propane bottoms are recycled to the cracking furnace. Debutanizer overheads form the C_4 product steam and bottoms are feed for the depentanizer. A C_5 product can be taken from the depentanizer. The final column is usually called an aromatic distillation column and produces an aromatic distillate overhead and a C_9 bottoms product.

The low temperature refrigeration system (methane, ethylene, propylene) is not shown on the flow sheet. These systems are usually a cascade arrangement using multistage centifugal compressors with steam or gas turbine drives. Steam demand and steam balance requirements determine the choice of drivers for compressors used in any ethylene plant.

Yields: Typical yields from various feed stocks, including recycle ethane-propane cracking have been reported in the literature as follows:

Feed Stock	Ethane	Propane	Normal Butane	Light Naphtha	Full Range Naphtha	Gas Oil
Ethylene, Wt. %	81.6	46.9	44.5	42.3	34.1	29.4
Propylene, Wt. %	2.0	18.7	17.2	15.9	16.0	11.6
Butadiene, Wt. %	3.0	2.9	4.4	4.7	4.9	4.9
Aromatics, Wt.%	1.0	4.0	4.5	8.3	11.4	10.6
Propylene to Ethylene Ratio at Moderate Cracking	. . . .	0.63	0.71	0.59	0.59	0.53

Overall ethylene yields vary with the feedstock used and the severity of cracking. Naphtha pyrolysis yields are characterized by a high degree of flexibility. Also, by-product yields can be varied over a range for a given feedstock by varying design parameters and operating conditions.

Economics: There are substantial differences in capital and operating costs of ethylene plants depending upon the type of feedstock used. These differences are due to different unit costs of various feedstocks and also to different yields. The yields affect the costs since a raw material such as ethane, with 81.6 percent weight yield of ethylene, requires smaller equipment because of the smaller volumes of materials that are processed compared with propane or naphtha. Also, the quantity and value of the co-products vary depending on the feedstock.

These prices were used in the calculation of ethylene manufacturing costs shown in the table: Fuel gas 20 cents/million Btu, Propylene 2.5 cents/pound (part polymer grade; part chemical grade), C_4 stream 4.5 cents/pound for butadiene content, C_5 and heavier 1.34 cents/pound. It can be seen from the table that the cost of the raw material is the most important single cost factor regardless of the type of feedstock; this cost varies from a low of 65 percent of total direct costs when using 3 cents/gallon ethane to a high of 80 percent of direct costs when using 7.5 cents/gallon naphtha. Utilities are the only other significant direct cost; they account for a low of 15 percent of total direct costs when using 7.5 cents/gallon naphtha to a high of 25 percent when using 3 cents/gallon ethane. Another important variable is capital—depreciation, general overhead, taxes and insurance—along with required return on investment account for the following percentages of required selling price, even with a one billion pound/year plant: Ethane feed, 30 percent; propane feed, 37 percent; 7.5 cents naphtha feed, 33 percent; 5.0 cents naphtha feed, 57 percent.

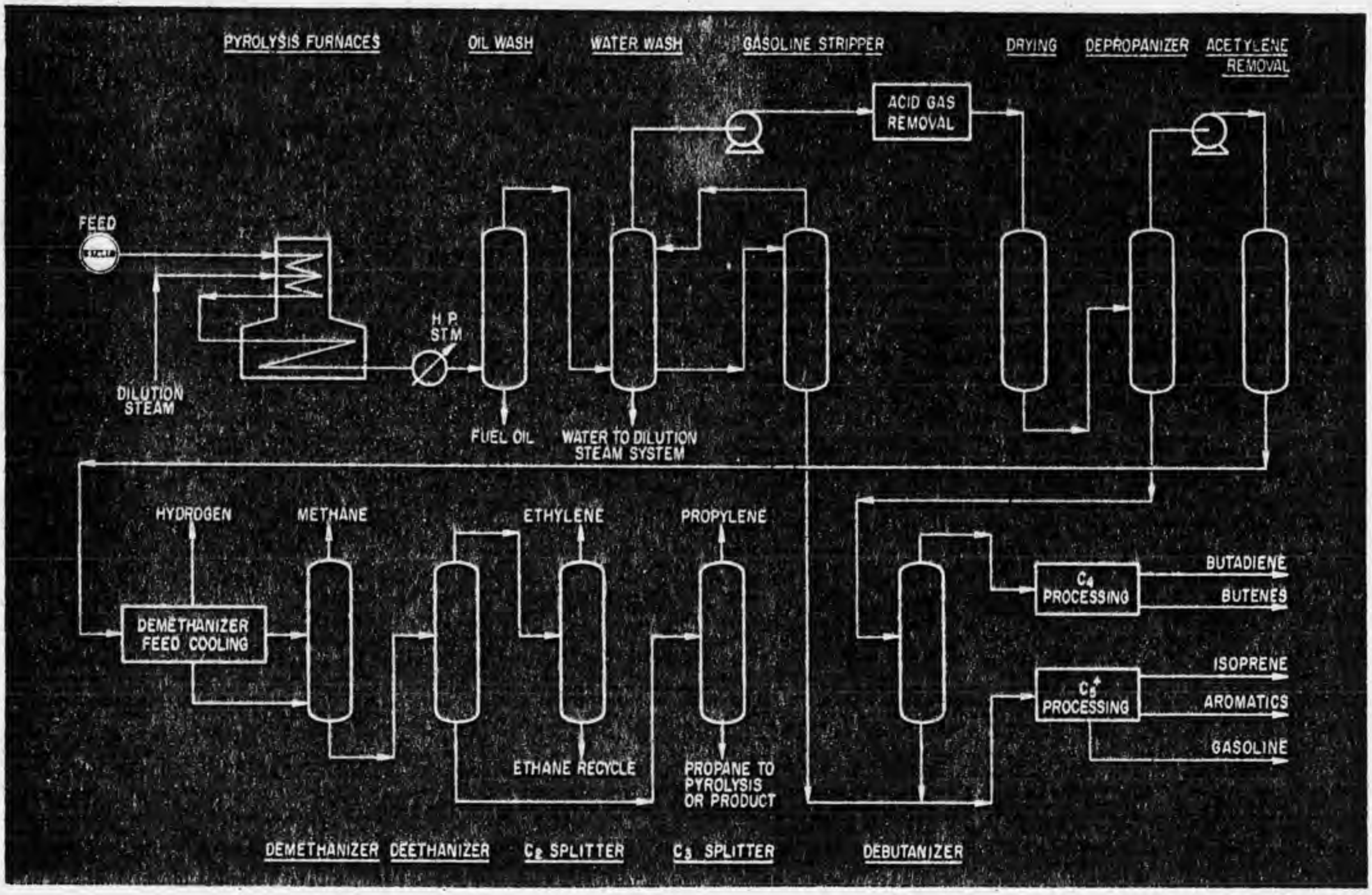
Ethylene Manufacturing Costs, One Billion lb./yr. Plant

($ Million, unless otherwise noted)

Feedstock	Ethane	Propane	Naphtha	Naphtha*
Capital investment	23.700	25.700	28.000	28.000
Feedstock, unit cost	3.0¢/gal.	4.0¢/gal.	7.5¢/gal.	5.0¢/gal.
Direct Costs				
Feedstock	12.000	21.995	38.096	25.400
Utilities (inc. fuel gas)	4.500	5.850	6.985	no change
Catalyst & chemicals	0.631	0.820	0.978	
Labor & supervision	0.572	0.629	0.660	
Maintenance (3¼% inv.)	0.770	0.835	0.910	
	18.473	30.129	47.629	34.933
Indirect Costs				
Depreciation (10% inv.)	2.370	2.570	2.800	no change
General overhead (2% inv.)	0.474	0.514	0.560	
Taxes & insurance	0.237	0.257	0.280	
	3.081	3.341	3.640	
Total costs	21.554	33.470	51.269	38.573
Credits				
Residue gas	1.140	2.890	2.210	no change
Propylene	0.625	8.150	12.750	
B-B	0.585	4.025	9.530	
C_5+	0.389	3.110	6.500	
Total credits	2.739	18.175	30.990	
Net cost	18.815	15.295	20.279	7.583
Net cost, ¢/lb. ethylene	1.88	1.53	2.03	0.76
Return on investment at 20% before taxes, in ¢/lb. ethylene*	0.47	0.51	0.56	0.56
Allowance for sales & admin. expense plus ROI on working capital ¢/lb. ethylene*	0.2+	0.2+	0.2+	0.2+
Minimum required sales price, ¢/lb. ethylene*	2.6	2.3	2.8	1.6

* These data from Stobaugh; remaining data from Eber H. Peters.

Commercial Installations: Ethylene plants number into the hundreds throughout the world. Major suppliers of ethylene plants include the following: The M. W. Kellogg Co., 711 Third Avenue, New York, New York 10017; The Lummus Company, 1515 Broad Street, Bloomfield, New Jersey 07003; Linde A.G., 8021 Hollriegelskreuth, Germany; C F Braun & Co., Alhambra, California 91802; Stone & Webster Engineering Corp., 225 Franklin St., Boston, Mass. 02107; Lurgi Gesellschaften, Postfach 9181, 6000 Frankfurt (Main) 1, Germany; Selas Corporation of America, Dresher, Pa. 19025; Foster Wheeler Corp., 666 Fifth Avenue, New York, New York 10019; Chemical Construction Corp.; The Badger Co., Inc., 363 3rd Street, Cambridge, Mass. 02142; Azote & Produits Chimiques s.a., 31-Toulouse 03, France; Badische Anilin-& Soda-Fabrik AG. 6700 Ludwigshafen, Germany; and Hoechst-Uhde Corp., 550 Sylvan Avenue, Englewood Cliffs, New Jersey 07632.



Ethylene — C F BRAUN & CO

Application: The schematic flow diagram shown is typical for naphtha feedstock and for economic criteria of low energy cost and short payout periods. The fractionation sequence can be varied to accommodate different feeds or different economic criteria. For example, for naphthas, high energy cost and long payout periods would favor a front end demethanizer.

Description: The schematic flow diagram shown is typical for a naphtha feedstock and is varied to accommodate the type of feed and requirements of specific plants.

Feedstocks are cracked in the presence of steam in tubular pyrolysis furnaces. The severity level is determined by economic studies which establish the optimum relation of byproducts to ethylene.

The furnace effluent is cooled in transfer line exchangers by generating steam at pressures up to 1800 psi. Heat recovered from the effluent gas and flue gas is used as an energy source. It permits steam balancing and enters into selection of the optimum combination of steam turbines, gas turbines, and electric motors.

The cooled gases are quenched with circulating oil and washed to remove fuel oil fractions. The last low-pressure quenching is by direct contact water cooling. Gasoline range materials are condensed in this step, along with the dilution steam from pyrolysis. The condensed water is vaporized and recycled as dilution steam to the cracking furnaces.

Uncondensed gases are compressed and treated to remove acid gases. Systems based on amine or other regenerative solutions have been used followed by caustic washing. The treated gas is dried with alumina or molecular sieves.

Acetylene is removed by catalytic hydrogenation in the C_3 and lighter stream from the depropanizer.

Demethanizer feed is chilled in successive stages to condense methane and heavier, leaving hydrogen as a gaseous product. Methane is separated from C_2s and heavier in the demethanizer. The hydrogen and methane tail gas streams may be further treated to meet high-purity specifications.

The deethanizer separates C_2s from C_3s and the C_2 stream is fractionated in a C_2 splitter to produce 99.9+ percent ethylene. Ethane is normally recycled to pyrolysis.

C_3s may be catalytically hydrogenated to meet chemical grade propylene specifications, or they may be fractionated in a C_3 splitter to produce polymer grade propylene of 99.5+ percent purity.

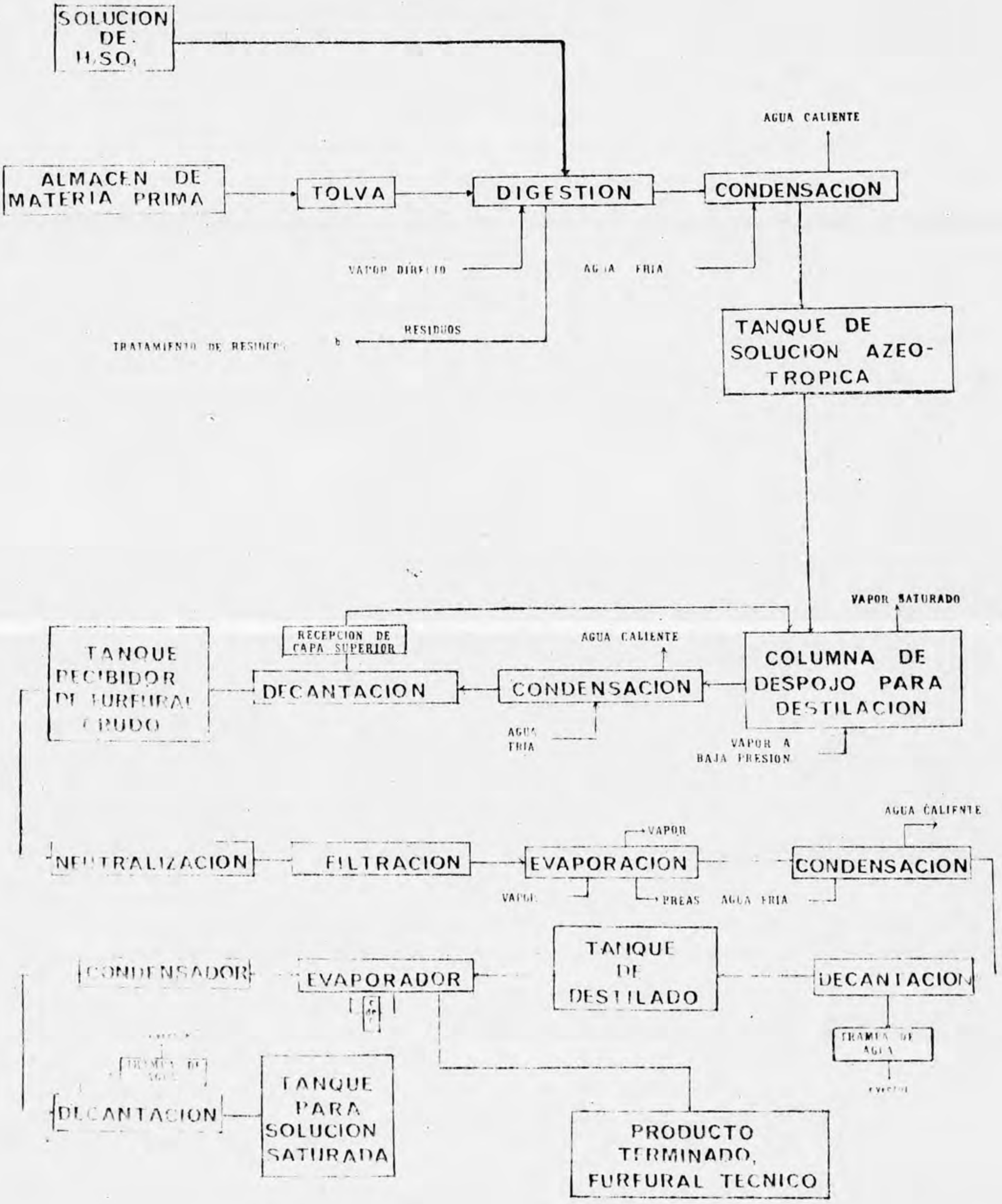
The debutanizer produces a C_4 overhead stream which may be processed to extract butadiene and other C_4 products. The C_5^+ material may be hydrotreated to produce stable gasoline or it may be further processed to recover aromatics or a C_5 fraction containing isoprene.

Refrigeration is supplied by a cascaded ethylene-propylene system which may be integrated with the C_2 and C_3 fractionation facilities to reduce equipment cost.

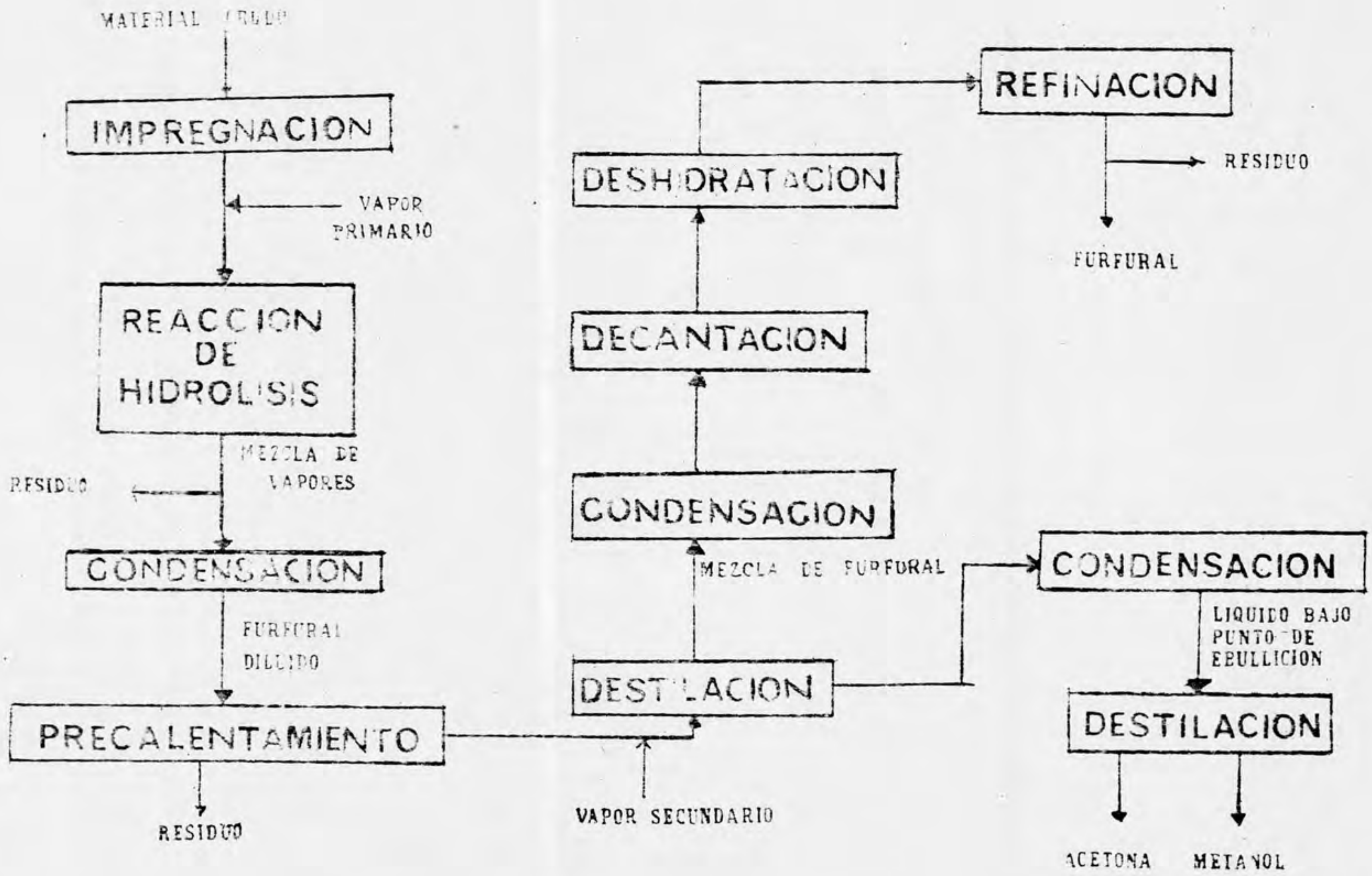
Yields: Over-all ethylene yields from the various feedstocks vary from about 80 weight percent for commercial ethanes, through 35 weight percent for light paraffinic naphthas, to below 20 weight percent for heavy gas oils. Pilot plant runs are made to verify product yields and set design parameters for the commercial pyrolysis coil.

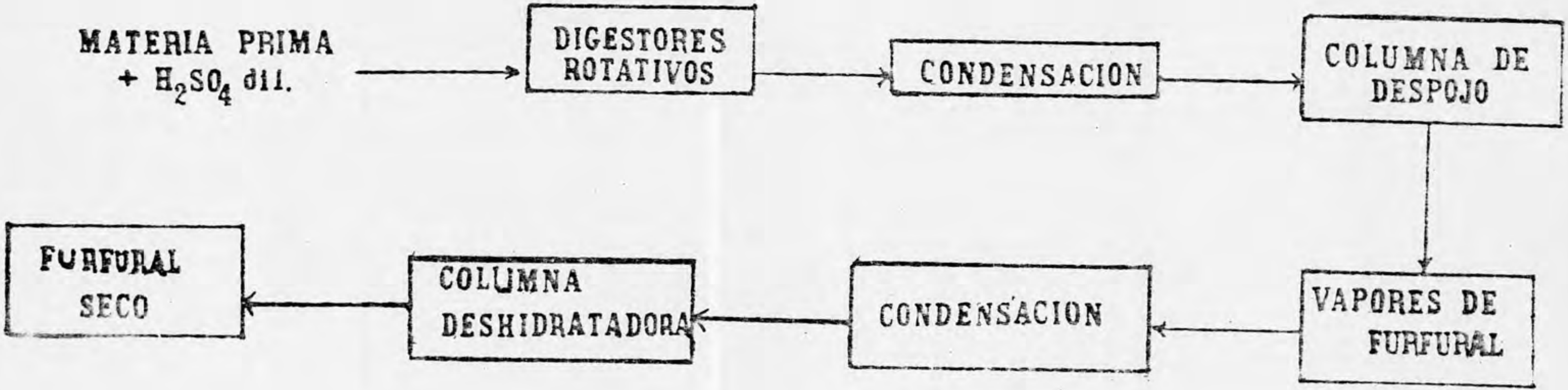
Commercial installation: Twenty-two plants have been designed or constructed with an annual capacity exceeding 7.5 billion pounds of ethylene.

PROCESO FYDSA



PROCESO ROSENLEW





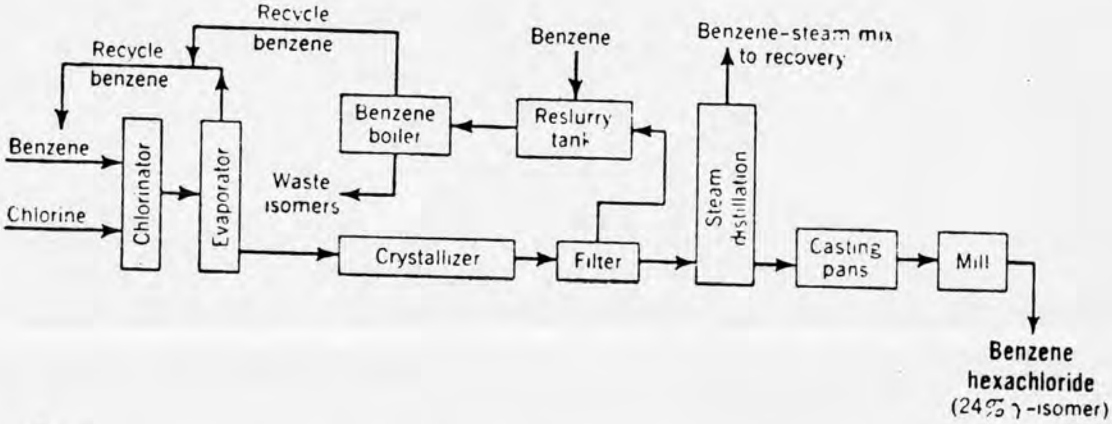
PROCESO SIMPLIFICADO DE QUAKER OATS

BENZENE HEXACHLORIDE

(BHC)

$C_6H_6Cl_6$

From Benzene and Chlorine



Reaction

$$C_6H_6 + 3Cl_2 \xrightarrow[\text{light}]{\text{Actinic}} C_6H_6Cl_6$$

95% yield

Material Requirements

Basis—1 ton benzene hexachloride (24% γ isomer)

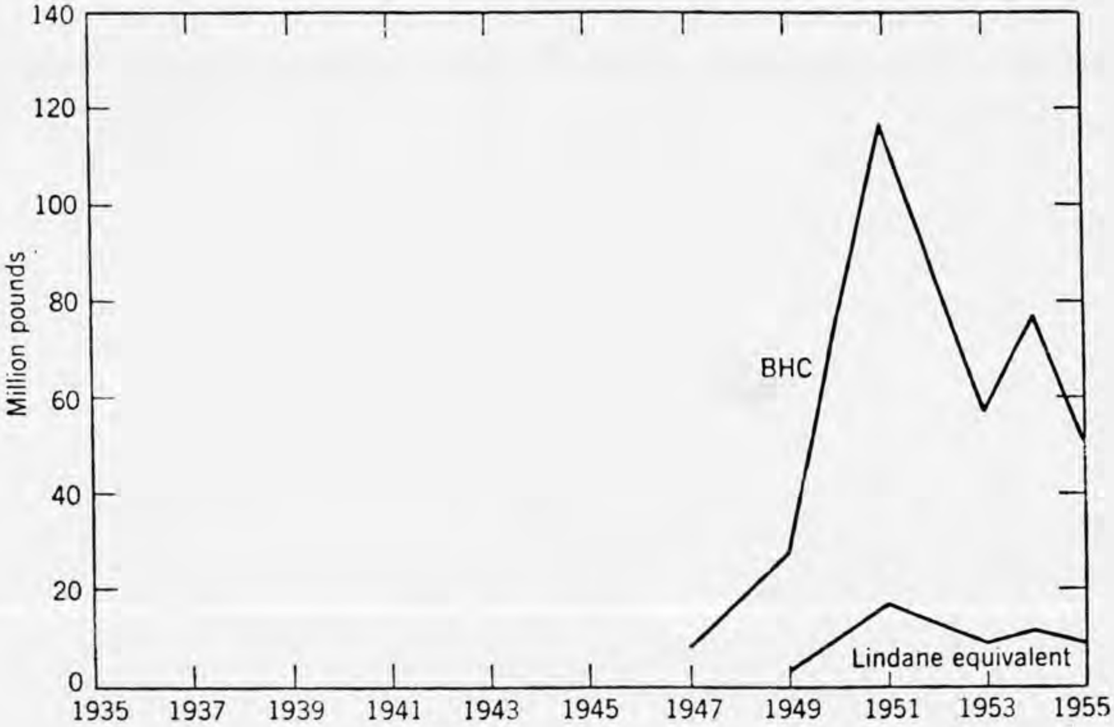
plus 1 ton waste isomers

Benzene	1,050 lb
Chlorine	2,950 lb

Process

Benzene hexachloride, commonly called BHC, is made by reacting chlorine and benzene in the presence of actinic light. Only one of the several isomers formed, the gamma isomer, is highly toxic to insects. Processes vary [illegible] the purification [illegible]

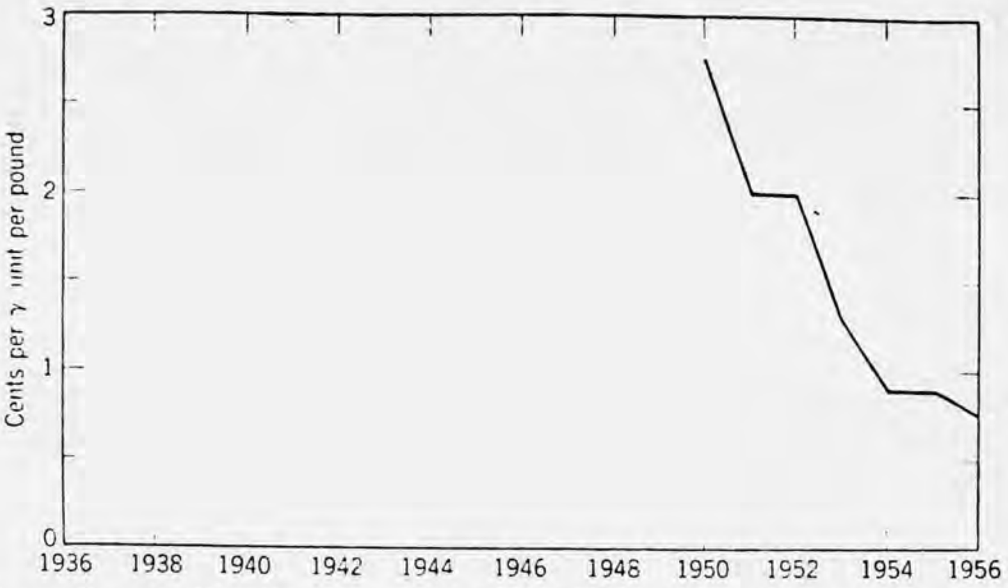
In a typical process chlorine is contacted with benzene continuously in a vessel fitted with a mercury-vapor lamp. The reactor is operated at or slightly above atmospheric pressure and a temperature of 20 to 60°C. The BHC concentration in the reactor is controlled at 12 to 15 per cent to prevent precipitation of the less soluble isomers. The reactor product is then concentrated by evaporating the benzene for recycle. Liquefied BHC (10–15% γ isomer) is then pumped to a crystallizer where, at 35 to 40°C, some of the α and β isomers crystallize. After filtration the filtrate is steam-distilled, and the molten bottoms are cast in metal pans, cooled, and ground to desired size. The product (about 24% γ isomer) is generally packed in fiber drums for shipment to an insecticide mixing plant. Further fractional crystallization yields lindane (99% γ isomer).



Production—Benzene Hexachloride

Use Pattern

Insecticide 100 per cent



Price—Benzene Hexachloride (Prior to 1950, BHC was not sold on γ-unit basis)

Miscellaneous

Properties. Colorless to yellow crystals or flakes. The crude product has a musty odor.

Mol. wt.	290.85	M.P.	(γ isomer) 112.5°C
Density		B.P.	decomposes

Soluble in alcohol (6.4 g per 100 g). Insoluble in water. Can be toxic to humans.

Grades. Technical BHC (sold on basis of γ isomer content as 14–16%, 23–24%, 36–40%, etc.) in powder or lump form. Lindane (99% γ isomer) in the form of colorless crystals.

Containers and Regulations. Paper bags and fiber drums of various sizes. No ICC shipping label required. Manufacturing Chemists Association requires warning label.

Economic Aspects

Benzene hexachloride, sometimes called gammexane and 666, and commonly called BHC, is an insecticide and classified generally as an agricultural chemical. This classification includes various fumigants, fungicides, growth regulators, herbicides, insecticides, pesticides, rodenticides, soil conditioners, etc. Before World War II most of these materials were inorganic compounds or naturally occurring organic compounds. During the war it was found that many synthetic organic chemicals containing chlorine in the molecule had insecticidal properties. This instigated a search for the most effective compounds and set in motion vast research resources which delved into all phases of the agricultural chemical field. Many new compounds were synthesized and found more effective for specific uses than any current materials. Accordingly, production of agricultural chemicals skyrocketed. One reason for this was real need. In 1952 despite widespread sorts of pesticides, crop losses to agricultural pests were 4 billion dollars by insects, 4 billion dollars by fungi, and 5 billion dollars by weeds.

The insecticidal properties of BHC were discovered in England and France in the early 1940's. Of the sixteen possible isomers, five have been isolated—α, β, γ, δ, and ϵ forms. Only the γ isomer is toxic. It destroys insects by external contact, ingestion into the stomach, and absorption through the respiratory tract. Between 65 and 85 per cent of production is used on the cotton crop, primarily to control the boll weevil. It is not suited for use on food crops because of the musty odor it imparts to the plant. To overcome the odor problem, lindane (at least 99% γ isomer) was developed. Lindane is a coined name selected by agreement between USDA authorities and the insecticide industry to distinguish highly refined BHC from lower grades. It is used primarily on food crops when DDT is not effective.

For most uses, BHC and lindane must compete with other chlorinated insecticides as well as DDT. These include chlordan (excellent for killing flies), toxaphene, dieldrin and aldrin, among others. The last three are especially effective against grasshoppers and cotton insects.

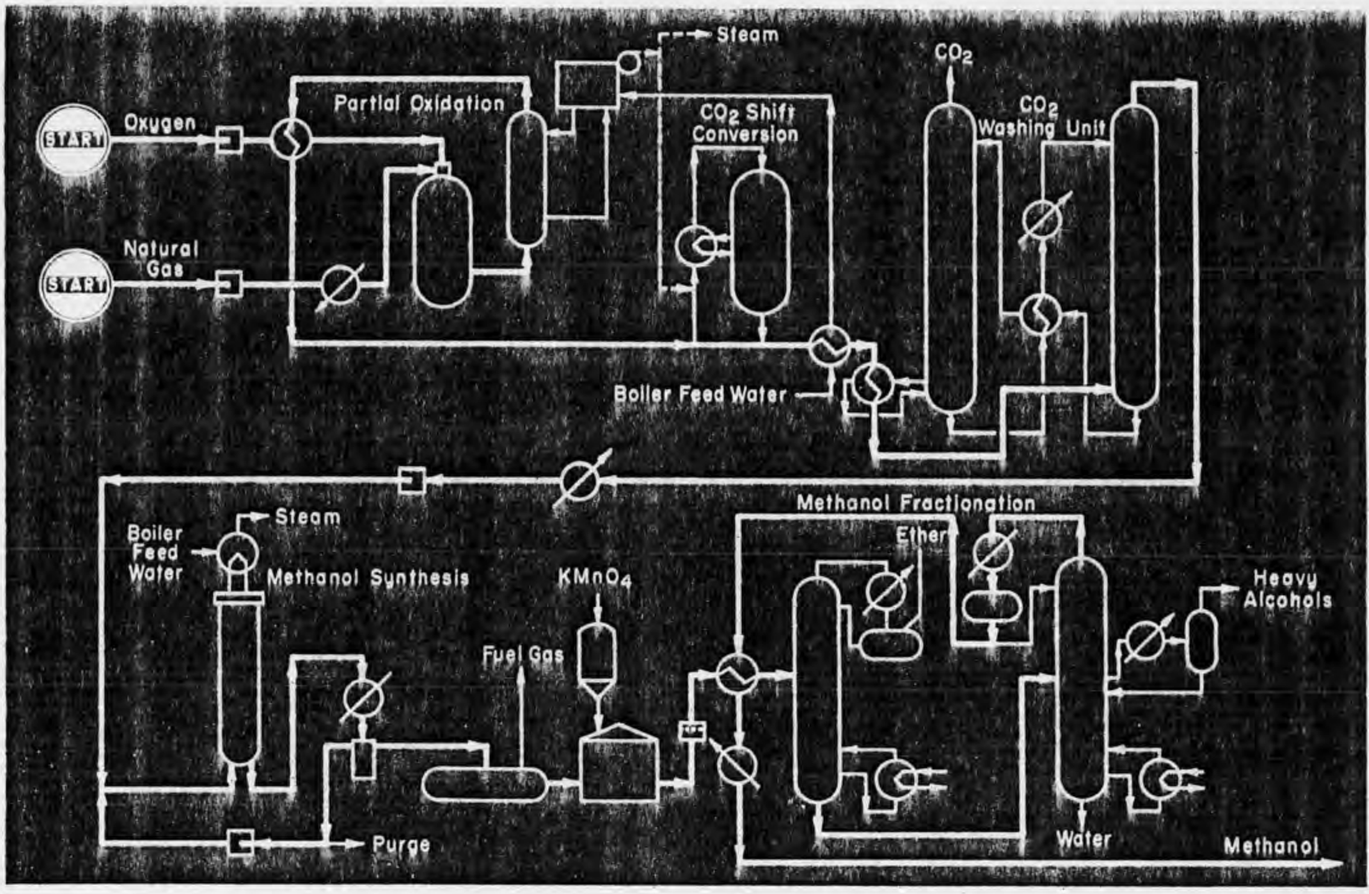
BHC, like other agricultural chemicals, is a seasonal product. Accordingly, large inventories must be built up in anticipation of the growing season. If the inventory for a given year is large and demand slackens, a drop in price usually results, with consequent lower profits. Accordingly, the successful venture in agricultural chemicals demands accurate forecasting, a sound financial position, and aggressive salesmanship.

Considerable work is under way on the development of process conditions that will lead to a larger fraction of γ isomer in the crude chlorinated product.

A plant manufacturing 5 tons of 25% γ-BHC per 24-hr day is estimated to cost $425,000 excluding building and site.

Manufacturers and Plant Sites

Allied Chemical & Dye Corp. (General Chemical Div.), Marcus Hook, Pa.
Columbia-Southern Chemical Corp., Natrium, W. Va.
Commercial Solvents Corp., Terre Haute, Ind.
Diamond Alkali Co. (Chlorinated Products Div.), Houston, Texas; Newark, N. J.
E. I. du Pont de Nemours & Co., Inc., La Porte, Texas
Ethyl Corp., Baton Rouge, La.
Food Machinery and Chemical Corp. (Westvaco Chlor-Alkali Div.), So. Charleston, W. Va.
Frontier Chemical Co., Wichita, Kans.
Geigy Chemical Corp., Cranston, R. I.; McIntosh, Ala.
Hooker Electrochemical Co., Niagara Falls, N. Y.
Montrose Chemical Co., Newark, N. J.
Olin-Mathieson Chemical Corp., Niagara Falls, N. Y.
Pennsalt Chemicals Corp., Natrona, Pa.; Calvert City, Ky.
Pittsburgh Coke and Chemical Co., Pittsburgh, Pa.
Stauffer Chemical Co., Henderson, Nev.
Tennessee Products and Chemical Corp., Nashville, Tenn.
Wyandotte Chemical Corp., Wyandotte, Mich.



Methanol—MONTECATINI

Application: A process for the manufacture of rectified methanol based on catalytic synthesis from a gaseous mixture of carbon oxides and hydrogen.

Charge: Any mixture of gaseous hydrocarbons, or acetylene off-gas; oxygen 98 percent pure.

Product: Methanol, 99.9 percent pure.

Description: The gaseous charge is first compressed at 450 psig, preheated and partially oxidized into a furnace operating at about 2300 °F. in order to obtain a low content in residual methane. For oxidization purposes highly pure oxygen (not less than 98 percent) is used, to limit the content in the final synthesis gas of inert components.

The gas leaving the furnace flows through a waste heat boiler in which saturated steam at 550 psig is produced in an amount exceeding the total requirements of the whole process.

The flow gas is essentially formed by a mixture of carbon monoxide and hydrogen, containing minor amounts of carbon dioxide, methane, nitrogen and water. The hydrogen to carbon oxides ratio in the oxidized gas is slightly lower than the stoichiometric value which can be foreseen from the reaction equations:

$$CO + 2H_2 \rightarrow CH_3OH$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

It is therefore necessary to remove a small amount of carbon oxides to obtain a slight excess of hydrogen which fosters the kinetic of the above mentioned reactions.

This is accomplished as follows: a small fraction of oxidized gas (20 to 25 percent when starting from natural gas) is sent to a shift converter in which carbon monoxide is converted to carbon dioxide, yielding hydrogen from steam.

The converted gas, mixed with the unconverted gas fraction flowing from the boiler, yields heat which can be used, for instance, for stripping the carbon dioxide absorbing solution; the gas mixture is then sent to a washing tower in which the carbon dioxide content is lowered dowr to 1-2 percent.

The washed gas is now compressed to about 4,200 psig, mixed with the recycle gas and finally enters the converter. The latter is identical in design to the well known Montecatini-Fauser ammonia converter.

This method gives strict temperature control and thus allows a good conversion and a high degree of purity in the obtained product. Water, circulated in the cooling elements placed inside the converter, is cooled in a waste heat boiler yielding steam at 100 psig.

The effluent gas from the converter is cooled in a condenser; here crude methanol is separated as a liquid phase and the unreacted gas is recycled by a compressor.

Crude methanol is pumped from the separator vessel to a let down tank, operating at about 200 psig, in which the dissolved gases are given off. From the let down tank the crude product is fed to the purification unit. Purification is carried out in three steps: first a diluted potassium permanganate solution is added to the crude methanol to oxidize the aldehydes, ketones and other impurities contained therein in small amounts. Secondly, the alcohol is pre-heated and fed to a distillation column in which light ends (essentially dimethylether) are removed. In a third step the bottoms of first column are fed to a second tower which separates pure methanol produced as top effluent, from water which is withdrawn as bottom effluent; higher alcohols are removed as a sidestream from the lower part of the fractionation tower.

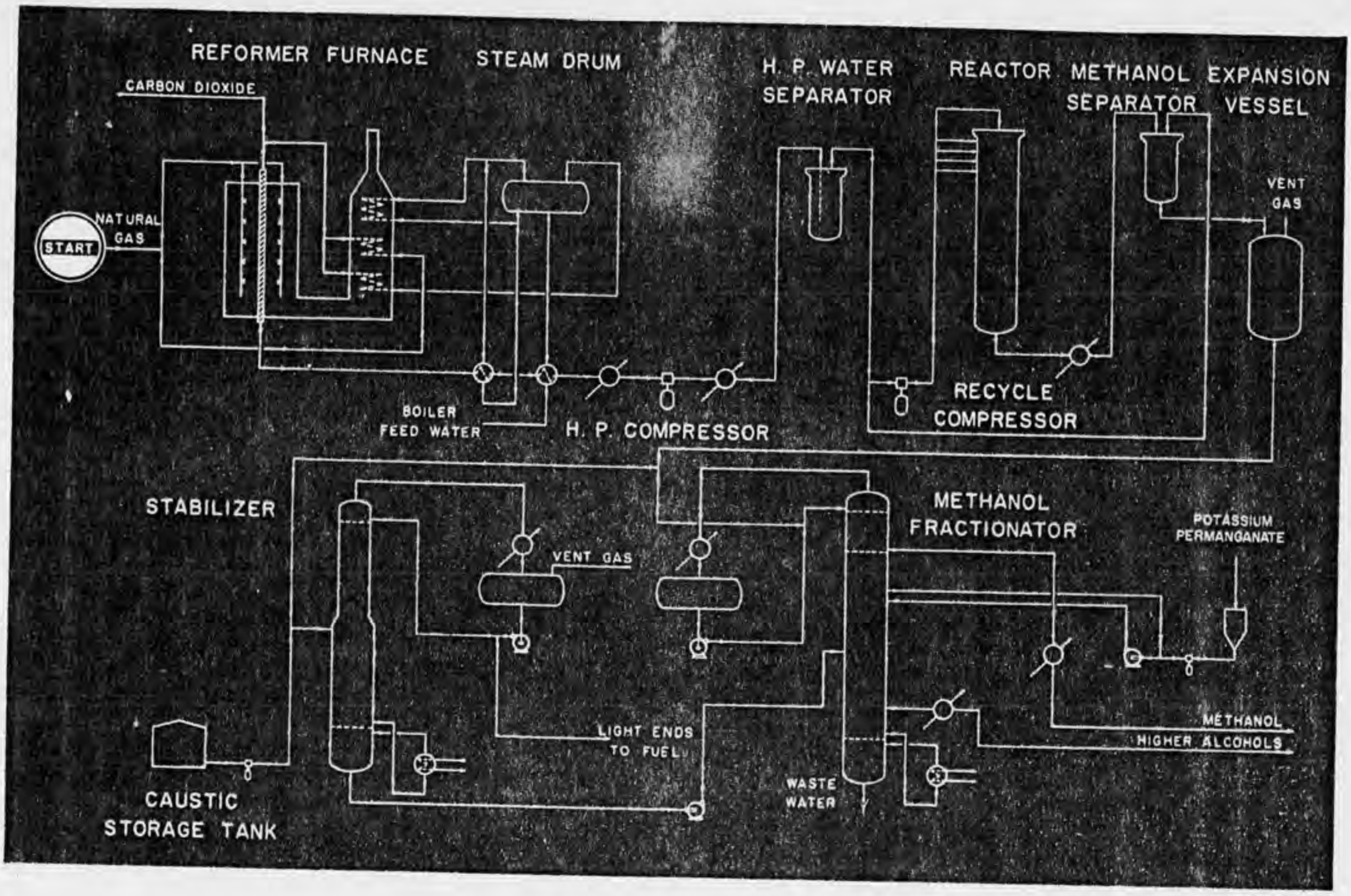
Operating conditions: The working pressures in the various stages of the cycle have been already indicated in the above description.

Temperatures are, approximately, as follows: in partial combustion furnace: 2300 °F.; in shift conversion of carbon monoxide and steam to CO_2 and H_2: 750 °F.; in methanol synthesis reactor: 740 °F.

Yields: For the production of 100 kg of rectified methanol 920 N cubic meters of 100 percent methane and 620 N cubic meters of 100 percent oxygen are required.

Commercial Installations: Montecatini has built a total of 10 plants for methanol production in five different countries.

One unit, having a capacity of 150 metric tons per day from acetylene off-gas is under construction at Brindisi-Italy.



Methanol (Uhde)—ARTHUR G. McKEE AND COMPANY

Application: A process for manufacturing synthetic methanol.

Charge: Natural gas, ethane, LPG, any light hydrocarbon.

Product: Pure anhydrous methanol.

Description: Methanol is produced by the reaction of carbon monoxide or carbon dioxide with hydrogen. The process is catalytic and carried out at elevated temperature and pressures. Any suitable source of H_2 and CO or CO_2 may be used to produce the synthesis gas. Under U.S. economic conditions the most favorable source is high-pressure reforming of natural gas with steam.

Steam-methane reforming produces a gas in which the ratio H_2/CO is higher than desirable for the methanol reaction. This ratio is theoretically 2.0, but a ratio of 2.25 is normal practice. To achieve the desired balance, carbon dioxide from any available outside source may be added in the H_2/CO_2 ratio of 3.25 to react with excess H_2.

In steam-methane reforming the natural gas at approximately 150° F is preheated to 850° F and mixed with steam likewise preheated to 950°-1000° F. Carbon dioxide required to achieve the desired $H_2/CO + CO_2$ ratio is added, and the mixture passes to a bank of catalyst tubes in the radiant section of a furnace. High temperatures favor the reforming reaction. Excess steam is used to insure complete utilization of the methane.

Leaving the catalyst tubes the mixture is quenched with water to bring its temperature below reaction temperature as quickly as possible. It then exchanges heat with boiler feed water and is cooled with water before going to the high pressure compressor. This compressor raises the pressure of the mixture to that of the reactor system, 4,600 psig.

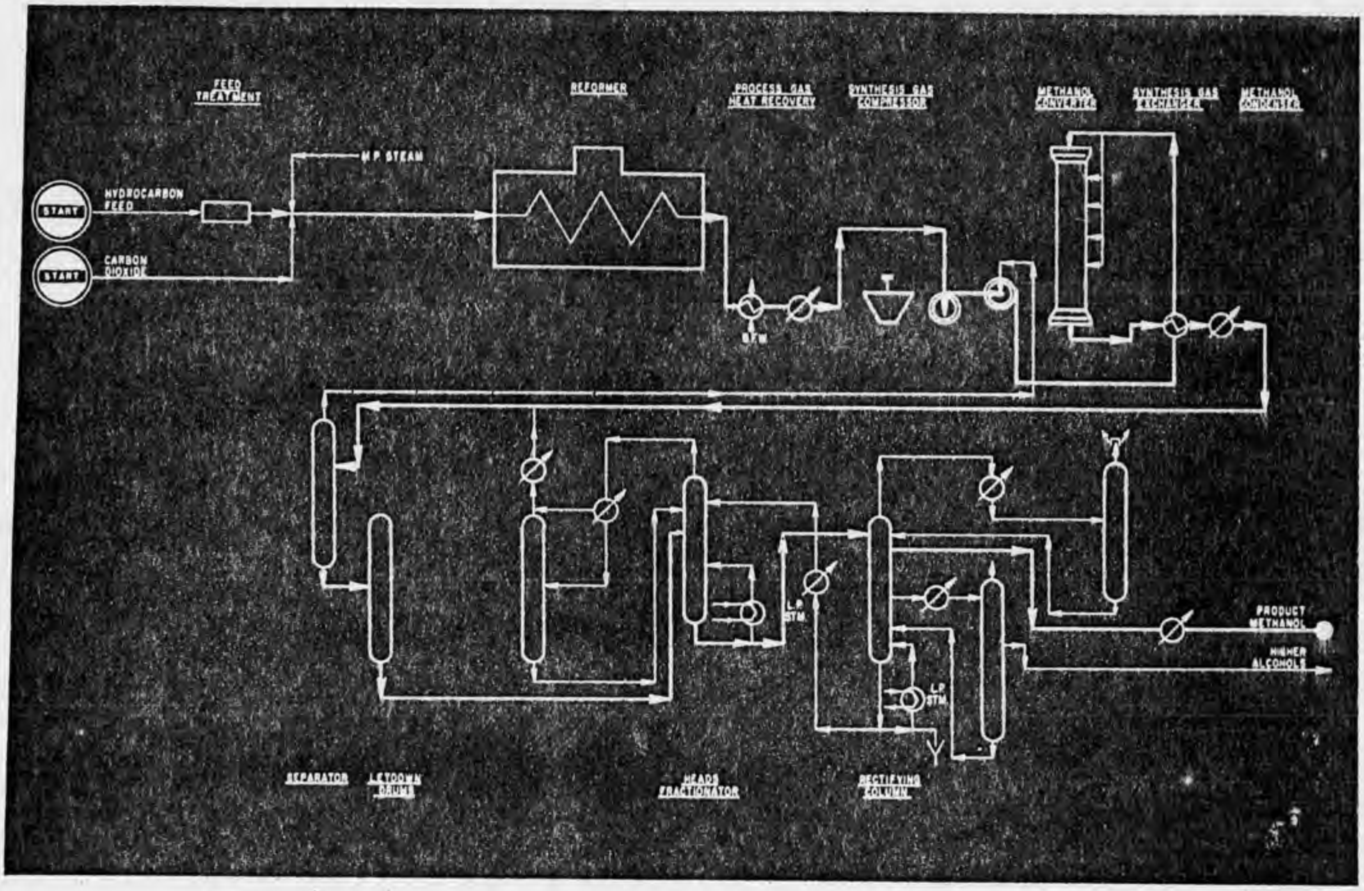
The Uhde methanol reactor consists of catalyst beds mounted in a high-pressure container. The main body of reacting gas enters at the top of the vessel and passes down along the shell through an annular space. This preheats the gas and keeps the pressure shell cool. The pressure shell is therefore constructed of heat-treated steel. A stainless steel or copper lining is used because of corrosion possible from the high partial pressure of CO. At the bottom the gas passes through the shell side of a shell-and-tube-type exchanger built within the pressure shell. Here it is heated by the reaction products leaving the convertor. Leaving the heat exchanger the feed gases pass through a central tube to the top of the reactor and then down through the first bed of catalyst.

The reaction of H_2 and CO is strongly exothermic. To regulate the temperature over the catalyst some of the feed gas by-passes the preheater. It enters directly into the space between the catalyst beds cooling the gases leaving the catalyst bed above.

The gases leaving the bottom catalyst bed pass through the tube side of the internal heat exchanger before leaving the reactor. They are then cooled with water and pass to the methanol separator where the condensed methanol is withdrawn. The unreacted gases are returned to the reactor by the recycle compressor. The methanol is depressured to an expansion vessel in which the dissolved gases are flashed and vented. It is then stabilized to remove light ends (ethers, hydrocarbons and noncondensibles). A small amount of caustic solution is added with the stabilizer feed to neutralize the acids formed as by-products.

The stabilized methanol is charged to the methanol fractionator for purification. A recycled sidestream withdrawn from the fractionator is treated with 1 percent potassium permanganate solution to remove aldehydes, etc., by oxidation. The overhead product of this fractionator is returned to the stabilizer where it joins the light ends stream. The purified methanol is withdrawn as a sidestream. Higher alcohols are withdrawn farther down the fractionator. The salts, MnO_2 and water are withdrawn to waste at the bottom of the tower.

Operating Conditions: The methanol synthesis is carried out at 4,600 psig. In the catalyst beds the reacting gases enter at approximately 615° F.



Methanol (CPI-Vulcan)— VULCAN-CINCINNATI, INC.

Application: A process for the manufacture of methanol from natural gas, refinery gas, naphtha, or light hydrocarbons, steam and carbon dioxide.

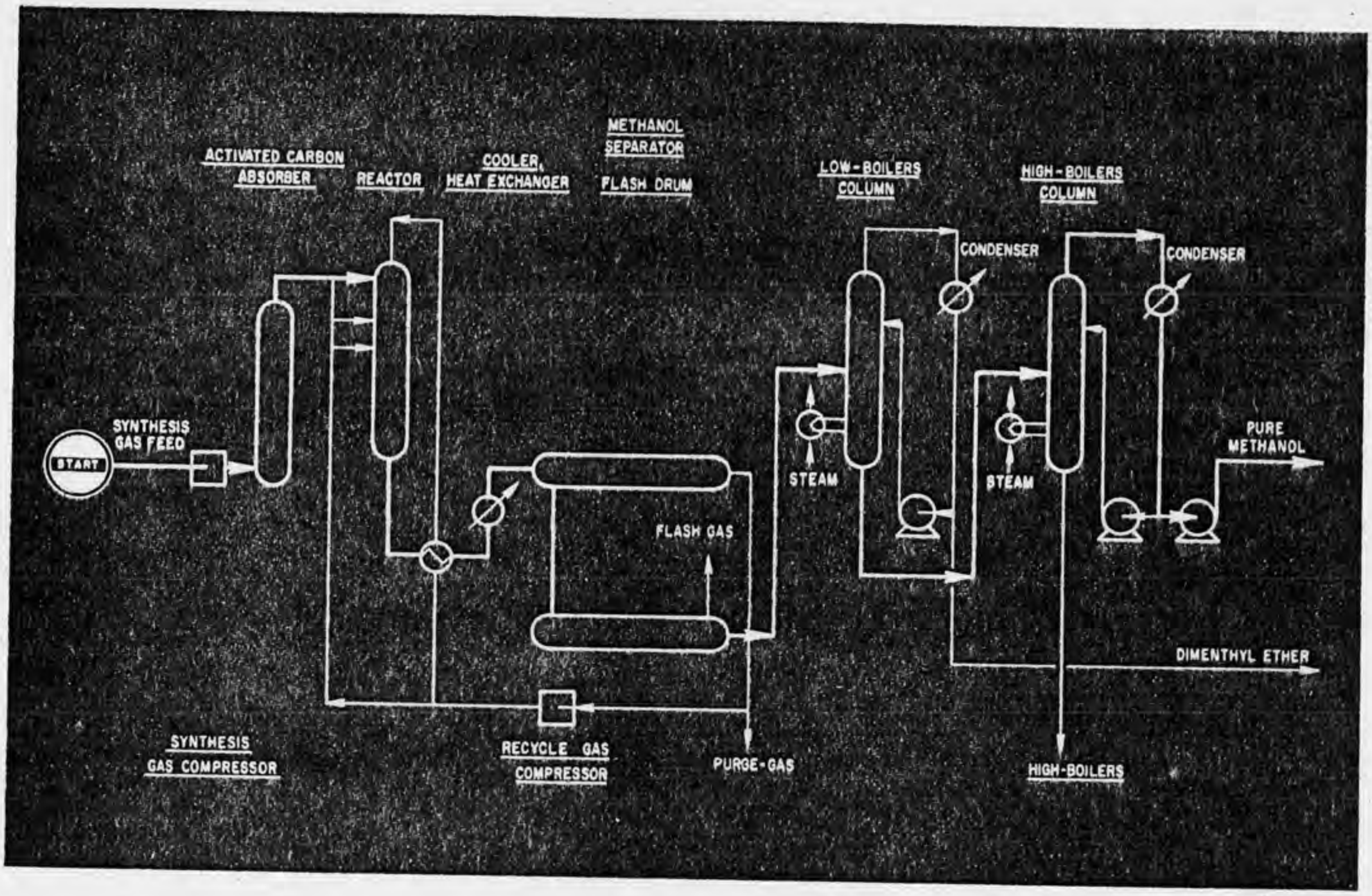
Description: Gaseous hydrocarbon feedstock is initially processed by catalytic or adsorptive means to remove sulfur impurities. The cleansed feedstock, along with steam and carbon dioxide, are brought to reformer pressure and catalytically reacted at elevated temperature to produce synthesis gas containing hydrogen and varying proportions of carbon oxides. Carbon-hydrogen ratios are adjusted to optimum levels prior to reforming. Fuel gas and process purge gas are used for reformer thermal requirements. Thermal energy in the resulting flue gas is effectively recovered in a series of exchangers for the production of high pressure superheated steam and boiler feedwater heating. Cooled flue gas is discharged to atmosphere. Synthesis gas is likewise used in boiler feedwater heating and the production of steam. Plant turbine drive requirements for synthesis gas compression use high pressure steam. Process heating and miscellaneous utility demands are best met with medium and low pressure steam. Centrifugal compression of the synthesis make-up and recycle gases boosts gas pressure to loop design levels prior to entering the multi-staged methanol converter. A unique converter control concept permits optimum thermal sensing and temperature controls over narrow spans of individual catalytic beds, that effectively promote reaction, resulting in high methanol yields and minimum byproduct formation. Development of a high-activity methanol catalyst permits operation at significantly lower pressures than ordinarily encountered in comparable units. Characteristics of this catalyst are high selectivity, low sensitivity to sulfur, broad operating temperature range, low initiation temperature and the added feature of pre-reduction which permits safe storage for long periods of time.

Gas leaving the converter gives up its exothermic heat of reaction to preheating the incoming synthesis gas. Additional cooling promotes condensation, and non-condensibles and crude methanol enter separators at loop pressure, where the unreacted gas is stripped off and returned to compression. Crude methanol is then let down in pressure prior to entering the purification section.

Crude methanol is refined by distillation. A "heads" fractionator and rectifying column are employed in producing high-purity methanol product. Light ends stripped off in the process are returned to the reformer furnace for fuel. Methanol product flows through a cooler exchanger and is then sent to storage.

In this process, reformer pressure, steam pressure and synthesis loop pressure are design variables used to develop an over-all plant design which will produce methanol at lowest cost.

Commercial Installations: Five plants onstream, several others in the design or construction phases. Capacities range from 30 to 2,000 tons of methanol per day.



Methanol (UKW Process)— LURGI CORP.

Application: A process for the manufacture of methanol from mixtures of CO, CO_2 and H_2 obtained from the gasification of solid fuels, liquid fuels, such as bunker-C-oil and naphtha or from the reforming of natural gas, refinery gas or other off-gases.

Description: Carbon monoxide, CO_2 and H_2 are converted to methanol at about 320-370° C and 300 atmospheres gauge in the presence of chrome oxide/zinc oxide catalyst according to the following equations:

$$2\,H_2 + CO \rightarrow CH_3OH$$
$$3\,H_2 + CO_2 \rightarrow CH_3OH + H_2O$$

The synthesis gas, after compression and removal of iron pentane carbonyl by adsorption on activated carbon, is charged together with recycle gas to the reactor accommodating several beds of catalyst. Quench gas is introduced between the catalyst beds to optimize the reaction temperature profile. The methanol-bearing gas leaving the reactor is cooled by heat exchange with recycle gas and finally with air or water. The condensed crude methanol is separated from unreacted gas which is recycled by the recycle compressor to the reactor. Inerts are removed by continuous purge of a portion of the recycle stream upstream of the recycle compressor.

The flashed and gas-free crude methanol from the separator is purified to the purity desired by distillation. Dimethyl ether, methyl formiate and other low boiling components are removed in the low boilers column while water and higher alcohols are removed in the high-boilers column.

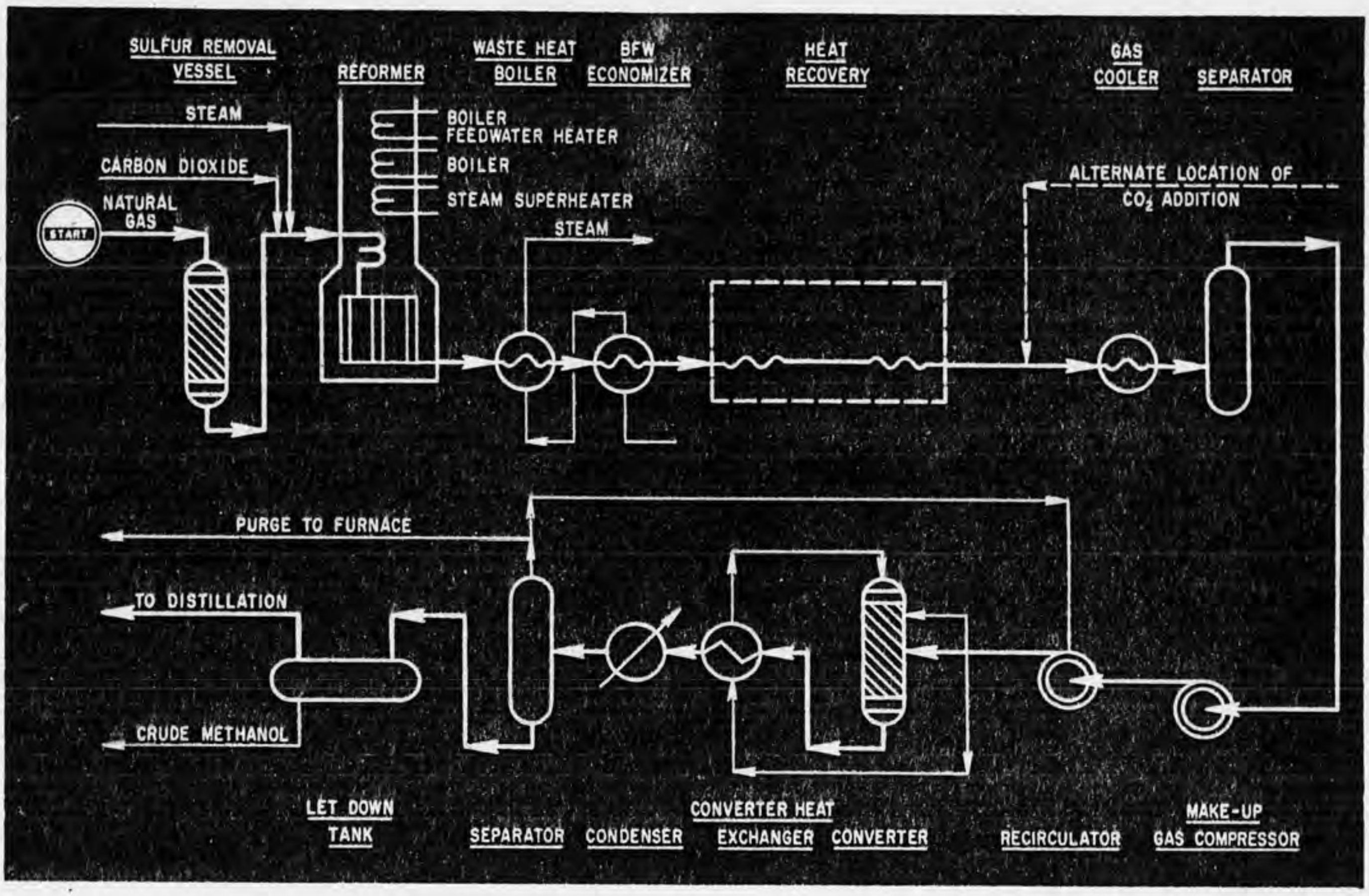
Technical Data: Operating requirements for gas production (RECATRO Process), methanol synthesis and distillation per ton of pure methanol using naphtha as starting material:

Naphtha	504 kg
Heating fuel	3.85 million kcal
Electric power	54 kWh
Heat to be removed by cooling	2.3 million kcal
Feed water	1.6 ton

Methanol Specification:

Sp. gravity 20°/20°	0.793 kg/l
Water content	0.035% wt.
Boiling interval	0.5° C
Permanganate number	60 min.

Commercial Installations: The installed capacity of plants operating by the UKW-Lurgi process is presently 600,0000 t/y of pure methanol. So far, Lurgi has built plants in Rumania, Czechoslovakia, Yugoslavia, Republic of Korea and Spain.



Methanol (ICI Low Pressure Process)—CHEMICAL CONSTRUCTION CORP.

Application: A process for the manufacture of 99.5-99.99% pure methanol from natural gas, steam, and carbon dioxide.

Description: Natural gas is first treated for sulfur removal by passing it over a bed of activated carbon.

The next step consists of "reforming" natural gas with steam to make a synthesis gas containing CO, CO_2, H_2, and CH_4. CO_2 is added before or after the reformer furnace to make up the carbon deficiency of synthesis gas normally made from natural gas and steam alone. As far as methanol production is concerned such synthesis gas is rich in hydrogen, and whenever CO_2 is readily available, it is used as described above to supply the balance of carbon. However, methanol can also be produced from a hydrogen rich synthesis gas, by purging excess hydrogen in the makeup gas.

Depending on the economics of raw materials available, the pressure and the temperature of reforming operations can be selected to optimize the process. The general range can be considered at 150-300 psig and 1,450°-1,600° F.

The heat in the synthesis gas leaving the reformer is recovered by making steam, heating up boiler feed water, and supplying part of the heat requirements of other sections of the plant. The gas is then cooled and compressed.

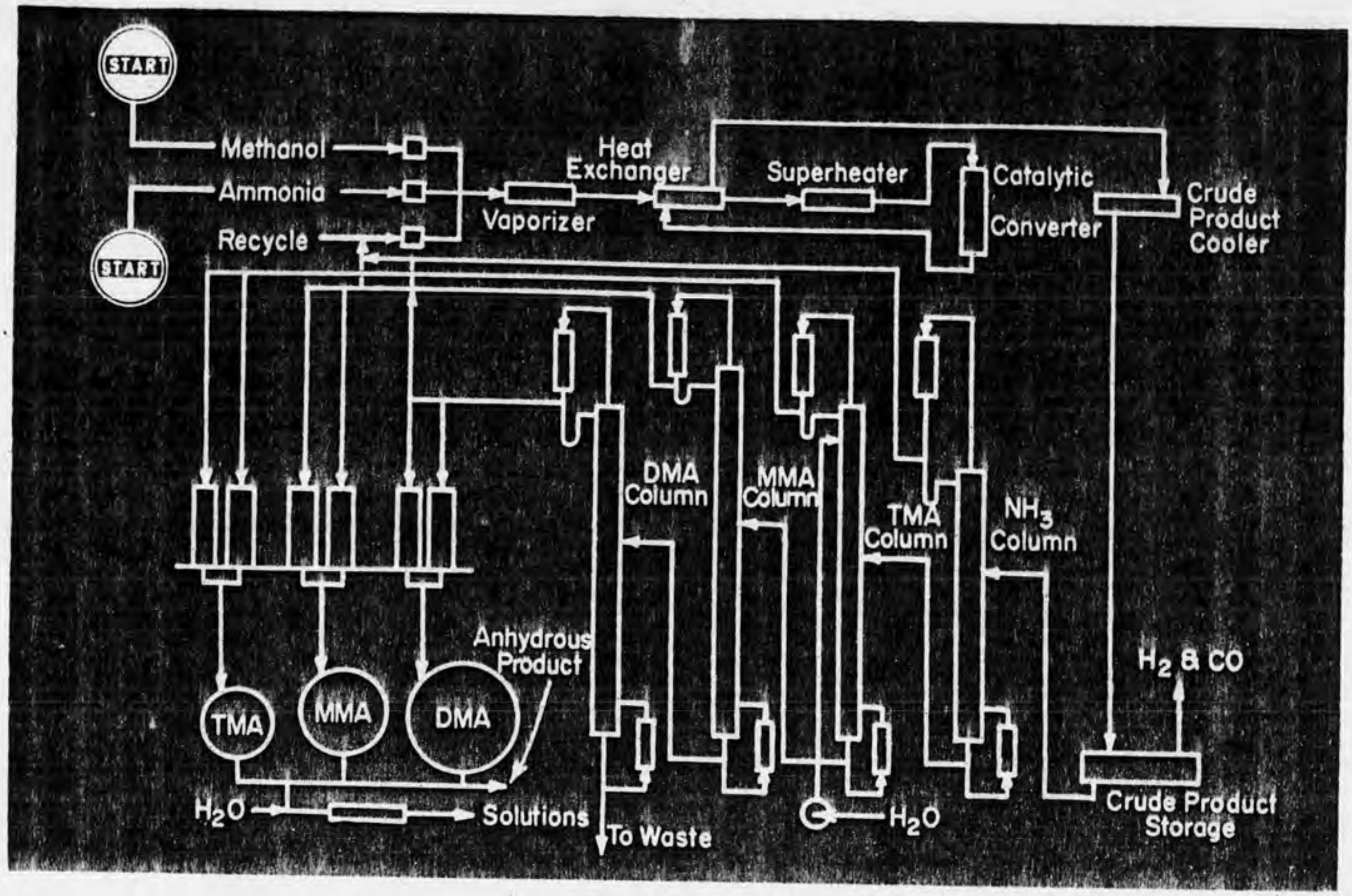
Compression-Synthesis: The gas is compressed to 680 psig in a centrifugal compressor and then mixed with recycle gas and further compressed to 750 psig in another centrifugal compressor. A major portion of the combined stream is heated up in the converter heat exchanger and sent to the converter where it flows over a continuous bed of catalyst. The portion of gas that is not heated in the converter exchanger is injected into the catalyst bed at appropriate depths through distributors of patented ICI design which provide very good mixing and still allow free passage of catalyst for charging and discharging.

The gas leaving the catalyst bed passes through the converter heat exchanger to heat up the unreacted gas going to the converter, and then flows through the methanol condenser where the methanol is condensed. The condensed methanol is separated from the noncondensed gas in a separator. The liquid methanol is let down in pressure and sent to distillation section as crude methanol, and the noncondensed gas is recycled to the converter after being compressed. Most of the inerts derived from the feed stock are purged from the loop and used as fuel. The balance of the inerts dissolved in the crude methanol stream are flashed in the let down tank. This flashed stream containing methanol is sent to the distillation section. The normal range of catalyst bed temperature is 482°-518° F.

Distillation: The low pressure process produces crude methanol with a considerable lower impurity than the crude from the high pressure process.

Installed Capacity: 1000 T/D in single plant.

Reference: Strelzoff S.: "Methanol—Its Technology and Economics." Paper No. 12 B, presented at the 64th National Meeting of A.I.Ch.E., New Orleans, La., March 16-20, 1969.



Methylamines— THE LEONARD PROCESS COMPANY

Application: A continuous process for the manufacture of mono, di, and tri-methylamines, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$.

Charge: Technical grade anhydrous ammonia, and synthetic methanol.

Products: Anhydrous or aqueous solutions of mono, di, and trimethylamine.

Description: Anhydrous ammonia, synthetic methanol, and recycle liquid are fed continuously at controlled rates to a vaporizer which converts the liquid to a gas stream which then flows successively through a heat exchanger and superheater and into a converter packed with an amination catalyst where the ammonia and methanol react to form the amines. The reaction is exothermic and part of this heat of reaction is recovered by passing the hot exit gases from the converter through the heat exchanger to heat up the forward gas flow. The gas stream from the heat exchanger passes into a condenser which liquefies the stream and permits storage of the crude product until it is distilled.

From the crude product storage, the mixture of NH_3, Mono, Di, and Tri-methylamines and water are fed to four distillation columns in series. The first column separates out the excess ammonia and part of the trimethylamine which forms an azeotrope with ammonia as an overhead stream which is recycled. The bottoms are fed to the second column into which water is fed near the top to perform an extractive distillation which permits pure trimethylamine to be withdrawn overhead and taken to product storage, or recycle as desired. The bottoms are fed to the third column where pure monomethylamine is taken off as a top product stream which can be piped to storage, or recycled as desired. The bottoms are fed to the fourth column where pure dimethylamine is taken off as an overhead product while the water is drained to waste from the column bottom.

Since the reaction system is a perfect equilibrium system, any amount of the tri, mono, or dimethylamine can be taken off as product from the system, and any amount not wanted as product can be recycled, and the recycled material suppresses the formation of an equivalent amount of that material. This permits great flexibility in the operation of the plant and gives the ability of meeting peak demands for sale of various products. All three products are better than 99 percent pure.

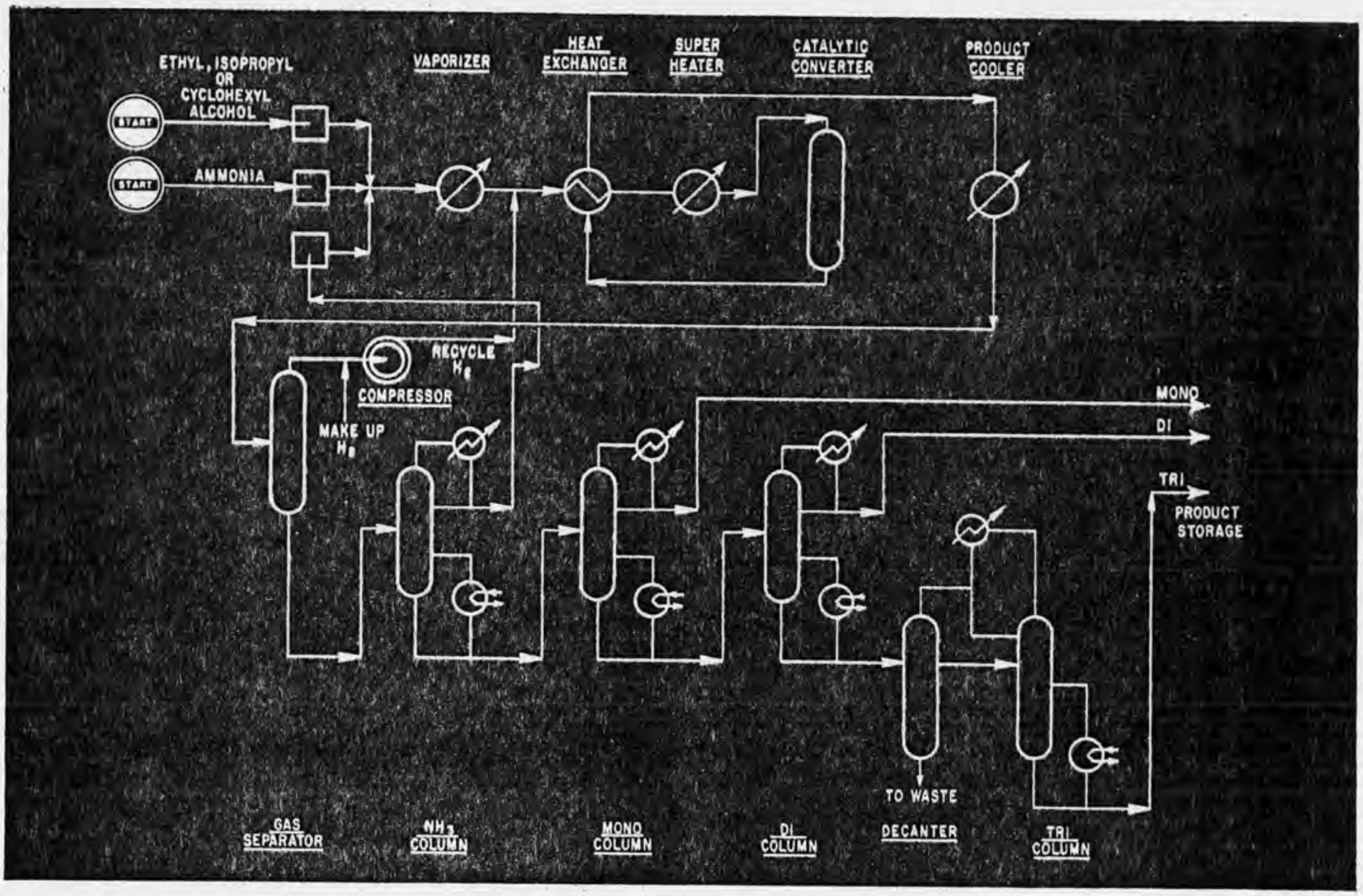
The entire operation is continuous and is instrumented so that one operator per shift controls the plant.

All process equipment and piping is fabricated of carbon steel which, since the methylamines are excellent corrosion inhibitors, lasts indefinitely.

Yields: Over-all yield of both ammonia and methanol is above 95 percent.

Commercial Installations: The Leonard Process Company, 137 Fifth Avenue, New York has two plants in operation in the U. S. (Commercial Solvent Corp. and Pennsalt Chemicals Corp.) and a new major plant under design for Escambia Chemical Corporation in the Far East, Nitto Chemical; in Italy, Persac Chemical; in Belgium, Union Chimique Belge's combination Methylamine-Dimethylformamide plant, under construction; in England, Imperial Chemical Industries, under construction.

Reference: PETROLEUM REFINER, Vol. 37 No. 9 Sept. 1958 pp. 373.



Combination Amines— THE LEONARD PROCESS CO., INC.

Application: A continuous process for the manufacture of ethyl, isopropyl, or cyclohexylamines in the same process plant from anhydrous ammonia and ethanol, isopropanol or cyclohexanol. Products include: anhydrous mono, di and triethylamine, or mono and diisopropylamine, or mono and dicyclohexylamine.

Description: Anhydrous ammonia, ethyl, isopropyl or cyclohexyl alcohol, and recycle liquid along with recycle and fresh hydrogen gas are fed continuously at controlled rates to a vaporizer which converts the liquids to gas which then flows through a heat exchanger and superheater to bring the gas stream up to reaction temperature before it enters the catalytic converter where a hydrogenation catalyst promotes the reaction forming the amines. The reaction is exothermic and part of this heat of reaction is recovered by passing the hot reaction gases through the heat exchanger to heat up the forward gas flow. The product gas stream then flows through a condenser, and then into a gas separator where the excess hydrogen separates and is largely recycled along with the fresh makeup hydrogen to the converter.

From the gas separator, the liquefied mixture of ammonia, amines and water feeds continuously to four columns in series. The first column separates out the excess ammonia and returns it to the reaction system. The second column separates out the mono product which may be taken off to storage, or returned to recycle if it is not desired as a product. The third column takes off di product to storage or recycle while the bottoms pass into a decanter to separate the excess water before the stream passes into the fourth column which takes off excess water overhead and returns it to the decanter while pure tri product is taken off the bottom to storage or returned to recycle if not wanted as product. This simplified four column distillation system has been made possible by a new catalyst which converts all alcohol fed to the converter to amines, so that the need for an azeotrope breaking and alcohol recovery column, as used in existing plants, are eliminated. This simplification reduces capital costs by 30% and reduces operating costs by 25% due to lower utility consumptions and better raw material yields.

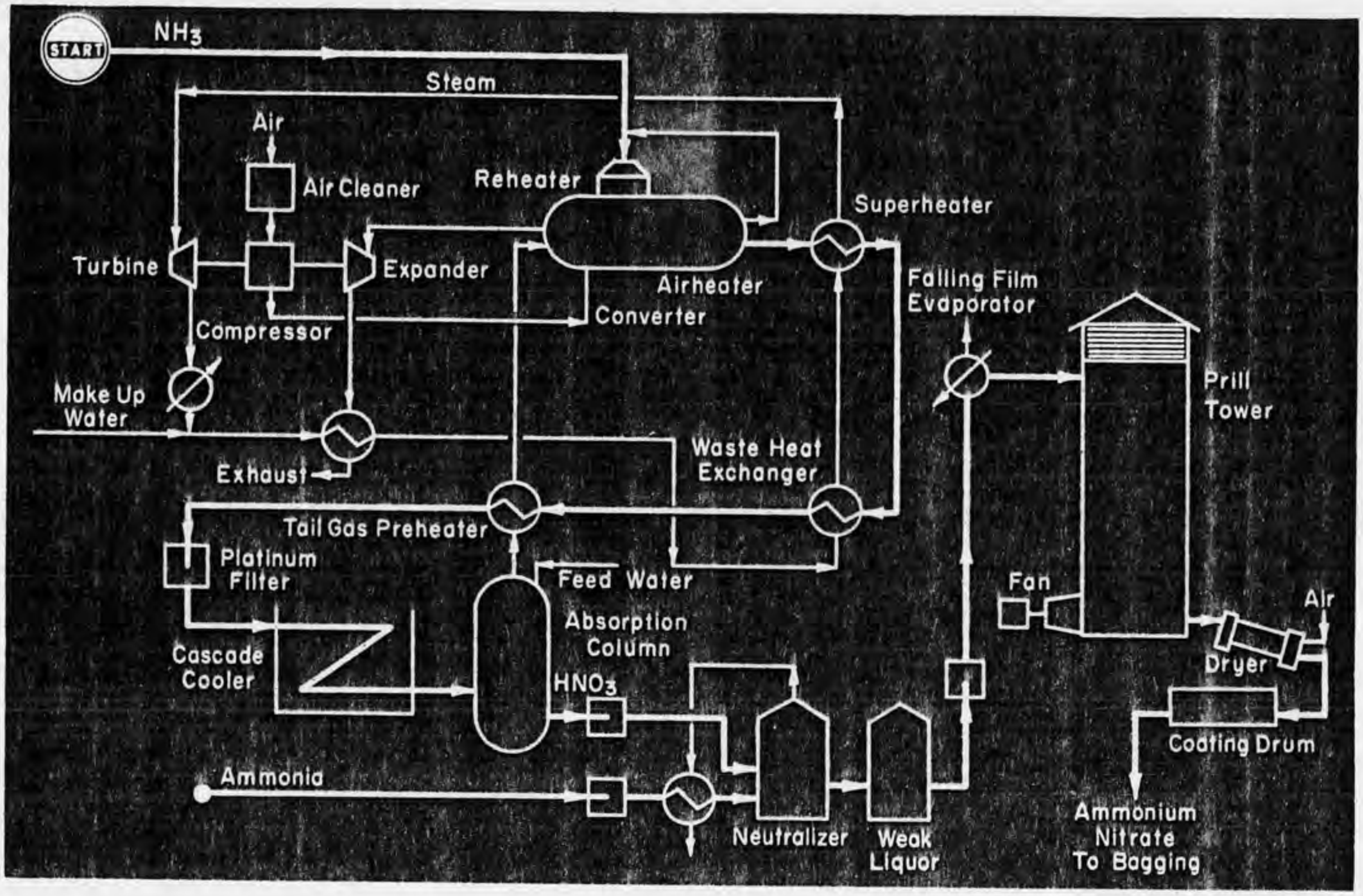
The foregoing description is based on ethylamines and the isopropyl and cyclohexylamines are processed in a similar manner.

The entire operation is continuous and instrumented so that one operator per shift controls the plant.

All process equipment and piping is fabricated of carbon steel which lasts indefinitely as the amines are excellent corrosion inhibitors.

Yields: Over-all yield of both ammonia and the alcohol used is above 91% as compared to the 75% yield obtained on existing plants.

Commercial Installations: Virginia Chemicals, West Norfolk, Va.; Union Carbide Corp., Taft, La.; Industrialimport, Bucharest, Rumania (under construction).



Ammonium Nitrate and Nitric Acid—THE CHEMICAL & INDUSTRIAL CORP.

Application: A process for manufacturing nitric acid and fertilizer grade ammonium nitrate.

Charge: Anhydrous liquid ammonia.

Product: 55 to 60 percent nitric acid and prilled ammonium nitrate with minimum nitrogen content of 33.5 weight percent.

Description: First, ammonia is oxidazed with air to produce oxides of nitrogen which are then absorbed in water to form nitric acid. The reactions may be written as follows:

$$4\ NH_3 + 5\ O_2 = 4\ NO + 6\ H_2O$$
$$2\ NO + O_2 = 2\ NO_2$$
$$3\ NO_2 + H_2O = 2\ HNO_3 + NO$$

Amonium nitrate is then formed by the reaction of nitric acid with ammonia as follows:

$$NH_3 + HNO_3 = NH_4NO_3$$

The necessary air is supplied by a steam turbine driven centrifugal compressor taking suction through an air filter. An expander operating on heated tail gas is used to recover the potential energy in the waste gas from the process. Compressed air is delivered to the air heater and heated to the proper temperature for combustion of ammonia. Anhydrous liquid ammonia is vaporized and superheated and fed into the mixer with the air stream from the air heater.

The mixture of heated air and ammonia enters the converter and burns on the platinum-rhodium catalyst. The oxidation mixture leaves through exchangers for heat recovery and the production of steam. A glass wool filter in the combustion gas stream collects the finely-divided platinum from the catalyst. Cooled gases are recovered in the absorption tower as nitric acid. Once started, the nitric acid plant is self-sustaining, requiring no outside power or steam.

Ammonia, vaporized by steam from the neutralizer, is sparged into the neutralizer along with nitric acid. The heat of neturalization evaporates part of the water and gives a solution of 83 percent ammonium nitrate.

Final avaporation to above 99 percent is done in a falling film evaporator located at the top of a low prilling tower. The resultant melt flows through spray nozzles and downward through the tower. Air is drawn upward by fans at the top of the tower. The melt is cooled enough to solidify, forming round pellets or prills of the desired range of sizes.

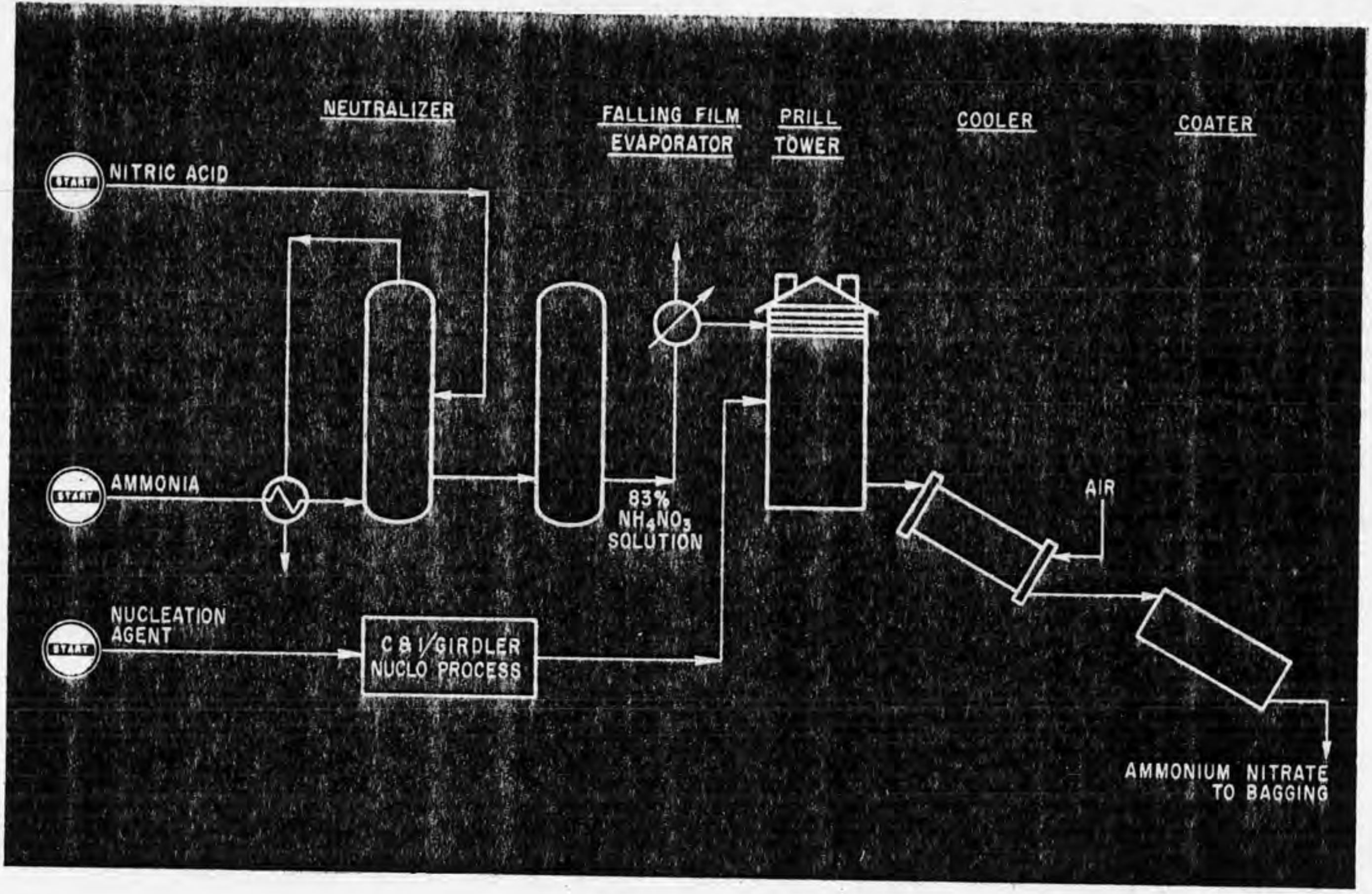
The prills are removed from the bottom of the tower and fed to a rotary cooler. Fines from the cooler are collected in a wet cyclone. The solution is eventually returned to the neutralizer.

After cooling, the prills are screened to size and the over- and under-size sent to a sump and returned to the neutralizer. Intermediate or product size prills are dusted with a coating of diatomaceous earth and sent to bagging.

Yields: The over-all yield of ammonia to ammonium nitrate is about 93 percent. This amounts to about 2.25 tons fertilizer per ton ammonia feed.

Commercial Installations: California Chemical Co., Ketona Chemical Corp., Cubana del Nitrogen, S.A., Mtanza, Cuba, and Fertilizantes del Istmo, S.A., Minatitlan, Mexico.

References: Industrial and Engineering Chemistry, Vo.. 23, p 860 (1931); Encyclopedia of Chem. Tech., Vol. 9, 333-5 (1952); Industrial & Engineering Chemistry, Vol. 45, No. 3, p 496 March (1953).



Ammonium Nitrate — C&I/GIRDLER INC.

Application: A process for manufacturing fertilizer grade ammonium nitrate from anhydrous ammonia or urea off-gas and 55 to 60% nitric acid.

Description: Ammonium nitrate is formed by the reaction of nitric acid with ammonia as follows:

$$NH_3 + HNO_3 = NH_4NO_3$$

Ammonia, vaporized by steam from the neutralizer, is sparged into the neutralizer along with nitric acid. The heat of neutralization evaporates part of the water and gives a solution of 83% ammonium nitrate.

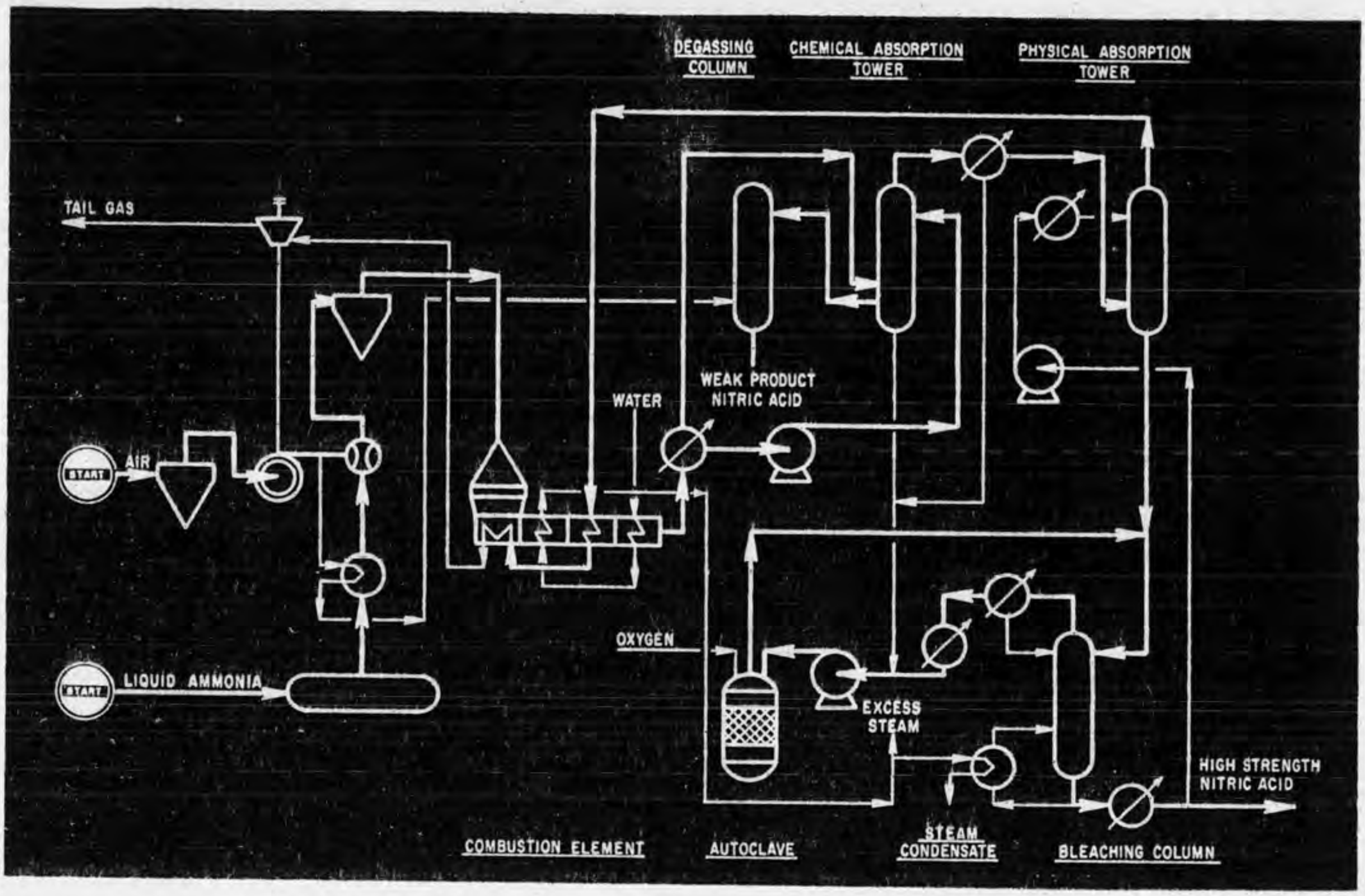
Final evaporation to above 99% is done in a falling film evaporator. A C&I/Girdler additive is mixed with the melt to stabilize the crystal formation and the resultant melt flows through special prilling devices downward through the tower. Air is drawn upward by fans at the top of the tower. The melt is cooled enough to solidify, forming round pellets or prills of the desired range of size.

The prills are removed from the bottom of the tower and fed to a rotary cooler. Exhaust air containing fines from the cooler is scrubbed and the solution is eventually returned to the neutralizer.

After cooling, the prills are screened to size and the over and under-size sent to a sump and returned to the neutralizer. Intermediate or product size prills can be sent to storage or shipping without coating.

Yield: The over-all yield of ammonia and nitric acid to ammonium nitrate is about 98% on a nitrogen basis.

Commercial Installations: There are more than 24 plants operating using this process with production capacity exceeding 8,000 tons per day of ammonium nitrate.



Nitric Acid (Hoko Process) — PINTSCH BAMAG AG

Application: A process for simultaneous production of high-strength nitric acid (98-99%) of high purity and weak acid (up to 65%) from ammonia and oxygen/air.

Description: This pressure process for the production of high-strength nitric acid and weak acid requires no dehydrating agents, such as sulfuric acid or magnesium nitrate for the high-strength part of production, and is thus more economical and needs less plant maintenance.

According to the local conditions, e.g. steam, electricity, ammonia and platinum prices, it has to be decided whether a medium pressure (approximately 50 psig) or a high pressure plant (approximately 110 psig) is more economical.

All the reaction water available from the process is worked up to weak acid and high-strength acid (Hoko). Thereby the top limit of the Hoko portion to be produced is fixed. It is about 60% of the total acid amount. Application of water-eliminating means enables an even higher portion of Hoko to be made. Below this limit any desired portion of Hoko can be produced.

Ammonia and air are converted under pressure on platinum-rhodium catalysts in a combustion element to form nitric oxide. Upon cooling-down of the hot gases in a number of heat exchangers and a waste-heat boiler most of the combustion water is condensed as weak acid. This acid is used for making weak acid by chemical absorption in an absorption tower. The main part of the acid product is degassed with air. The nitric oxides remaining in the gas are re-oxidized and then separated by physical absorption with Hoko. The remaining tail gas contains approximately 200 ppm NO + NO_2.

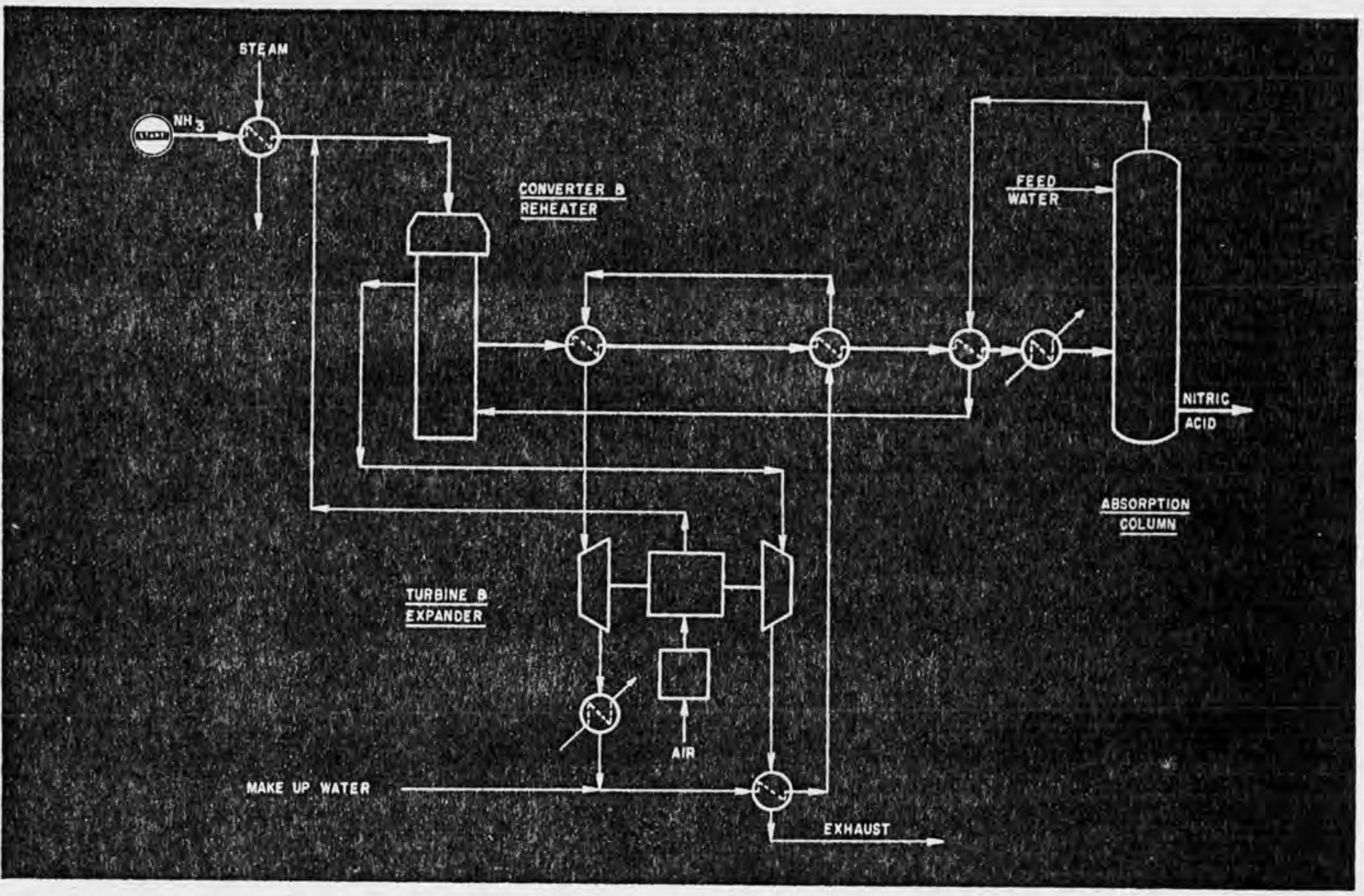
The high-strength acid with dissolved dinitrogen tetroxide is fed to the bleaching column where nitrogen dioxide is separated. Nitrogen dioxide is condensed in liquefiers. The pure high-strength acid is drawn off from the bottom, a part of which is recycled to the absorption column.

Part of the weak nitric acid coming from the chemical absorption column and dinitrogen tetroxide from liquefiers are fed to autoclave where at a high pressure these react with the fed oxygen to form nitric acid. Since this acid contains excess tetroxide, this too is fed to the bleaching column. The final product is a pure and clear acid of 98-99% concentration.

Pintsch Bamag also offer various processes for separate production of Hoko and weak acid.

Yields: Over-all yield, ammonia to nitric acid 94%.

Commercial Installations: Since 1916 more than 100 weak nitric acid plants and since 1925 more than 50 high-strength nitric acid plants have been supplied by Pintsch Bamag to different countries.



Nitric Acid — C&I/GIRDLER, INC.

Application: A process for manufacturing 55 to 67% nitric acid from anhydrous liquid or gaseous ammonia or urea off-gas.

Description: Ammonia is oxidized with air to produce oxides of nitrogen which are then absorbed in water to form nitric acid. The reactions may be written as follows:

$$4\,NH_3 + 5\,O_2 = 4\,NO + 6\,H_2O$$
$$2\,NO + O_2 = 2NO_2$$
$$3\,NO_2 + H_2O = 2\,HNO_3 + NO$$

The necessary air is supplied by a steam turbine or motor driven centrifugal compressor taking suction through an air filter. An expander operating on heated tail gas is used to recover the energy in the waste gas from the process. Anhydrous liquid ammonia is vaporized and superheated and fed into the mixer with the air stream from the compressor.

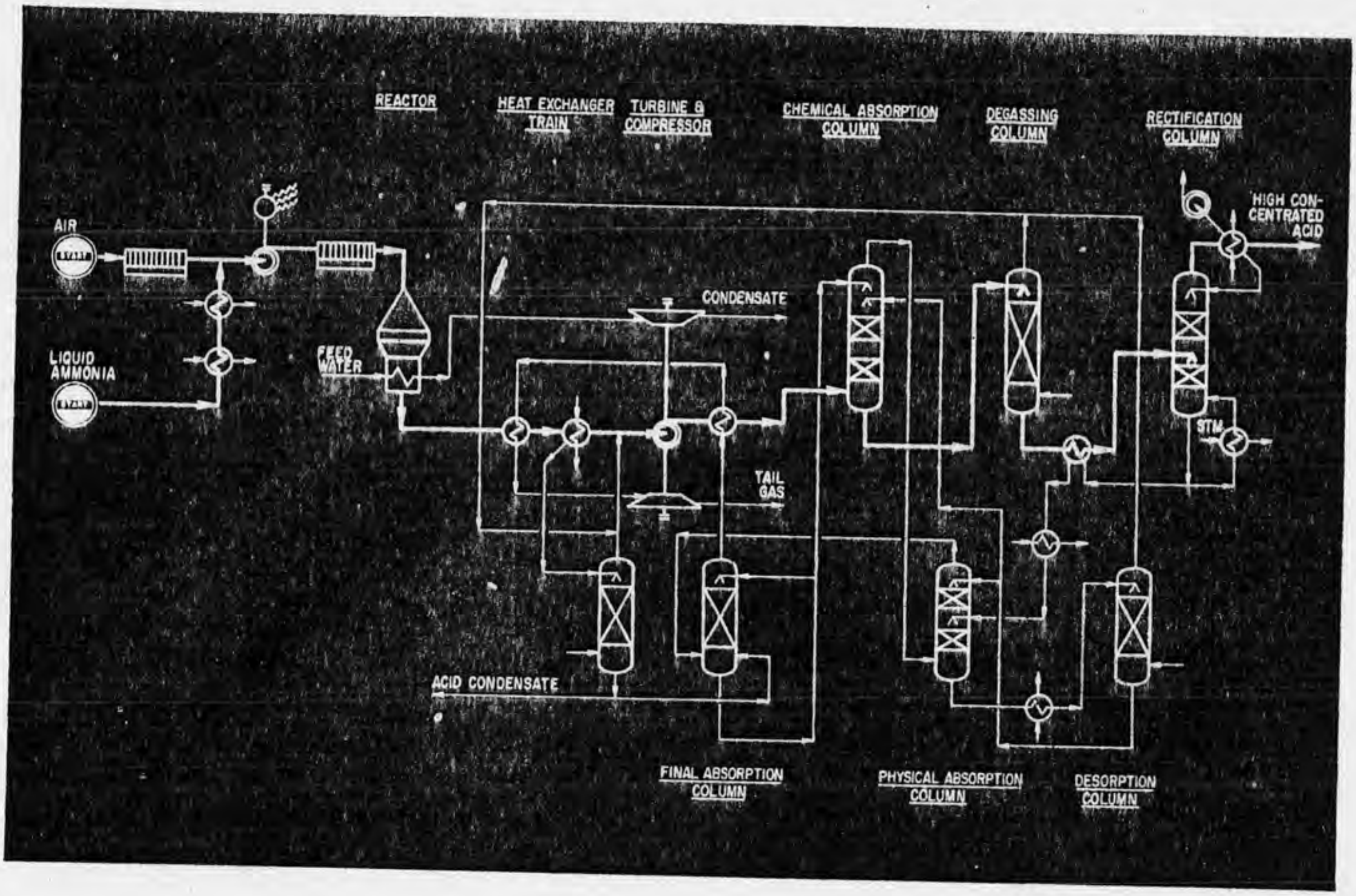
The mixture of air and ammonia enters the converter and is catalytically oxidized. The oxidation mixture leaves through exchangers for heat recovery and the production of steam. Cooled gases are recovered in the absorption tower as nitric acid. Plants can be designed for self-sustaining operation, requiring no outside power or steam.

The tail gas from the plant normally contains 0.1 to 0.2 volume percent NO_2. This can be reduced by appropriate fume abatement equipment in which a fuel (commonly natural gas) is catalytically burned in the tail gas. The energy from this reaction is recovered in the expander or as additional steam.

The process uses the regular platinum-rhodium gauze or a new non-noble pelleted oxide catalyst system. Utilizing the newer catalyst system simplifies the process equipment and provides an extended operating period before catalyst replacement is required. This results in greater total production and lower over-all production and maintenance costs.

Yield: The over-all yield, using either catalyst system, is about 3.5 tons of nitric acid per ton of ammonia feed.

Commercial Installation: Eighty commercial installations exist with a total daily capacity in excess of 15,000 tons on a 100 percent HNO_3 basis.



Nitric acid (SABAR Process) — DAVY POWERGAS GmbH

Application: A process for producing nitric acid (80-99% HNO_3) from ammonia and air. It does not require oxygen, refrigeration energy, dehydrating agents (sulfuric acid or magnesium nitrate). Nitric oxides in the tail gas can be reduced below 200 ppm by absorption. Weak acid at any rate and concentration can be produced simultaneously.

Description: Gaseous ammonia is mixed with air and converted to nitric oxides in the reactor on platinum-rhodium catalysts. Ammonia conversion is at atmospheric pressure so that the reaction water—most of which must be passed out of the process—can be condensed without absorption of nitric oxides. The atmospheric pressure conversion gives low platinum loss and a high yield. The reaction heat is used to produce steam and to preheat the tailgas prior to expansion. The reaction gases are finally cooled in the gas cooler condenser where the main portion of the reaction water is separated as 2% nitric acid condensate. After addition of secondary air which contains recycled nitrogen dioxide the nitrous gas is compressed to between 6-13 atm. abs.

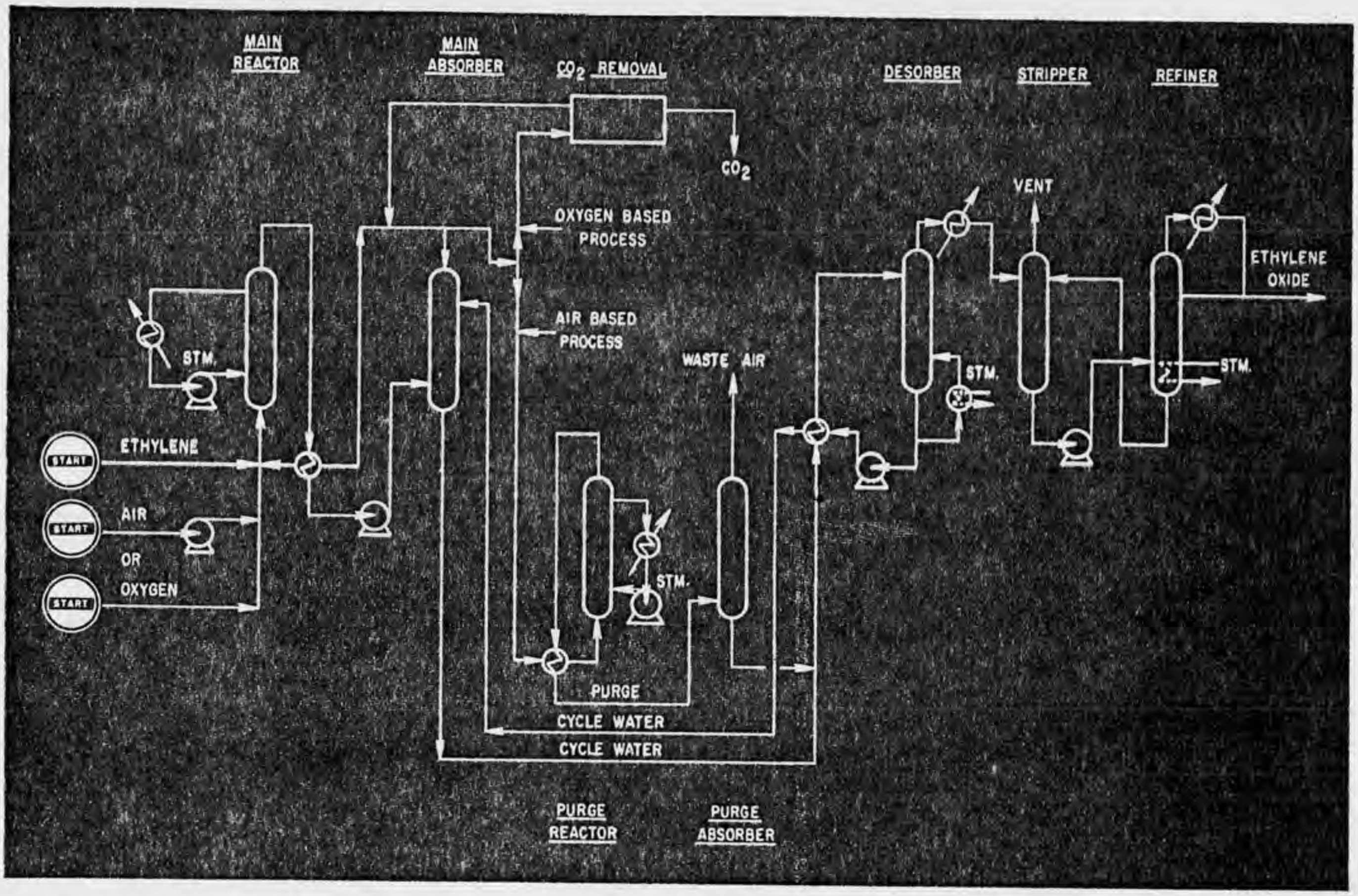
The compressed gas enters the chemical absorption section where superazeotropic acid is formed. The nitrogen dioxide remaining in the gas after the chemical gas absorption is physically absorbed in the physical absorption column in the nitric acid. The nitric acid loaded with nitrogen dioxide from the physical absorption section enters a desorber where nitrogen dioxide is stripped by secondary air which is recycled to the main gas stream ahead of the compressor.

The tail gas from the physical absorption is freed from nitric acid vapors, preheated and expanded in the tail gas turbine.

The superazeotropic acid is freed from nitrogen dioxide by secondary air and sent to rectification where it is separated into high concentrated and azeotropic acid. The latter is recycled to the chemical absorption section.

Economics: Investment costs are substantially lower than the "HOKO" process (which requires oxygen and refrigeration units) and operating costs are lower unless oxygen and refrigeration are available at extremely low prices.

Commercial installations: The first 120-metric-ton/day SABAR Process plant is under construction for startup in late 1973.



Ethylene Oxide — SCIENTIFIC DESIGN CO., INC.

Application: A process for manufacture of ethylene oxide from ethylene using either air or oxygen as the oxidizing agent.

Description: The flowsheet shown is only one of the many possible process schemes. Compressed air or oxygen, ethylene and recycle gas are mixed and fed to a multitubular catalytic reactor. The temperature of oxidation is controlled by an organic cooling medium shown. From the reactor the effluent gases, which contain ethylene oxide, are cooled and further compressed. The cooling is accomplished by recuperative exchange with the recycle gases. The gases then pass to a scrubber where ethylene oxide is absorbed in a dilute aqueous solution. Most of the unabsorbed gases are returned to the reactor via the previously mentioned recuperative exchanger, thus completing a closed circuit. When air is used as the oxidant, a portion of these gases is diverted to the secondary reactor, to purge accumulated inert gases. The secondary reactor scavenges the remaining ethylene. From the secondary reactor the effluent gases are cooled as before. The ethylene oxide is absorbed in a scrubber, and the residual gases are discharged from the system. When oxygen is used, the secondary system is unnecessary; instead a portion of the recycle gas is diverted through a Co_2-removal system before being returned to the reaction system. Ethylene oxide is stripped from the combined dilute aqueous scrubber streams and recovered in a fractionation train.

Also possible and already being done by some companies is the conversion of an existing air-based plant to an oxygen-based plant. Since the systems are flexible and similar, this can be accomplished in minimum downtime.

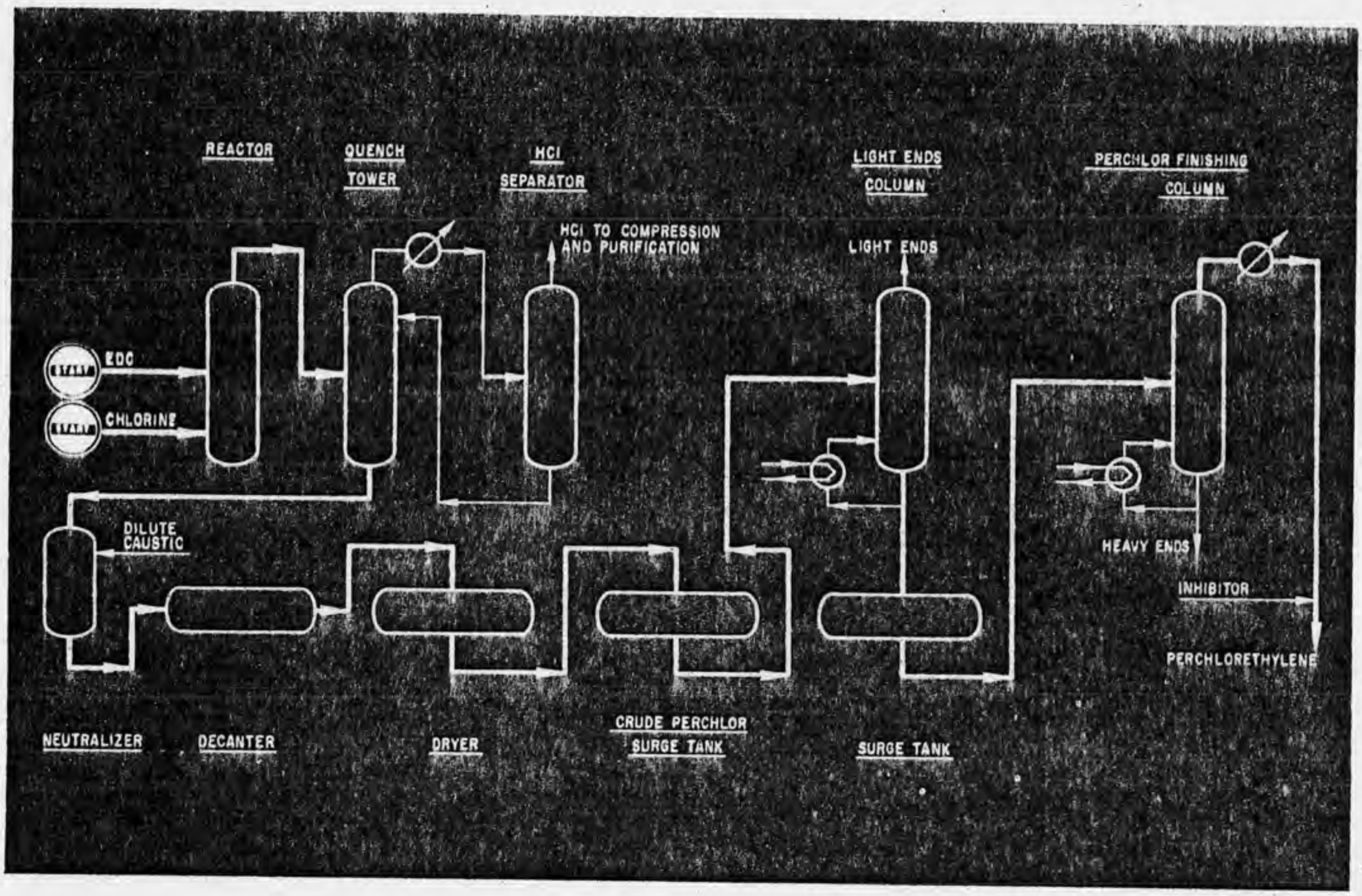
The catalyst contains silver and its long life and high productivity have been commercially proven, resulting in significant savings in capital and operating costs.

Yields: The weight yield, expressed as pounds of ethylene oxide produced per pound of ethylene consumed, is well over 100% in plants of normal design.

Oxygen or Air: By its long experience in ethylene oxide plant design, SD can determine through complete process optimization for each new plant or expansion, whether air or oxygen would be the most economical oxidant. SD's oxygen and air-based processes are fully commercialized. Three plants using oxygen are operating and two are under construction.

Commercial Installations: Forty ethylene oxide plants in 12 countries have been completed or are being designed for 21 companies. This represents total design capacity of over 2.6 billion pounds of ethylene oxide per year, which represents over one-third of the world's total.

References: HP/PR, Vol. 32, No. 9 September 1953, p. 146.



Perchlorethylene — DIAMOND SHAMROCK CORP.

Application: A process for making perchlorethylene from ethylene dichloride, or other C_2 feedstock, and chlorine.

Description: In the simultaneous chlorination and dehydrochlorination of ethylene dichloride (EDC), liquid EDC and dry Cl_2 are fed to a fluidized catalyst reactor. Organics from product distillation section are recycled to the reactor.

Gaseous reaction products are quenched and most organics condensed. HCl in the condensed crude is neutralized with dilute caustic. The crude perchlorethylene is decanted from the aqueous phase, and after drying, distilled.

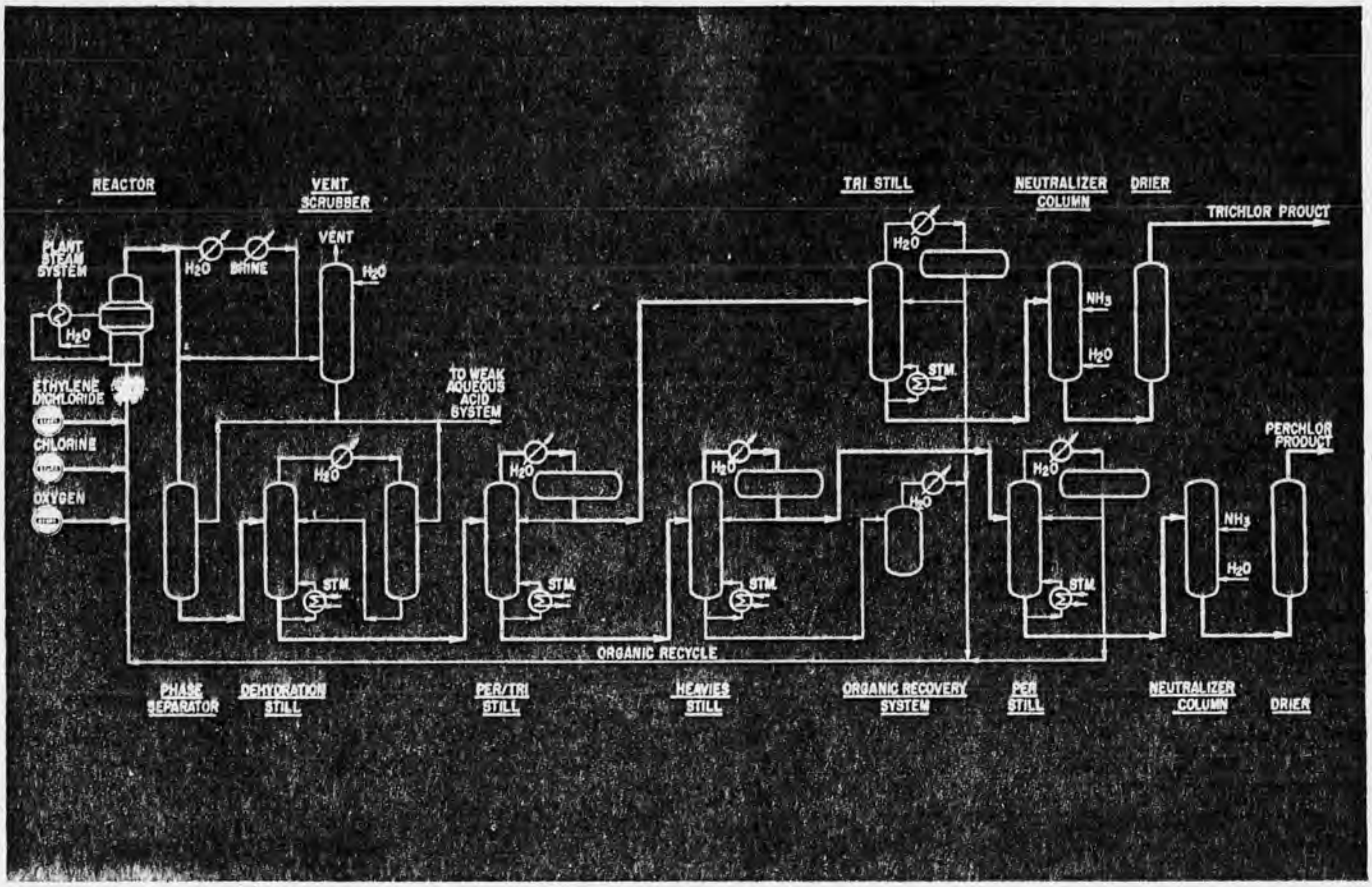
Light end organics (e.g., trichlorethylene and carbon tetrachloride) are condensed and recycled to the reactor. Bottoms (perchlorethylene and higher boiling impurities) are separated and the perchlorethylene distillate neutralized, dried and inhibited.

With different reactor operating conditions and additional distillation equipment, trichlorethylene can be produced along wth perchlorethylene.

Anhydrous HCl: The perchlor quench tower vapor is chilled to remove most of the organics. The condensed fraction returns to the quench tower and the remaining gas (mostly HCl) is compressed to 90-95 psig, scrubbed and chilled again and available for other process use or sale at 85 psig.

Yield: Efficiencies are based on 96-97% Cl_2 and 99+% EDC. Approximate conversion efficiencies of Cl_2, C, and H_2 in the raw materials to perchlorethylene and HCl are: 96.5%, 93% and 95%. Over-all yield is about 96.3%. With EDC feed, about 0.9 ton HCl/ton of perchlorethylene is produced. Typical perchlor purity is 99.8%. For special applications, an additional purification procedure provides 99.995% perchlorethylene.

Commercial installation: Diamond Shamrock Corp. produces perchlorethylene, trichlorethylene and HCl at Deer Park, Texas. The process has been licensed to others in the United States and abroad.



Perchlor and trichlor (per/tri) — PPG INDUSTRIES

Application: A single stage oxychlorination process for perchloroethylene and trichloroethylene from ethylene and/or chlorinated C_2 organics. Adjustment of feeds varies product ratios from all perchlor to nearly all trichlor while maintaining high utilizations. The process can be tailored to feed any C_2 chlorocarbon mixture with hydrogen chloride (HCl) and/or chlorine (Cl_2). The process can accept chlorocarbons normally considered wastes from processes such as vinyl chloride.

Description: An inexpensive fluid bed catalyst is used in the highly exothermic multistep reaction.

$$2\,C_2H_4Cl_2 + 5\,Cl_2 \rightarrow C_2H_2Cl_4 + C_2HCl_5 + 5\ HCl\ \text{(chlorination)}$$

$$C_2H_2Cl_4 + C_2HCl_5 \rightarrow C_2HCl_3 + C_2Cl_4 + 2\,HCl\ \text{(cracking)}$$

$$7\,HCl + 1.75\,O_2 \rightarrow 3.5\,H_2O + 3.5\,Cl_2\ \text{(Deacon)}$$

$$2\,C_2H_4Cl_2 + 1.5\,Cl_2 + 1.75\,O_2 \rightarrow C_2HCl_3 + C_2Cl_4 + 3.5\,H_2O$$

Use of oxygen (low-cost) greatly simplifies product recovery by eliminating noncondensables.

The process shown is for ethylene dichloride (EDC), chlorine and oxygen feeds. Condensed crude and weak acid are phase separated and the crude dried by azeotropic distillation to produce a noncorrosive still line feed.

The first column (per/tri) splits the crude into trichlor-rich and perchlor-rich streams. The trichlor-rich stream is fed to the trichlor product column (tri) where low boilers are removed overhead. The trichlor product is removed at the bottom. It is treated with NH_3, washed and dried.

The perchlor-rich stream contains both mid-boilers and heavies. It is fed to the heavies column first. The high boilers are removed at the bottom and flashed to remove any tars and carbon. Tars and carbon can be incinerated and byproduct muriatic acid produced.

Perchlor from the product still bottom is treated the same as trichlor. The mid-boilers are removed overhead; the lights, heavies and mids consisting of saturated and unsaturated C_2 chlorocarbons are recycled.

The still line arrangement was designed for minimum cost and is unique. Both products are removed at a still bottom and are color-free.

Product quality: Both products are 99.9 + wt.% and meet quality standards of the metal degreasing and dry cleaning industries when appropriately stabilized.

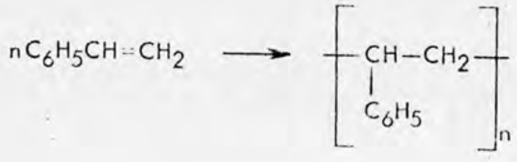
Energy requirements: Steam is generated by the reactor. The low-inert reactor off-gas is easily condensed with water cooling. Refrigeration loads for secondary recovery are very low since large volumes of HCl and N_2 are not handled. An optimum purification arrangement also leads to low utilities.

Commercial installations: The process is used in the U.S., Europe and Japan. Total combined capacity of plants in operation or under construction is one billion pounds/year. PPG also produces EDC by oxychlorination.

References: *Chemical Engineering,* Dec. 1, 1969, pp. 90-91; *Hydrocarbon Processing*, Nov. 1972, pp. 109-110; *Chemi-Ing.-Techn.* 43, Annual 1971, pp. 184-187.

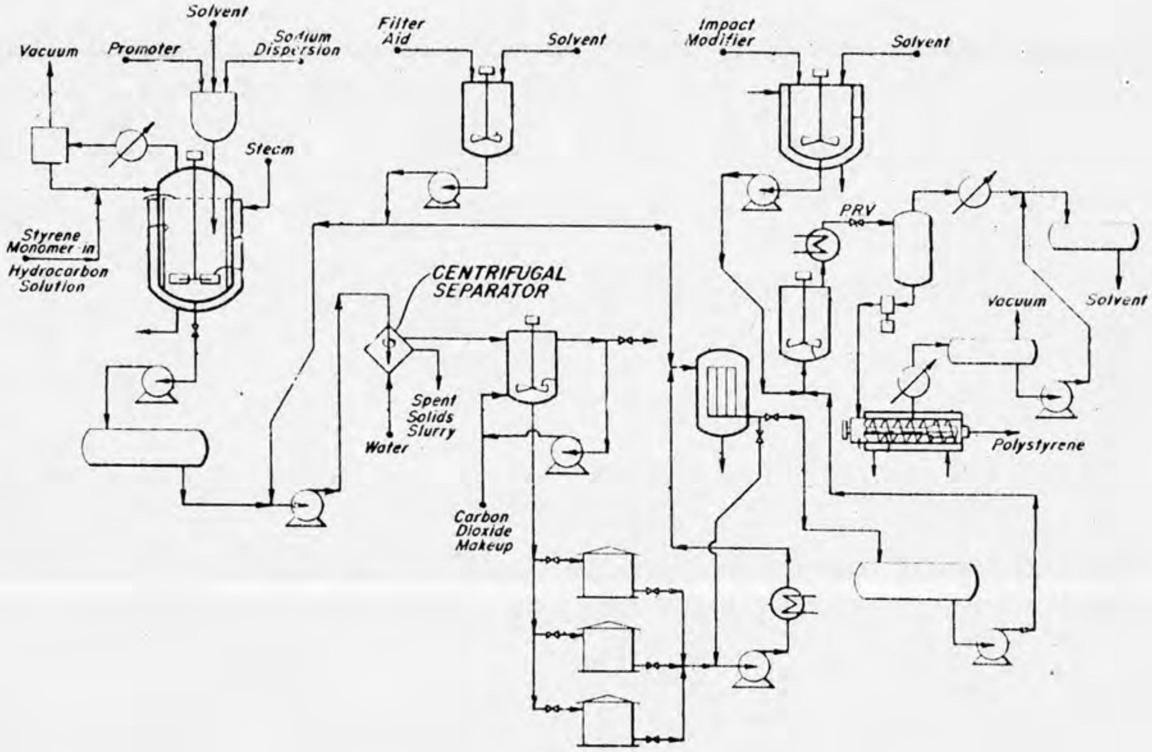
POLYSTYRENE

Reaction:



$$nC_6H_5CH{=}CH_2 \longrightarrow \left[-\underset{\displaystyle C_6H_5}{\underset{|}{C}H}-CH_2-\right]_n$$

(where n = 500-1,000)



Feed Materials:
Styrene

Coproducts:
-

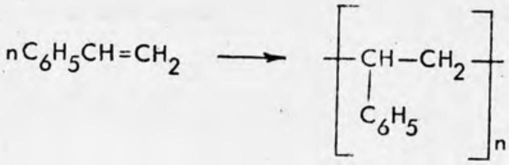
Catalyst:	Sodium
Phase:	Liquid
Reactor type:	Stirred, Jacketed Kettle
Solvent used:	None
Temperature, °C:	72
Pressure psi:	1.5 psia
Reaction time:	1.5 hours
Heat Required:	-
Heat evolved:	Yes
Product yield:	98%
Product purity:	
Materials of Construction:	Stainless Steel

Major Product Uses: One of three major thermoplastic materials for fabrication of plastic products.

Reference: U.S. Patent 2,980,661 by W.W. Twaddle et al (to Standard Oil Co., Indiana) (April 18, 1961)

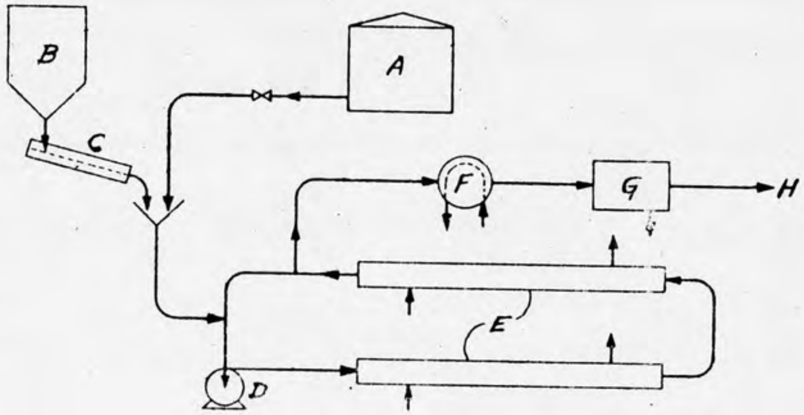
POLYSTYRENE (LOW M. W.)

Reaction:



$$n\,C_6H_5CH{=}CH_2 \longrightarrow \left[\begin{array}{c} -CH-CH_2- \\ | \\ C_6H_5 \end{array}\right]_n$$

(where n = 20)



A-Styrene Feed Tank
B-Catalyst Hopper
C-Vibrator Feeder
D-Circulating Pump
E-Reactor
F-Cooler
G-Filter
H-Product

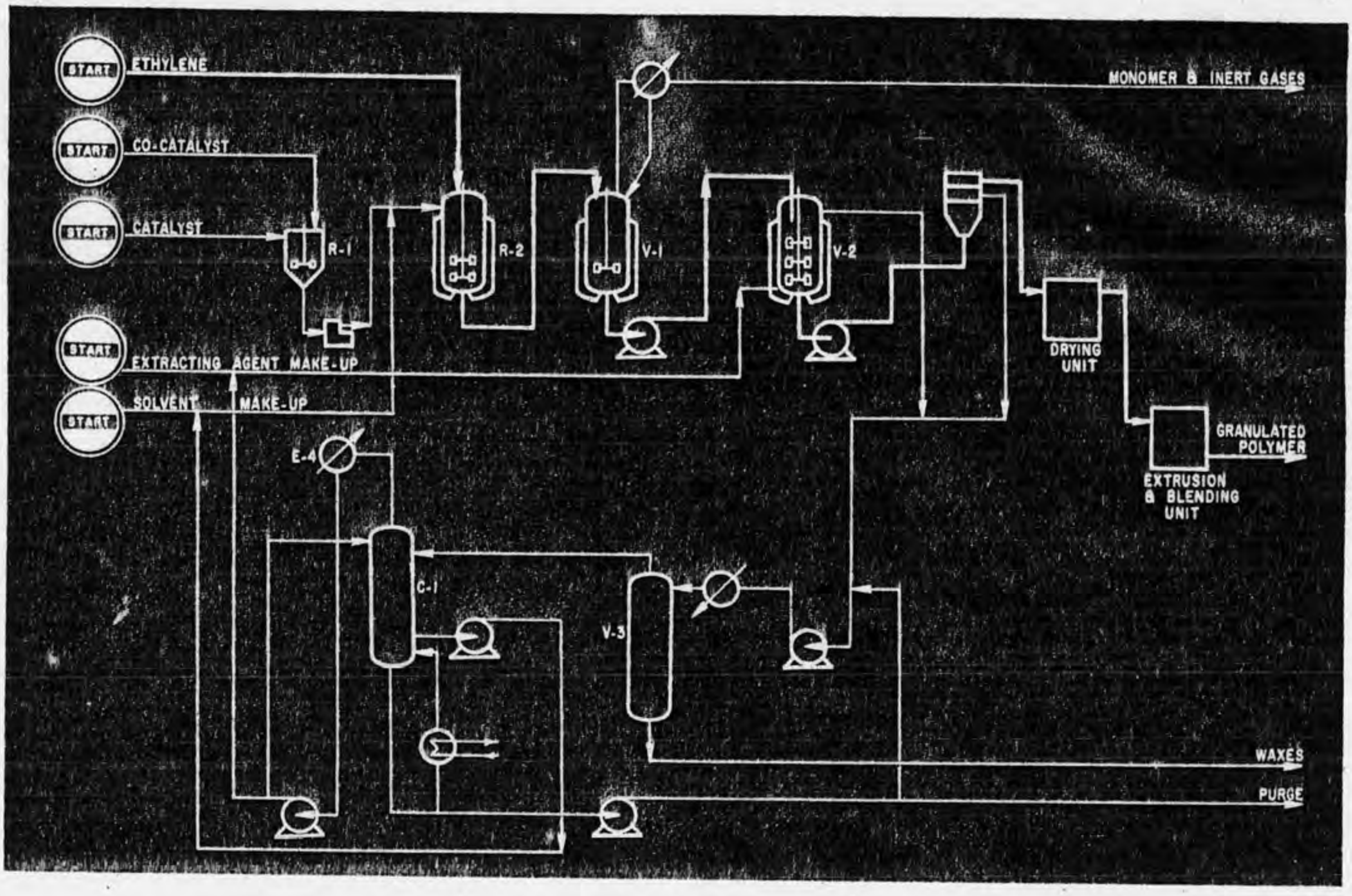
Feed Materials:
Styrene

Coproducts:

Catalyst: Activated Clay
Phase: Liquid
Reactor type: Tubular
Solvent used: None
Temperature, °C: 50-110
Pressure psi: 50
Reaction time: 8 minutes
Heat Required: -
Heat evolved: Yes
Product yield: 30%
Product purity:
Materials of Construction:

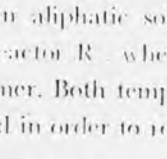
Major Product Uses: High molecular weight styrene with good mold flow properties.

Reference: U.S. Patent 3,052,664 by W.J. Cleland et al (to Shell Oil Co.) (Sept. 4, 1962)



Polyethylene— SNAM PROGETTI

Application: A process for the production of high density (0.959-0.968) polyethylene from 99% ethylene using a two-component catalyst system consisting of: (1) a titanium halide and (2) a cocatalyst based on a new class of aluminum hydride compounds:



$$\left[\begin{array}{cc} & R \\ & | \\ Al & N \\ | & \\ H & \end{array}\right]_n$$

Description: The catalyst from the preformation tank R_1 is suspended in an aliphatic solvent and then continuously fed to the reactor R_2 where is also sent a continuous flow of monomer. Both temperature and pressure are carefully controlled in order to retain polymer quality.

The polymer slurry, discharged from the reactor, is conveyed to a flash vessel (V_1) where the reaction is stopped and unreacted monomer and inerts are separated, and finally washed in V_2 with an extracting agent, which is recycled from the distillation unit, in order to remove catalyst residues.

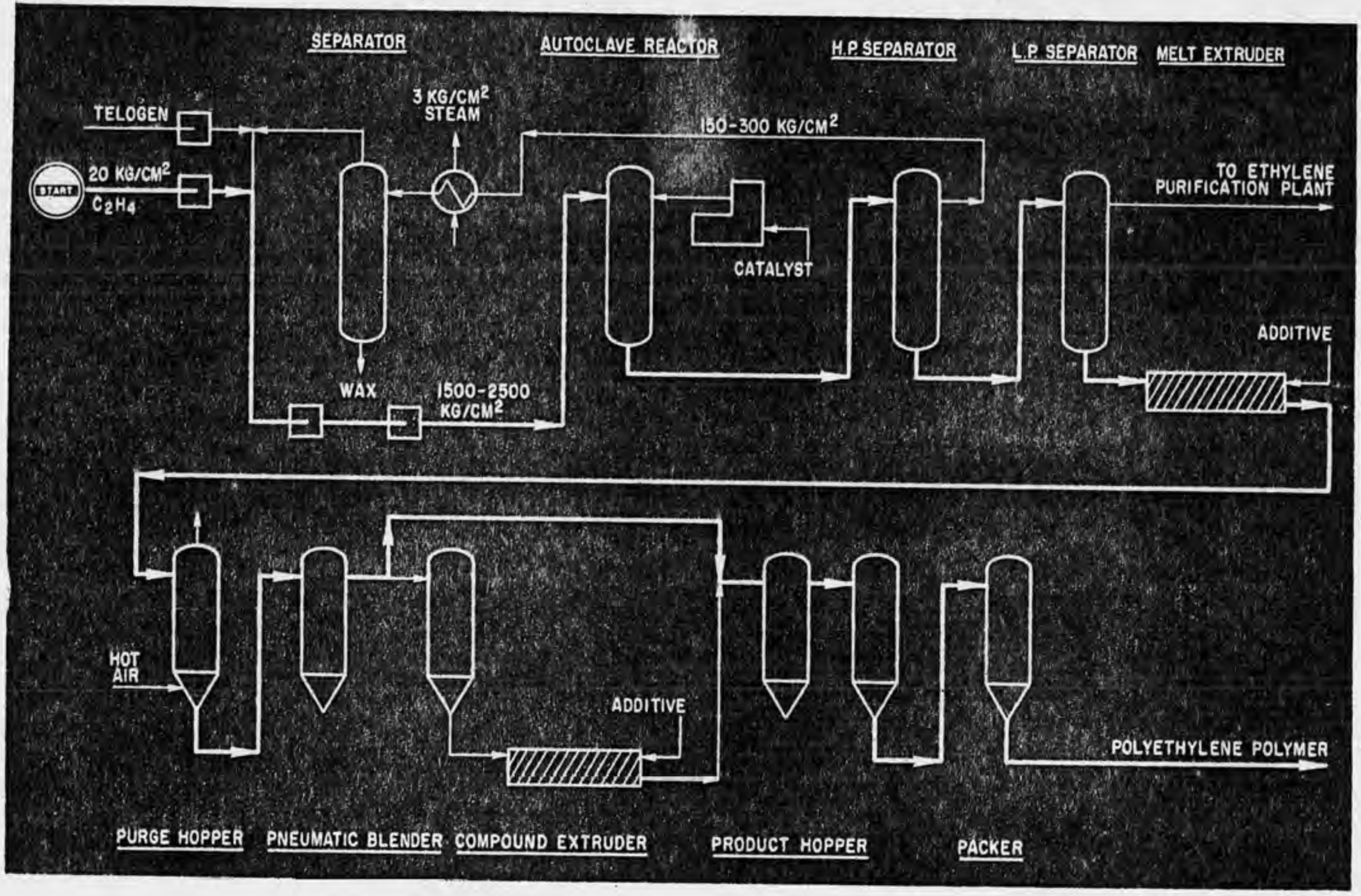
The polymer, separated from the solvent and dried, is sent to a conventional blending and extrusion section.

Solvent and extraction agent from the separation and drying units are conveyed to the recovery plant where waxes are removed (V_3); finally in the C_1 column the recycle solvent is obtained as bottom, and the extraction agent as overhead.

Raw Material and Utility Consumption (Per metric ton of pelletized polyethylene):

Ethylene, 100% Kg	1.090
Solvent, Kg	50
Catalyst and chemicals, $	48
Low pressure steam, Kg	2.000
Electric power, Kwh	500
Cooling water, m^3	250
Fuel, Mkcal	700

Commercial Installation: Engineering is under way for an industrial plant of 40,000 Mt/y capacity envisaged to operate at Gela (Italy).



Polyethylene—MITSUI TOATSU CHEMICALS, INC.

Application: A process for producing polyethylene from ethylene at elevated pressures and temperatures by use of single autoclave reactor with large capacity.

Description: The radical polymerization of ethylene under high pressures and at elevated temperatures can be represented by the following equations.

Over-all Reaction:

$$nCH_2 = CH_2 \rightarrow -(CH_2 - CH_2\text{-})\text{-}_n$$
$$-\Delta H = 22.15 \text{ kcal/mole } C_2H_4 (500°\text{K})$$

Elementary Reactions:

Initiation:

$$ROOR \rightarrow 2\,RO\,\bullet$$
$$RO\,\bullet + CH_2 = CH_2 \rightarrow RO - CH_2 - CH_2\,\bullet$$

Propagation:

$$-CH_2 - CH_2\,\bullet + CH_2 = CH_2 \rightarrow$$
$$-CH_2 - CH_2 - CH_2 - CH_2\,\bullet$$

Chain Transfer and Repropagation:

$$-CH_2 - CH_2\,\bullet + R - CH_2 - R' \rightarrow -CH_2 - CH_3 + R - \dot{C}H - R'$$
$$R - \dot{C}H - R' + CH_2 = CH_2 \rightarrow R - \underset{\displaystyle R'}{\underset{|}{CH}} - CH_2 - CH_2\,\bullet$$

Termination:

$$-CH_2 - CH_2\,\bullet + -CH_2 - CH_2\,\bullet \rightarrow$$
$$-CH_2 - CH_3 + -CH = CH_2 + -CH_2CH_2CH_2CH_2-$$

High-pressure ethylene and peroxide solution (catalyst) are fed into a strongly agitated autoclave, in which the polymerization proceeds at a controlled temperature. The reaction is extremely exothermic and the heat generated is cooled with cold feed ethylene in such a way as to keep the reaction temperature constant. A failure in temperature control stops the polymerization, or causes an explosion because of the decomposition of ethylene into carbon and methane, which is also exothermic ($-\Delta H = 30.44$ kcal/mole C_2H_4). The ethylene conversion to polyethylene is usually kept under 20%.

Several grades of polyethylene can be produced by changing reaction conditions: pressure, temperature, and types and amount of telogens.

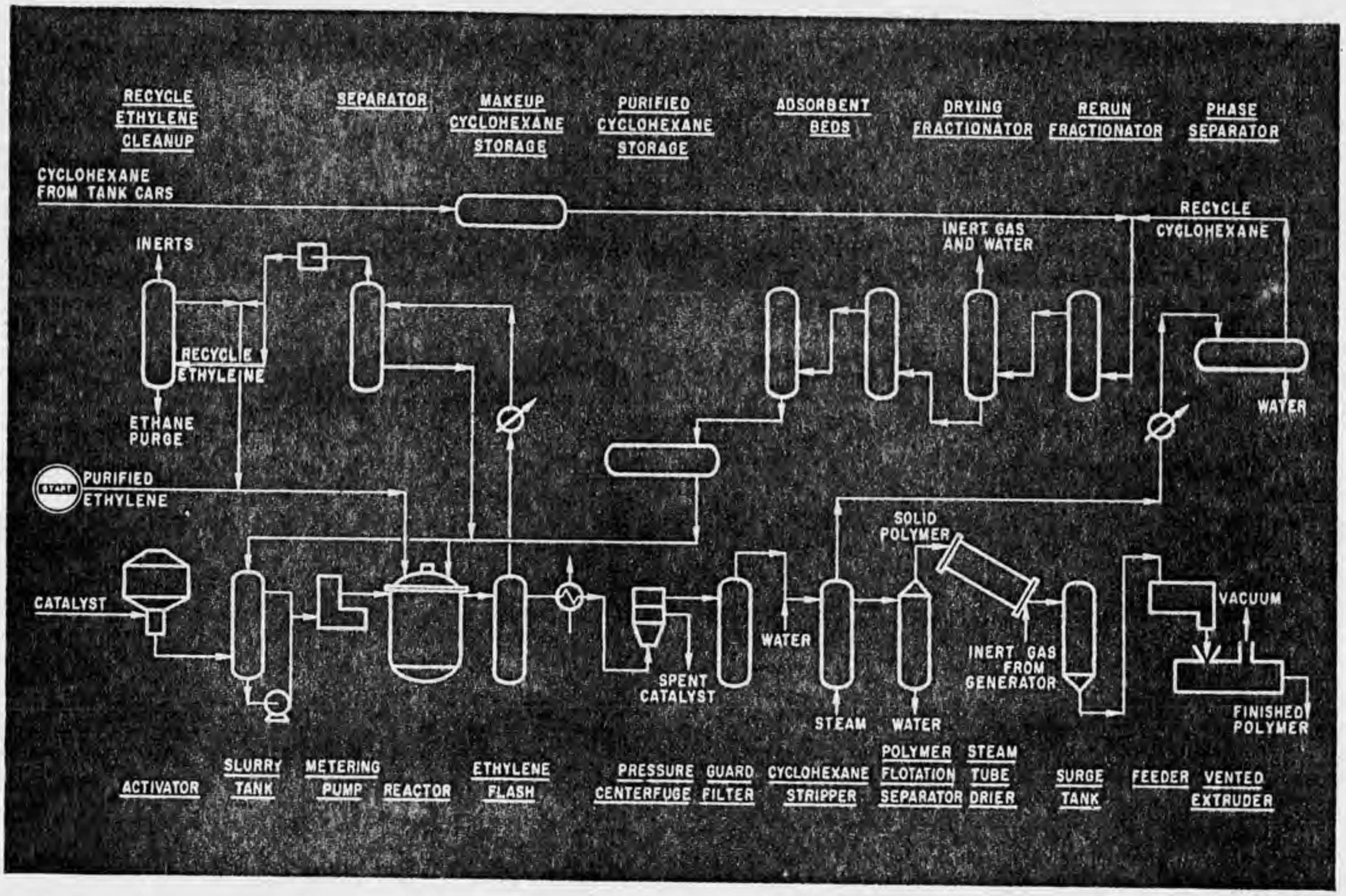
The important process conditions are listed as follows:

Temperature	160-250°C
Pressure	1500-2500 kg/cm²
Types and amount of telogens	Light Hydrocarbons, several percent
Types of peroxides	Di-tert-butyl peroxide Tert-butyl perbenzoate Decanoyl peroxide

The process is suited not only for extrusion coating grade, but also for film grade with excellent optical properties superior to ones produced by any tubular reactors. Injection and blow molding grades, and ethylene-vinyl acetate copolymer are also available.

Commercial Installation: The process will be in commercialized use by Mitsui Toatsu Chemicals.

References: *Chem. & Engr. News,* May 15, 1967 p. 38-40.



Polyethylene — PHILLIPS PETROLEUM CO.

Application: A relatively low-pressure process for the continuous production of polyethylene from ethylene gas of 99% purity.

Description: This is a process in which solid catalyst and a solvent are present in the reactor as a slurry, and the polymer is maintained in solution until after the catalyst is removed from the reaction mixture.

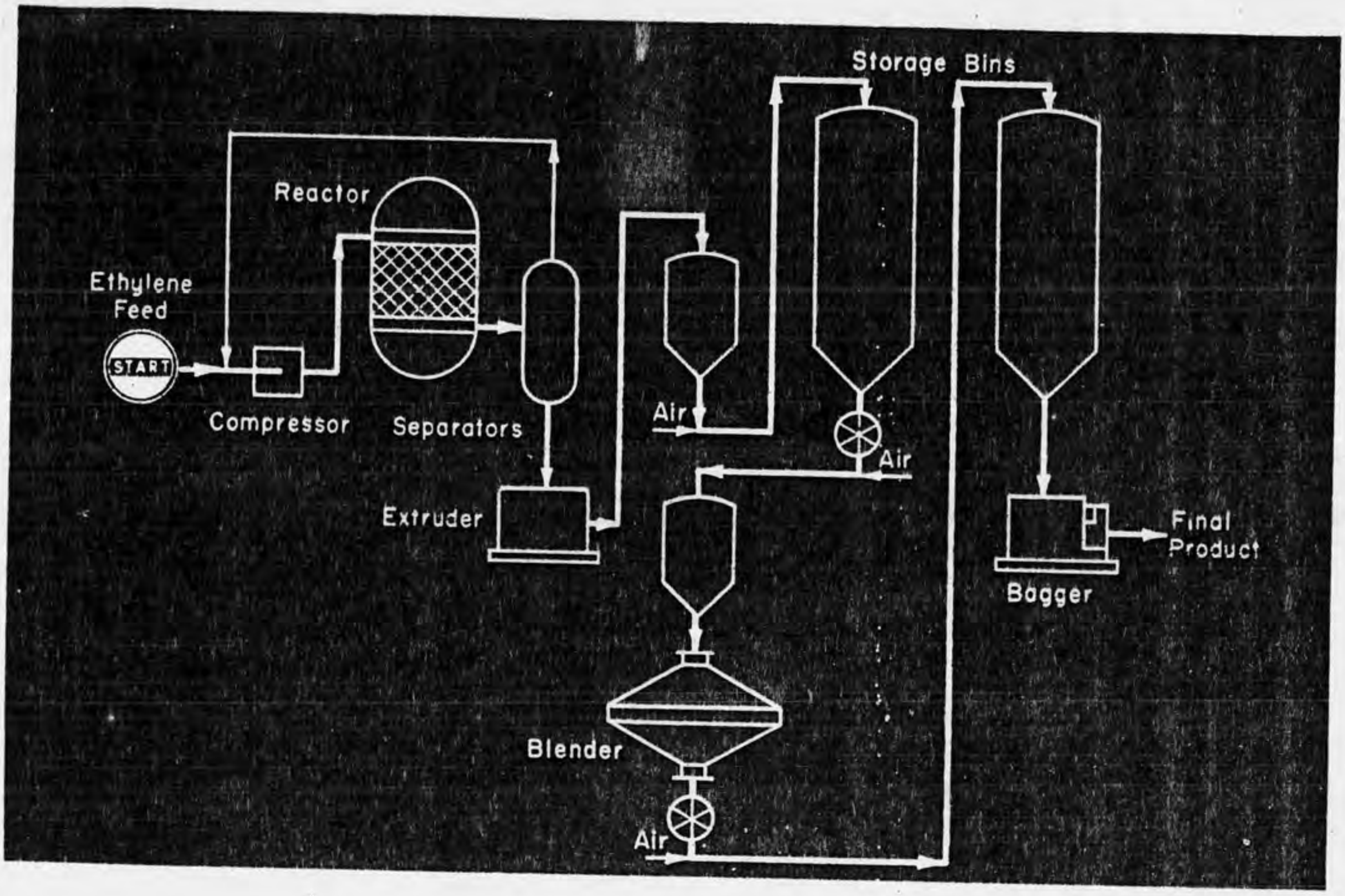
The ethylene charge gas, free of sulfur compounds, is treated for removal of catalyst poisons such as water, oxygen and carbon dioxide.

The treated ethylene and cyclohexane solvent are charged to the reactor at rates to give the equivalent of around 5 weight percent ethylene. A suitable catalyst, such as chromium oxide (CrO_3) on a silica-alumina support, is maintained at a concentration of 0.5 percent or less (based on weight of solvent). The solvent serves several functions in addition to its role as a solvent for ethylene and polyethylene. It protects the growing polymer chain from chain-breakers, controls the viscosity of the solution, controls the rate of ethylene consumption to promote good polymer growth, and it serves as a medium for dissipating the heat of reaction. The reactor is maintained at a temperature of 200° to 300° F and a pressure in the range of 100 to 500 psig.

The reactor effluent is sent to a flash drum for removal of some of the excess solvent and ethylene. The polymer solution is then centrifuged and filtered to recover an essentially ash free polymer solution. The polymer is precipitated from the solution in a stripper to form a slurry. The polymer is separated from the slurry, dried and finished as polyethylene pellets.

Yields: The conversion of ethylene to polymer is virtually 100 percent, and recovery of solid polymer is in excess of 98 percent.

Commercial Installations: The following plants utilize the process described here: Celanese Corp. of America, Pasadena, Texas; Allied Chemical Corp., Baton Rouge, La.; National Petro Chemicals Corp., Deer Park, Texas; Phillips Petroleum Co., Pasadena, Texas; Union Carbide Chemicals Co., Seadrift, Texas, and Chemplex Co., Clinton, Iowa. Licensees also are in England, France, Spain, Germany, Belgium, Italy, Brazil and Japan.



Polyethylene (AGFO)—SCIENTIFIC DESIGN COMPANY, INC.

Application: A process for the manufacture of high pressure polyethylene.

Charge: High-purity ethylene; 99.9 percent preferred.

Product: Pelletized polyethylene, density approximately 0.91-0.93.

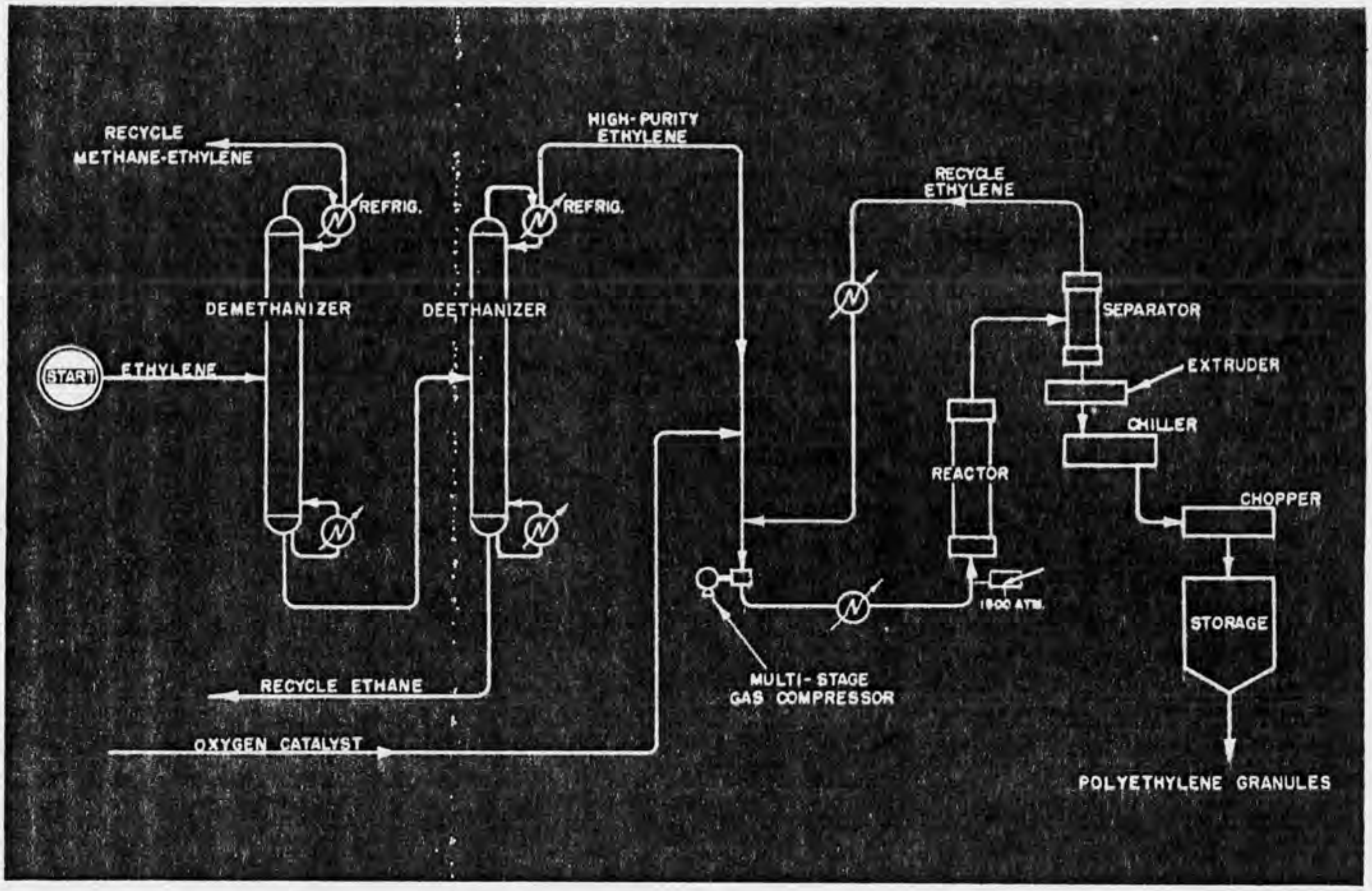
Description: Ethylene feed is mixed with catalyst and with a recycle stream from the polymer separators, then compressed to very high pressure with intermediate and final cooling. This stream is fed continuously to a tubular reactor where careful temperature control is maintained by circulating high pressure water in the jacket. The mixture of ethylene and molten polymer is passed through a separator where the unconverted gas is removed for recycling. To remove from the system the inerts present in the feed, a small bleed stream is taken from the recycle. This is returned to the ethylene purification unit which supplies the feed ethylene.

Molten polymer from the low pressure separator is fed directly to an extruder which lends uniformity to the product. The extruder has a granulating head which reduces the polymer to pellets.

The capacity of a production line is fixed by the characteristics of the process. High capacities are achieved by installing parallel production lines.

The finishing section is very flexible in design and its nature will depend on the desired product distribution. In general, it will include refining extruders, blenders, and storage bins. The polyethylene pellets are transported from one unit to another by means of an air transport system operated by remote control. Coloring facilities may also be included as part of the over-all installation. The product is bagged or shipped directly in special tank cars.

Commercial Installations: Foster Grant Co., Inc., Beaumont, Texas (under construction).



Polyethylene (High Pressure-ICI)

Application: A process for the continuous manufacture of polyethylene.

Charge: Ethylene gas of 90-95 percent purity.

Product: Solid polyethylene.

Description: Polyethylene manufacture requires high purity ethylene and the first step is to purify the ethylene plant product.

The first purification column is the demethanizer in which the overhead, consisting of methane-ethylene, is taken back to the ethylene plant and the bottoms to the second tower where 99.8-99.9 percent ethylene is taken overhead with the bottoms going back to the ethylene plant.

In the *mass polymerization* process, an operating pressure of about 1500 atmospheres and a temperature of about 375° F is used. A free radical yielding catalyst, such as oxygen, is added to the feed and the compressed mixture is fed to the reactor. Once initiated the reaction proceeds quite rapidly with about 25 percent of the ethylene being converted to high molecular weight polymer. Special means are provided to maintain essential isothermal conditions of 375° F.

The effluent from the reactor passes to a separator vessel in which unconverted ethylene is removed and recycled to an intermediate stage of the charge gas compressor. This ethylene contains no oxygen which, though serving as catalyst or initiator, is consumed in the reaction.

The liquid from the separator is water-white polyethylene with a very high viscosity. It is extruded in a form which can be quickly chilled and solidified, such as a continuous ribbon. Final steps in the process are chopping, bin storage, sacking and shipping.

In the *water-solvent polymerization* process, an operating pressure of about 1,000 atmospheres is used. An aromatic hydrocarbon is added as a solvent to improve polymer solubility in the reaction zone and thus permit easier and quicker removal of the formed polymer before it is attacked by growing polymer chains. A mixture of fresh and recycle ethylene, plus about 20 ppm oxygen catalyst, is dissolved in a benzene-water mixture at 375° F. The major constituents in the charge have a weight ratio of about 1.0:1.0:1.5 ethylene:benzene:water. The water contains 100 ppm of oxygen. The charge is fed to a stainless-steel tubular reactor and during the course of reaction additional water is injected to maintain a more constant catalyst concentration throughout the reactor. About 17 percent of the ethylene is converted to polymer. Isothermal conditions of 375° F are maintained. The effluent from the reactor passes to a separator where the unconverted ethylene is removed and recycled as in the mass process. The liquid, consisting of polymer, benzene, and water is sent to a distillation unit where benzene and water are ultimately separated from the heavier polymer.

In the water-solvent process, water carrying additional initiator is injected at multiple points along the reaction tube in order to attain a higher conversion of the ethylene per pass through the reactor. The "half-life" of these initiators normally used is low and consequently it is necessary to continually add initiator to maintain the rate of polymer formation.

The separated polymer is handled as described above for mass-polymerized ethylene.

The product polymer has a molecular weight of 18,000-30,000.

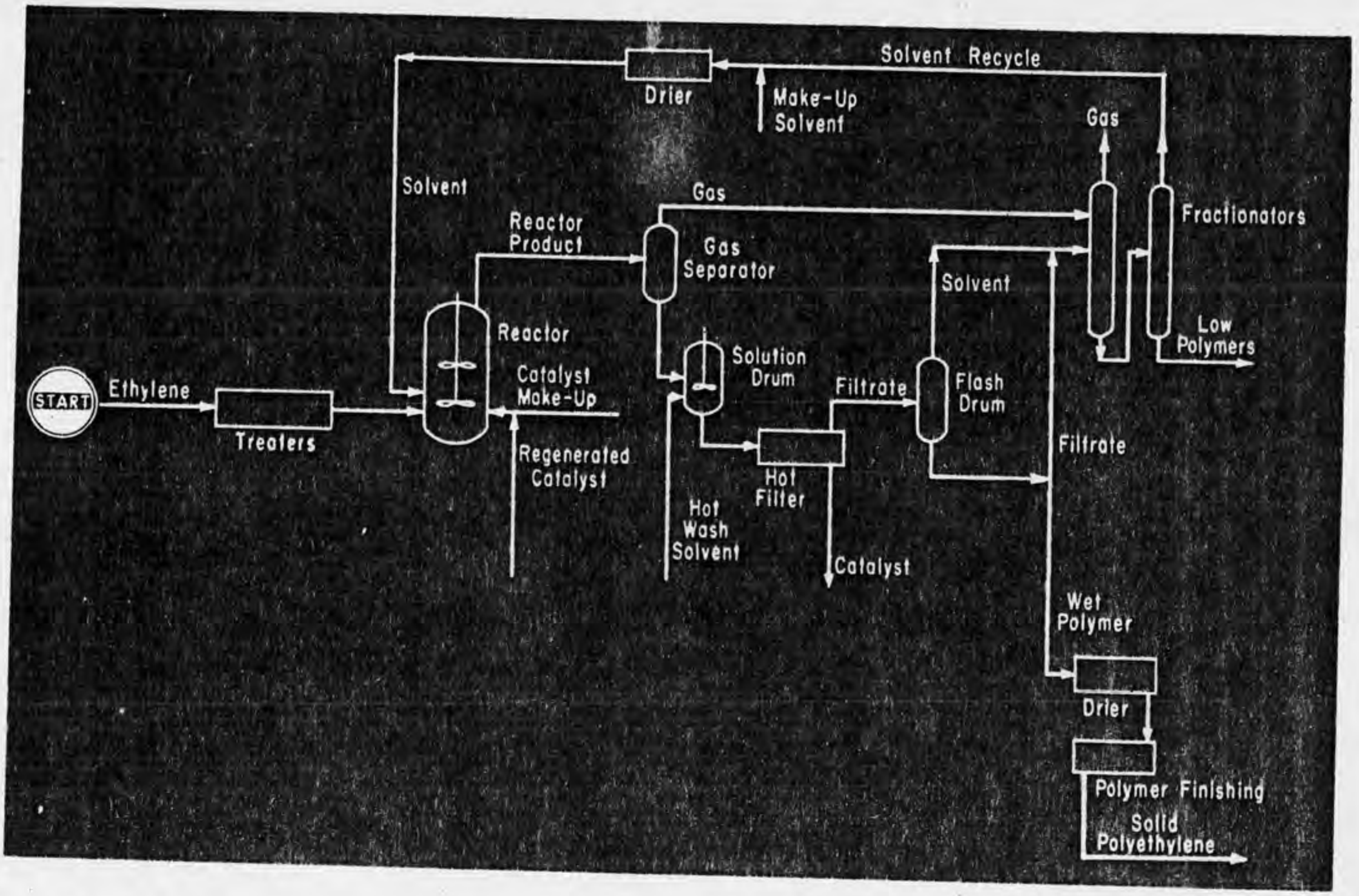
The typical processes described above are subject to variations imposed by the particular properties of polymer desired and the research findings of individual producers. Operating pressures range from 1,000 to 2,000 atmospheres. Autoclave reactors may be used. Free radial generating catalysts which may be used, in addition to oxygen, would include organic peroxides such as benzoyl peroxides and di-tertiary butyl peroxide. Azo compounds and metal alkyls are also effective.

Operating Conditions: Typical values are given above.

Yields: Over-all yield from ethylene is about 95 percent.

Commercial Installations: Union Carbide Chemicals Company, Charleston, W. Va.; Texas City, Texas; Seadrift, Texas; Torrance, Calif., Whiting, Ind. E. I. du Pont de Nemours & Company, Orange, Texas. Canadian Industries, Ltd., Edmonton, Canada. Spencer Chemical Company, Orange, Texas. The Dow Chemical Company, Freeport, Texas. Texas Eastman Company, Longview, Texas. Monsanto Chemical Company, Texas City, Texas. U. S. Industrial Chemicals Co., Tuscola, Ill., Pasadena, Texas, and Koppers Co., Inc., Port Arthur, Texas.

References: "Polyolefin Resin Process," Marshall Sittig, Gulf Publishing Co.



Polyethylene (Low Pressure-Slurry-Solution Process)

Application: A relatively low-pressure process for the continuous production of polyethylene.

Charge: Ethylene gas of 99 percent purity.

Product: Solid polyethylene.

Description: This is a process in which solid catalyst and a solvent are present in the reactor as a slurry, and the polymer is maintained in solution until after the catalyst is removed from the reaction mixture.

The ethylene charge gas, free of sulfur compounds, is treated for removal of catalyst poisons such as water, oxygen and carbon dioxide. Conventional treating may be employed, such as hot metallic copper for oxygen, anhydrous calcium sulfate or alumina for water and supported caustic for carbon dioxide.

The treated ethylene and a suitable hydrocarbon solvent are charged to the reactor at rates to give the equivalent of around 5 weight percent ethylene. A suitable catalyst, such as hexavalent chromium oxide (Cr_2O_3) on a silica-alumina support, is maintained at a concentration of 0.5 percent or less (based on weight of solvent). The solvent may be a C_5 to C_8 paraffin, a naphthene or an aromatic such as toluene or xylene. The aromatics have higher solvency toward polyethylene than the other solvents. The solvent serves several functions in addition to its role as a solvent for ethylene and polyethylene. It protects the growing polymer chain from chain-breakers, controls the viscosity of the solution, controls the rate of ethylene consumption to promote good polymer growth, and it serves as a medium for dissipating the heat of reaction. The reactor is maintained at a temperature of 200° to 300° F and a pressure in the range of 100 to 500 psig.

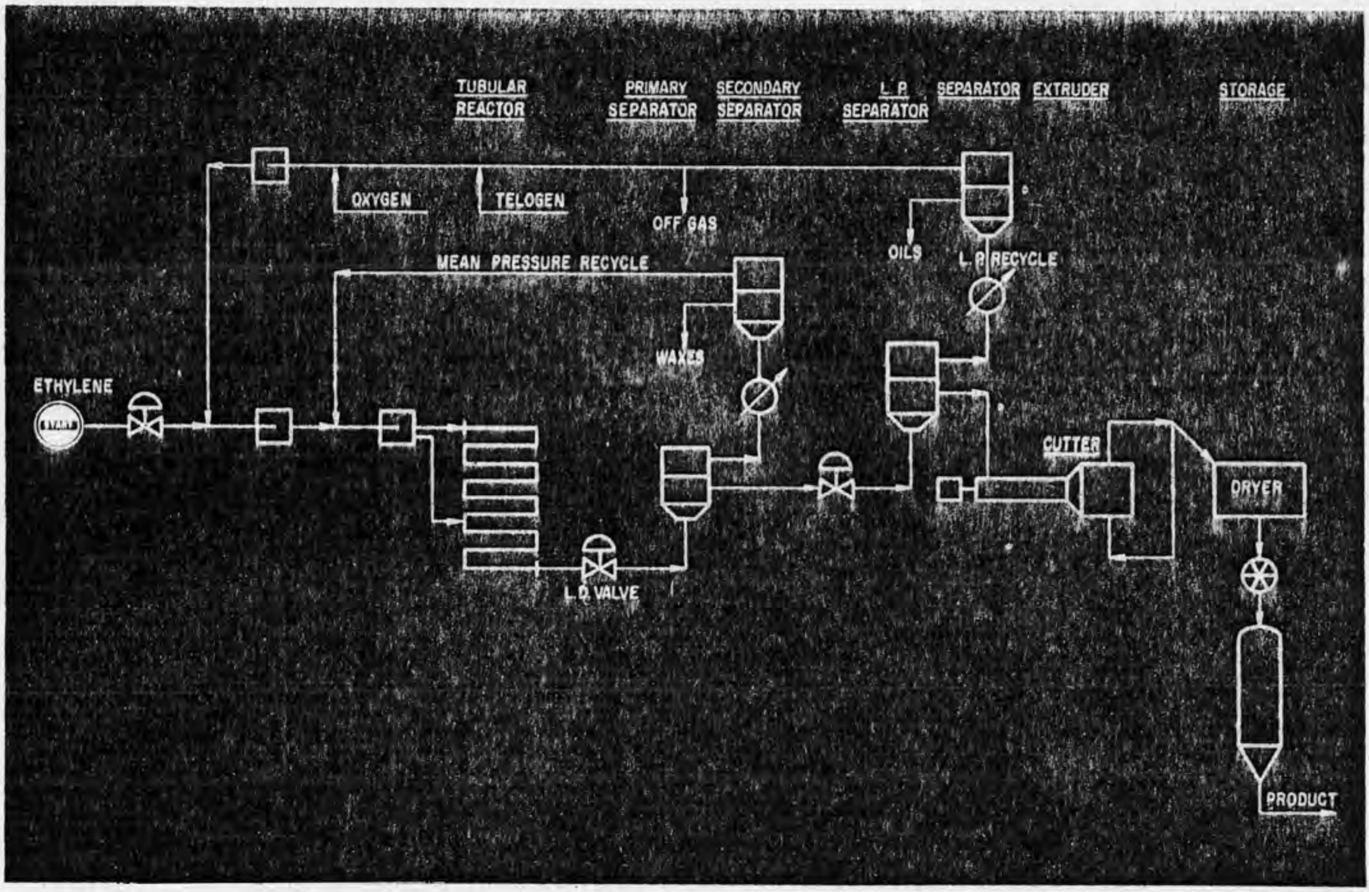
The reactor product is sent to a gas separator and then to a solution drum where additional hot solvent from the deresining operation is added to insure that all of the polymer is in solution. The mixture is then filtered to remove the catalyst which is sent to a deresining chamber where residual polyethylene is recovered from the catalyst. The spent catalyst is regenerated and returned to the reactor.

The hot filtrate is sent to a flash drum for removal of some of the solvent and then to a chiller where the temperature is reduced to 75° to 150° F. The increased polymer concentration and temperature reduction causes the high molecular weight polymer to precipitate and form a slurry. Anti-solvents, such as propane, alcohols or water are usually employed at this step to facilitate separation of the polymer from the solvent. The slurry is filtered to recover an essentially ash-free polymer which is dried and finished as polyethylene pellets. The filtrate and flashed solvent streams are combined and sent to fractionators, along with the separator gas, for solvent recovery and purge of inert gas and low polymers. The solvent is combined with make-up solvent, dried and sent to the reactor.

Operating Conditions: The ranges of the principal operating conditions are given in the foregoing description. They are influenced by the properties of the solvent employed.

Yields: The conversion of ethylene to polymer is virtually 100 percent, and recovery of solid polymer is in excess of 98 percent.

Commercial Installations: The following plants utilize variations of the process principles described here: Celanese Corp. of America, Pasadena, Texas; W. R. Grace and Co., Baton Rouge, La.; Phillips Chemical Co., Pasadena, Texas, and Union Carbide Chemicals Co., Seadrift, Texas.



Polyethylene (LD) — ATO CHIMIE

Application: A process for high pressure polymerization of ethylene using gaseous oxygen as catalyst.

Description: Ethylene feed combined with recycle, catalyst and chain transfer agent is compressed in a multistage compressor to about 280 bars. It is then mixed with the medium pressure recycle and compressed in the secondary compressor to more than 1,800 bars. It then enters the jacketed tubular reactor passing through three zones: preheating, reaction and cooling. The reactor effluent passes through a special valve to the primary separator where the stream is split into medium and low pressure segments. The medium pressure stream (containing mostly unreacted ethylene at 300 atm) is cooled and taken to other separators for wax separation before being recycled to the hyper compressor. The low pressure stream goes to the low pressure separator and to the extrusion line. Residual gas is cooled and waxes separated, and has catalyst and chain transfer agents added before going back to the booster compressor.

Yields: Conversion rates higher than 21% are obtained.

Economics: Requirements for one ton of pelletized polyethylene are:

Ethylene, kg	1.030
Chemicals, FF*	8
Additives, FF* (average)	7.50
Electric power, kWh	1,000 to 1,200
Cooling water, m³ (ΔT = 10° C)	160-180
Steam, tons	0.65

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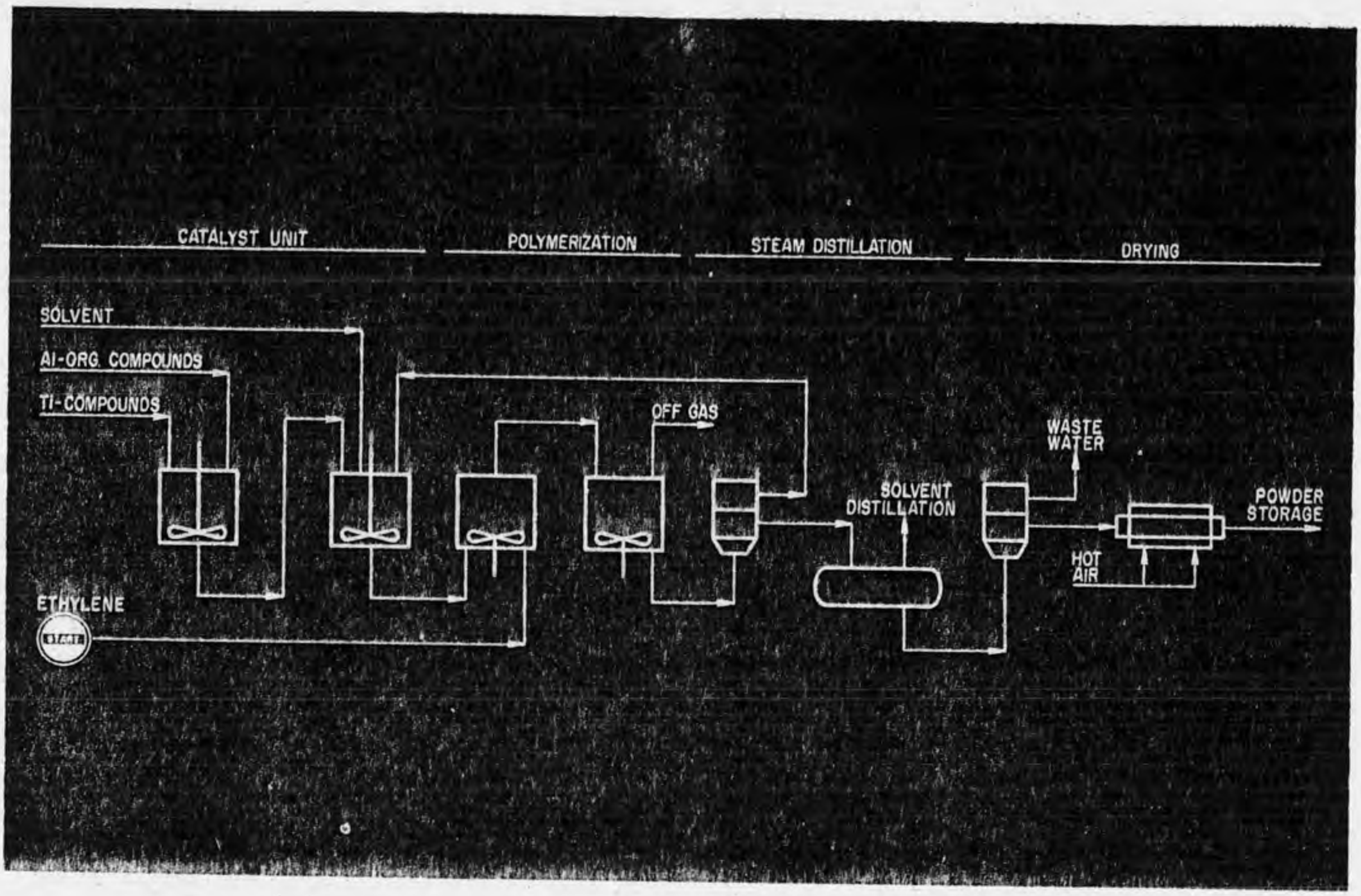
* French francs

Commercial installations: ATO has eight plants with total capacity of 250,000 t/y. The most recent plant startup was in February 1972 at Gonfreville, France. Three additional trains will start in 1973-74: 60,000 t/y at ATO in Gonfreville and two of 35,000 t/y in Tarragone, Spain. Three other plants are under license with a total capacity of 105,000 t/y.

Licensor: ATO CHIMIE.



Polyethylene (HD) — FRIEDRICH UHDE GMBH

Application: A process to produce high density polyethylene at low pressure starting from ethylene.

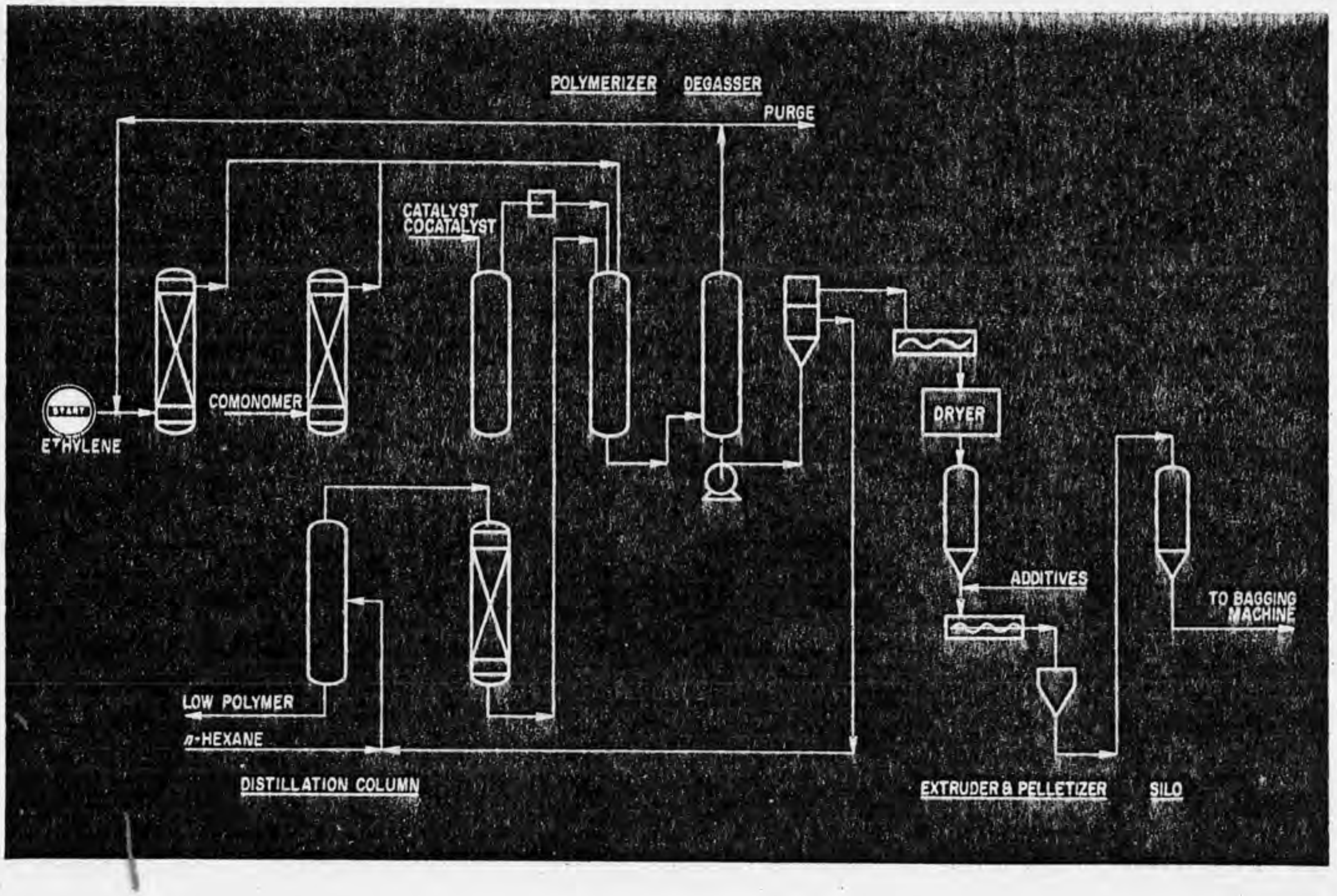
Description: Ethylene in addition with small quantities of other olefins, such as butylene or propylene, and hydrogen is continuously fed with catalyst and diluent into large-size reactors. The reaction takes place in a slurry and the polymer is obtained in the form of powder. The polymerization normally runs at pressures below 10 bar at temperatures between 80° and 90°C. The catalyst used in the reaction shows a very high activity. Therefore in large scale industrial use the catalyst is added in such small quantities, that any removal of catalyst can be avoided. Due to almost complete reaction of the ethylene this process does not need any ethylene recycling or monomer recovering. Most of the diluent is removed from the polymer by centrifuging, and can be re-used in the process without purification.

The resulting HDPE product finally is treated by steam in order to remove the last traces of diluent from the polymer. Drying is achieved in a concurrent air drier like a fluidized bed drier. This step does not require any nitrogen blanketing. Therefore, the HDPE powder can be used for further processing without nitrogen protection directly or it can be first granulated to natural or colored granules according to a large number of product-types and formulae available. The non-caking HDPE powder itself with normal bulk weights between 430 and 510 kp/m^3 is stored in powder bins, where additional handling like suitable stabilization or homogenizing can take place.

Raw materials and utilities: (per 1,000 kg HDPE powder)

Steam (12 bar), kg	1,300
Cooling water, m^3	130
Electric power, kWh	200
Nitrogen, Nm^3	35
Ethylene, including comonomers, kg	1,035
Hydrogen, kg	1
Diluent, kg	25
Catalyst, DM	10

Commercial installations: Plants with a total capacity onstream, over 600,000 metric tons/year at end of 1973.



Polyethylene (HD) — MITSUBISHI CHEMICAL INDUSTRIES LTD.

Application: A process for producing a wide range of high density polyethylene.

Description: After removing such catalyst poisoning components as water, oxygen, sulfur, etc., feed gas is supplied to the reactor system.

n-Hexane, passed through the same kind of purification process as the feed gas, is used as a vehicle. New *n*-hexane, for makeup of losses and a vehicle generated in the process, is distilled to remove low and high-boiling materials formed in the process, and given chemical and physical treatments, before being sent to the reactor system.

By varying the catalyst systems, a wide range of resins for all kinds of applications can be obtained in a single production line. Catalyst starting materials are all generally available. The catalyst produced is supplied to the reactor system in the form of a hexane slurry.

The reactor is equipped with a specially designed agitator and a cooling device for removal of polymerization heat. Temperature is kept within 30-90°C for good slurry polymerization.

The polymerization slurry is reduced to nearly normal pressure in a degassing vessel, releasing unreacted gas, which is recompressed and recycled. Total volume of recycled gas is small due to the high conversion per pass. After degassification, catalyst activity is stopped, and the polyethylene slurry is separated by a centrifuge into cake and mother liquor. The separated vehicle is returned to the vehicle purification section and the polymer cake sent to the drying section. Drying is performed in a fluidized bed to remove the small amount of hexane in the polymer cake. After adding the necessary stabilizers, the dried powder is extruded into pellets and bagged.

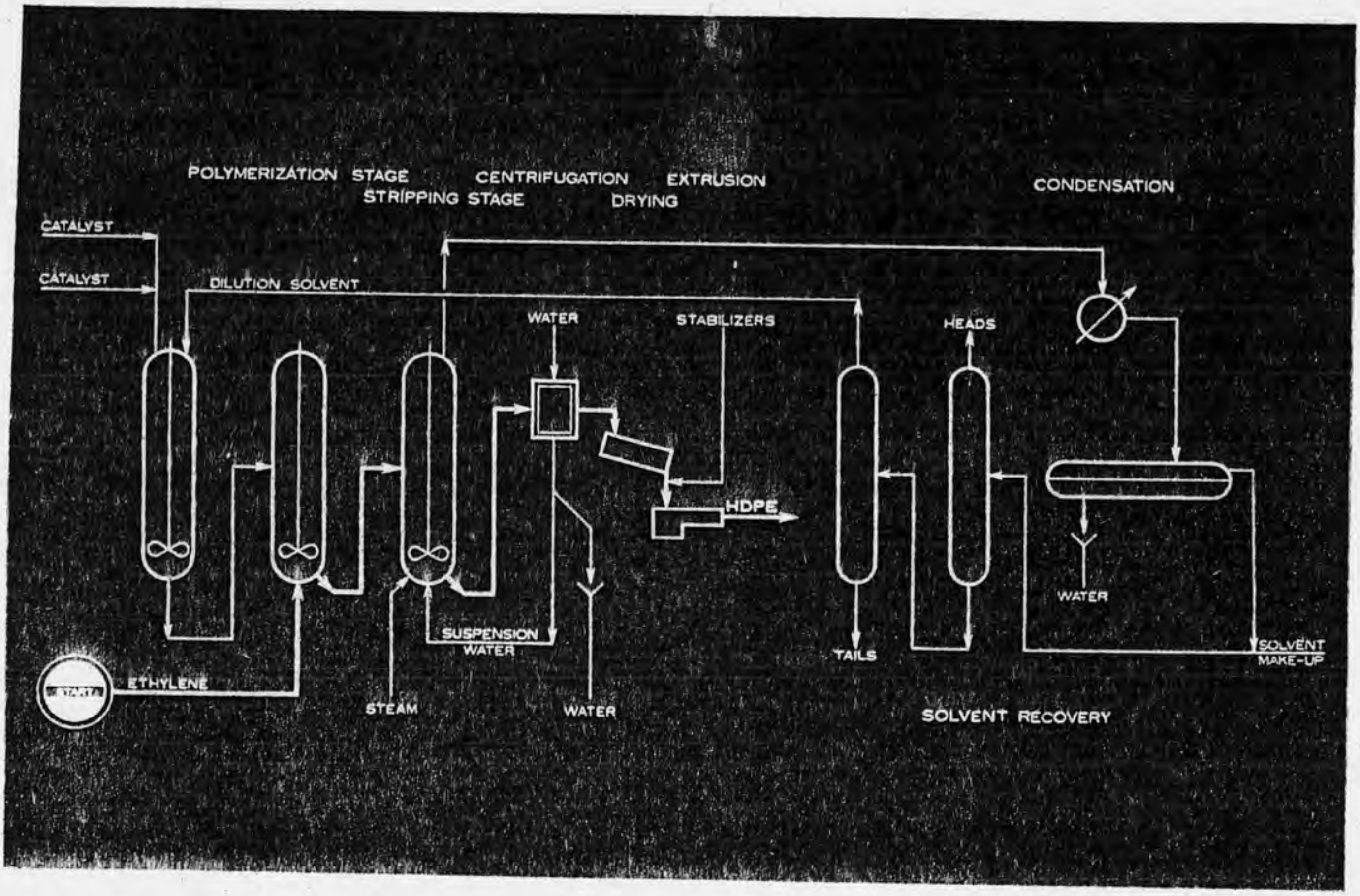
Some co-polymers can also be produced by this process.

Economics: (per metric ton of product)

Ethylene, kg	1,060
n-Hexane, kg	35
Catalyst and chemicals (including stabilizer), Yen	2,000
Electricity, kWh	875
Steam, ton	1.4
Cooling water, ton	410

Commercial installation: A plant of 60,000 metric tons per year is in operation in Japan.

Reference: *Hydrocarbon Processing,* November 1972, Vol. 51, No. 11, p. 97-98.



Polyethylene (HD) — MONTEDISON S.p.A.

Application: A process to produce high density polyethylene from ethylene.

Description: The catalyst, a mixture of supported, solid, titanium compound and an aluminum trialkyl, is fed to the reactor along with polymerization grade ethylene, a diluent (hexane is preferred), and MW regular (hydrogen). When copolymers are to be produced, a second olefin (propylene, butene-1, etc.) is fed to the reactor. Polymerization conditions are mild: temperature between 50° and 100° C; pressure lower than 15 atm.

The polymerization slurry is transferred to the steam-stripping. Hexane is separated as a gas, condensed, decanted from water, purified by distillation and recycled to polymerization. The polymer-in-water suspension is centrifuged; the wet polymer is then dried.

The polymer powder is stabilized and pelletized in a conventional granulation section.

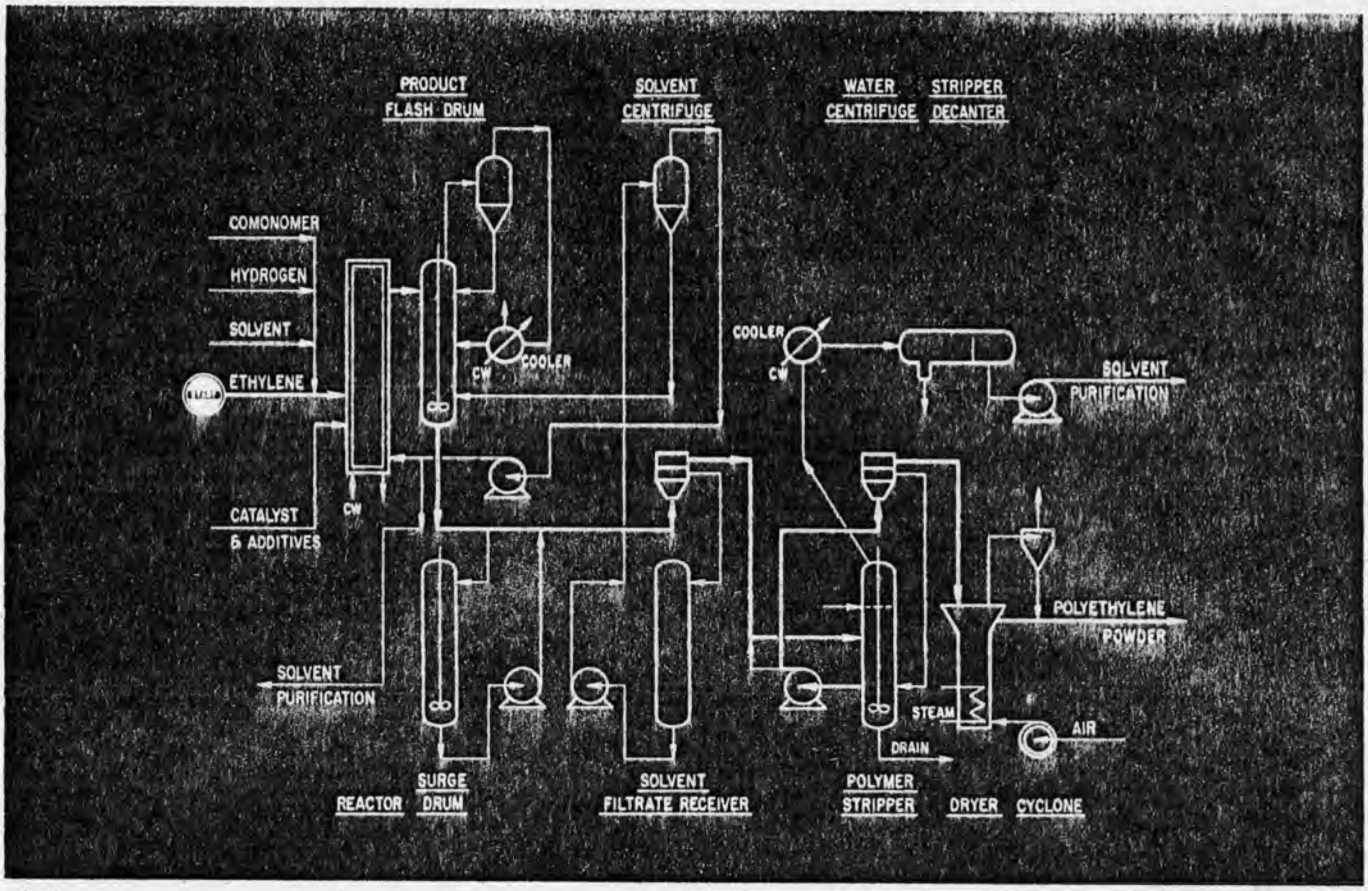
A particularly convenient characteristic of the catalytic system is that it does not produce the very low molecular weight fraction (waxes), which impair the mechanical properties of the polymer and the heat-exchange through the reactor walls.

Raw materials and utility consumption: (per 1,000 kgs of pelletized injection grade polymer. Slightly different values in the case of copolymers and of bottle-grade polymers):

Ethylene, kg	1,050
Solvent, kg	30
Hydrogen, kg	1.5
Catalyst, $	6
Chemicals, $	3
Steam, kg	2,700
Cooling water, m³	400
Electric power, kWh	600
Nitrogen, Nm³	100

Product properties: The process offers the possibility of independent control of density, MW, and MW distribution. A full range of homo and co-polymers may be produced: Density: from 0.965 to about 0.940 g/cm³; MW: from lower than 0.1 to more than 40 g/10′; MWD: from very narrow to very large.

Commercial installations: One plant, 120,000 t/y nominal capacity, on two lines, was started up at the beginning of 1972 in the Brindisi factory of the company. TECNIMONT S.p.A. (Piazza Türr 3, Milano) is the engineering company of the Montedison Group and is recommended contractor for this process.



Polyethylene (HD) — SOLVAY & CIE.

Application: A process for producing medium and high density polyethylene from ethylene.

Description: HD polyethylene is produced using a supported catalyst system which has a very high activity and selectivity. The process can produce a range of homo and copolymers with characteristics which can be uniquely tailored for a wide variety of applications.

Dry feedstock ethylene, hydrogen and comonomer in hexane diluent combine in an isothermal closed-loop tubular reactor to produce a slurry of polymer "fluff" in hexane. Catalyst and additives are fed to the reactor and mostly remain in the polymer produced. Reaction conditions are in the region 120-195° F and 425 psig.

The reactor products are depressurized to slightly above atmospheric pressure in a steam-stripper where hexane, unreacted ethylene, comonomer and hydrogen are separated from the polymer/water slurry. Hexane vapors are condensed and collected in a wet hexane decanter. Unreacted ethylene and part of the comonomer are recompressed, dried, roughly purified (separation of light gases) and returned to the reactor.

The polymer/water slurry from the stripper is separated in a pusher-type centrifuge and final drying of the polymer fluff is achieved in an air fluidized bed dryer.

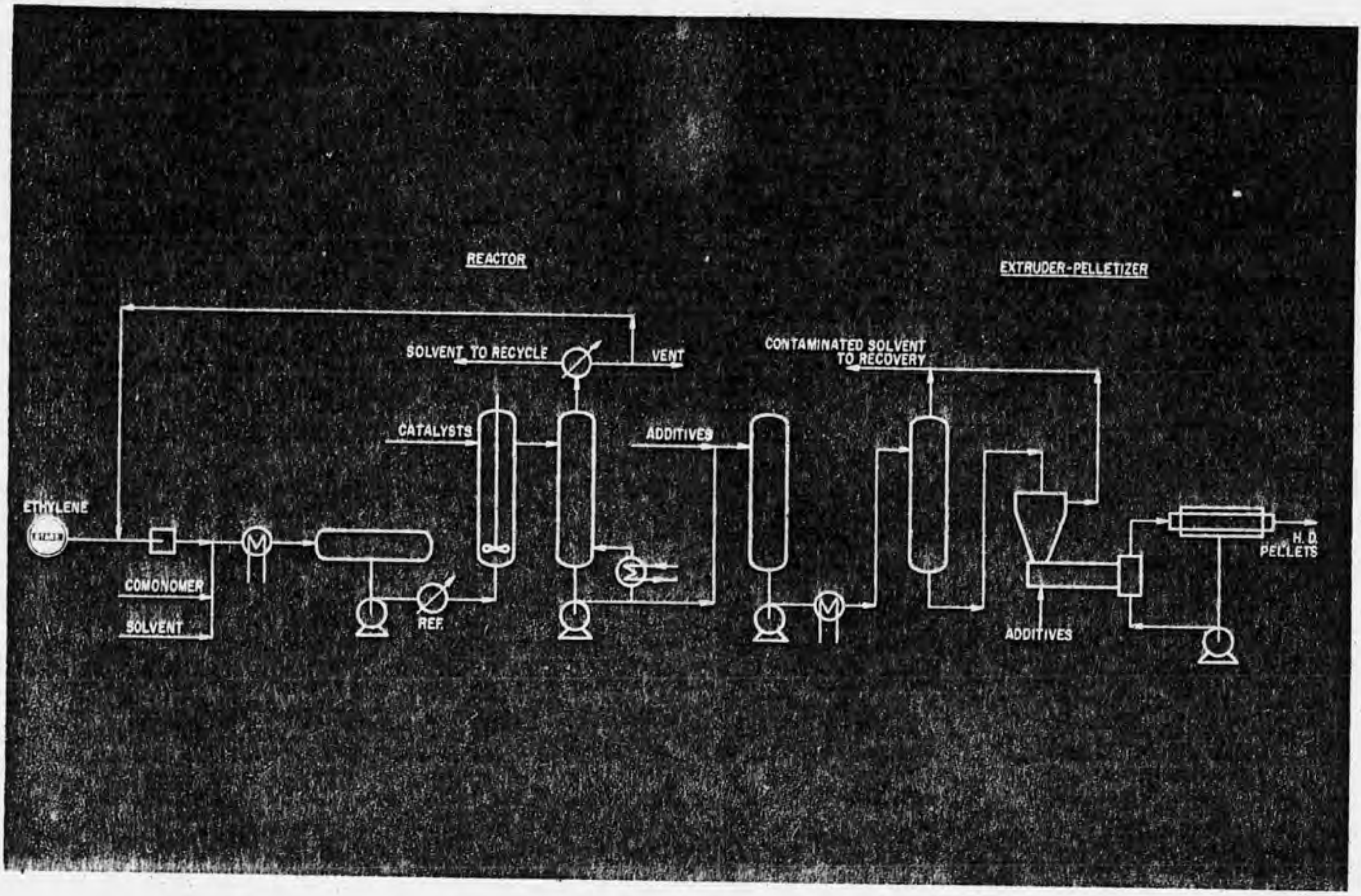
Hexane recovered from the wet hexane decanter is recycled to the reactor via a purification unit in which light gases and heavy components are removed.

Raw materials and utilities consumption per 1,000 pounds of PE comprising 50% homo and 50% copolymers:

Ethylene consumption, lbs.	1,030
Comonomer, lbs.	20
Hydrogen, lbs.	1-2
Hexane, lbs.	25
Low and medium pressure steam, lbs.	2,000
Cooling water, U.S. gals.	30,000
Electric power, kWh	100
Inert gas, scf	500
Catalysts and chemicals, $ U.S.	≃ 2.25

Commercial installations: Solvay, Sarralbe, France; Solvay, Rosignano, Italy; Eletroteno, Brazil; National Petrochemicals Co., U.S.A.; Chubu Chemical, Japan.

Power-Gas Ltd. is an approved engineering contractor for this process.



Polyethylene (HD) — STAMICARBON BV

Application: A solution polymerization process for production of high- and medium-density polyethylene.

Description: Polymerization grade ethylene is absorbed in naphtha. By refrigeration of the feed, adiabatic operation of the reactor is achieved. Catalyst is fed to the reactor directly from the storage. The ethylene conversation is 95% per pass. The reactor product is concentrated in a first flash step. Flash gas passes through a condenser, from which liquid solvent and unconverted monomer are recycled direct. The polymer flow is mixed with additives, after heating freed from solvent in a subsequent flash step, producing a pure polymer which is extruded and pelletized. The pellets are dried in a special unit of Stamicarbon design.

The solvent from the second flash step is recovered and purified by extraction and distillation, to be recycled to the reaction section.

By metering a suitable comonomer to the monomer flow, the required copolymers can be produced.

Products: Different grades of polyethylene for injection-moulding as well as for blow-moulding may be produced. The melt-index can be varied from 0.2 to 30, or even higher if desired.

The density can be varied from 0.93 to 0.97, i.e. including the medium density range.

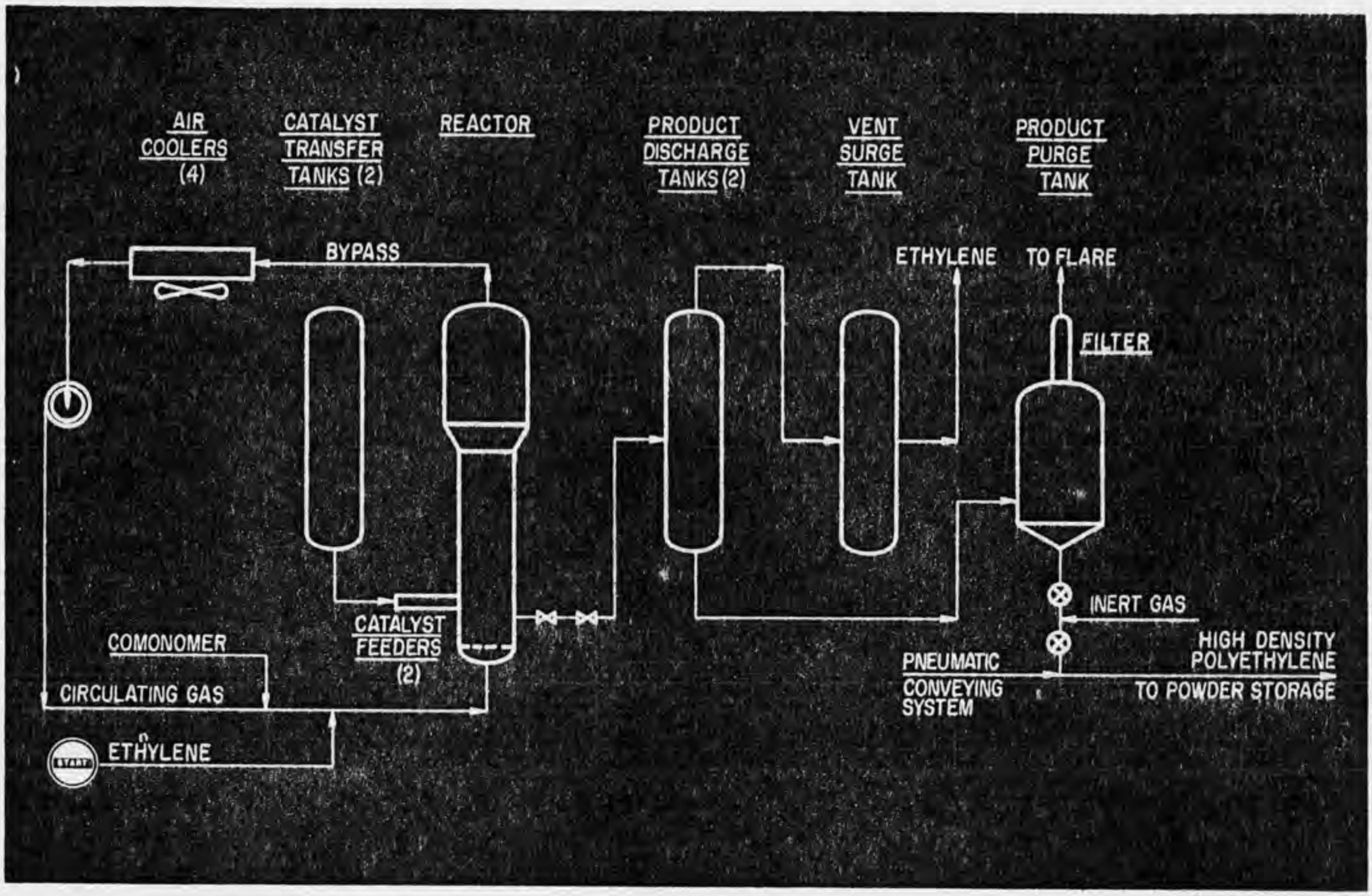
MWD can be varied over a broad range, including very narrow distributions.

Consumption: (per metric ton of final product)*

Ethylene, kg.	1025 kg
Solvent, kg.	36 kg
Steam, kg.	1150 kg
Power, kWh	670 kWh
Chemicals, Dutch Guilders	18.60
Hot oil heating, kcal.	400,000

*(Average for 50% injection and 50% blow moulding mix.)

Commercial installations: The first commercial plant with a design-capacity of 30,000 mtpa was built for DSM and commissioned in March 1971. The "compact-process" was licensed to Sinclair-Koppers, USA.



Polyethylene (HD) — UNION CARBIDE CORP.

Application: A gas phase process for the manufacture of high density polyethylene (HDPE) from ethylene.

Description: High density polyethylene is produced in a fluidized bed using a new series of supported chromium-containing catalysts which permit production of a full commercial range of HDPE polymers. The few pieces of major equipment required for this process lead to operating simplicity and, consequently, improved product consistency. Design capacity of a single polymerization line is flexible. A single reactor with an annual capacity rating of 160 MM pound/year is scheduled for 1974 startup by Union Carbide Corp.

This gas phase process differs from conventional processes in that no solvent or diluent is required in the polymerization step. Gaseous ethylene and catalyst in the form of a dry powder are fed continuously to a fluidized bed reactor. Reaction is nominally 300 psi and controlled between 85 and 100°C, depending on the product desired. Circulating gas fluidizes the bed of growing polymer, supplies monomer for reaction, and provides a medium for heat removal. After passing through the reaction zone, the velocity of circulating gas is reduced in an expanded section of the reactor to permit disengagement of fine particles. Heat of reaction is removed from the stream in an air cooler. Motive force for circulation is provided by a single stage centrifugal compressor of standard design.

Granular polymer product is intermittently removed from the reactor through a gas-lock chamber equipped with sequenced valves. Most of the approximately 5 wt. % monomer accompanying the discharged material may be recovered during depressurization, and can either be recompressed and fed to the reactor or used for other purposes. Product is purged of residual monomer prior to air conveying to conventional extrusion equipment.

Polymer density is controlled by incorporation of comonomer, while melt index and molecular weight distribution are controlled by catalyst selection and/or modification, and by varying operating conditions. High catalyst efficiencies (approximately 600,000 pounds of polymer/pound of metallic chromium) eliminate the need for catalyst removal or downstream purification.

Raw materials and utilities consumption: (per lb. polymer unless otherwise noted)

Ethylene, lb.	1.017*
Comonomer	0.02
Catalyst materials, $	0.001-0.002†
Steam	Negligible
Electricity, kwh	0.20
Cooling water	Negligible
Nitrogen, scf	0.12
Inert gas, low purity, scf	1.3

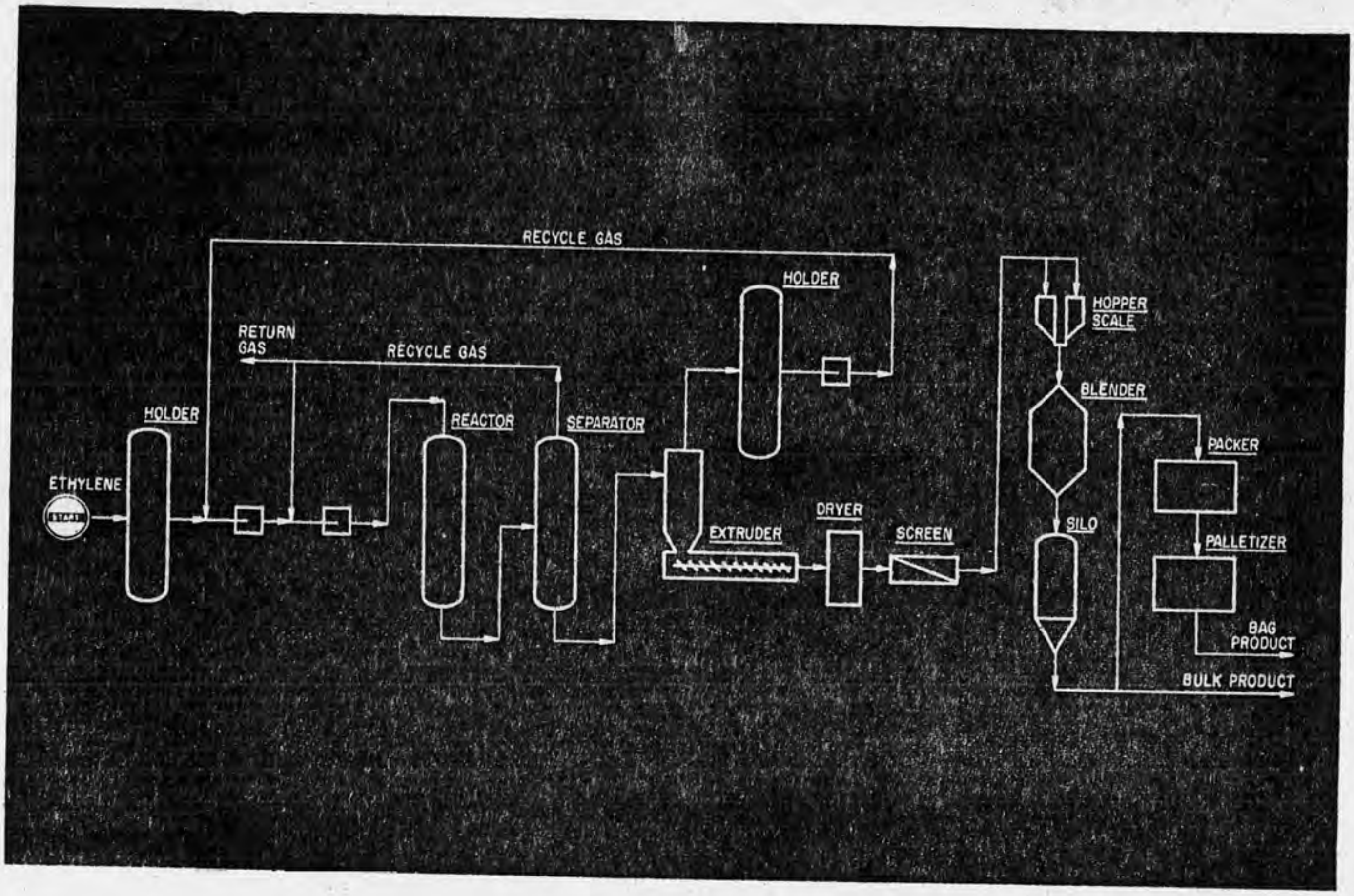
*Assumes recompression of recovered monomer and excludes any solids handling losses downstream of polymerization.

†Catalyst material costs depend on specific catalyst species.

Commercial installation: The first plant, operated by Union Carbide, began production at Seadrift, Texas, in 1968. Two others are now in operation in Sweden and Australia, and ground has been broken for a third in Czechoslovakia.

Licensors: Union Carbide Corp. is using the services of Fluor Corp. and CJB Projects, Ltd., to facilitate licensing the technology used in this process.

Reference: Rasmussen, D. M., "High Density Polyethylene Polymerized in Gas Phase," *Chemical Engineering*, Sept. 18, 1972.



Polyethylene (LD) — SUMITOMO CHEMICAL CO., LTD.

Application: A process for the production of low density polyethylene (LDPE) from ethylene.

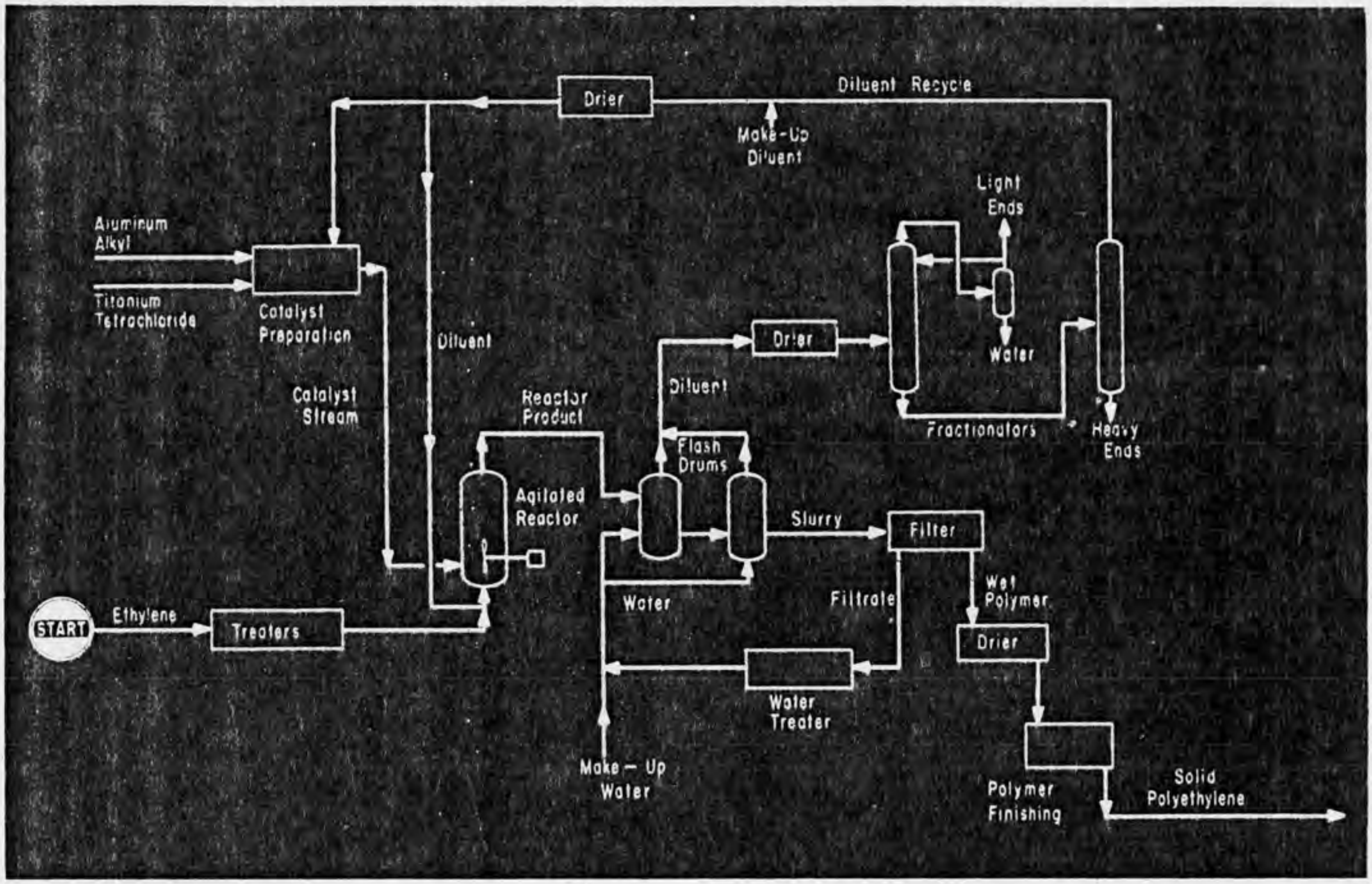
Description: Feed ethylene is combined with compressed recycle gas from the extruder and compressed further. This stream is joined by recycle gas from the separator and compressed to reaction pressure. Reactor product flows to the separators, and unconverted ethylene is recovered for recycle to the compressors. From the extruder the polyethylene is dried and screened before going to the hopper scale, blender and to storage silos.

Operating conditions of the reactor are controlled by a computer system to prevent off-grade product.

Reactor: Sumitomo operates two types of reactors—vessel reactors and tubular reactors. Single train capacities using the vessel reactor are 60,000 metric tons/year and with tubular reactors, 30,000 metric tons/year. A 60,000-metric ton/year tubular reactor is under construction scheduled for operation mid-1974.

Conversion rate: Conversion rates for vessel reactors is 21-24 percent compared to conventional processes having 15-16 percent. Tubular reactors are over 20 percent conversion, the highest value being more than 26 percent. The process is easily started up and completely free from any danger of explosion.

Product quality: Both reactor systems produce a broad range of product. Products from the zoned reactor are excellent general purpose grades. Also, various kinds of copolymers can be produced. Diversified additives recipes can also improve product quality easily and at low cost.



Polyethylene and Polypropylene (Low Pressure-Ziegler)

Application: A low pressure process for the continuous production of polyethylene (or polypropylene).

Charge: Ethylene gas of 99 percent purity for polyethylene. (Propylene of similar purity for polypropylene.)

Product: Solid polyethylene (or polypropylene).

Description: The accompanying flowsheet describes the principles of the low pressure polyethylene process that employs Ziegler catalysts. Many details of the process are still confidential, especially those related to catalyst preparation and to catalyst and ash removal after the polymer is formed. Numerous catalyst combinations are possible; however, the popular combination consists of aluminum triethyl, which promotes the polymerization, and titanium tetrachloride, which in combination with aluminum triethyl forms a finely divided precipitate which catalyzes the anionic polymerization. The catalyst constituents are extremely reactive to water and oxygen; therefore, since only a trace of catalyst is required, it is carried in a carefully dried diluent under conditions that make it safe to handle.

The ethylene charge gas is treated for removal of sulfur compounds, oxygen, water and carbon dioxide, and is then charged to the reactor. The diluent may be a C_5 to C_7 paraffin or naphthene or one of the lower aromatics. The catalyst is charged as a very dilute stream. The reactor is maintained at a pressure in the range of one atmosphere to 100 psig and a temperature of 140° to 170° F.

The reactor product is sent to a series of flash drums to remove the diluent. These drums are maintained at conditions in the range of 3 to 5 psig and the appropriate temperature to flash the diluent. Water is added to the flash drums to destroy the catalyst and slurry the polymer. The diluent is sent to a drier to remove entrained water and then charged to a fractionator where light ends and water are removed as an azetrope. The bottoms is sent to a second fractionator for removal of heavy ends, and the diluent is recovered for recycle.

The water-polyethylene slurry is filtered, and the aqueous filtrate is treated and recycled to the flash drums. Alcohol may be used in place of water to destroy the catalyst and wash it from the polymer. Additional filtration steps and special treating agents may be employed to help remove the catalyst. The solid polyethylene is dried, extruded and finished to form polyethylene pellets. Higher boiling diluents may be used. In this case a different diluent recovery system would be required.

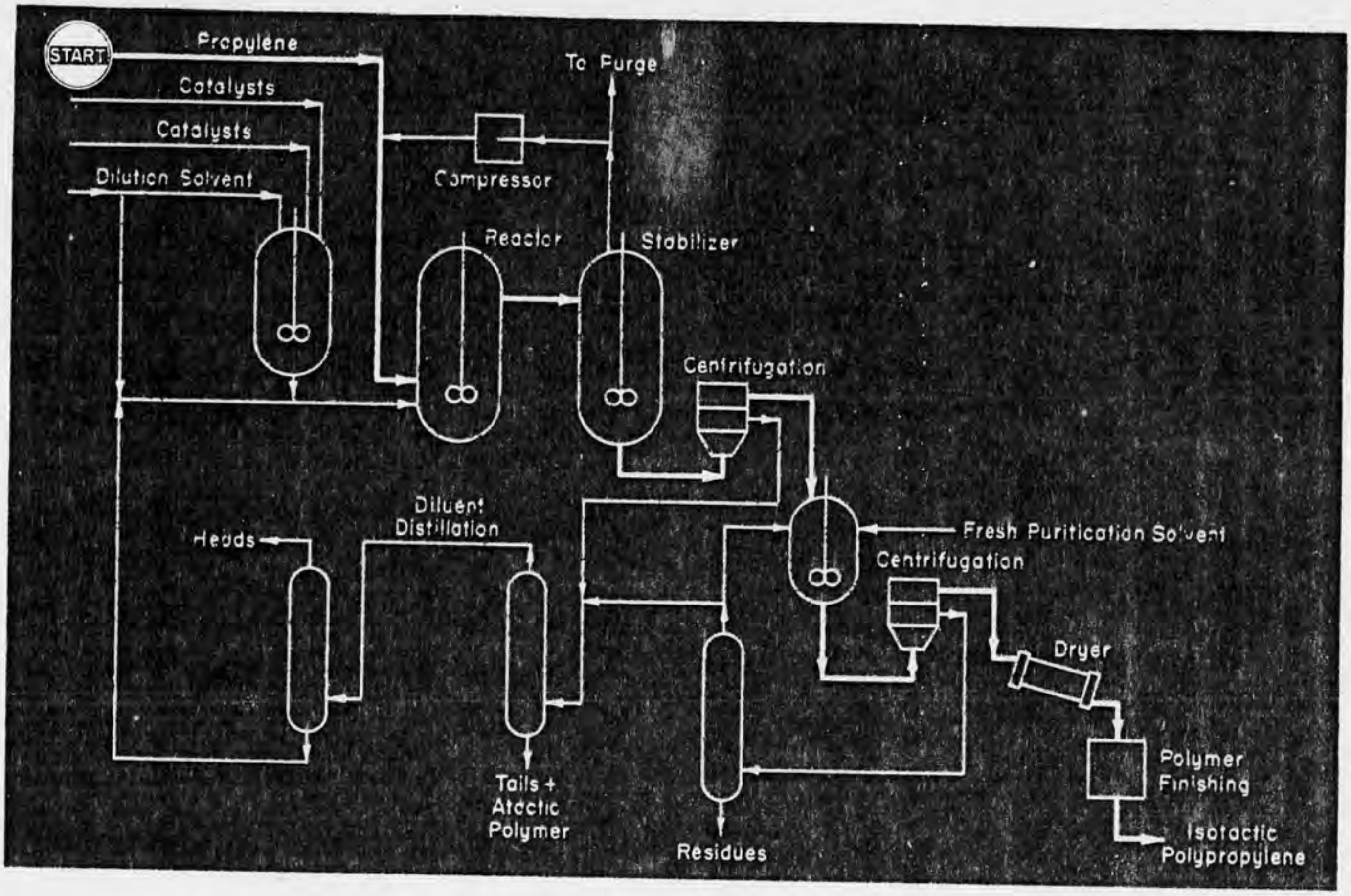
Operating Conditions: The operating conditions given above are influenced by the physical properties of the diluent.

Yields: The over-all yield of polymer is around 95-98 percent of the ethylene consumed.

Polypropylene: This polymer is made from propylene in essentially the same process and under nearly the same conditions except that titanium trichloride is used in place of titanium tetrachloride. This increases the yield of polymer to over 90 percent based on the olefin charged.

Commercial Installations: *Ziegler Polyethylene:* Dow Chemical Co., Bay City, Mich.; Hercules Powder Co., Parlin, N. J.; Koppers Chemical Co., Port Reading, N. J.; and Union Carbide Chemicals Co., Institute, W. Va.

Polypropylene: Hercules Powder Co., Parlin, N. J.



Polypropylene—MONTECATINI

Application: A continuous process for manufacturing isotactic polypropylene, by low pressure stereospecific polymerization of propylene.

Charge: Propylene "polymerization grade" 99 percent pure. Solvents. Catalysts.

Product: Solid isotactic polypropylene in pellets.

Description: Polypropylene is produced by means of catalytic polymerization in the presence of catalysts obtained by reaction of metallorganic compounds, particularly aluminum-alkyls, with titanium halides.

The propylene monomer used is highly concentrated and processed so as to reduce to allowable values the content of impurities which can negatively influence the catalyst activity.

The catalyst components are reacted in a hydrocarbon medium and the resulting complex is fed to the reactor.

Paraffinic hydrocarbons, such as C_6^+, C_7^+ are generally used as reaction diluent substances.

The reactor works at a pressure of 1 to 10 atm. and it is thermostatized in order to maintain the temperature in the range from 50 to 100° C.

All reagents are fed continuously to the reactor and the reaction product is also continuously transferred as a suspension to a stabilizer where unconverted monomer is flashed and recycled to the reactor after a suitable purge in order to keep the amount of inert gases within an acceptable value.

The stabilized reaction suspension is centrifuged and washed with a proper mixture of organic solvents with the purpose of removing the greatest part of the reaction diluent and of deactivating and consequently eliminating the residual catalyst.

The diluent used in the reaction and depration steps are then recycled, after having been suitably purified by means of distillation.

The polymer coming from a second centrifugation step is dried, stabilized, extruded and finally hot granulated in lens-shape.

Operating Conditions: The above mentioned operating conditions have only a pure indicative value. They may be changed depending on the characteristics wanted in the final product.

Product Characteristics: Average characteristics of a polymer obtained by the outlined process are as follows:

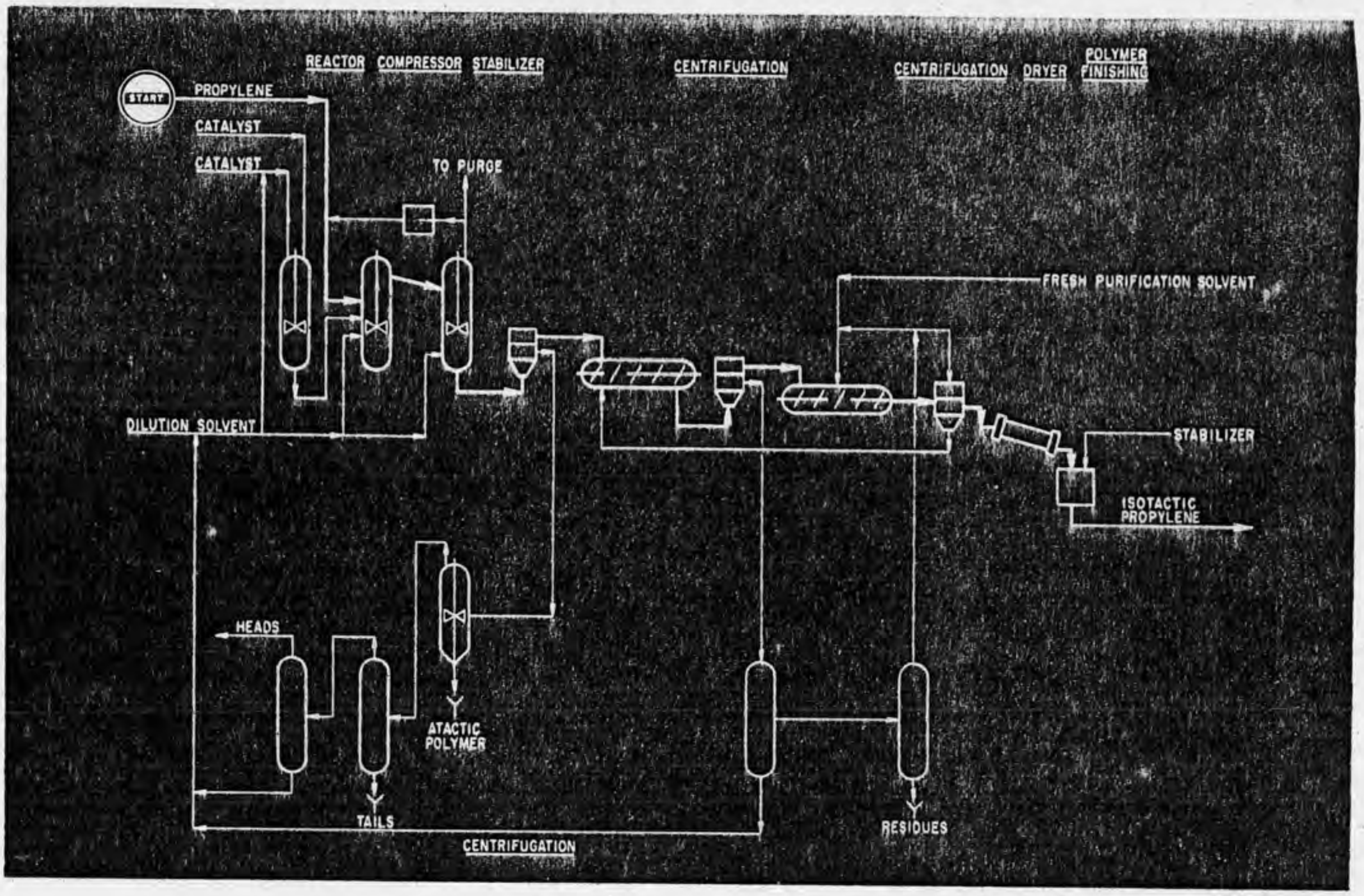
isotactic index	90 — 98	
tensile strength	3,250 — 4,800	psi
ultimate elongation	300 — 600	%
flexing stiffness (flexural elastic modulus)	14,000 — 10,000	psi
Vicat softening point (1 kg)	302	F°
distortion temperature (ASTM-66 psi)	212 — 266	F°
Rockwell hardness	60 — 65	L scale
ashes	<0.05	%
dielectric constant (18 MHz)	2 — 2.2	
dissipation factor (18 MHz)	0.0003 — 0.0010	
dielectric stiffness (rigidity) short time test	32	KV/mm

Commercial Installations: Polypropylene is now produced, by the above mentioned continuous process, at Montecatini Factory in Ferrara (Italy) and at Danubia Factory in Schwechat (Vienna).

A Montecatini plant using the same process is going to operate at Neal (West Virginia U.S.A.) under the name of Novamont Corp.

Other Montecatini plants for polypropylene production are under construction in the new petrochemical factory at Brindisi (Italy).

The process has been licensed to Imperial Chemical Industries and Shell Co. in Great Britain; to Rotterdamse Polyolefinen Maatshappij in Netherland; to Esso Svenska Co. in Scandinavian Countries and to Mitsui, Mitsubishi and Sumitomo in Japan for polypropylene production.



Polypropylene— MONTECATINI EDISON SPA

Application: A process for manufacturing isotactic polypropylene by low pressure stereospecific propylene polymerization in a paraffinic hydrocarbon (C_6^+ and C_7^+) diluent. Metallorganic compounds (aluminum alkyls with titanium halides) are used as catalysts.

Description: Propylene is polymerized in the liquid phase in the temperature range 50° C to 100° C at a pressure in the range 1 to 10 kg/cm^2 abs. Polymerization is carried out by feeding continuously all the reagents to the reactor. The reaction product is also continuously transferred as a suspension from the reactor to a stabilizer where the unconverted monomer is flashed and recycled to the reactor after a suitable purge to keep inerts within an acceptable value. The stabilized reaction suspension is centrifuged and washed with proper mixture of organic solvents which remove most of the reaction diluents and deactivate and eliminate the residual catalyst. The diluents used in the reaction are transferred to the solvent recovery unit, purified and recycled to the polymerization un

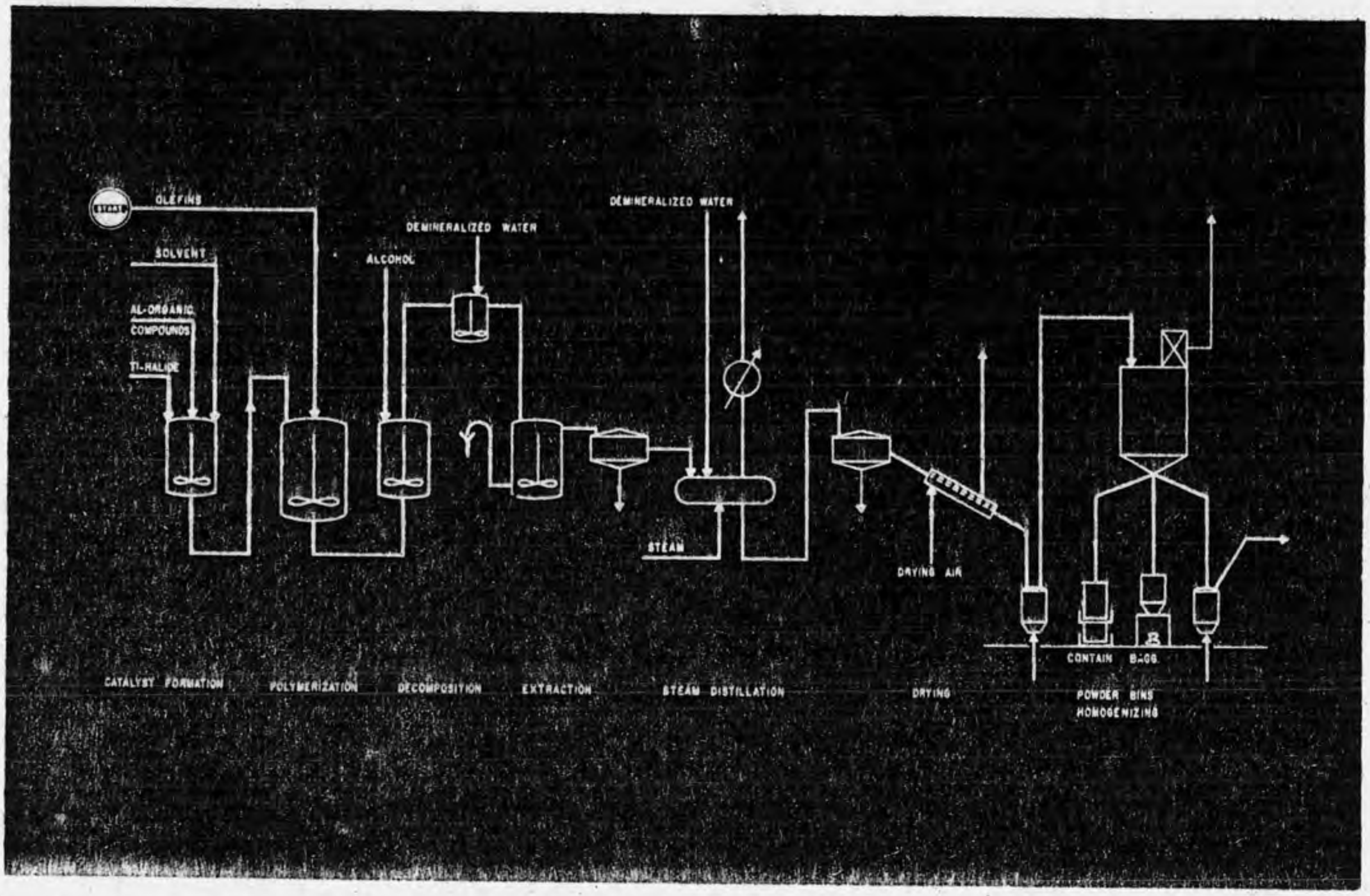
The washed polymer is again centrifuged and conveye to the polymer drying system. Stabilized, it is then e truded and finally hot granulated in lens-shape.

The polypropylene produced has high molecular weig and a high isotacticity index give the product excelle mechanical properties.

Consumptions per 1,000 kg pelletized polypropyle produced are:

Polymerization grade propylene (on 100% basis)	1,150 l
Chemicals (including catalyst, solvents and other chemicals)	25 U.S.

Commercial Installations: Polypropylene is produced the Montecatini Edison factories of Ferrara and Ter Italy, with a total capacity of more than 100,000 met tons/year. The process has been licensed to more than companies throughout the world.



Polypropylene (FWH Process) — FRIEDRICH UHDE GMBH

Application: A process to produce polypropylene homo and co-polymerisates from propylene using a catalyst which consists of titanium III-halide and an aluminum-organic compound as co-catalyst.

Description: The catalyst prepared in R_1 is reacted in R_2 with propylene and other olefins in an aliphatic hydrocarbon. After subsequent decomposition and extraction of the catalyst, the powdery product is separated by filtration from the main portion of the diluent, and purified in a steam distillation from the residual diluent. After further filtration, the moist product is dried with air, stored in a powder silo, and granulated.

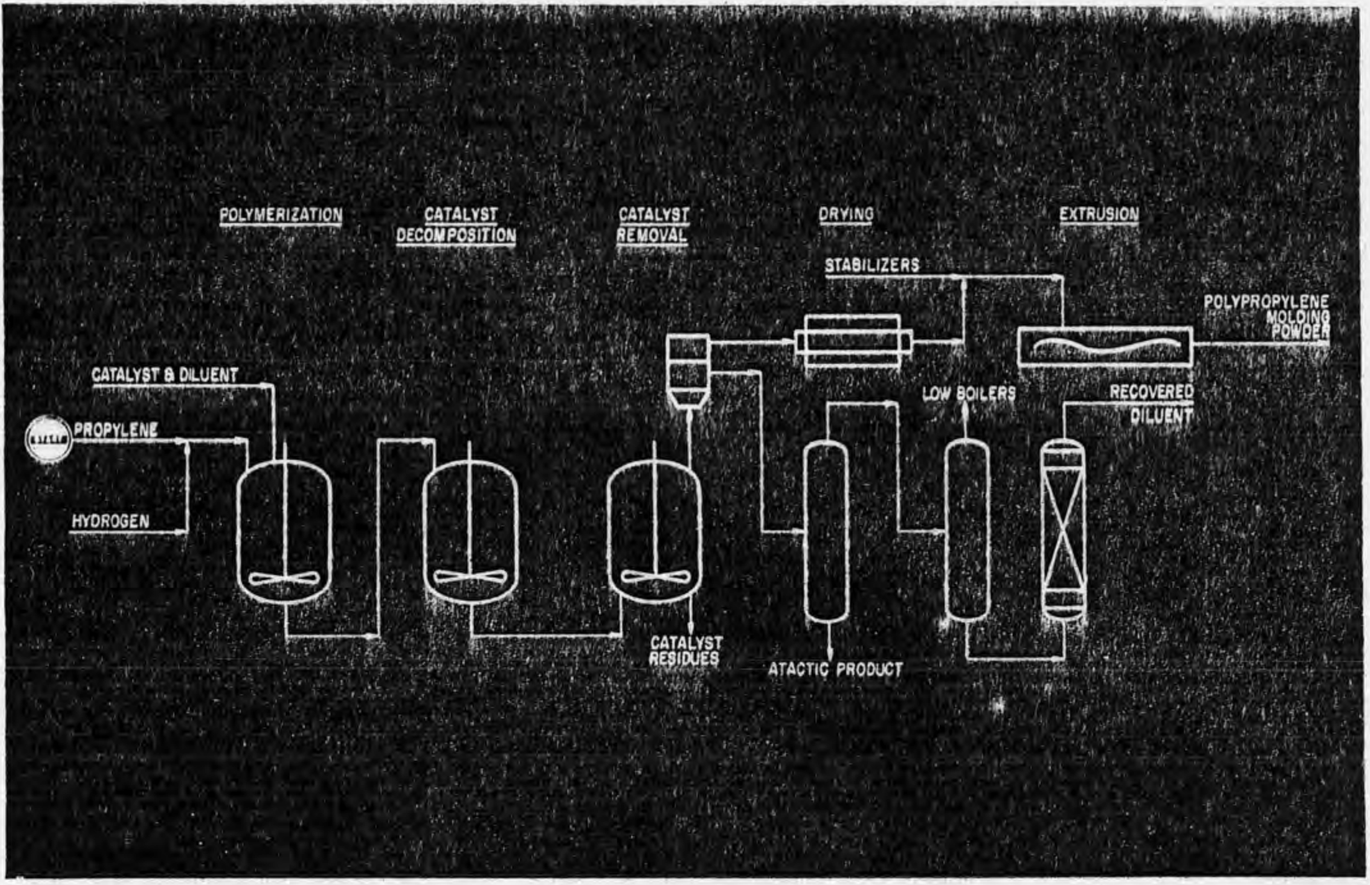
The diluent separated during the process is purified in a solvent distillation: low-molecular polymer portions and low-boilers are removed.

Raw material and utility consumption:

(Per one metric ton of pelletized polypropylene)

steam (16 bar), kg	1,400
steam (3 bar), kg	1,600
cooling water, m^3	230
electric power, kWh	200
demineralized water or condensate, m^3	2.5
nitrogen, Nm^3	50
propylene including comonomers, kg	1,060
hydrogen, Nm^3	2
catalysts and polymerization auxiliaries, DM	43
diluent, kg	55
alcohol, kg	5

Commercial installations: Plants with a total capacity onstream: 300,000 metric tons/yr. (end of 1973); 100,000 metric tons/yr. under construction.



Polypropylene — HERCULES INC.

Application: A slurry process in hydrocarbon diluent for the manufacture of polypropylene from propylene using a catalyst prepared from titanium tetrachloride and an aluminum alkyl.

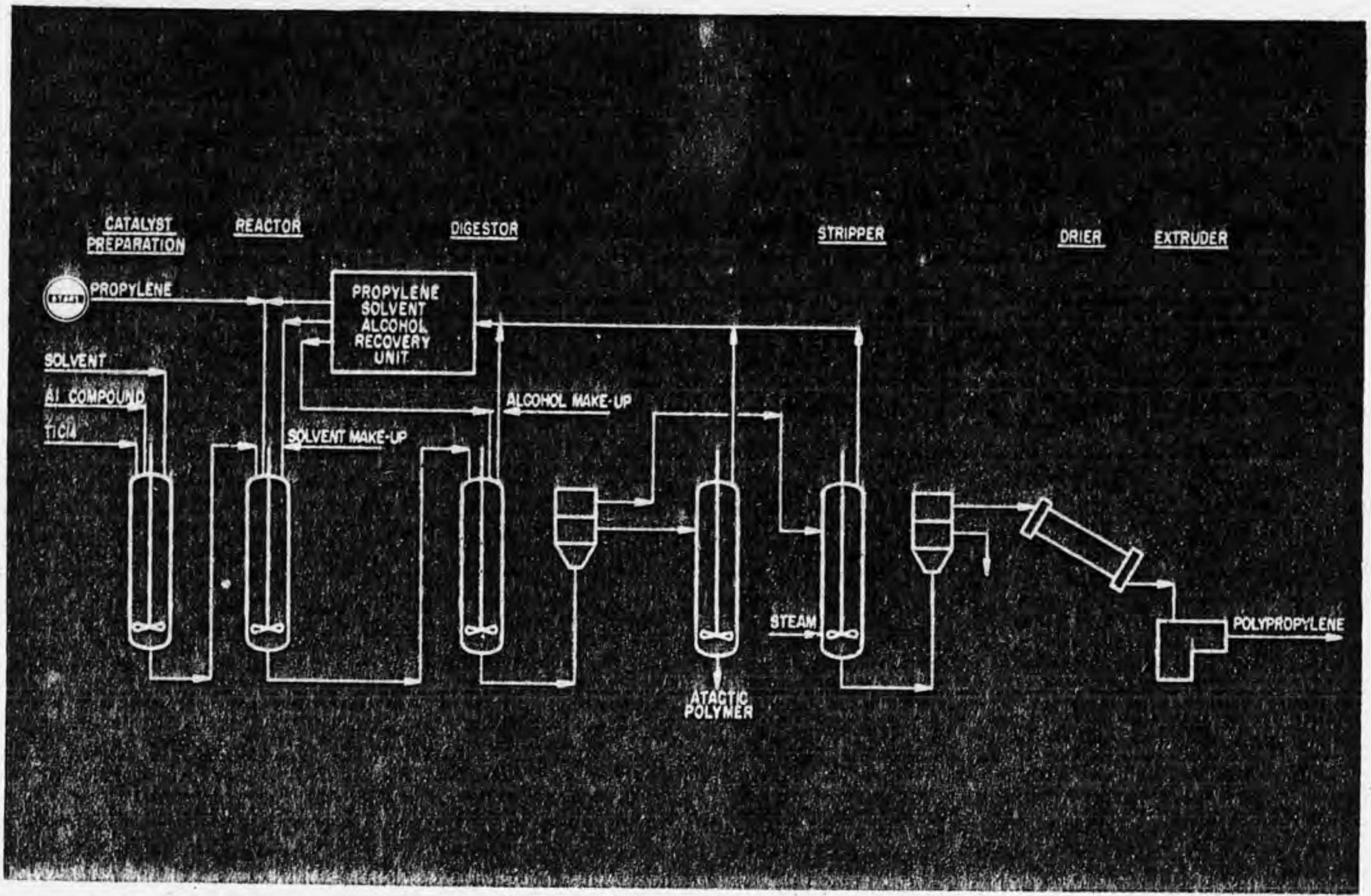
Description: The catalyst system and hydrocarbon diluent are added continuously to the polymerization reactor. Propylene of high purity is fed to the reactor at a controlled rate. Typical polymerization conditions are temperatures in the range of 50 to 100° C and pressures of 5 to 30 atmospheres. The crystalline polymer formed under these conditions is insoluble and precipitates as a finely divided granular solid enveloping the catalyst particles. Molecular weight control is achieved by addition of hydrogen, a chain-transfer agent, to the monomer system.

The catalyst is deactivated and solubilized catalyst components are removed from the polymer-hydrocarbon phase in an extractor. The polymer granules are separated from the bulk of diluent and dried. The polymer is then stabilized and extruded into molding pellets.

In the production of 1000 pounds of polymer, depending on type, generally somewhat more than 1050 pounds of monomer is consumed.

Commercial installations: Plants at Lake Charles, La.; Bayport, Texas (1974), and Montreal, Que. (1975) with over one billion pounds capacity.

References: Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 14, Second Ed., pages 282-309, 1967.



Polypropylene — MONTEDISON S.p.A.

Application: A process to produce propylene homopolymers and plastic copolymers with ethylene from propylene, using titanium trichloride and an aluminum alkyl compound as catalyst.

Description: Polymerization grade propylene, hydrocarbon solvent and catalyst suspension in the same solvent are continuously fed to the reactor.

The polymerization is carried under mild conditions (pressure under 12 atm.; temperature between 50 and 80° C), in presence of hydrogen as molecular weight regulator.

The polymerization slurry is fed to a "digestor," where unreacted propylene is separated and then recycled to reactor. In the digestor, catalyst is decomposed and solubilized in the hydrocarbon solvent by addition of an alcohol.

The polymer is separated from the hydrocarbon solvent by centrifugation. Atactic polypropylene is separated by evaporation of the solvent, which is recycled.

The polymer is steam-stripped in order to separate the solvent; the wet polymer is dried.

The dry powder is pellettized in a conventional granulation section.

By use of a suitable catalyst, whose process is available to Montedison, a polymer in powder form, narrow particle distribution, may be produced, which may be used instead of the granulate.

The process is somewhat modified in the case of production of plastic copolymers.

Raw materials and utility consumption: (per 1,000 kgs of pelletized polymer):

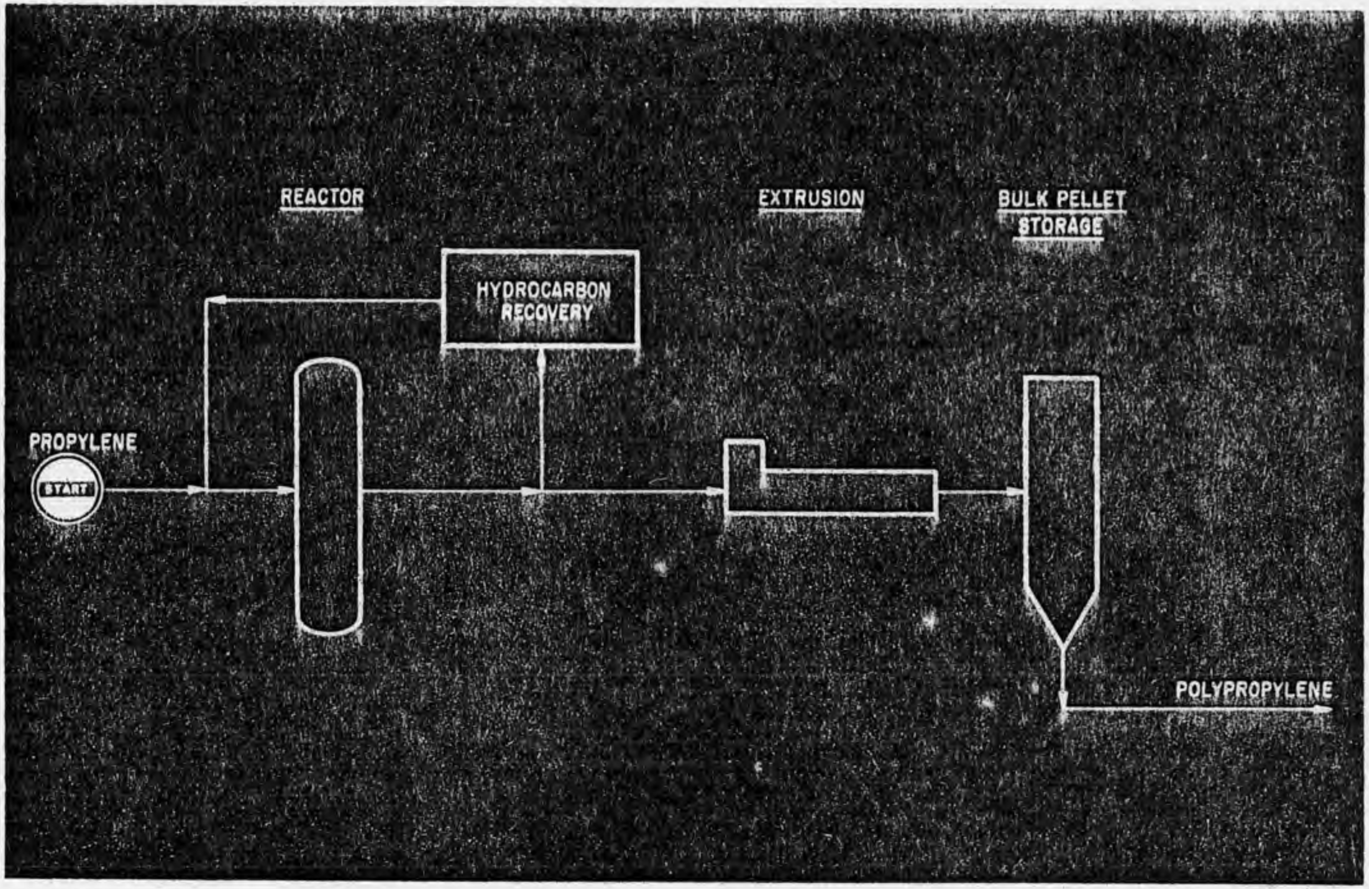
Propylene, kg	1.125
Solvent, kg	25
Alcohol, kg	4
$TiCl_3$ kg	1.2
Al compounds, kg	2.4
Chemicals, U.S. $	1.3
Steam, kg	3.200
Cooling water, m^3	400
Electric power, Kwh	500
Nitrogen, Nm^3	70
Credit: Atactic polypropylene, kg	85

(Somewhat different values in the case of production of plastic copolymers.)

Product properties: A wide range of homo and copolymers may be produced. Melt index may be varied from low values (0.1-0.3 g/10′), as required for the extrusion grades to the medium values (2-8 g/10′) required by the injection molding grades, film grades, etc., to the high values required by the fibre grades (20 g/10′).

Medium and high impact block copolymers may be produced, as well as random copolymers. Ashes content is very low; isotactic content very high (95% or more).

Commercial installations: Montedison has four polypropylene plants in Italy, with capacity 200,000 t/y; has licensed its processes and know-how to three Japanese companies, one U.S., one Austria, 1 Spain, 1 India and 1 U.S.S.R. TECNIMONT S.p.A. (Piazza Türr 3, Milano) is the engineering company of the Montedison Group is recommended contractor for the process.



Polypropylene — PHILLIPS PETROLEUM CO.

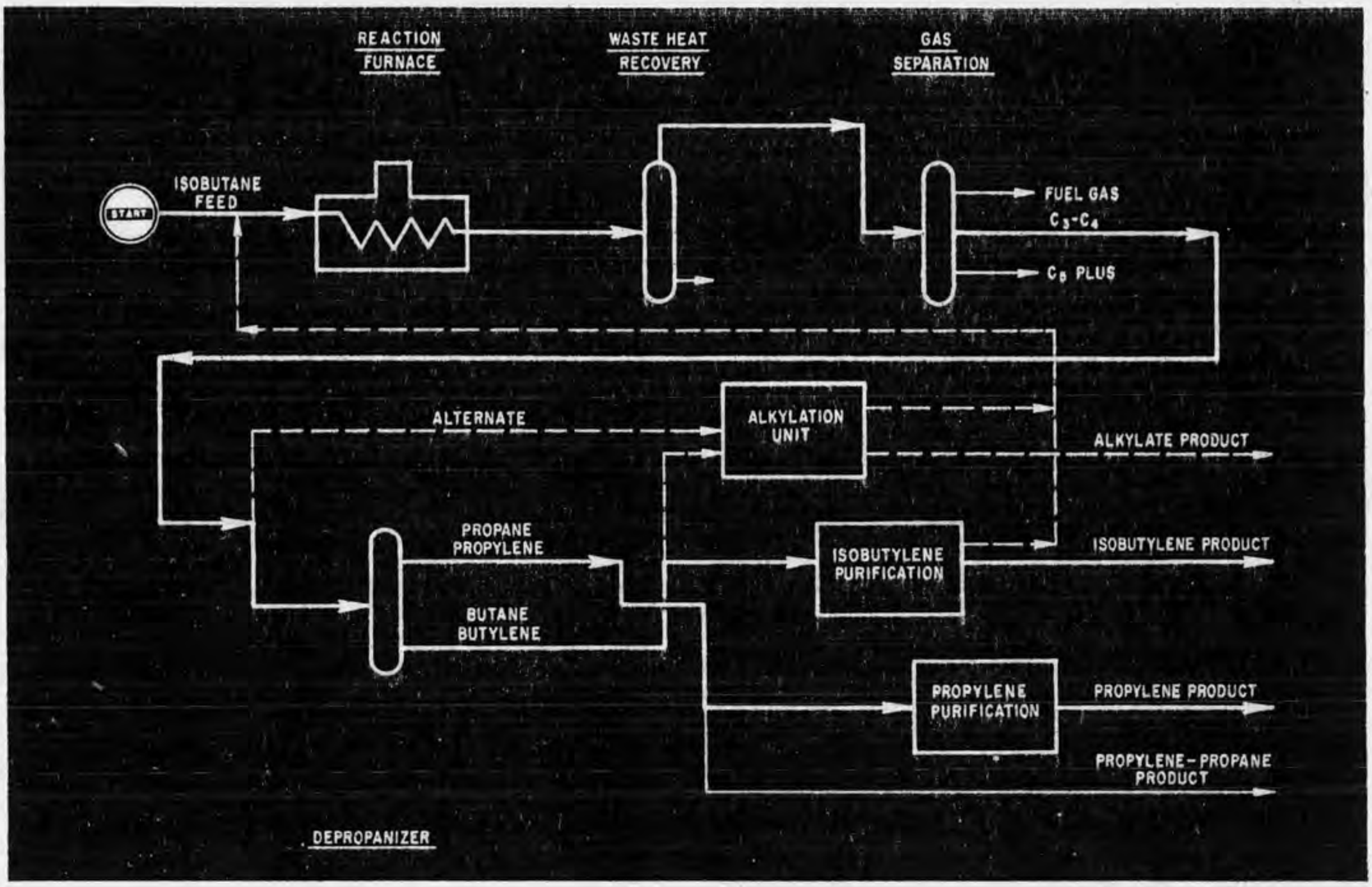
Application: A process to produce polypropylene homopolymer and copolymers continuously from propylene.

Descripiton: Fresh and recycle monomer is introduced into the reactor with the catalyst. Polymerization occurs at relatively low temperatures. The product, whether homopolymer or copolymer, is withdrawn continuously for separation from the hydrocarbon. Separation of residues and soluble polymer is performed in a very unique system incorporated in the process. Soluble polymer in the product can be varied to meet market requirements. The product in powder form is stabilized and pelleted.

The process is ultimate in simplicity and, therefore, service factors are high.

Impact grade copolymers of product, as well as the homopolymers, fill the known market applications.

Commercial installations: Diamond Shamrock Corp., Deer Park, Texas; Phillips Petroleum Co., Pasadena, Texas; and Pertamina, Pladju, Sumatra.



Isobutylene & Propylene (Coastal States Petroleum Co.) — FOSTER WHEELER CORP.

Application: A process for the production of isobutylene and propylene from isobutane feed.

Description: Isobutane feed is cracked under carefully controlled conditions. Reaction section effluent is passed through a heat recovery section to a gas recovery area where fuel gas and small amounts of heavy components are separated from the C_3-C_4 stream.

The C_3-C_4 product stream can be sent directly to an alkylation unit or to purification systems to produce high purity isobutylene and propylene.

The mixed propylene-C_4 stream can be fractionated several ways depending upon the products required. For example, the isobutylene-rich mixture can be fractionated to produce a relatively rich (about 95%) isobutylene and an isobutane-rich stream.

The isobutylene-rich mixture can be sent to extraction or extractive distillation to produce high purity isobutylene (99^+%) and an isobutane-rich stream.

The entire C_3/C_4 stream can be sent to an alkylation unit or to a cat poly unit and the unreacted isobutane recycled to extinction.

Yields: Typical yields are expressed by the following tabulation, based on a plant to produce high purity propylene and a 27% isobutylene and uncoverted isobutane. The latter stream can be treated further if desired.

Stream	Feed	C_3 Product	C_4 Product	Offgas	C_5^+
bpsd	5,000	760	3,520	(3.35 MMscfd)	65
Component analysis, %					
Propylene		92			
n-butane	5				
Isobutane	95		67		
n-butene			2		
Isobutylene			27		
Mole Wt				13.7	
°API					43.9

The ratio of propylene to isobutylene produced can be varied within limits by modification of operating conditions.

Utilities: The utilities listed below are typical for the battery limits plant. Fuel gas requirements may be offset by the offgas from the plant.

Cooling water	5,800 gpm
Electric Power	190 kwh/hr.
Fuel gas	90 MM Btu/hr.
Boiler feed water	93 gpm
Steam	2,500 lbs./hr.

Commercial Installations: Coastal States Petrochemical Co. is operating the process at Corpus Christi, Texas. The Coastal States Isobutane cracking process is licensed exclusively through Foster Wheeler Corp. Further information may be obtained from Foster Wheeler Corp., Livingston, N. J.

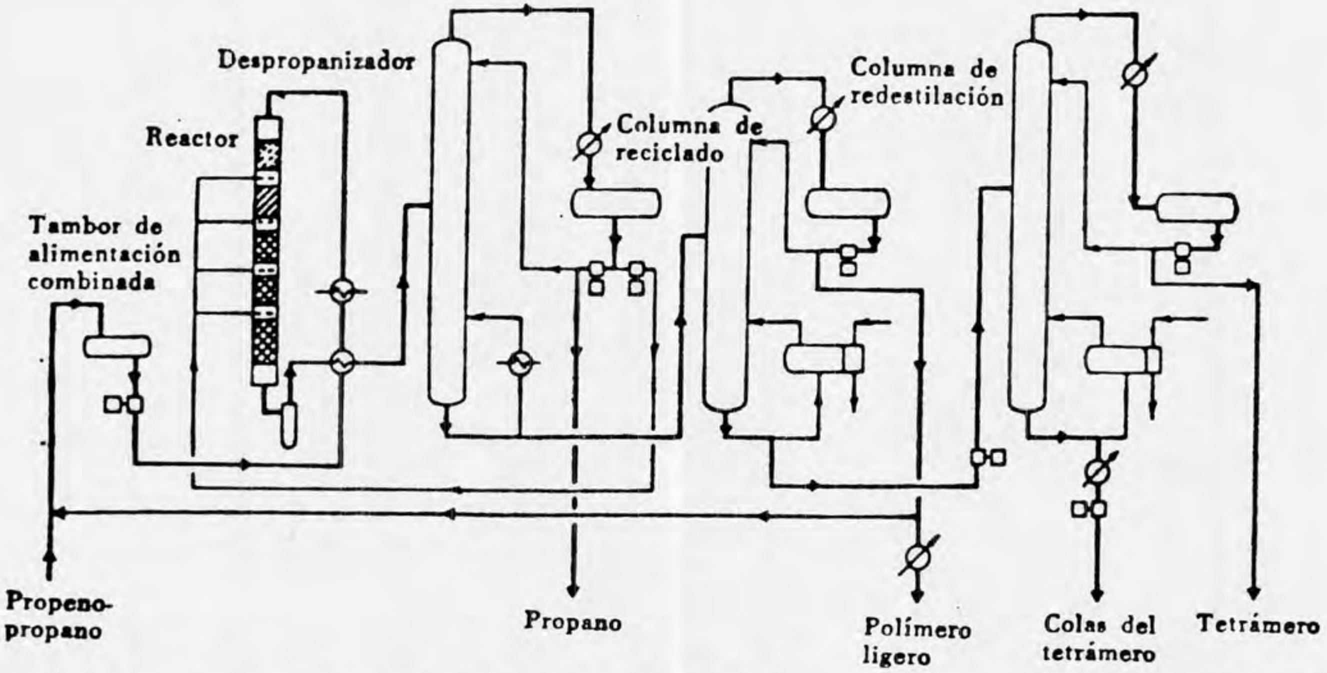
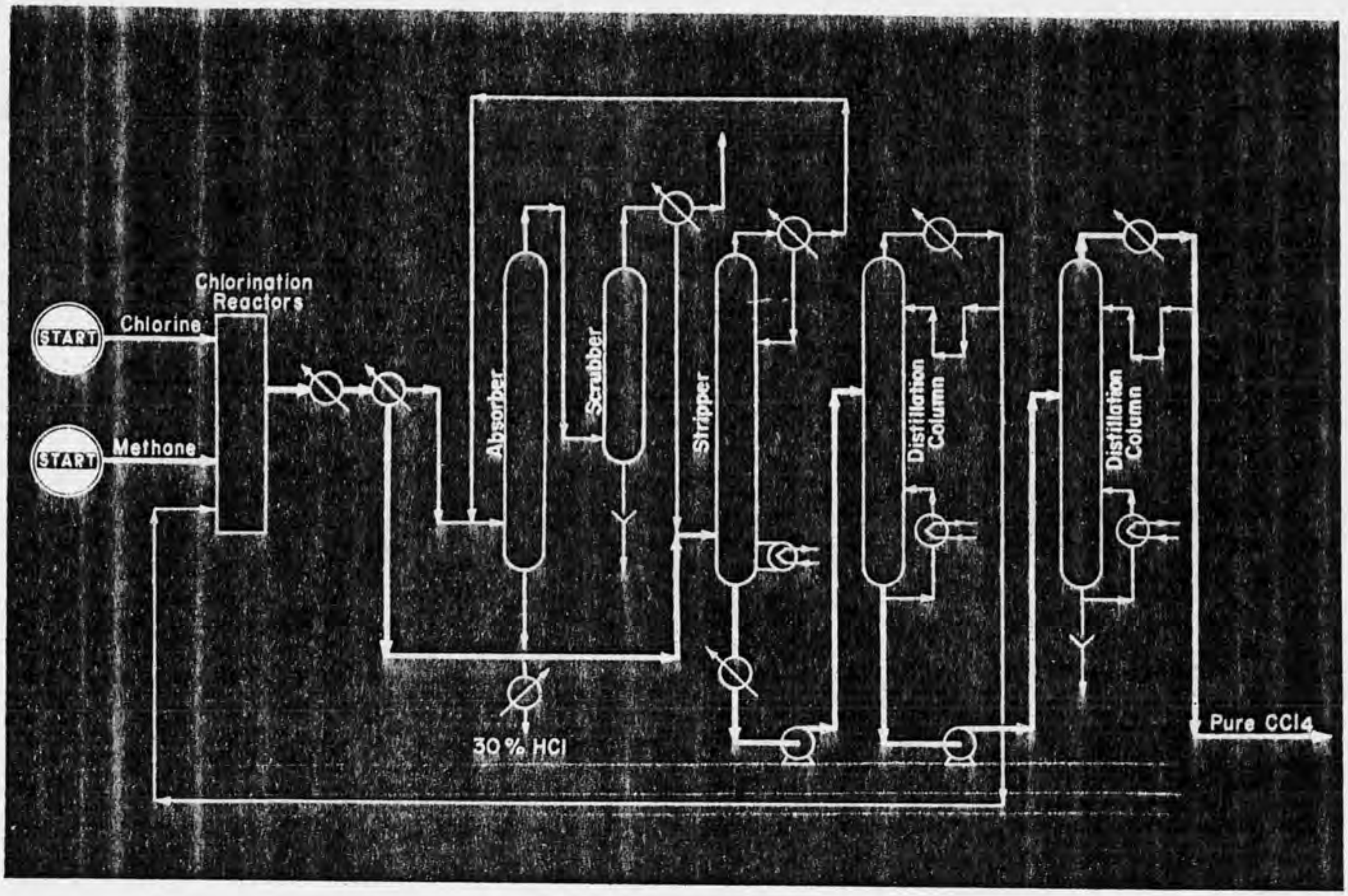


FIG. 25.14. Proceso para la obtención del tetrámero de propeno. (*Pet. Ref.*, 36, núm. 11, 278, 1957; copyright *Gulf Pub. Co.*)



Carbon Tetrachloride (Hoechst Process) — HOECHST-UHDE CORPORATION

Application: A process for carbon tetrachloride production by the thermal chlorination of methane.

Description: The chlorination of methane to form carbon tetrachloride takes place according to the following reaction:

$$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl + 89 \text{ Kcal}$$

This exothermic reaction is carried out continuously in reactors of special design. The effluent gas consists largely of carbon tetrachloride and hydrogen chloride. The HCl is absorbed in water. The raw CCl_4 is condensed and purified by distillation. The lower chlorinated methanes are obtained as overhead and may be recycled to the reaction section.

With a variation in the design of the recovery system, by-product HCl may be obtained as a gas, containing a small amount of CCl_4 and the inerts introduced with the methane and chlorine feed streams.

Raw Materials: The methane fed to the reactors must be dry and substantially free of higher hydrocarbons which reduce the yield and cause corrosion in distillation equipment. The concentration of inerts (N$_2$ an CO$_2$) should be as low as possible. The chlorine gas mu be dry and substantially inert free.

The following quantities of methane and chlorine a consumed per ton of CCl_4 produced:

Cl_2	3800 lb.
CH_4	223 lb.

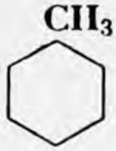
These figures correspond to yields of 97 percent of the retical based on chlorine and 93 percent based methane.

Products: The carbon tetrachloride product is free HCl, Cl_2, and organic impurities. The HCl is obtain as 30 percent hydrochloric acid and amounts to 1900 HCl per ton of CCl_4 produced.

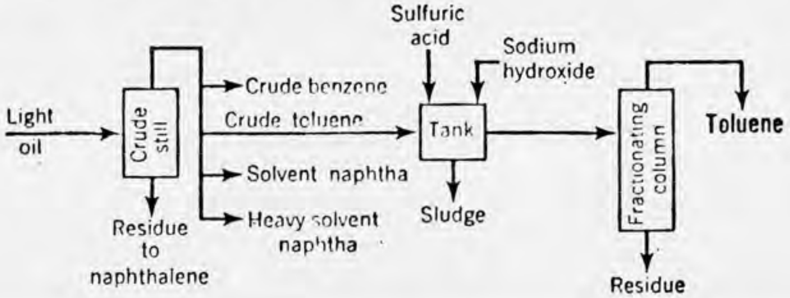
Commercial Development: The process was develop in a 10 T/D semi-works unit at the Hoechst plant Farbwerke Hoechst AG in Germany. A 60 T/D comme cial unit is in operation at Hoechst.

TOLUENE

(TOLUOL)



From Coal Gas and Tar Light Oil



Yield

1 ton of coal yields about 0.5 gal toluene

Process

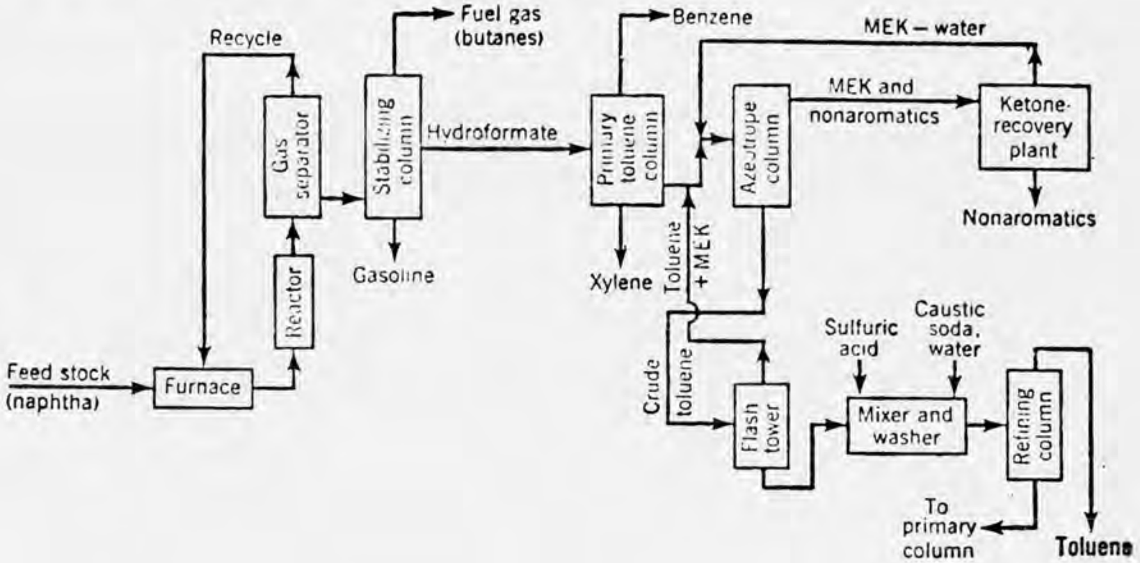
Toluene or toluol (the crude product) is obtained from light oil by fractional distillation. The light oil, formed by coal carbonization (see *Coke*), is recovered by cooling and scrubbing the by-product coke-oven gas. The light oil, which condenses with the tars (about 5 per cent of the tar), is recovered by rectification. (See *Naphthalene* for coal-tar distillation and *Benzene* for light-oil distillation.)

The light oils (containing 12 to 20 per cent toluene), scrubbed from coke-oven gas and distilled from tar, are combined and fractionally distilled in continuous or semicontinuous units. Between 0.1 and 0.2 gal of toluene is obtained per gal of combined light oil distilled. Generally, four fractions are taken in the crude distillation. The second cut, from about 95 to 125°C, consists of crude toluene which is sent to an acid-resistant agitator for wash-

[illegible] also related compounds. Usually, between .3 and 0.7 lb of sulfuric acid is used in 4 to 6 portions per gal of oil. The toluene is treated with a sufficient quantity of 10 per cent sodium hydroxide solution to remove the free acid.

The washed toluene is fractionally distilled in batch vacuum columns to yield refined toluene.

From Petroleum by Hydroforming



Reaction (Typical)

$$\underset{\text{Methyl cyclohexane}}{C_6H_{11}CH_3} \rightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + 3H_2$$

80–90% conversion

Material Requirements

Basis—1 ton toluene

Naphtha feed stock
Sulfuric acid
Caustic soda
Methyl ethyl ketone
} Widely variable, depending on feed stock

See *Benzene* for typical yields using Platforming process.

Process

Toluene is produced from specially selected fractions of petroleum, rich in naphthenes, by catalytic reforming (also known as hydroforming). This involves catalytic dehydrogenation in the presence of hydrogen (which reduces coke formation) to yield a mixture of aromatic hydrocarbons, chiefly toluene.

For the synthesis of toluene, the hydroformer raw material should be rich in dimethylcyclopentane, methylcyclohexane, and ethylcyclopentane (the [illegible] dimethylcyclohexane, will yield benzene and xylene, respectively. The feed stock also contains paraffin hydrocarbons, of which normal heptane and dimethylhexane are typical. These compounds pass through the hydroformer essentially unchanged and consequently contaminate the toluene hydroformate.

Crude petroleum and natural gasoline are processed by distillation to yield the hydroformer feed stock. For example, a California crude oil containing about 1.45 per cent synthesis hydrocarbons and 0.56 per cent natural toluene, is fractionally distilled, and a so-called heart cut is taken between 190 and 240°F. Natural and straight-run gasoline may also be processed by heart cutting to yield the maximum volume of feed stock obtainable.

The feed stock (a selected naphtha fraction) is preheated in heat exchangers and is then totally vaporized at 1,050°F in a furnace. Here it is joined with hydrogen-rich (70 per cent) recycle gas at 1,070°F, and the mixture is passed through a reactor with a contact time of about 15 sec. The reactor contains a dehydrogenation catalyst consisting of 10 per cent molybdenum dioxide on alumina. The reaction takes place at a temperature of 1,000 to 1,070°F, a pressure of 150 to 300 psi, and space velocity of 0.6 (volume of feed per hour divided by the volume of catalyst in the reactor). The ratio of recycle gas (70 per cent hydrogen) is about 6,000 cu ft per bbl of reactor charge (a barrel equals 42 gal in the petroleum industry).

The reaction gases pass through heat exchangers (preheating the feed stock) to a gas–liquid condenser and separator. Here a large portion of the separated wet gas is compressed (75 to 200 psi) and is recirculated to the furnace and reactor to increase the hydrogen concentration. The hydrogen tends to reduce coke deposition and thus maintain catalyst activity. The remaining gas and liquid pass to conventional absorption and stabilizing columns (fractionators), which produce fuel gas (butanes, etc.), gasoline, and hydroformate. The latter contains about 21 per cent toluene and may be recirculated through the reactor for maximum conversion to obtain a two-pass hydroformate containing 38 per cent toluene.

Two or more reactors are necessary for continuous operation because of the inactivating coke formation on the catalyst. One reactor is used for the dehydrogenation operation, while the second is being regenerated by burning with air or oxygen-containing flue gases. Generally, air is bled into an inert gas (mostly nitrogen and carbon dioxide) so that the mixture contains about 1.5 per cent oxygen. The latter combines with the coke, forming carbon dioxide and water, while the inert gas removes the heat of combustion. In passing through the catalyst bed the temperature is raised from 700° (inlet) to 1,100°F. The hot gases pass to waste heat boilers. The regenerated catalyst is reheated by hot flue gases, and then the inert gases, as well as water, are removed by purging with wet gas from the gas separators at atmospheric pressure.

The two-pass hydroformate (38 per cent toluene) is fed to the toluenepectively. The heart cut, containing about 65 per cent toluene, is fed into an azeotropic distillation tower. If one-pass hydroformate (21 per cent toluene) is used, the heart cut contains about 39 per cent toluene. A mixture of methyl ethyl ketone (90 per cent) and water (10 per cent) is added to the azeotrope tower. This azeotrope loosely associates with the paraffins and naphthenes and carries them out the top of the tower to the ketone-recovery plant. The toluene, because of its higher-boiling point, moves down the tower and is removed from the bottom as crude toluene. The crude material is run to a column (flash tower), where the remaining methyl ethyl ketone plus some toluene is removed as the head cut. This fraction is returned to the azeotrope tower. The ketone-free toluene is then charged into a mixer, where it is washed with 98 per cent sulfuric acid (about 5 lb per bbl), settled, water-washed, and caustic-washed to remove small amounts of olefins. The washed toluene is run to a refining column, where it is redistilled to produce nitration-grade toluene.

The methyl ethyl ketone recovery plant separates the ketone and nonaromatic hydrocarbons by countercurrent extraction with water. The ketone extract is separated from the water by distillation and is returned to the azeotrope tower. The nonaromatic raffinate from the water extraction is distilled to eliminate the water and ketone, leaving ketone-free nonaromatic hydrocarbons.

Alternate Catalytic Reforming Processes

Several catalytic reforming processes have been developed by various organizations. The processes differ in design details, operating conditions, and type of catalyst used. Some of these processes are listed below.

The *Fluid Hydroforming process* (licensed by the Standard Oil Development Co.) uses a fluidized solids technique in the reactor and continuous regeneration of the molybdenum-on-alumina catalyst in a separate vessel.

In a typical run a 214 to 291°F virgin naphtha was reformed at 934°F and 250 psig. A total aromatics yield of 39.6 per cent by volume was effected. By-product hydrogen amounted to 740 cu ft per bbl of naphtha processed. The yield of individual aromatic hydrocarbons (by volume) was: benzene—1.6%; toluene—15.8%; C_8 aromatics—15.4%; C_9 aromatics—6.8%. Overall liquid yield was 83 per cent, of which butanes were 6.9 per cent by volume and pentanes 7.2 per cent. The remaining depentanized liquid (68.9 per cent volume yield) could be processed for aromatics or used as aviation gasoline blending stock.

Platforming is a fixed-bed process using several reactors in series with intermediate reheating. This process, licensed by Universal Oil Products Co., uses a platinum-on-alumina catalyst. It is described in detail in the chapter on *Benzene*.

grade—99 to 100 per cent, industrial grade—95 to 98 per cent. Lower grades are known as crudes, or by special names, e.g., aviation gasoline blending stock.

Containers and Regulations. Tank cars, drums, pails, cans, and bottles. Red ICC shipping label required.

Economic Aspects

Toluene has two large end uses, explosives (TNT) and aviation gasoline. Because both of those are highly essential in wartime, toluene production historically has been high in wartime and low in peacetime. During World War I, the coke and gas industries were able to recover sufficient toluene for TNT manufacture, but, during World War II, that effort would have been picayune. The Army Ordnance Department, therefore, turned to the petroleum industry and had built ten hydroforming and six recovery plants, with a total capacity of approximately 20,000,000 gal toluene per month. Since the raw-material feed for recovery plants must contain toluene, the number of such plants is limited. The limit for hydroforming (more properly "catalytic reforming") plants, on the other hand, was not nearly reached. It was fortunate, however, that these plants could be converted readily to the manufacture of aviation gasoline, because demand for toluene fell sharply. But with the expansion of air transportation and the increased demand for high-octane motor fuel, hydroformer capacity was soon exceeded by the demand for the "reformate," so many more facilities were built. Then when the so-called "Korean emergency" came along, demands increased for benzene, toluene, and xylene as well as for aviation gasoline. The coke-oven industry could not expand, and so again more petroleum facilities were built. Accordingly, as demand has increased for aromatics, larger and larger percentages have come from petroleum. With toluene, this percentage has increased from 59 per cent in 1949 to 77 per cent in 1954.

Unlike benzene and xylene, however, toluene is not used to a very great extent in chemical synthesis (except for TNT). Development of processes based on toluene is precarious unless the product end-uses are as essential in wartime as aviation gasoline and high explosives. As late as 1953, 90 per cent of petroleum-derived toluene and 70 per cent of that from coal tar went to military use. During World War II lack of toluene for solvent use led many users to develop alternate solvents that continued to displace toluene after the war.

Catalytic reforming plants recovering toluene as such vary in capacity from 2,000 to 21,000 B/SD (barrels per stream day) of feed stock. Toluene production depends, of course, on the nature of the feed. Catalytic reformer investment costs are $125 to $300 per daily bbl capacity, depending on size and specific design. Although only about 20 reformers are in toluene service licensed by Atlantic Refining Co. Other fixed-bed catalytic reforming processes using a platinum catalyst are *Houdriforming* (licensed by Houdry Process Co.), *Ultraforming* (licensed by Standard Oil Co. (Indiana), and *Powerforming* (licensed by Esso Research and Engineering Co.).

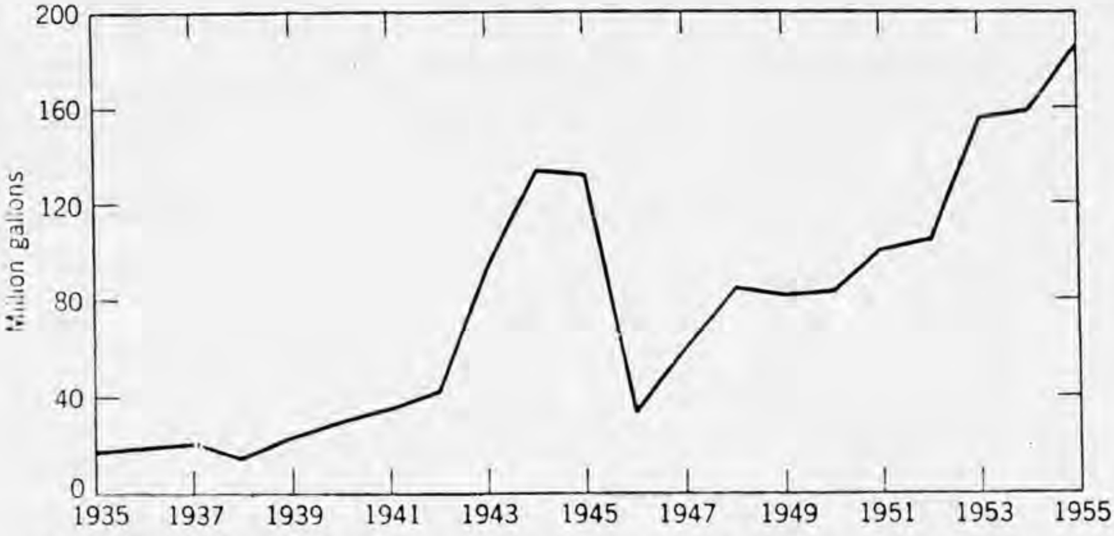
Separation Processes

The aromatic hydrocarbon values of reformates cannot be separated easily from nonaromatics of similar or close boiling points. Accordingly the processes most widely used are extractive distillation, azeotropic distillation, solvent extraction, and selective adsorption. Azeotropic distillation makes use of aqueous methyl ethyl ketone (described previously), nitromethane, methanol, or dioxane. In extractive distillation the usual solvents are phenol, cresols, furfural, aniline, and alkyl phthalates. Selective adsorption processes include the Sun Oil Co.'s Arosorb process using activated alumina as the adsorbent and California Research Corporation's process in which silica gel is used.

Two of the most widely used processes are liquid–liquid extraction processes. One uses liquid sulfur dioxide and the other (the Udex process) makes use of aqueous diethylene glycol (see *Benzene*). A typical separation by the Udex process is as follows:

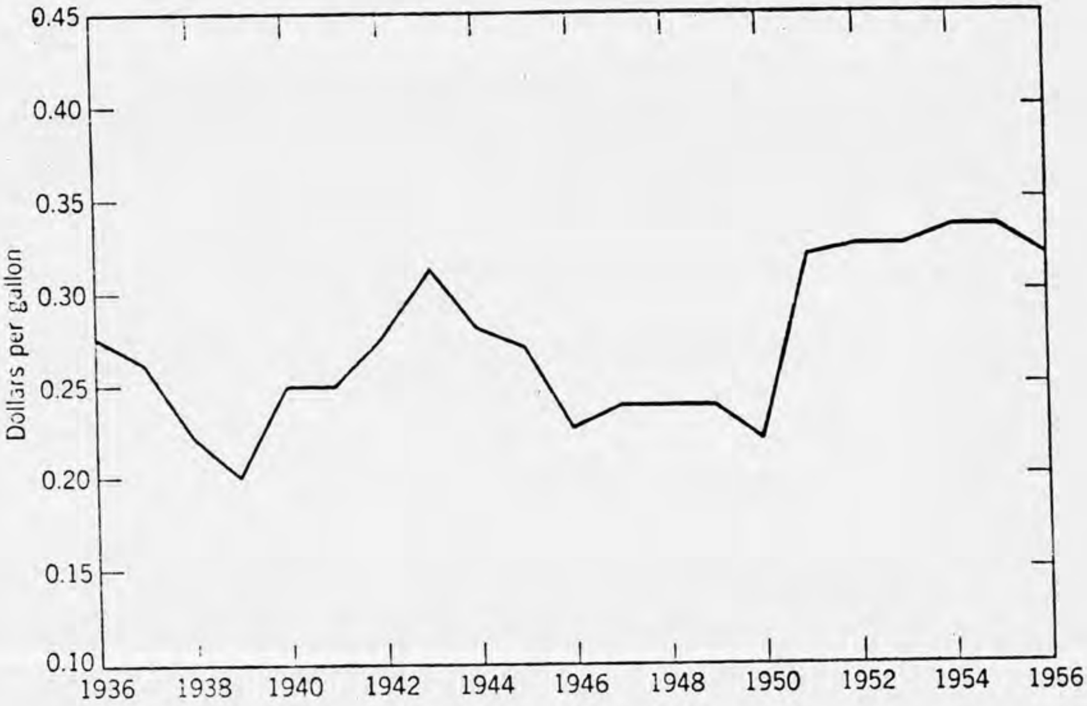
Feed: 51.3 per cent aromatics (7.6 per cent benzene, 21.5 per cent toluene, 21.0 per cent xylene, and 1.2 per cent C_9 aromatics).

Recovery: benzene—99.5 per cent; toluene—98 per cent; xylenes—95 per cent; and C_9 aromatics—80 per cent. Diethylene glycol loss was 0.05 lb per bbl aromatic products. With clay treatment used prior to final distillation (0.24 lb per bbl product), the benzene and toluene recovered were of nitration grade. The xylenes in this particular plant were of industrial grade only.



Production—Toluene (Crude and refined—not including ordnance plants)

	1955 (est.), per cent
Aviation gasoline	47
Solvent	22
Explosives	13
Other	18
	100



Price—Toluene

Miscellaneous

Properties. Colorless, refractory, flammable liquid with a benzenelike odor.

Mol. wt.	92.13	M.P.	−95.1°C
Sp. gr.	0.866 20°C/4	B.P.	110.8°C

Weight per gallon	7.21 lb (20°C)

Soluble in absolute alcohol, ether, acetone, and benzene. Insoluble in water (0.19 per cent at 20°C).

Flash point (closed cup)	40°F
Ignition temperature	1,026°F
Vapor density (air = 1)	3.14
Explosive limits (% by volume in air)	Lower 1.27 Upper 7.0
Maximum allowable concentration (ppm by volume)	200

now, another 100 catalytic reformers could be made available for toluene production with only comparatively slight modifications.

Manufacturers and Plant Sites

Catalytic Reforming Installations Recovering Toluene:
American Oil Co., Texas City, Texas
Ashland Oil and Refining Co., Buffalo, N. Y.
Continental Oil Co., Lake Charles, La.; Ponca City, Okla.
Cosden Petroleum Corp., Big Spring, Texas
Delhi-Taylor Oil Corp., Corpus Christi, Texas
Great Southern Chemical Corp., Corpus Christi, Texas
Humble Oil and Refining Co., Baytown, Texas
Pure Oil Co., Toledo, Ohio
Roosevelt Oil and Refining Co., Mt. Pleasant, Mich.
Shell Oil Co., Wilmington, Calif.; Wood River, Ill.; Houston, Texas
Sinclair Refining Co., Marcus Hook, Pa.
Standard Oil Co. of California, El Segundo, Calif.; Richmond, Calif.
Standard Oil Co. (Indiana), Whiting, Ind.
Sun Oil Co., Marcus Hook, Pa.
Suntide Refining Co., Corpus Christi, Texas

By-Product Toluene (Noncoke Oven):
Dow Chemical Co., Midland, Mich.; Freeport, Texas
Monsanto Chemical Co., Texas City, Texas
Union Carbide Chemicals Co., Institute, W. Va.
Velsicol Corp., Marshall, Ill.

For coke-oven producers, see *Benzene*.

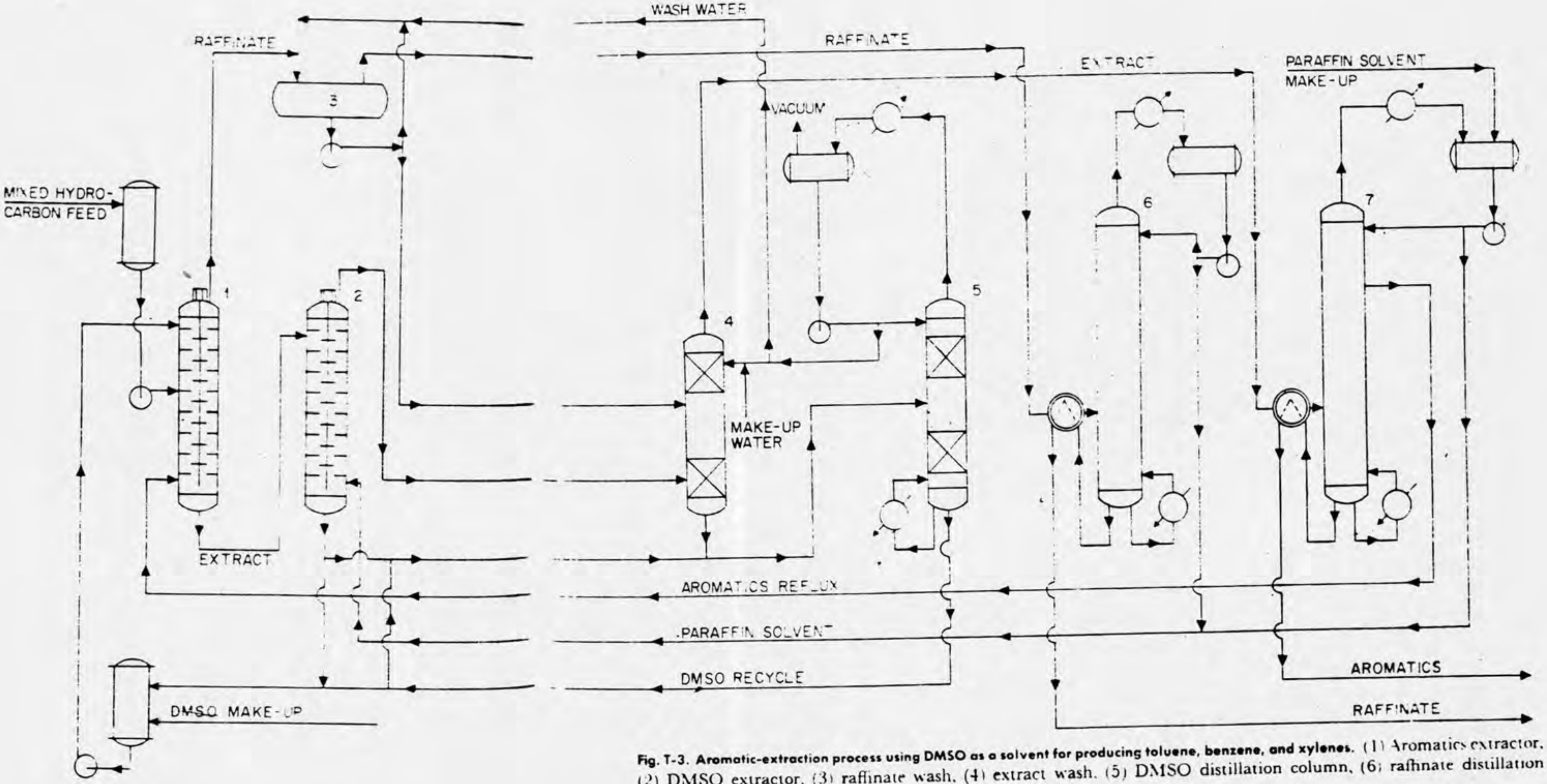
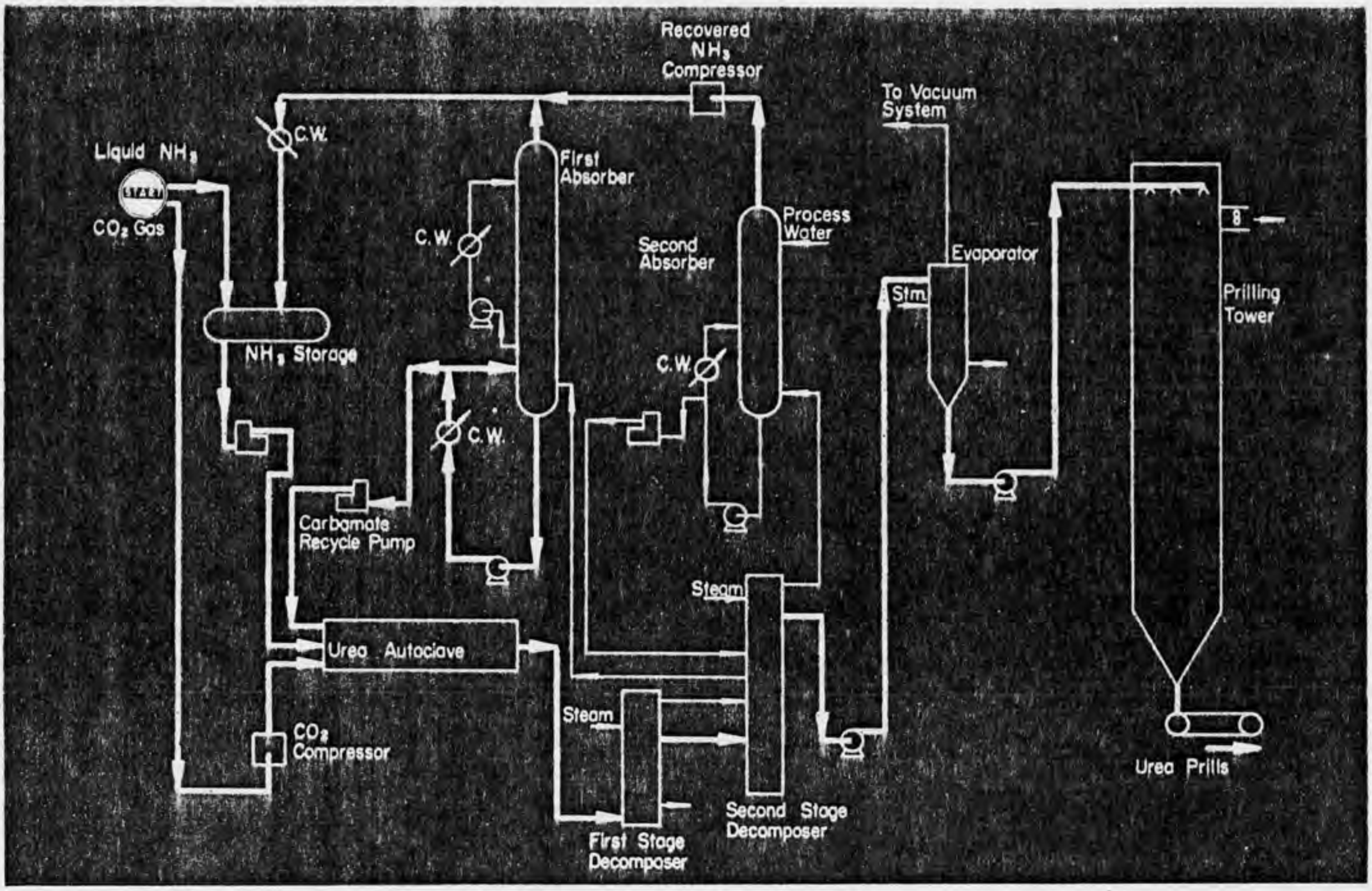


Fig. T-3. Aromatic-extraction process using DMSO as a solvent for producing toluene, benzene, and xylenes. (1) Aromatics extractor, (2) DMSO extractor, (3) raffinate wash, (4) extract wash, (5) DMSO distillation column, (6) raffinate distillation column, (7) aromatics distillation column.



Urea — CHEMICAL CONSTRUCTION CORPORATION

Application: A process for the manufacture of urea.

Charge: Ammonia and carbon dioxide.

Description: Urea is produced by reacting ammonia and carbon dioxide at elevated temperatures and pressures to form ammonium carbamate as an intermediate compound. The carbamate is simultaneously dehydrated to produce urea. The reactions are as follows:

$$2 NH_3 + CO_2 = NH_2COONH_4$$

$$NH_2COONH_4 = NH_2CONH_2 + H_2O$$

Although the first reaction to carbamate is complete at reaction conditions, the second reaction to form urea is incomplete under all practical conditions. In this process, using a ratio of ammonia to CO_2 of about 3.5:1, a 60 percent conversion of ammonium carbamate to urea is achieved.

CO_2 gas at about 2 psig is compressed to 3200 psi in a 4 stage, water cooled, motor driven, reciprocating type compressor. The CO_2 gas undergoes multistage compression with inter and after stage cooling and separation of water and oil.

The compressed CO_2, liquefied NH_3 from the liquid NH_3 feed pump, and recycled ammonium carbamate solution from the carbamate recycle pump are fed to the urea autoclave where they react to form urea, ammonium carbamate and water.

The autoclave effluent is reduced in pressure to about 300 psig and passed into the tube side of the steam-heated first stage decomposer where unconverted ammonia and CO_2, in the form of ammonium carbamate, are partially decomposed and separated from the urea solution along with most of the excess ammonia. The urea solution, containing dissolved ammonia and CO_2, is reduced to 15 psig and passed through the tubes of the second stage decomposer where most of the residual ammonia and CO_2 are driven off. Gases separated in the first stage decomposer are partially absorbed in dilute ammonium carbamate from the 2nd absorber in the shell of the 2nd stage decomposer providing the heat for decomposition. The urea solution is further degassed by heating with steam.

Ammonium carbamate solution and unabsorbed gas from the shell of the 2nd stage decomposer are passed to the first absorber, operating at a pressure of approximately 250 psig. The gases are partially condensed in the lower packed section by contacting them with a circulating carbamate solution. The heat of reaction is removed in an exchanger by cooling water operating under careful automatic control. The upper packed section operates at a lower temperature in order to condense the residual CO_2 as aqueous carbamate. Heat is removed in an exchanger by cooling water. Pure NH_3 gas leaving the top of the first absorber is condensed and delivered to the NH_3 storage tank.

Gas separated from the urea solution in the second stage decomposer, containing NH_3, CO_2 and water vapor, enters the second absorber. The CO_2 is condensed in the packed section of the tower and the resulting carbamate solution is pumped to the shell of the 2nd stage decomposer. A small amount of process water is added to maintain over-all water balance. Pure NH_3 gas leaving the top of the second absorber is compressed, condensed and returned to the NH_3 storage tank.

Urea solution from the second stage decomposer is pumped to the evaporator where it is concentrated to 99.7 percent under vacuum. The concentrated urea solution is pumped through the spray heads in the prilling tower. The streams formed break up into droplets which congeal to form solid spherical granules.

Process Advantages: (1) Maximum conservation of steam and cooling water through unique method of heat exchange using condensing off gases to decompose carbamate;

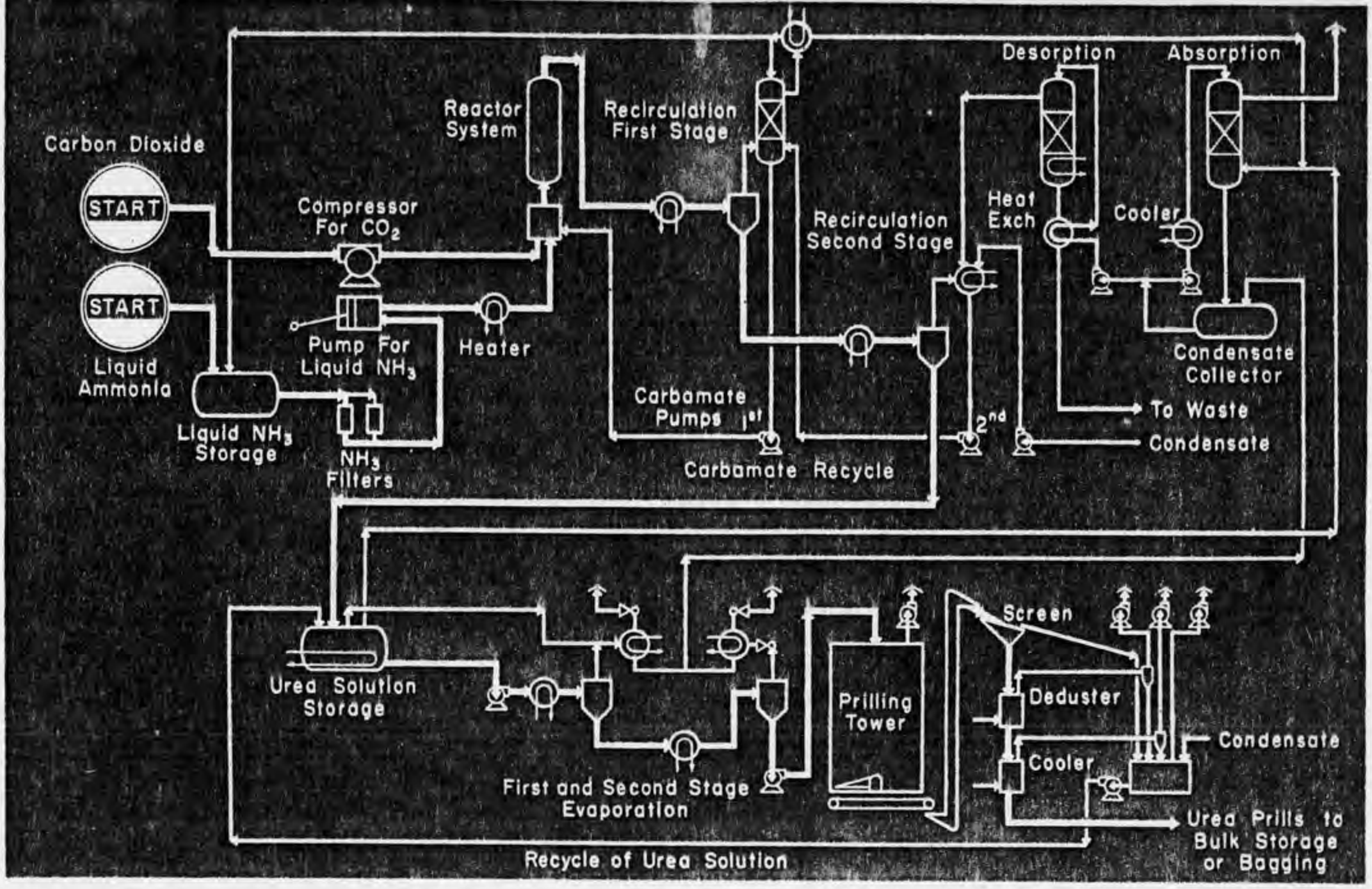
(2) No water from external sources is required for operation of the absorption system. The only water required is a small quantity for maintaining the over-all water balance.

Utilities: The following consumption figures are per short ton of prilled urea in a complete recycle plant.

Electricity	165 KWH
Steam (150 psig saturated)	4,000#
Cooling water (20° F rise)	20,000 gallons

Product: Urea solutions, prills for fertilizer and cattle feed supplement and crystals of high purity for plastics manufacture.

Commercial Installations: Sumitomo Chemical Co., Japan; Nihon Gas Co., Japan; Monsanto Chemical Co., Arkansas; Cyanamid of Canada, Ontario; Co-op. Farm Chem. Association, Kansas; Kobe Steel Co., Pakistan; Fertilizer Corp. of India, Ltd., India.



Urea (DSM)— DUTCH STATE MINES

Application: A process for the manufacture of urea.

Charge: Liquid ammonia and gaseous carbon dioxide.

Products: Urea is produced as aqueous solutions, as prills for fertilizer or cattlefeed-supplement, or as crystals with exceptionally low biuret content for plastics or foliar application.

Description: Three process schemes are available to convert raw materials to products with conversion efficiencies of 45 percent to about 100 percent. Once-through design gives the lower conversions, partial recycle gives intermediate conversions, and total recycle gives the higher conversions. Choice from among these three schemes enables the most economic utilization of ammonia for production of urea or coproduction of urea and ammonium salts such as nitrate or sulfate.

The main difference in three schemes is in the recovery section of the plant. The designs of the reaction section and the finishing section are the same for all schemes. Specifications for raw materials and products are the same for all schemes.

Reactions: Carbon dioxide reacts rapidly and completely with ammonia in the liquid phase to form ammonium carbamate. At reactor operating conditions of about 2,800 psig and 350° F, part of the ammonium carbamate decomposes into urea and water. The extent of decomposition depends mainly upon the amount of ammonia that is present in the mixture. High ammonia concentrations favor decomposition up to about 70 percent. At the stoichiometric ratio of ammonia to carbon dioxide in the reactor mixture, about 45 percent of the carbamate decomposes to urea and water.

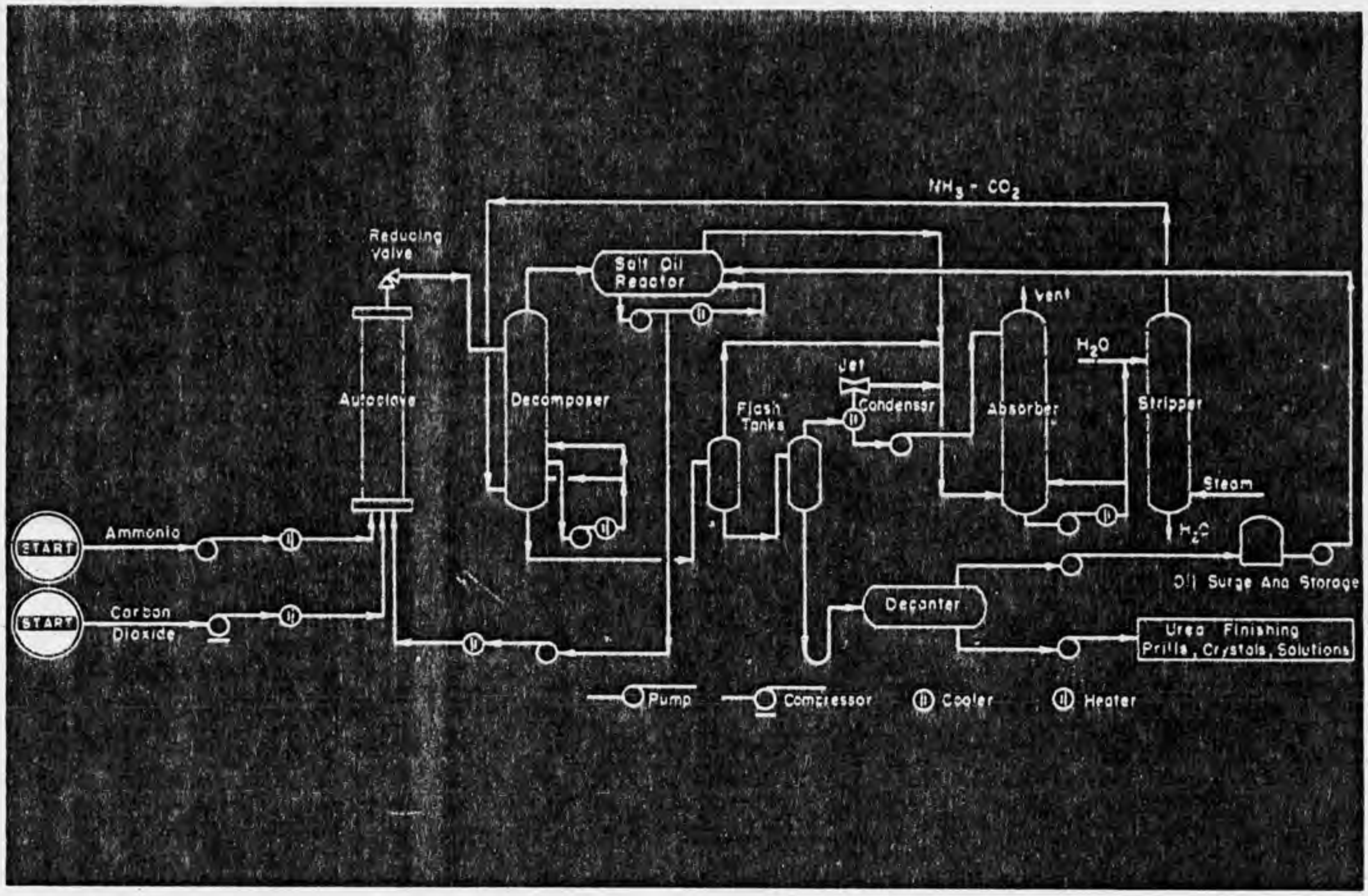
Recovery: In the total recycle process, excess ammonia is flashed from the reactor effluent, condensed and recycled to the reactor. Residual ammonia and carbon dioxide are desorbed from the reactor product and reabsorbed in water in two recirculating stages. At atmospheric pressure, the last traces of ammonia are absorbed in water and concentrated by desorbing under pressure, and then reabsorbing in the second recirculation stage. The carbamate solution is pumped from the second recirculation stage to the first, and finally returned to the reactor. The bottoms product from the ammonia stripper consisting of residual ammonium carbamate, urea, and water, is flashed to near atmospheric pressure in the decomposer to allow further stripping of ammonia and carbon dioxide. The remaining liquid consists of approximately 80 percent urea and 20 percent water.

Finishing: The main separation in the finishing section is between water and urea. Water is evaporated in two stages under progressively higher vacuum. The molten urea product from the second evaporator contains less than 0.3 percent moisture, and the resultant prills contain about 0.6 percent biuret. No further drying of product is necessary. Molten urea is prilled, cooled, and bagged or conveyed to bulk storage. In bulk storage, in a closed shed without air conditioning, the uncoated prilled product does not cake. A modification in the design of the evaporation section gives a prilled product containing less than 0.3 percent biuret.

Yields: For a total recycle process, 100 tons a day of urea computed on 46 percent nitrogen requires about 58 tons of ammonia and 76 tons of carbon dioxide. These quantities allow for nominal losses. For a partial recycle or a once-through plant, the required raw materials are proportional to the conversion efficiency. At 70 percent conversion of ammonia, 100 tons of urea require about 83 tons of makeup ammonia. At 45 percent conversion, makeup ammonia is about 129 tons. For a 100-ton urea plant, offgas ammonia to ammonium salt production is 0 for total recycle, 25 tons for 70 percent conversion, and 71 tons for 45-percent conversion.

Materials: Materials for the reactors, decomposer, evaporators, and other equipment in high temperature service are stainless steels of the 300 Series. Linings of lead, silver, or other precious metals are not used. The use of oxygen under U.S. Patent 2,727,069 controls corrosion at a negligible rate.

Commercial Installations: Seventeen plants are presently in operation or under construction in eleven different countries. Total Capacity is about 5,000 tons per day, or equivalent to 1.7 million tons a year. Plant sizes range from 70 tons a day to about 500 tons a day. The bulk of the production is by the total recycle design. Arthur G. McKee & Co. has designed and is constructing a plant for Solar Nitrogen Chemicals Inc. The first commercial plant producing prills with less than 0.3 percent biuret, is being engineered and designed by C F Braun & Company, and will start production in 1962



Urea— FOSTER WHEELER CORPORATION

Application: A process for the manufacture of urea.

Charge: Ammonia and carbon dioxide.

Products: Prilled solid urea, technical grade crystals, solutions.

Description: Urea synthesis, in the Pechiney-Grace process, essentially is achieved by the non-catalytic reaction of ammonia and carbon dioxide at a pressure of 3000 psig. The outstanding feature of the process is the use of a neutral oil in which unconverted feed gases in the form of an ammonium carbamate slurry is recycled to the reactor. The products of the reaction are highly corrosive and the neutral oil circulating medium minimizes attack of metal parts and also moderates temperature variations in the reactor.

Carbon dioxide compressed to reaction pressure, treated to remove any residual sulfur and oxygen, is preheated and charged to the reactor. Liquid anhydrous ammonia is preheated and also enters the reactor. The recycle stream containing 35-40 percent ammonium carbamate solid in a highly dispersed slurry-in-oil also enters the reactor. The primary reaction is to form ammonium carbamate from ammonia and carbon dioxide.

This is a highly exothermic reaction and supplies the heat for the secondary reaction, the dehydration of carbamate to urea and water, which is endothermic. The oil carrier thus serves as a thermal fly wheel storing the heat liberated by the first reaction and releasing it for the second reaction.

The effluent from the reactor, viz., urea, unreacted carbamate, water and carrier oil flows through a pressure reducing valve from the 3000 psig reactor pressure to approximately 60 psig and into the decomposer where heat is applied to decompose carbamate into ammonia and carbon dioxide.

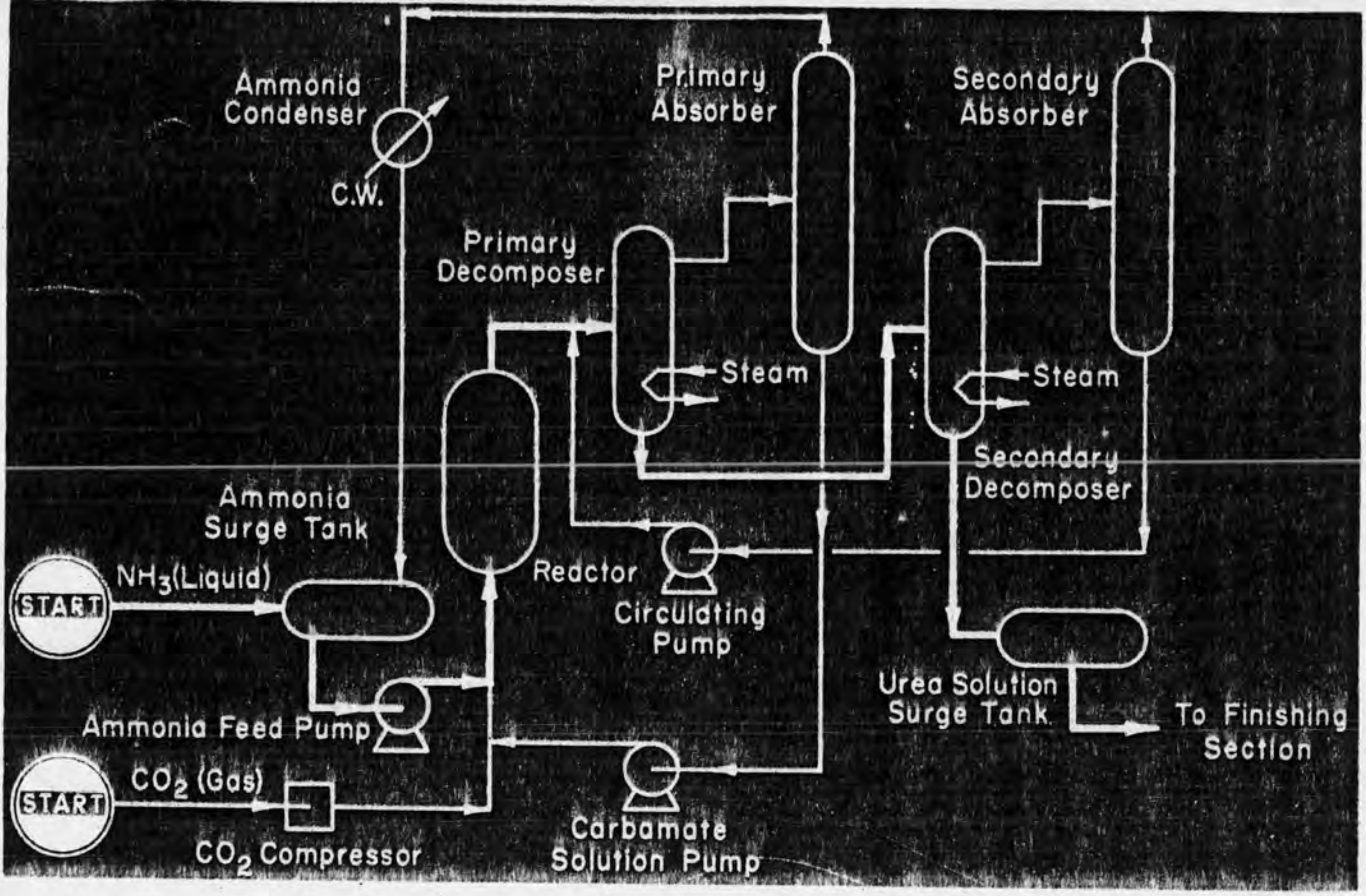
The aqueous urea solution and oil flows through atmospheric and sub-atmospheric flash systems to the decanter where the carrier oil settles as a top layer and is pumped to the oil surge and storage tank. The aqueous urea solution withdrawn from the bottom of the decanter is pumped to the urea finishing sections.

Uncoverted ammonia and carbon dioxide gases, from the decomposer, flow to the salt oil reactor where they combine to form solid ammonium carbamate finely dispersed in the circulating oil. This recycle stream of ammonium carbamate and oil is pumped back to the synthesis autoclave.

Ammonia and carbon dioxide gases released in various parts of the unit flow to an absorption-recovery section and are recycled to the decomposer.

Operating Conditions: Essential operating conditions are given in the above description.

Commercial Installations: Grand River Chemical Division of Deere and Company, Pyor, Okla., Grace Chemical Co., Division of W. R. Grace & Co., Memphis, Tenn. and 330 Ton/day installation by Government of Indonesia.



Urea (Lummus-Lonza)— THE LUMMUS COMPANY

Application: A process for the production of urea.

Charge: Gaseous carbon dioxide and liquid ammonia.

Production: The production of urea in various forms such as prills, crystals, molten mass and solutions of varying concentrations.

Description: The flow diagram illustrates the Lummus-Lonza Urea Process for the production of urea based on the total recycle of unconverted ammonia and carbon dioxide. The process may also be utilized for once-through and partial recycle operation.

Liquid ammonia and gaseous carbon dioxide in a selected ratio together with recycled carbamate are introduced into the reactor. The proper selection of feed ratios and reactor temperatures and pressures permit the synthesis reaction to occur at optimum conditions of conversion. Under these selective conditions approximately 70 percent of the carbon dioxide is reacted and therefore a minimum amount of carbamate need be recycled. The reaction between ammonia and carbon dioxide takes place between 160 to 220° C and 200 to 350 atmosphere. The reaction is exothermal and shown by the following equations:

$$2\,NH_3 + CO_2 \rightarrow NH_4CO_2NH_2$$

$$NH_4CO_2NH_2 \rightarrow (NH_2)_2CO + H_2O$$

The urea synthesis operation is carried out in a minimum sized high pressure vessel. Construction of the reactor is with a commercially available alloy liner.

The effluent from the reactor containing urea, ammonium carbamate and water is reduced to an intermediate pressure in the primary decomposer. Ammonia and carbon dioxide are flashed, separated from the residual liquid and flows to the primary absorber. The liquid flows to a secondary decomposer operating near atmospheric pressure where it is heated to complete the decomposition of carbamate. Ammonia and carbon dioxide from this decomposition step are absorbed in the secondary absorber.

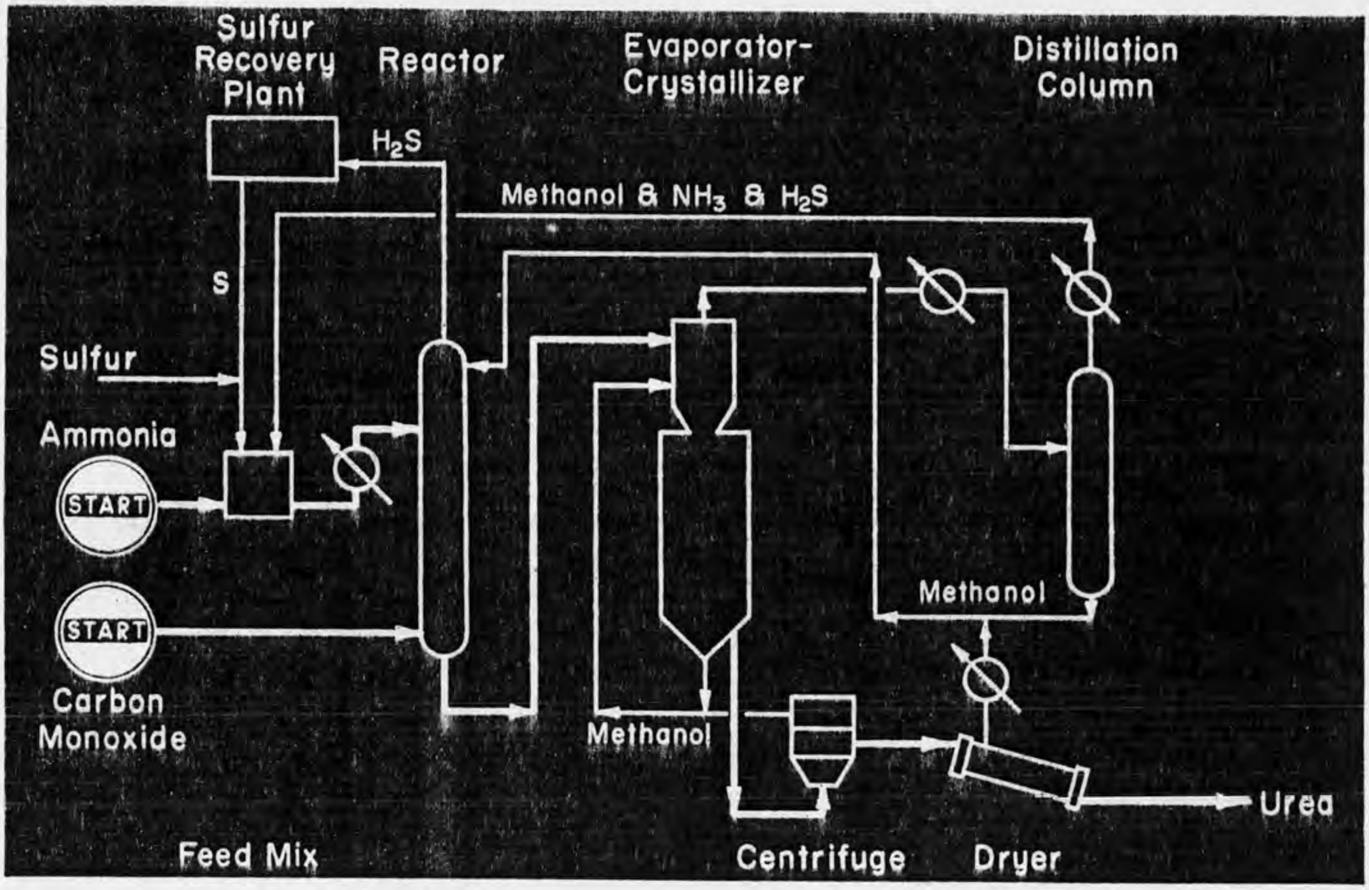
The urea solution from the secondary decomposer flows to a surge tank to be pumped to the finishing section for evaporation and solidification into desirable product form.

The gases from the first decomposer are recovered in the primary absorber in an aqueous solution. The tower is designed to concentrate most of the ammonia which leaves overhead and after condensation is combined with fresh ammonia feed. The separation takes place at a pressure which permits the use of cooling water for the condensation of ammonia and eliminates the need for refrigeration. The carbamate solution leaves the bottom of the tower and is recycled back to the reactor.

The gases from the secondary decomposer are recovered in the secondary absorber as an aqueous solution. This solution is returned to the primary decomposer.

The use of a water solution in the recovery of ammonia and carbon dioxide provides a recycle stream free of any contaminating material not previously fed to the system. Carbon dioxide pressure costs are reduced as the carbon dioxide is recycled as a liquid instead of as a gas. The recovery and recycle system described here permits 99 percent conversion of both the ammonia and carbon dioxide fed.

Commercial Installations: Fertilizantes del Bajio, Salamanca, Mexico (under construction).



Urea — MONSANTO CHEMICAL COMPANY

Application: A new synthesis of urea under mild conditions of pressure and temperature.

Charge: Gaseous ammonia, sulfur, carbon monoxide, solvent methanol and hydrogen sulfide.

Products: Crystalline urea of 99.6 percent purity and gaseous hydrogen sulfide.

Description: The Lion Oil Company, a division of Monsanto Chemical Company has developed a pilot plant process for the production of urea from ammonia, sulfur and carbon monoxide. In contrast to the conventional urea processes, the pressures are low, ranging from 200-300 psig, while the temperature is usually held at 212° F. The stoichiometric equation is

$$CO + 2\,NH_3 + S \rightarrow NH_2CONH_2 + H_2S$$

The sulfur is recovered from the hydrogen sulfide by one of the conventional processes and recycled.

The reaction is carried out in the presence of a solvent such as methanol. It has been found convenient to make up a feed solution by dissolving the sulfur in ammoniacal methanol and adding some hydrogen sulfide so as to get a more concentrated sulfur solution. The hydrogen sulfide does not take part in the reaction. The sulfur may be best handled in the melted state.

The reaction is conducted in a specially designed sieve-plate reactor made of stainless steel. It is operated in a counter-current manner.

Feed: Carbon Monoxide: Although a feed gas containing lower concentrations of carbon monoxide may be used, gases having 85 to 95 percent are preferred. Small amounts of inerts such as nitrogen do not interfere. Iron carbonyl and carbon dioxide are undesirable.

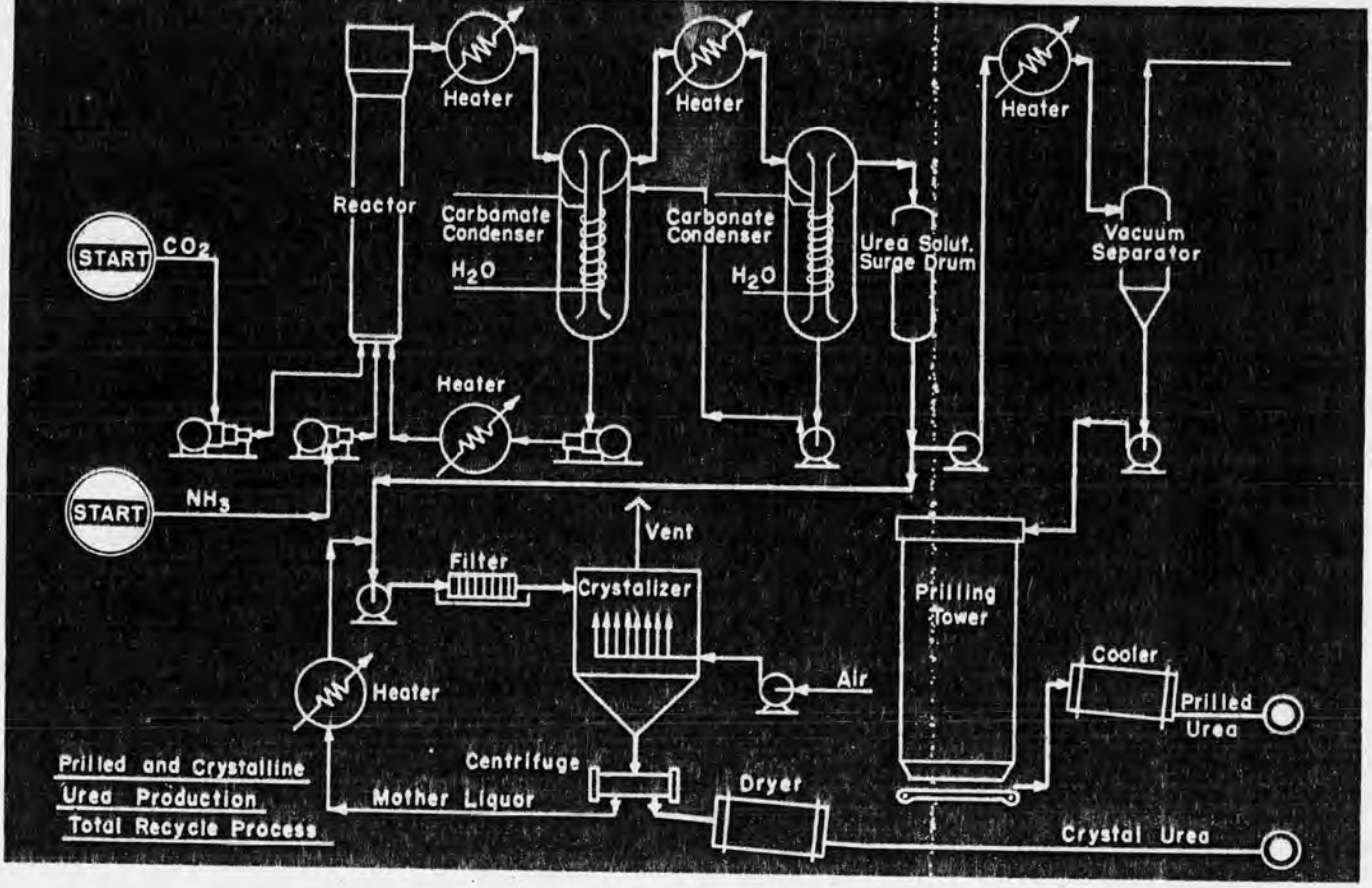
Sulfur and Ammonia: A feed solution having the following composition gives satisfactory results:

NH_3 25 percent, H_2S 4 percent, S 20 percent, and methanol 51 percent.

This is fed at a temperature of 136° F to the reactor by a pump made of nickel-molybdenum alloy, while the carbon monoxide is injected near the bottom at a pressure of 250 psig. The temperature is held at 212° F in the reaction section. The urea product containing excess ammonia and some hydrogen sulfide passes to the evaporator-crystallizer where the methanol, ammonia and hydrogen sulfide are removed overhead. The distillation column separates pure methanol which recirculates to a recovery section in the reactor preventing losses of ammonia from the reactor. The urea crystals from the crystallizer are centrifuged and dried to recover methanol. The product contains more than 99 percent urea.

Yields: Conversions per pass of sulfur to urea approach 100 percent, for ammonia usually 85-95 percent and for carbon monoxide 60-75 percent. Ultimate yields based on ammonia and sulfur are better than 99 percent under good operating conditions. The carbon monoxide is usually not recycled due to the presence of other impurities.

References: U.S. Patents 2,857,431; 2,857,430; British Patent 818,864.



Prilled and Crystalline Urea Production Total Recycle Process

Urea — MONTECATINI

Application: A process for the manufacture of synthetic urea.

Charge: Liquid ammonia and gaseous carbon dioxide free from sulfur compounds and having, at least, a 97 percent purity.

Product: Fertilizer grade urea in spherical granules or technical grade urea in crystals.

Description: Ammonia and carbon dioxide are pressurized into the reactor where, at a pressure of 2700 psig and at a temperature of 360° F. they react forming ammonium carbamate, which in turn is converted into urea plus water.

It is necessary to maintain in the reactor, because of its favorable influence upon the conversion of carbamate into urea, an excess of ammonia in respect of the stoichiometric value. In fact, the extent of urea formation is limited by equilibrium considerations so that in the reactor effluent there are, in addition to urea and water, some carbamate and free ammonia. The last two components must be separated from the urea solution.

The reactor effluent is first expanded to 300 psig. During this operation a gaseous mixture of NH_3 and CO_2 is freed and after condensation is recycled to the reactor. By means of this liquid recycle it is possible to return to the reactor a large portion of unreacted ammonia and carbon dioxide as an aqueous solution. The remaining NH_3 and CO_2 are vaporized from the urea solution by means of a second expansion step to about atmospheric pressure.

The gaseous mixture which is thus made available is condensed and sent back to the cycle by introducing it into the carbamate condenser.

This method of recycling NH_3 and CO_2 as an aqueous solution represents a substantial improvement over other methods which recover the same components in the gaseous state and recycle them to the reactor after compression. In this way, remarkable savings can be achieved in electric power consumption and greater simplicity in the construction design of the plant.

The urea solution, free from NH_3 and CO_2 is further concentrated in a vacuum concentrator and is then pumped to sprayers in a prilling tower. Here the solution is subdivided in the form of small droplets which, falling vertically in an air stream flowing upwards, are solidified, forming prills.

Prilled urea is particularly suitable for agricultural uses. The crystalline product having a higher purity is preferred for technical uses and is obtained from the concentrated urea solution by means of crystallization and centrifugation.

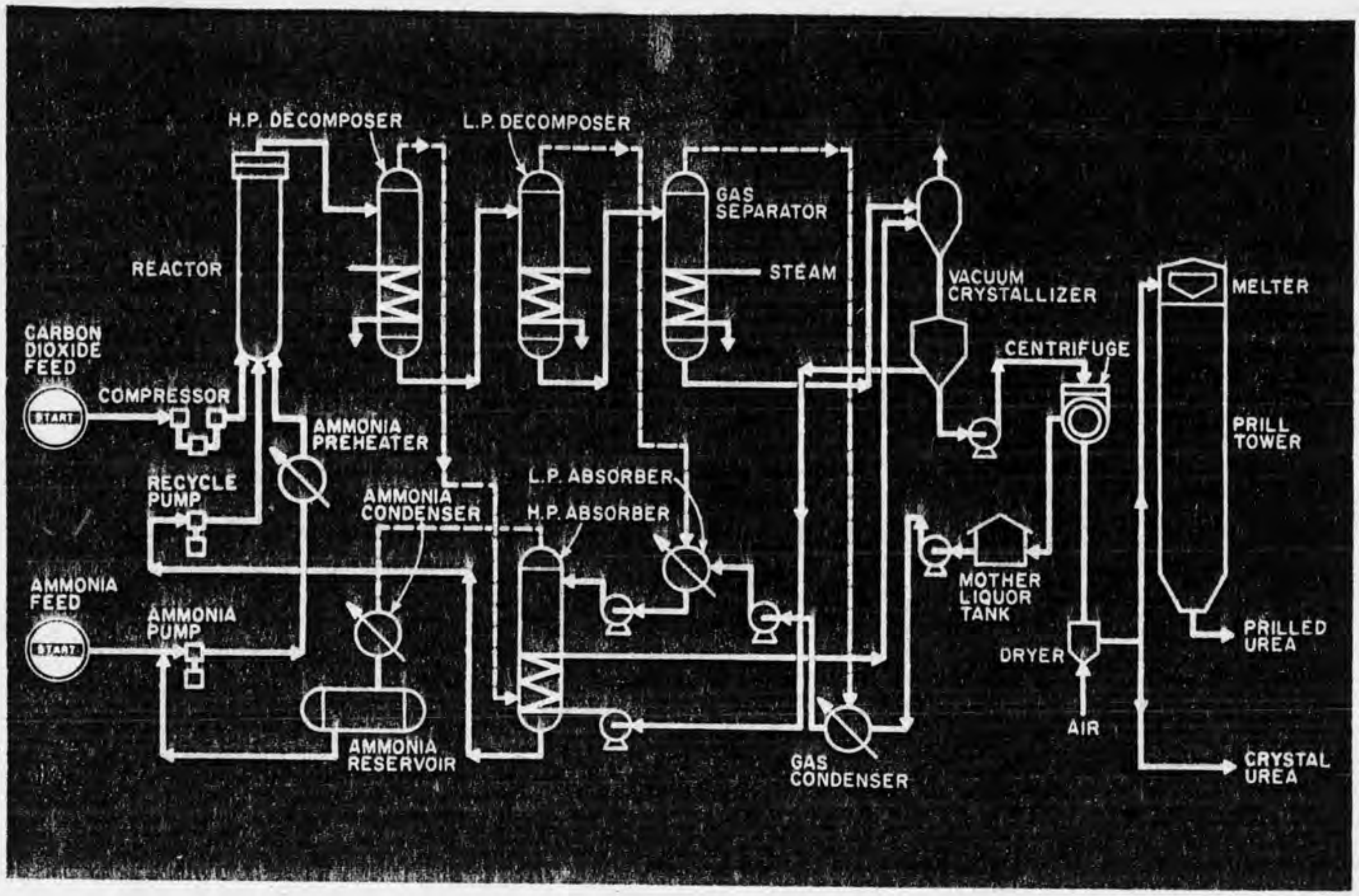
Operating Conditions: As already mentioned, the reactor pressure is from 2500 to 2800 psig and a temperature of 350° to 360° F. is maintained.

Yields: Conversion of ammonia and carbon dioxide into urea is total. Raw material requirements per ton of urea (46 percent N_2) are 0.600 ton of NH_3 and 0.770 ton of CO_2.

Corrosion Problems: Mild and carefully controlled reaction conditions are used in this new process to eliminate corrosion, a major problem in urea plants. By careful selection of composition and temperature in the reactor, it is possible to use with excellent results, commercially available stainless steel for reactor lining and for other surfaces exposed to corrosion.

Commercial Installations: 35 commercial plants are presently in operation or under construction all over the world, with a total annual capacity of 1 million metric tons of urea.

U.S. Plants in Operation: Shell Chemical Corp., Ventura, Calif.; Spencer Chemical Co., Vicksburg, Miss.; Spencer Chem. Co., Henderson, Ky.; SunOlin Chem. Corp., North Claymont, Del. Under construction: Armour & Co., Cherokee, Ala.



Urea (Mitsui Toatsu Process)— THE M. W. KELLOGG CO.

Application: A process for the manufacture of urea from liquid ammonia and gaseous carbon dioxide.

Description: Four basic processes, designed to meet a wide range of urea production needs, are offered. Each arrangement is based on the reaction of excess ammonia with carbon dioxide at about 3,500 psig at 365° F to form a mixture of urea and water, ammonium carbamate and surplus ammonia. The high carbon dioxide-to-urea conversion achieved reduces the amount of ammonium carbamate to be decomposed.

Once-Through Process. The reaction products are fed first into a high and then to a low pressure decomposer where NH_3 and CO_2 are separated. Conversion of CO_2 is about 73% and that of NH_3, about 32%. Ammonia in the off-gas can be sent to a fertilizer byproduct plant.

Partial Ammonia Recycle: Over-all conversion of NH_3 is increased to as much as 56% with the addition of an NH_3 separator to the basic once-through process. In this case, the reactor effluent flows through the let-down valve into the separator where most of the excess NH_3 is recovered and recirculated back to the synthesis reactor.

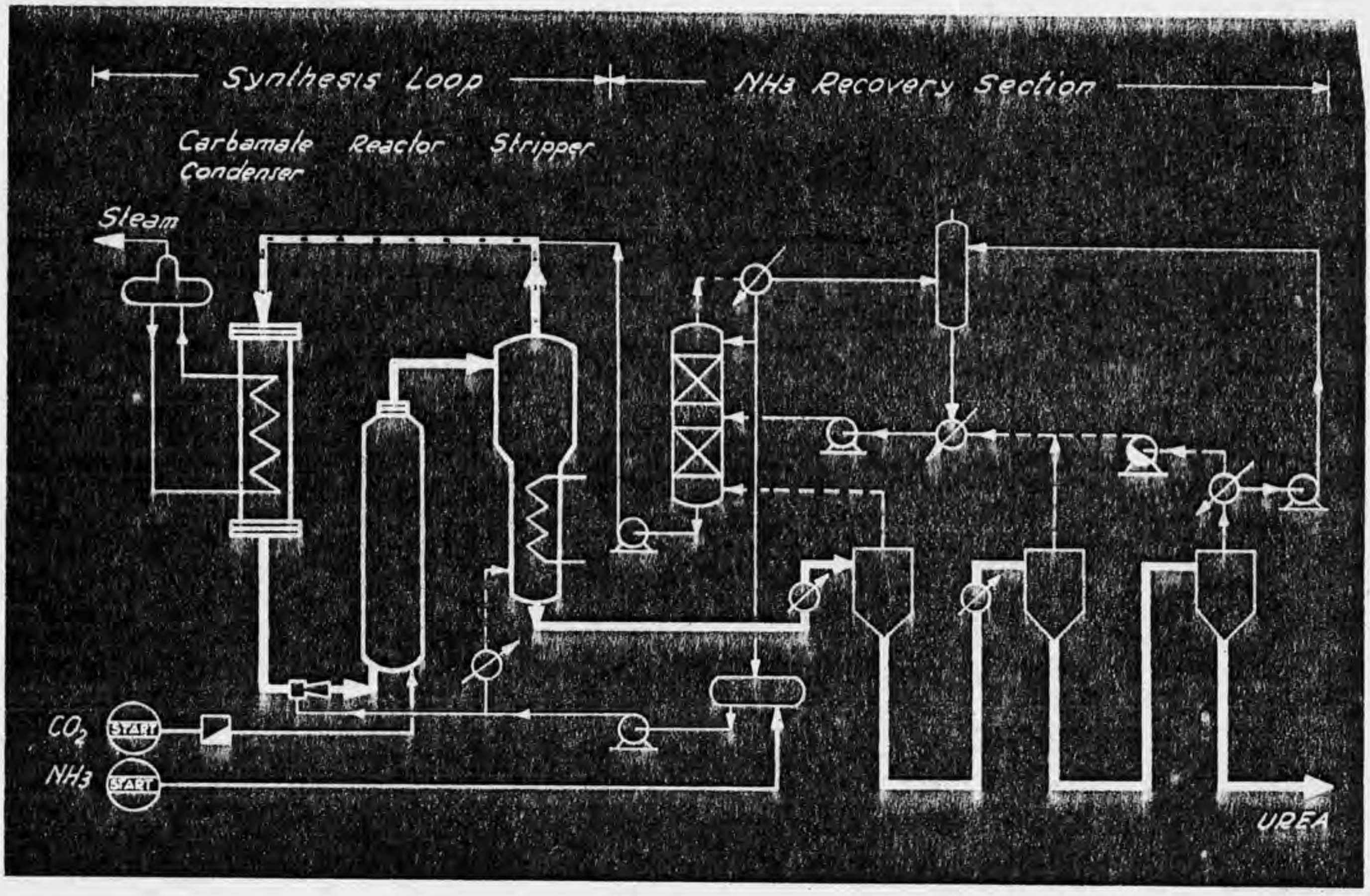
Partial Solution Recycle: NH_3 and CO_2 from a high pressure decomposer, together with the NH_3 gas from the NH_3 separator, are sent to a high pressure absorber and the resulting aqueous ammonium carbamate solution is recirculated back to the synthesis reactor. Overhead gas from the absorber is pure NH_3 gas which is also returned to urea synthesis in the partial NH_3 recycle process. Conversion of feed is increased to 80% for CO_2 and 70% for NH_3.

Total Solution Recycle: CO_2, recovered carbamate solution, and liquid NH_3 are first reacted and then sent to a high pressure decomposer. The untreated carbamate is decomposed, and the urea solution leaving the tower contains a minimum of unseparated NH_3 and CO_2. The solution is further treated in the low pressure decomposer and gas separator where the small remaining quantities of NH_3 and CO_2 are perfectly separated from the urea solution. All NH_3 feed and CO_2 are converted into urea in this process.

Commercial Installation: 9,300,000 mt/y with 53 plants in 20 countries; the total capacity of those urea plants using Mitsui Toatsu urea process is reaching one-third of the world urea production.

Raw Material and Utilities Requirements Units Per Short Ton of Uncoated Prilled Urea

				TOTAL RECYCLE		
Urea Process	Once Through	Partial Ammonia Recycle	Partial Solution Recycle	Vacuum Crystallization	Atmospheric Crystallization	Direct Prilling
Liquid Ammonia						
In urea and losses, tons	0.570	0.572	0.574	0.575	0.580	0.575
In off gases, tons	1.216	0.571	0.187			
Fresh feed, tons	1.786	1.146	0.761	0.575	0.580	0.575
Gaseous Carbon Dioxide						
In urea and losses, tons	0.749	0.749	0.760	0.768	0.773	0.768
In off gases, tons	0.270	0.270	0.066			
Fresh feed, tons	1.019	1.019	0.826	0.768	0.773	0.768
Electric Power, kwh	182	182	161	146	155	146
Steam, lbs.	2,000	2,200	2,700	2,400	2,800	2,900



Urea — SNAM PROGETTI

Application: A process for the manufacture of urea from liquid ammonia and carbon dioxide.

Description: Ammonia and carbon dioxide react at 150 kg/sq. cm to yield urea and ammonium carbamate. The carbamate content of the reactor effluent is completely decomposed and separated in a single-stage high pressure carbamate recycle operating at reactor pressure. Gravity is the motive power to return the high pressure carbamate solution to the reactor in the synthesis loop avoiding the use of a pump.

Head is added to gravity by means of an ejector (feed ammonia is the driving medium) to obtain steady operating conditions even with the carbamate condenser installed at ground level. This layout is essential for large plants.

Part of the feed ammonia is sent to carbamate decomposer (stripper) as stripping medium to obtain complete disassociation of carbamate. The overhead vapors pass to the high pressure carbamate condenser, in which the condensation permits the production of steam.

Operating at 185° C and NH_3/CO_2 feed mole ratio of 3.5:1 in the reactor and at 200° C in the carbamate decomposer, the CO_2 total conversion in the synthesis loop exceeds 95%.

NH_3 Recovery: The urea solution leaving the carbonate decomposer is expanded and heated in two stages at successively low pressure where residual ammonia and the CO_2 traces are flashed off.

The bulk of NH_3 is sent to a recovery column and recycled as anhydrous NH_3 to the reactor; the small amount of CO_2 is recycled as ammonium carbonate solution to carbamate condenser.

Finishing: Production of 0.6% biuret prills, suitable for most fertilizer applications, involves vacuum concentration of the 75% urea solution coming from the NH_3 recovery section and prilling. Production of low biuret prills (0.25%) involves: vacuum crystallization, separation of mother liquor and crystals in a centrifuge, crystals drying, melting and prilling. Part of the mother liquor, rich in biuret, is fed into the stripper where the high ammonia concentration transforms it into urea.

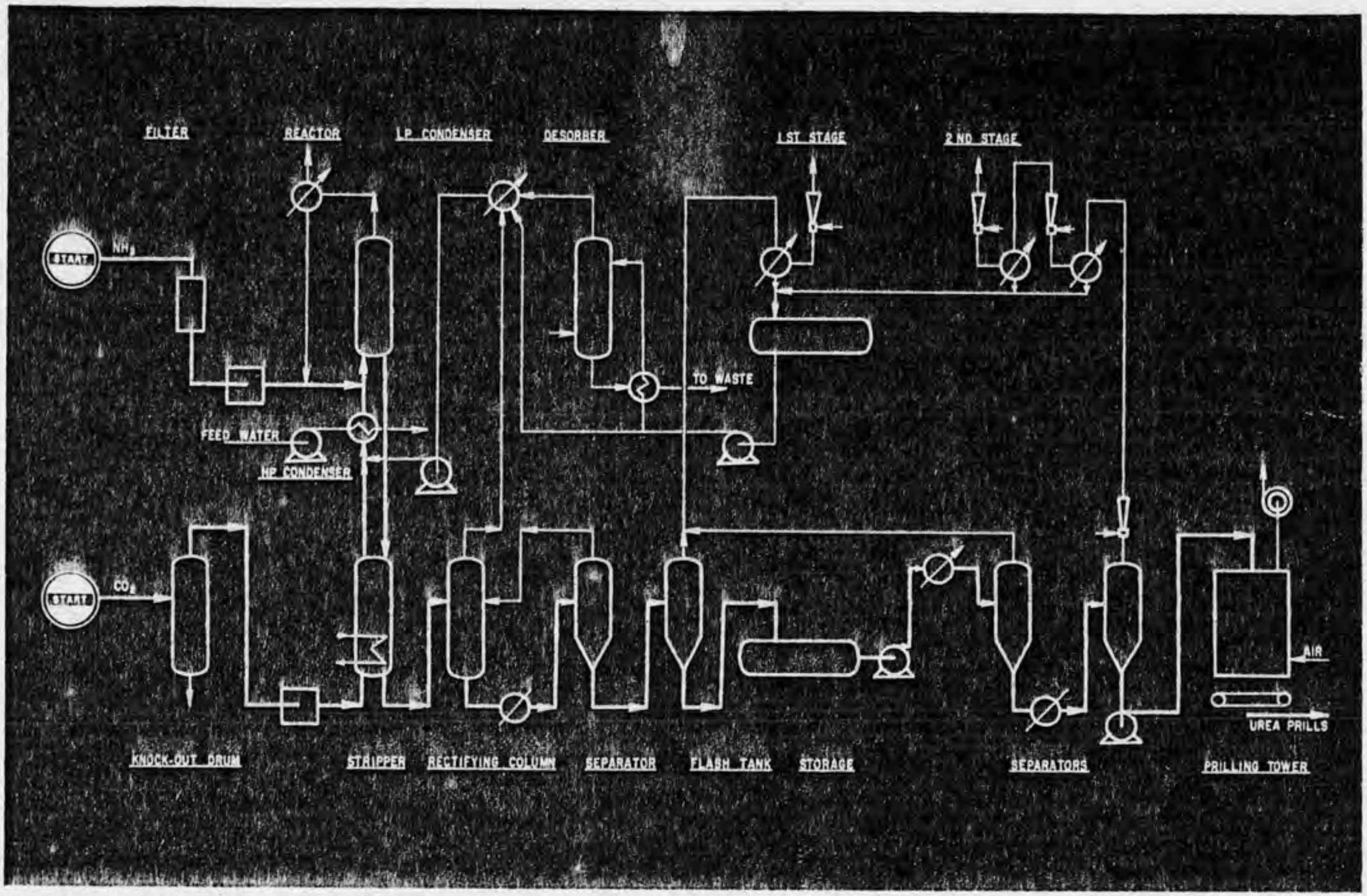
Corrosion Problems: The synthesis loop operates at moderate temperatures and pressures, with a high excess of NH_3. So corrosion problems are completely eliminated.

Yields: Over-all conversion of NH_3 and CO_2 into urea is 99.5%.

Utilities required per metric ton of prilled urea:

	via concentration	via crystallization
Steam (25 kg/sq. cm g) metric tons	0.9	1.0
Electric power, kwh	120	130
Cooling water (25° C) cu. meters	65	65

Commercial Installations: One commercial plant has been in operation since 1966; five plants with capacity ranging from 300 mt/d to 900 mt/d are now under construction. The process has been licensed to C&I Girdler, Fluor, Pintsch Bamag, and Woodall-Duckham.



Urea (DSM) — STAMICARBON N.V.

Application: A process for the manufacture of urea with ammonia efficiencies of from 45 to about 100% from NH_3 and CO_2.

Description: In the reactor, operating at 130-150 atm.g. with temperatures of 170-190° C and at over-all NH_3/CO_2 ratios of 2.8-2.9, a part of the incoming NH_3 and CO_2 is reacted into ammonium carbamate, which, together with incoming ammonium carbamate already formed in the high pressure (H.P.) condenser, is partly decomposed into urea and water. Reactor effluent is stripped with fresh CO_2 at synthesis pressure in a specially developed stripper with external heat supply.

In the stripper the bulk of the non-converted carbamate is decomposed and also the bulk of the excess ammonia is vaporized. The resulting gases, NH_3 and CO_2, are recycled to the H.P. condenser, where the main part of these gases is already reacted into ammonium carbamate. This carbamate and the non-condensed gas, are, together with fresh liquid NH_3, fed to the reactor where the above-mentioned reactions take place.

Recovery: Stripped urea solution, still containing minor quantities of ammonia and carbon dioxide, is expanded and heated at a pressure of between 2 and 5 atm.g. Resulting gases are removed and condensed in a low pressure carbamate condenser.

Finishing: For a final prilled product containing 0.7-0.8 % biuret, water is evaporated in two stages under progressively higher vacuum. For a final prilled product containing 0.2-0.25 % biuret, the urea is crystallized under vacuum. The resulting crystals are dried and molten. In both cases the resulting molten urea, containing about 0.2% moisture, is prilled. No further product drying is necessary.

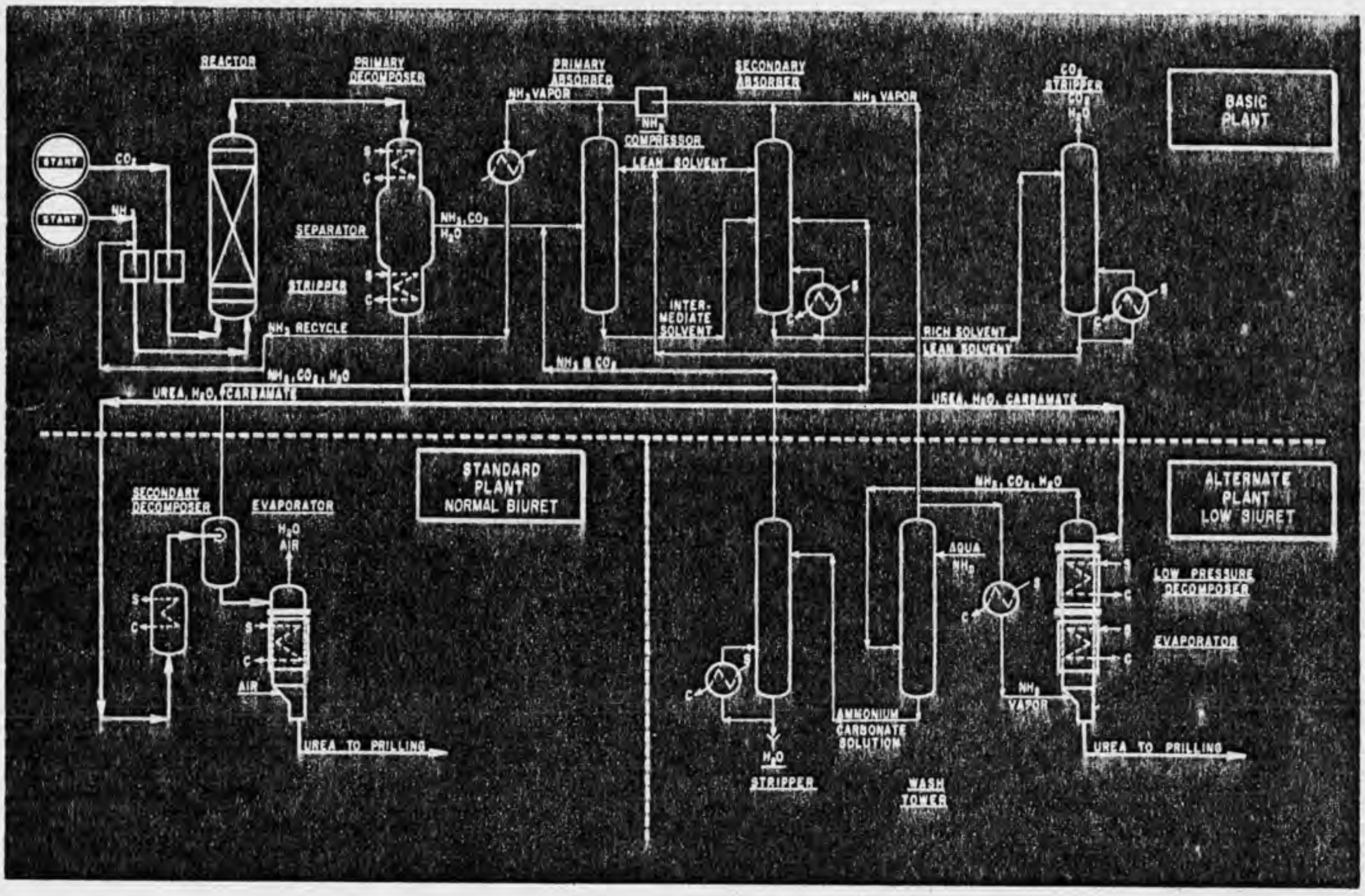
Materials: Materials for reactor, stripper, condensers, decomposers, evaporators and other equipment in high temperature service are stainless steels of the 300 series.

Commercial Installations: 60 plants and 10 extensions are in operation or under construction in 29 countries, among them two 1,400-metric-ton-per-day plants. Total capacity amounts to about 25,900 tons per day.

Typical Consumptions: For a total recycle urea plant (stripping process) producing fertilizer grade prills, typical consumptions are:

	biuret content	
	0.7-0.8 %	0.2-0.25 %
kgs CO_2	755	755
kgs NH_3	570	570
kwh power	125	135
kg steam (25 atm.g.)	1000	1050
m³ cooling water (Δt = 11° C)	55	55
production of 3 atm.g. saturated steam	150-200	350-400

References: Chem. Eng. Sc: Chem. Reaction Engineering symposium, Brussels, Sept. 11, 1968 (to be published).



Urea (CPI-Allied Chemical)— VULCAN-CINCINNATI, INC.

Application: A process for the manufacture of urea from ammonia and carbon dioxide.

Description: Urea synthesis is based on the exothermic reaction of NH_3 and CO_2 to form ammonium carbamate which simultaneously undergoes a partial dehydration to urea.

CO_2, make-up NH_3 and recycle NH_3 enter the zirconium-lined reactor, which is operated above 400° F and 5,000 psi. The NH_3 to CO_2 ratio is kept between 4:1 and 5:1. The CO_2 conversion to urea is about 85%. The urea melt and unconverted carbamate pass into the primary decomposer, a cocurrent heat exchanger designed for high-velocity flow.

Decomposition products (NH_3 and CO_2) and water vapor are flashed off and pass as overhead from the separator. The urea solution passes into a small, steam-heated, falling-film counter-current stripper, where NH_3 still present in the solution is further removed and flows back into the separator.

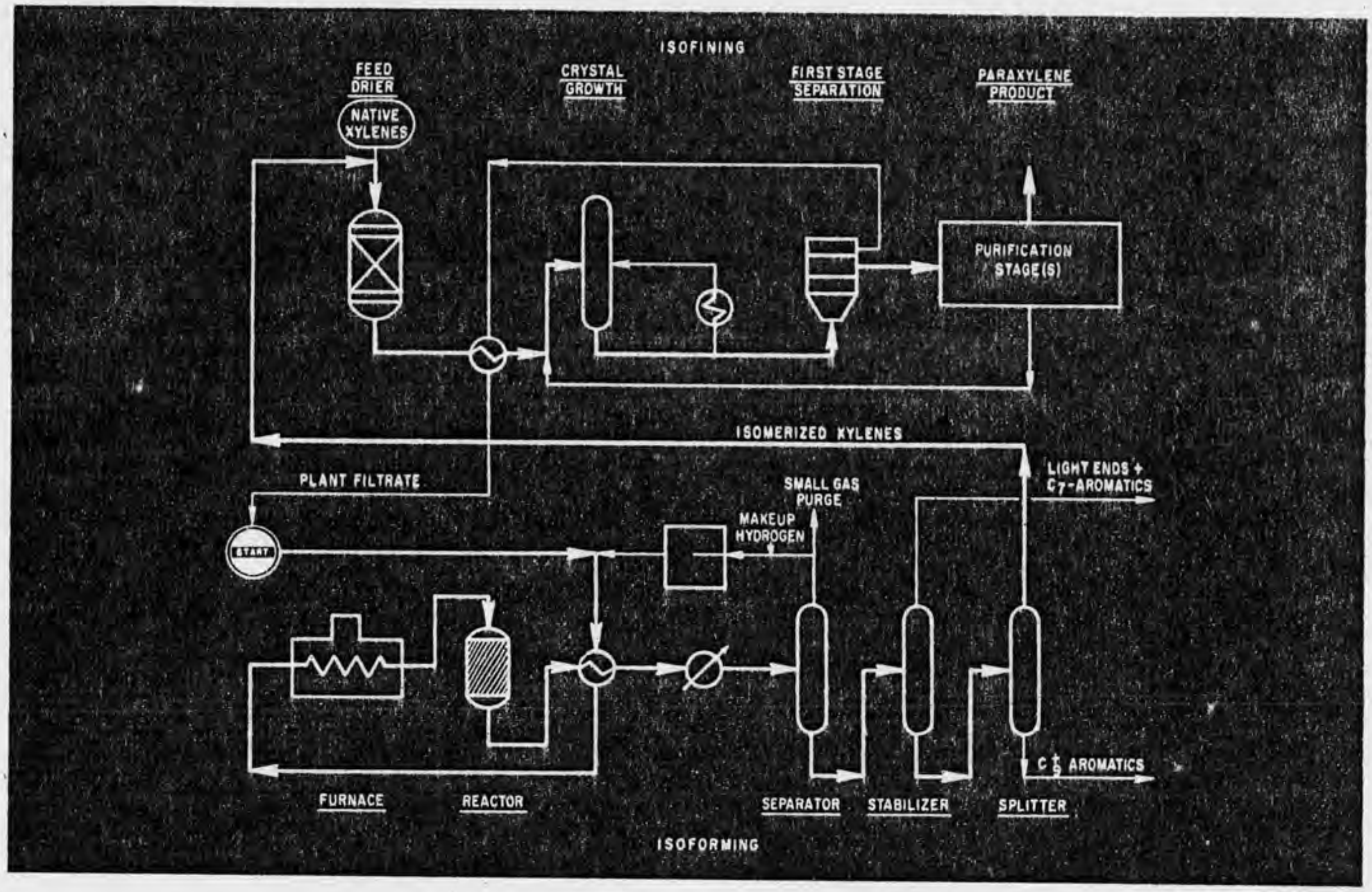
At the operating conditions of the primary decomposer, about 90% of the carbamate disassociates into CO_2 and NH_3 so that the final CO_2 content (as carbamate) in the urea stream going to the secondary decomposer is quite low—about 1.5% of the original CO_2 fed to the reactor. Since the decomposition of carbamate takes place in the presence of the excess ammonia in the reactor off-gas, the tendency for biuret formation is minimal.

For **normal biuret** content urea product, the aqueous urea now passes into the secondary decomposer, where disassociation of any remaining carbamate occurs at about atmospheric pressure. Then, while the overhead streams from the primary and secondary decomposers go to the absorption unit, the urea solution is sent to an evaporator. This evaporator is a steam-jacketed, centrifugal, thin-film unit equipped with rotating discs and baffles. A stripping stream of air flows counter-current to the downward flow of urea solution. Dehydration is carried out rapidly (contact time is a few seconds) and at a low temperature to minimize biuret formation. The product's biuret content is usually below 0.7% by weight, with about 0.20% water. The urea melt effluent from the evaporator is then ready for prilling.

For **low biuret** content urea product, the urea melt from the primary decomposer passes into a low pressure decomposer and evaporator system. A stripping stream of NH_3 vapor instead of air moves counter-current to the downward flow of urea melt. Final decomposition of carbamate and dehydration are carried out under an NH_3 atmosphere, rapidly and at a low temperature to prevent any biuret formation in this step. The product's biuret content is usually below 0.35% by weight, with about 0.20% water. The urea melt effluent from this system is then ready for prilling.

The products of disassociation (NH_3 and CO_2) from the primary and secondary decomposer, or low pressure decomposer and evaporator system, are treated with monoethanolamine solvent which selectively absorbs all of the CO_2, leaving pure NH_3 that is returned to the urea reactor.

Commercial Installations: Twenty-three plants are in operation embodying design features of the CPI-Allied Chemical urea process.



p-Xylene (Isofining and Isoforming Processes)

— ESSO RESEARCH AND ENGINEERING CO.

Applications:

Isofining is a staged counter current crystallization process for the separation and purification of paraxylene from a mixture of its isomers. **Isoforming** is a fixed bed catalytic hydroisomerization process to isomerize an isomer depleted xylene stream back to a near-equilibrium mixture.

Process Description: **Isofining**—Xylenes feed is dried, prechilled, and sent to the crystallization section for growing crude paraxylene crystals under controlled conditions via indirect refrigeration. There is no contamination by direct refrigerants or additives. The crude paraxylene crystals are separated from the mother liquor by centrifugation. No further refrigeration is required after this point. Before leaving the crystallization unit, filtrate from this centrifugation is used to precool the feed.

The relatively impure paraxylene separated in the first centrifugation is then purified to the desired level in one or more stages of partial remelting and recrystallization, and centrifugation, by contacting it with higher purity recycle filtrate from succeeding stage(s). This countercurrent system, which operates similar to a fractionator with reflux, gives the desired flexibility in product purity, feed composition changes, and capacity while minimizing the refrigeration load.

Isoforming—A C_8 aromatics feedstock, which has been depleted of one or more of the xylene isomers, is mixed with a hydrogen-rich stream and heated by exchange and a furnace to reaction temperature. The mixture is charged to a fixed bed reactor containing the unique Isoforming catalyst, which promotes the desired isomerization back to a near-equilibrium mixture. The reactor effluent is cooled and the near-equilibrium xylenes stream is separated from the hydrogen-rich gas. After taking a small purge, the separated gas is recycled to the reactor along with a small amount of makeup hydrogen.

The cooled liquid effluent is then charged to fractionators where heart-cut isomerized xylenes are separated from the small amounts of C_7 and lighter and the C_9 and heavier aromatics byproducts produced in the Isoforming reaction. The heart-cut is recycled to the xylene isomer removal process(es).

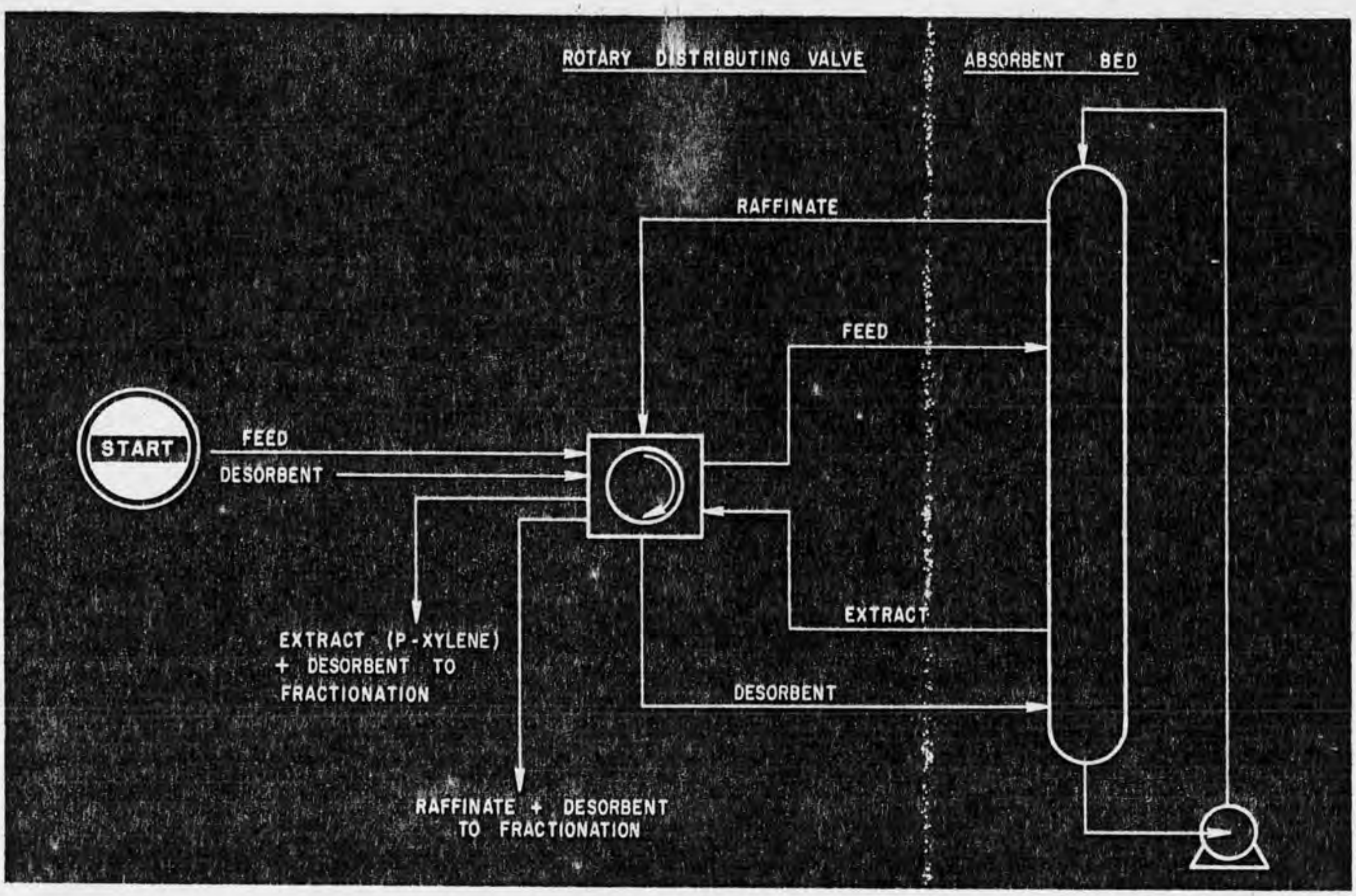
Isoforming operating conditions range from 600-850° F, 200-500 psig, liquid hourly space velocity of 0.5 to 3.0, hydrogen to oil ratio of 3/1 to 8/1, and hydrogen purity (50 to 85+%). Such flexibility gives important economic advantages in tailoring the process to specific situations.

Economics: Prime contract onsite investments for **Isofining** normally vary from 2¢ to 3.5¢ per lb/Y of design capacity for 99.5% *p*-xylene, depending on plant capacity, location, and feed composition.

Isoforming prime contract onsite investments including associated fractionation facilities usually vary from $145 to $200 per BCD of design feed rate. Operating cost for catalyst can be expected to average around 0.5¢/barrel of feed or less.

Commercial Installations: There are four Isofining plants and three Isoforming plants in commercial operation.

References: Chemical Engineering, 10/7/68. Oil & Gas Journal, 7/15/68, p. 102.



p-Xylene Separation (Parex)— UNIVERSAL OIL PRODUCTS CO.

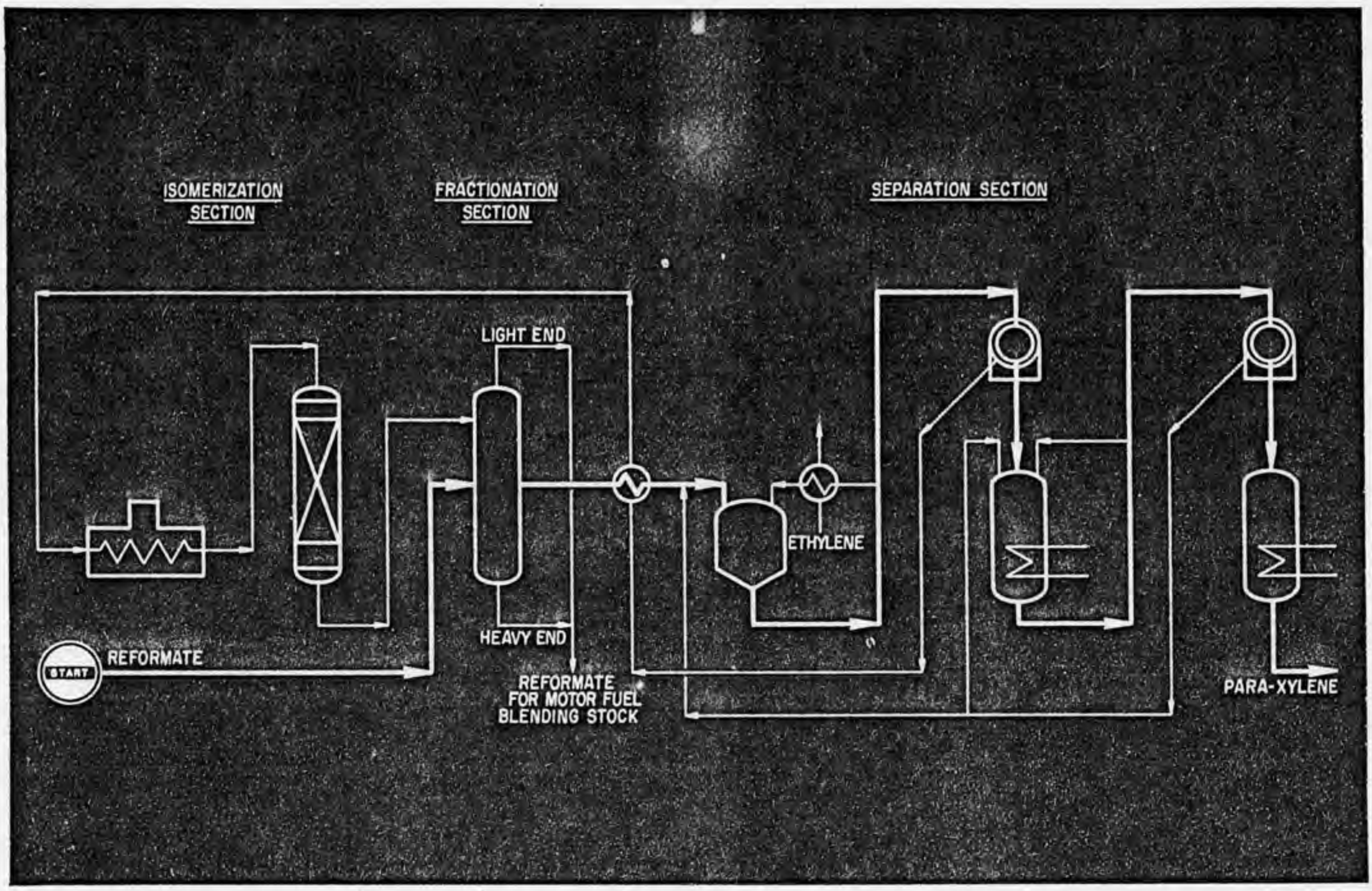
Application: A process for separating *p*-xylene from mixtures with other xylene isomers, ethylbenzene and non-aromatic hydrocarbons. The *p*-xylene is recovered at a purity in excess of 99.5%, and extraction efficiency can be above 95%.

The process can be operated to extract *p*-xylene in a once-through operation from either a C_8-aromatic mixture derived from extraction or from a C_8-cut of reformate. Alternatively, it can be operated in conjunction with xylene isomerization process to yield any required proportion of the C_8-aromatic products as *p*-xylene.

Process Description: *Para*-xylene is recovered by adsorption from the liquid phase in a fixed bed of solid adsorbent. The adsorbed *p*-xylene is then recovered from the adsorbent by washing it with a desorbent liquid having a boiling point different from that of any of the C_8-aromatics. The products are separated from the desorbent by fractionation. The process arrangement simulates continuous contercurrent flow of adsorbent and liquid, without actual movement of the solid. A single bed of adsorbent is used, and the flow of feed and products to and from the bed is continuous.

Operating Conditions: Temperatures are in the range of 250-300° F and pressures are moderate. Carbon steel is used throughout the plant. No refrigeration or conveyance of solids is required.

Commercial Operations: Two Parex units have been licensed and are in the design stage. Both will operate in conjunction with xylene isomerization and fractionation facilities, to yield both *o*-xylene and *p*-xylene as net products.



p-Xylene — MARUZEN OIL CO.

Application: A process for crystallizing and isomerizing mixed xylene streams to high purity *p*-xylene from reformate feedstock. The heavy and light aromatics may be used as gasoline blending stocks.

Description: The reformate feedstock (RON 97 to 98 range is used) is first split into light ends and heavy ends with the heart-cut xylene rich stream being taken for this process. Recycle styrene are also run through this fractionator along with fresh feed. This heart-cut is interchanged with first stage *p*-xylene crystalizer lean recycle stream and mixed with second stage *p*-xylene crystallizer wash and chilled by ethylene refrigeration. First stage *p*-xylene crystallizer effluent is centrifuged and partially remelted and fed to the second stage centrifuge where pure (99.5+ percent) *p*-xylene is produced. The *p*-xylene lean stream is pre-heated and isomerized over a fixed bed silica-alumina catalyst under atmospheric pressure with steam to an equilibrium xylene mixture. The catalyst has excellent selectivity and maintains full recovery of aromatics without the use of hydrogen. The isomerized stream is mixed with fresh feed and the cycle continued.

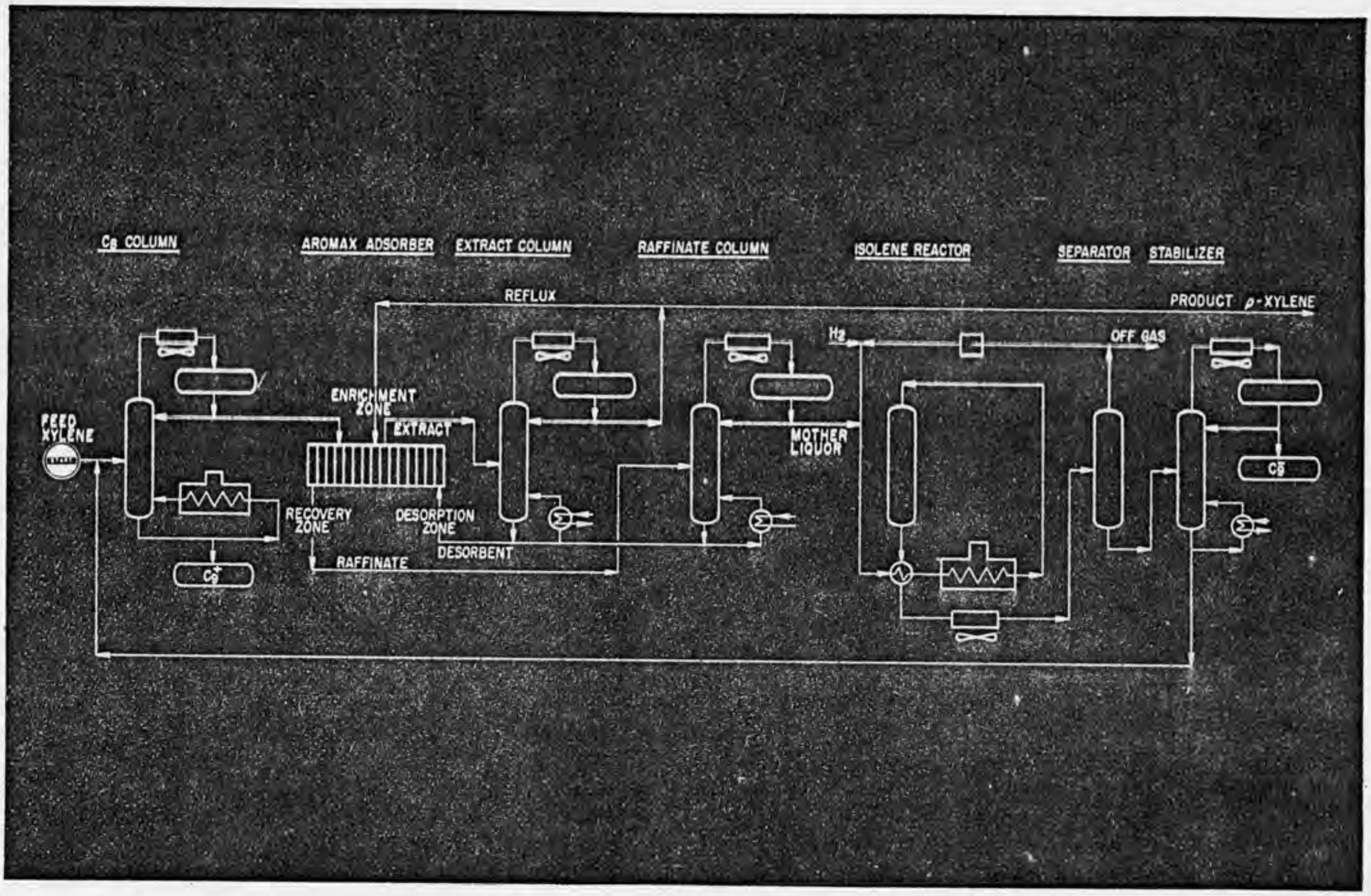
Feed: Reformate of RON 97-98 range is used. Liquid recovery of 96% with no loss of aromatic rings is expected.

Utilities: For each metric ton of *p*-xylene produced:

Steam, kg	160
Electricity, kwh	463
Cooling water, tons	98
Fuel oil, Kcal	3.7×10^6
Catalyst and Chemical	$3.3
Labor, men/shift	3
Catalyst life, years	2

Economics: For a 100,000-metric-ton/year *p*-xylene plant, $11.5 million (U.S.) in Japan excluding engineering fee and royalty.

Commercial installations: 10,000-metric-t/y Matsuyama refinery (1950), 20,000 metric t/y (1951), expanded to 60,000 metric t/y (1971). Kuray Yuka, 23,000 metric t/y (1967). Isomerization section only licensed to Bulgari (1968). All units use extracted chemical grade xylenes as feedstock. Maruzen's next expansion will be based on straight reformate without solvent extraction step.



p-Xylene (Aromax and Isolene) — TORAY INDUSTRIES, INC.

Application: A process for manufacture of *p*-xylene from mixed xylenes.

Description: The process consists of *p*-xylene recovery (Aromax) and isomerization of xylene (Isolene).

Aromax: The adsorbent column consists of a series of independent chambers. Mixed xylene is introduced to the adsorber and raffinate, which containes small amount of remaining *p*-xylene, is withdrawn at a point several chambers downstream of the feed chamber, while *p*-xylene is selectively adsorbed. This takes place in the so-called recovery zone. Reflux, primarily *p*-xylene, is introduced to the adsorber several chambers upstream of the feed point and it increases purity of the *p*-xylene adsorbed. This takes place in the enrichment zone. Above the reflux chamber, the adsorbed *p*-xylene is desorbed by a desorbent, purge material, introduced to the top of the desorption zone, and it is withdrawn from the adsorber as extract. The desorbent is recycled to the adsorber after distillation in the extract and raffinate columns. The adsorption flow is similar to a rectification operation except that the desorption operation is incorporated in adsorption process. In the adsorption column, the adsorbent bed contacts the xylene stream countercurrently. Since it is economically impractical to have a moving adsorbent in commercial operation, the countercurrent flow of adsorbent and xylene can be accomplished by switching the inlet and outlet position of xylene streams periodically by using a sequence of automatic on-off valves.

Isolene: Mother liquor from the Aromax is mixed with hydrogen, heated to reaction temperature, and then enters a single adiabatic fixed-bed reactor. The isomerized reactor effluent is cooled and separated into liquid and gaseous phase. Hydrogen-rich gas from the separator, after a small amount for fuel being withdrawn to maintain hydrogen purity, is mixed with make up hydrogen and recycled back to the reactor. Liquid drawn from the separator is fractionated and C_7^- and C_9^+ components are recovered. Product xylene recycles to the Aromax.

Raw materials and utilities consumption: (100,000 metric tons/year *p*-xylene):

Feed mixed xylenes, tons/yr.	116,000
Catalyst & chemicals consumption, Yen/yr.	69×10^6
Utilities: Steam, tons/hr.	13
Heat duty (absorbed) kcal/h	55×10^6
Electric power, kW	3,900
Cooling water, tons/h	150

Plant construction cost: $2,280 \times 10^6$ Yen.

Initial catalysts and chemicals cost: 730×10^6 Yen.

Commercial installation: Isolene plant of 120,000 t/yr and Aromax plant of 110,000 t/yr as *p*-xylene are in operation at Kawasaki, Japan. Aromax-Isolene technologies were licensed to People's Republic of China.

References: *Chemical Economy & Engg. Review,* 3 (6), p 56 (1971); *Oil & Gas Journal,* Sept. 4, p 116 (1972); *Chemical Engg.,* Sept. 17, p 106 (1973).

PROYECTOS DE INVERSION GRANDE
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added to the eluate develops color, the absorbance of which is recorded. Each amino acid is identified from the retention volume, and the quantity is determined from the peak area. See also **Chromatography.**

Industrial Production. There are three principal ways to manufacture commercially valuable amino acids in substantial quantities: (1) by extraction from natural proteins, (2) by fermentation, and (3) by chemical synthesis.

Extraction Methods: Although most high-production amino acids, such as monosodium glutamate (MSG), now are produced by other methods,* there are four amino acids, as described next, which still are produced by the extraction method because no bacterial strains have been discovered to produce them in high yields by fermentation, or because no appreciable market has been found to stimulate consideration of the chemical synthesis route.

L-Leucine, easily extractable in quantity from any kind of vegetable protein hydrolyzates, may continue to be produced by this method. L-Cystine generally is extracted from the human-hair hydrolyzate. L-Histidine is available from blood of beasts in quantities, but it may be produced by fermentation in the near future, since some suitable artificial mutants of bacteria have already been discovered. The sole commercial source of L-hydroxyproline is now gelatin.

Almost all the 22 kinds of amino acids previously listed and included in Table A-11 are manufactured commercially.† Three natural amino acids, which usually are not contained in proteins but which are effective in medicine, also are listed in Table A-11. These are citrulline, ornithine, and dihydroxyphenylalanine.

Fermentation Methods: There are many kinds of microorganisms which are able to synthesize amino acids necessary to support their life from a simple carbon source and an inorganic nitrogen source, such as ammonium or nitrate salts, or nitrogen gas. With the remarkable progress carried out recently in the field of biochemistry and microbiology, a large amount of information on the biosynthetic pathways of amino acids in these microorganisms and also on the controlling mechanisms working in these pathways has been accumulated. The production of amino acids through microbiological processes has been accomplished by making practical use of this accumulated information.

In 1956, Japanese microbiologists succeeded in developing the first industrial production of L-glutamic acid through a microbiological process. Since then, the development and improvement of microbiological processes have continued. Currently, almost all common amino acids can be produced by *amino acid fermentation* at a low cost on an industrial scale. For example, monosodium glutamate was produced by the fermentation route at a rate of 180,000 metric tons in 1969, accounting for 90% of world production. See Fig. A-38.

The amino acid fermentation process is relatively simple. A physiologically active isomer of amino acid, L-amino acid, can be obtained exclu-

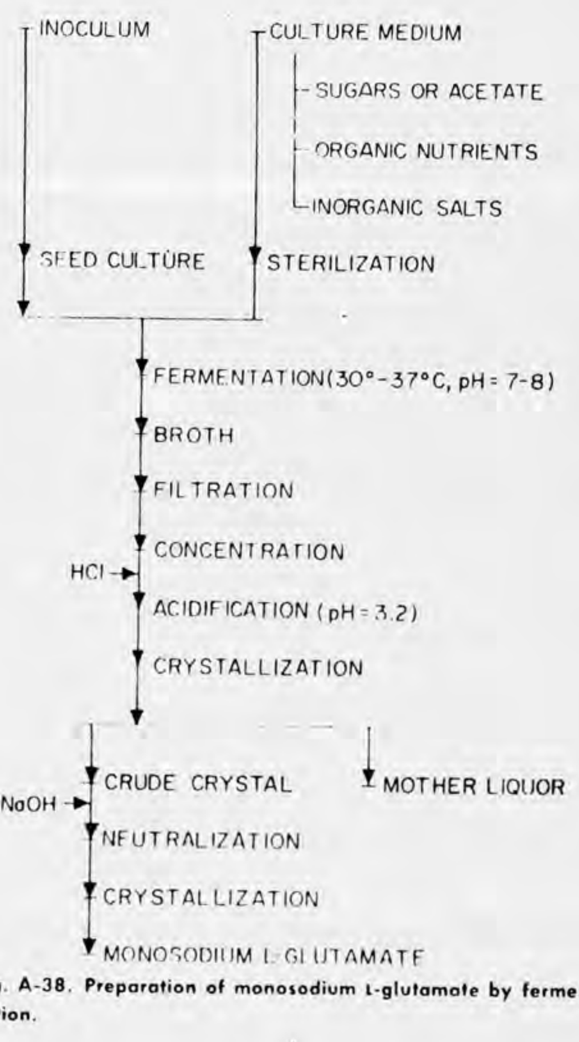

Fig. A-38. Preparation of monosodium L-glutamate by fermentation.

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*Some MSG production by extraction may remain in connection with utilizing glutamine contained in sugar beets

†As, for example, by Ajinomoto Co., Inc., Kawasaki, Japan.

sively and directly. This is an advantage over other methods of amino acid manufacture.

The amino acid fermentation processes are classified as follows:

- *A.* Methods involving simply the cultivation of a microbial strain
  1. Isolated from a natural source, or a wild microbial strain, or
  2. Improved by some genetic methods, or an artificial mutant
- *B.* Method involving the conversion of a certain precursor to the corresponding amino acid with microbiological enzymes

Method with a Wild Microbial Strain: Through a series of microbiological studies, it has been found that some microbial strains isolated from natural sources possess excellent abilities to excrete and accumulate a large amount of a particular amino acid in the cultural broth under specifically controlled conditions.

The production of glutamic acid previously mentioned is a typical case. When a certain bacterial strain is cultured aerobically for about 24–48 hr in a chemically defined medium containing carbon sources, such as sugar or acetate, and nitrogen sources, such as ammonium salt, more than 50 wt % of the carbon sources is converted to glutamate. S. Kinoshita and his coworkers discovered that such a high yield of glutamate can be attained only when the growth of the used bacterium is controlled to a certain level by the limited supply of biotin, a vitamin required by the glutamate-producing bacterium. An excess amount of biotin in the medium can be controlled by the addition of certain antibiotics or detergents. This phenomenon has been explained in terms of the change of cellular permeability of glutamate. The limited supply of biotin or the addition of antibiotic or detergent increases the cellular permeability of glutamate. The glutamate thus formed inside the cells is excreted easily through the cell membrane and accumulated in the cultural broth.

Other amino acids produced by this method on a commercial scale are listed in Table A-42.

Method with an Artificial Mutant: Soon after the glutamate producing bacterium was isolated and the concept of amino acid fermentation first materialized, microbiologists studied ways to improve the ability of microorganisms to accumulate amino acids by the use of *genetic techniques.* From biochemical observations, it is known that the accumulation of amino acids takes place (1) if a metabolic flow of amino acids in the cells is blocked at a certain step by a genetic method and/or (2) if some biochemically controlled mechanisms (such as feedback inhibition and repression, regulating the biosynthesis of amino acids in the cells) are modified or destroyed. In fact, some excellent strains have been found among auxotrophic and/or drug-resistant mutants obtained so that the above conditions are fulfilled in these mutants.

Some amino acids produced in this way also are listed in Table A-42.

Conversion of a Precursor to Amino Acid: Several amino acids are manufactured from their direct precursors by the use of microbially produced enzymes. Bacterial L-aspartate β-carboxylase is used for the production of L-alanine from L-aspartic acid. Bacterial aspartase responsible for the amination of fumaric acid is employed to produce L-aspartic acid. Tyrosine is produced through a process in which the condensation of phenol and serine is catalyzed by bacterial β-tyrosinase.

Some amino acids are produced by means of a slightly modified method of this type. The conversion of a certain precursor to the aimed amino acid takes a longer and rather complicated pathway than the action of a single enzyme. In the case of the fermentative production of isoleucine, α-aminobutyric acid is added to the culture. Similarly, anthranilic acid is used for the production of tryptophan.

The amination of α-keto acids to form their corresponding amino acids with transaminase or dehydrogenase will be utilized in the future.

As previously outlined, all protein-constituting amino acids except sulfur-containing amino acids can be produced by the amino acid fermentation process. The microbiological process for the production of sulfur-containing amino acids is now under investigation.

Isolation of Amino Acids from the Fermentation Broth: Amino acid accumulated in the fermentation broth should be isolated as pure crystals for the market. There are several physicochemical methods available for this purpose, but only a few are used for the industrial production of amino acids.

1. *Ion-Exchange Resin:* The chromatographic separation of an amino acid mixture using ion-exchange resins is one of the most common purification methods. Usual fermentation broths contain contaminating amino acids as well as bacterial cells. Isolation of the relevant amino acid from other components is easily done by

flowing the broth through an ion-exchange resin column. This method also is used for the recovery of an amino acid from the mother liquor of the amino acid crystal.

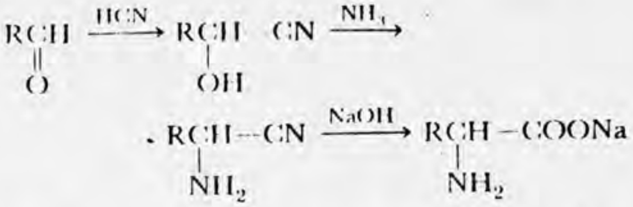
2. *Precipitation:* Compounds which give insoluble salts with amino acids are selected for the separation and purification of amino acids. Picrate has been used for the purification of proline, which is difficult to purify because of its high solubility.

3. *Crystallization:* An amino acid is least soluble when the pH of the solution is adjusted to the isoelectric point. If the solubility is sufficiently low at this point (as in the case of glutamic acid), adjustment of the pH of fermentation broths serves to separate a pure amino acid in crystalline form. The polymorphism and polytypism of the crystals often are observed. The way of controlling supersaturation (agitation, temperature, existence of minute amounts of impurities, seed crystals, hysteresis of the solution, and other factors) is important in obtaining the required purity of the separated crystals. In the case of glutamic acid, the L-form crystal is unstable, and thus it is necessary to observe rigorously the subtle optimal conditions needed for the production of good pure crystals. Concentration and cooling are used most frequently in the final stage of production of pure amino acid crystals. See also **Crystallization.**

Some physiological testing is done for the production of medical preparations. As test animals, cats are chosen for checking blood-pressure depression and rabbits for the pyrogen test.

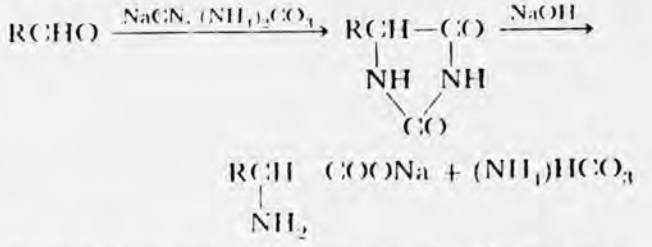
Chemical Synthesis. There are many laboratory methods for amino acid synthesis, but only a few appear to offer industrial potential. The synthetically produced amino acids listed in Table A-12 are made mostly from aldehydes. Glycine and DL-alanine are produced by the Strecker synthesis, starting from formaldehyde and acetaldehyde, respectively. *β*-Cyanopropionaldehyde, the raw material for glutamic acid, is produced by hydroformylation of acrylonitrile. This aldehyde contains isomeric *α*-cyanopropionaldehyde, but the ratio of *α* to *β* is smaller than 1:10. Following are two ways for the synthetic production of amino acids from aldehydes. The hydantoin process has an advantage over the Strecker synthesis in giving higher yields generally. In the case of glutamic acid, the conversion of glutamic acid (in solution) from *β*-cyanopropionaldehyde by the hydantoin process is nearly quantitative.

Strecker Synthesis: Aldehydes react with hydrogen cyanide and excess ammonia to give aminonitriles, which in turn are converted into *α*-amino acids on hydrolysis.



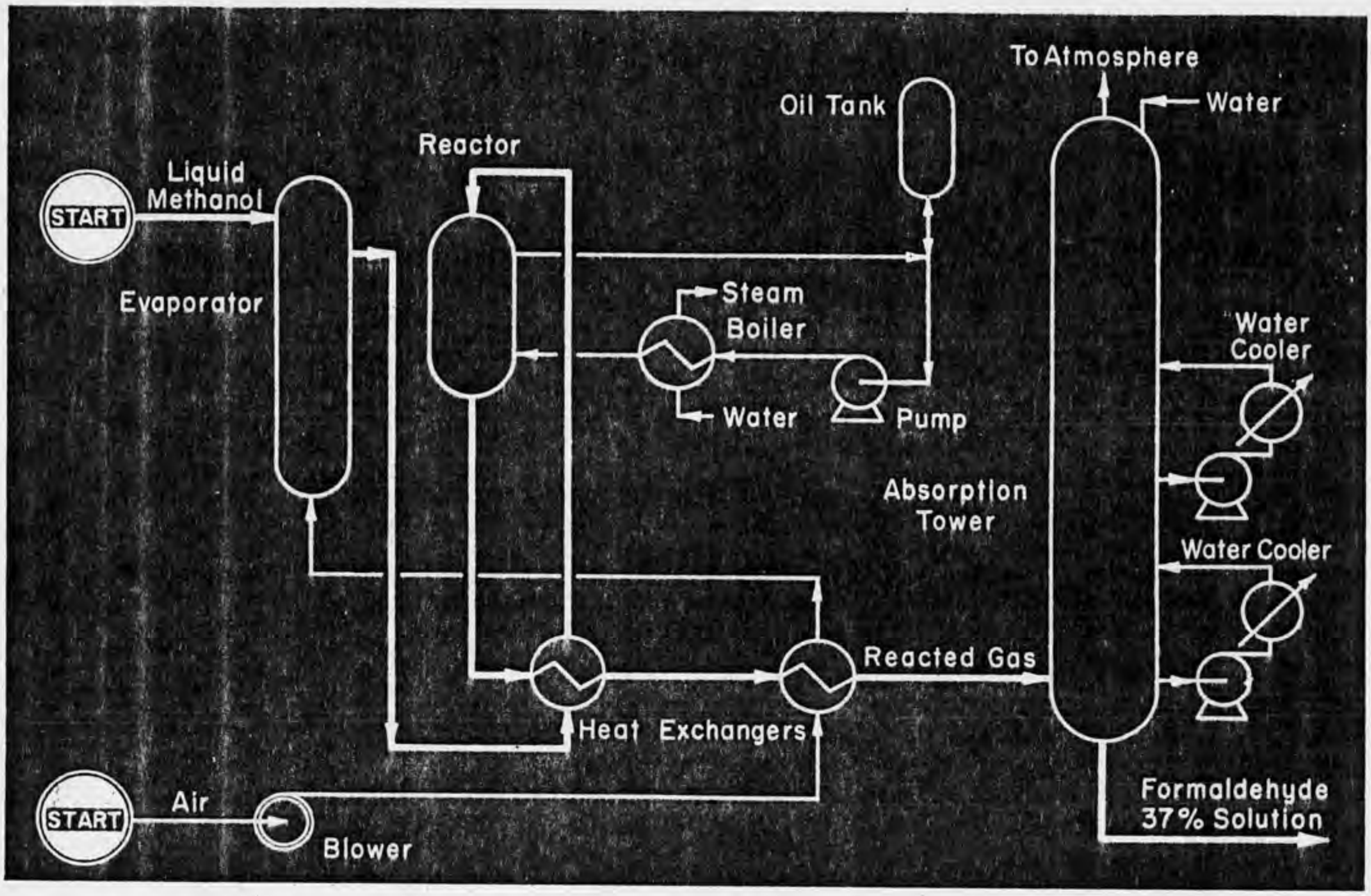
$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{RCH}} \xrightarrow{\mathrm{HCN}} \underset{\substack{| \\ \mathrm{OH}}}{\mathrm{RCH}}-\mathrm{CN} \xrightarrow{\mathrm{NH_3}} \underset{\substack{| \\ \mathrm{NH_2}}}{\mathrm{RCH}}-\mathrm{CN} \xrightarrow{\mathrm{NaOH}} \underset{\substack{| \\ \mathrm{NH_2}}}{\mathrm{RCH}}-\mathrm{COONa}$$

Hydantoin Process: Aldehydes react with sodium cyanide and ammonium carbonate to give hydantoins. It will give *α*-amino acids on hydrolysis with alkali.



$$\mathrm{RCHO} \xrightarrow{\mathrm{NaCN,\ (NH_4)_2CO_3}} \begin{array}{c} \mathrm{RCH-CO} \\ |\qquad | \\ \mathrm{NH\ \ NH} \\ \diagdown\ \diagup \\ \mathrm{CO} \end{array} \xrightarrow{\mathrm{NaOH}} \underset{\substack{| \\ \mathrm{NH_2}}}{\mathrm{RCH}}-\mathrm{COONa} + (\mathrm{NH_4})\mathrm{HCO_3}$$

In this case, excesses of carbon dioxide and ammonia are easily removed from the reaction mixture by treating with a little amount of alkali under high temperature and pressure.



Formaldehyde—MONTECATINI

Application: A process for the manufacture of formaldehyde solution, based on vapor phase catalytic oxidation of methanol by air.

Charge: Rectified methanol (99 percent pure) and atmospheric, non-purified air.

Product: Formaldehyde aqueous solution from 37 to 42 percent by weight, according to desired requirements, containing less than 1 percent by weight of methanol and less than 0.010 percent by weight of formic acid as impurities.

Description: Air, compressed at about 3 psig, is preheated in a first shell-and tube heat exchanger, in which heat from the reacted gases is recovered, and is then conveyed to a methanol evaporator. Feed of methanol is carefully controlled to ensure that the concentration does not exceed 8 percent in the air-methanol mixture.

The mixture leaves the evaporator at about 105 °F. and enters a second shell and tube exchanger, which is also heated by a hot reactor gas stream.

Here the mixture is heated to the desired reactor-feed temperature before entering the converter. Employment of two heat exchangers, one before and one after the vaporizing step, increases recovery of heat from reactor products and requires less exchange surface than a single unit as formerly used.

The air-methanol gaseous mixture flows into the reactor where, in the presence of a special oxidation catalyst composed of metallic oxides, the following basic reaction takes place:

$$2CH_3OH + O_2 \rightarrow 2CH_2O + 2H_2O + 38.06 \text{ Kcal/gmol.}$$

The reaction temperature is controlled to strict limits by a thermostatic oil circulation system. Oil absorbs heat from the reactor and is then cooled in a boiler where the reaction heat is recovered in the form of high pressure steam (280 psig); after cooling, oil is recycled in closed circuit to reactor.

The reacted gases, containing formaldehyde vapors, nitrogen and steam flow through the two heat exchangers and then reach a multistage absorption tower.

This is fed from the top with water. The absorption heat is removed by means of formaldehyde aqueous solutions circulated in a closed circuit, in the first two stages of the tower. Said solutions are cooled in heat exchangers located outside the tower.

The formaldehyde solution produced is directly conveyed to storage tanks and does not need final distillation of excess methanol nor reduction in formic acid content since the process is adjusted to give a high quality product.

Operating conditions: Complete safety against explosion dangers in the gaseous air-methanol mixture is obtained by a suitable choice of mixture components ratio.

Up-to-date control equipment is widely used, so that only one man per shift is needed in running the plant.

A wide range of space velocities can be used, provided the temperature of catalyst and methanol concentrations are kept constant, without impairing formaldehyde yields.

At reduced space velocity, methanol reacts completely, but some CO and CO_2 are formed as byproducts.

At higher space velocities the amount of byproducts decreases but some methanol remains unreacted.

In plant operation, the most suitable conditions are selected in such a way as to ensure that methanol content in the final product is usually kept between zero and 1 percent by weight.

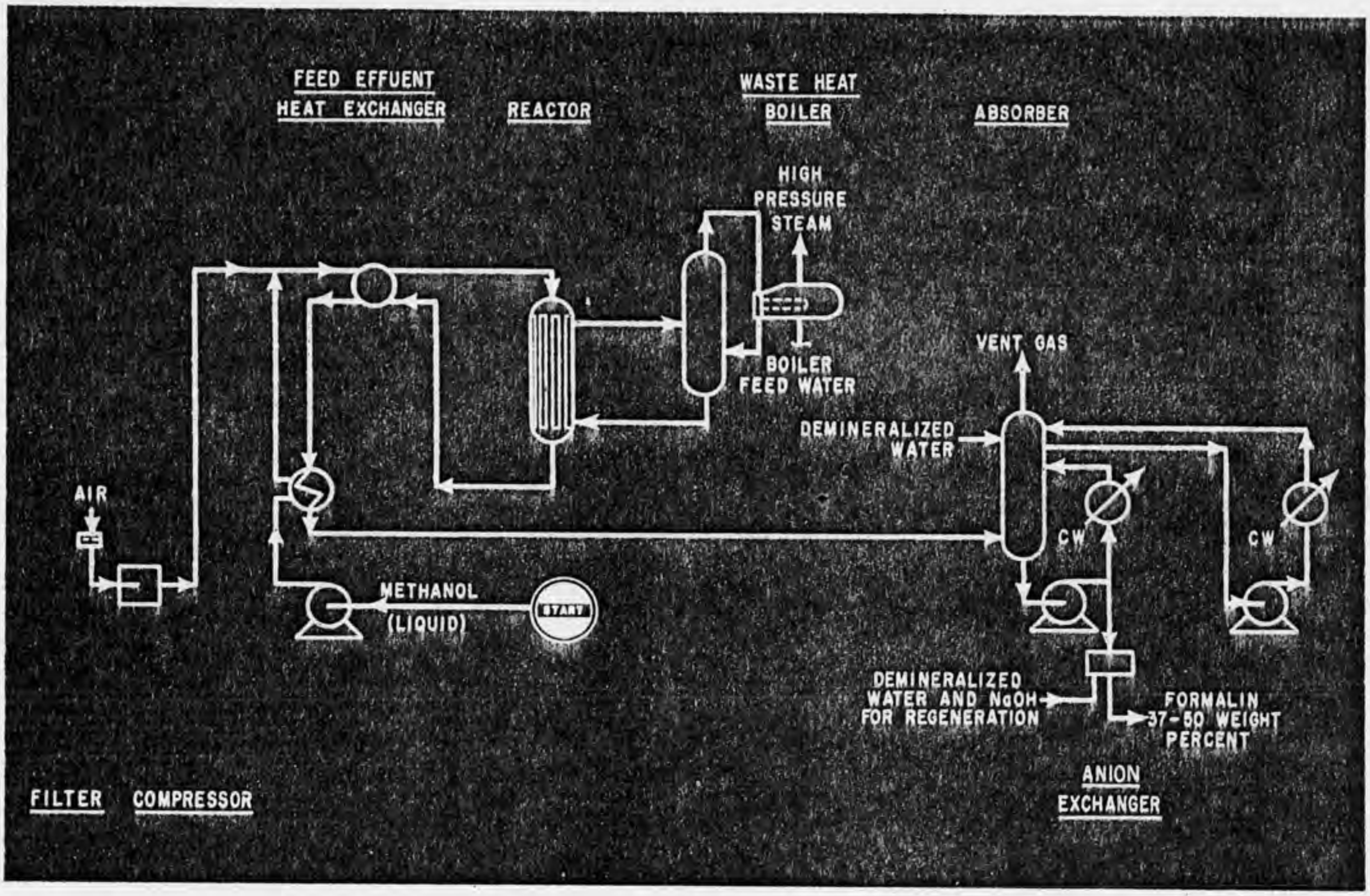
Yields: Over-all yield based on methanol fed is higher than 90 percent on a stoichiometric basis. Heat recovering yields high pressure steam (280 psig), reaching 0.35 metric ton per ton of 37 percent product solution.

High selectivity of the catalyst, prepared by a special process, not only ensures a high purity in the final product, but also allows a long useful life of the catalyst itself (more than 18 months). A specific production of more than 9 metric tons of 37 percent formaldehyde solution for each lb. of catalyst used is standard practice in Montecatini's plants.

Commercial installations: A large industrial plant, composed by four units and having a total capacity of 270 million lbs./year of 37 percent solution is in operation at Montecatini's Works at Castellanza, near Milan, Italy.

Four additional plants of this kind, having a capacity of 55 million lbs./year each are in operation or in advanced construction stage in Belgium, Rumania, The Netherlands and Brazil.

Reference: Chem. & Eng. News, May 26, 1958, p58; Chemical Engineering, Feb. 6th, 1961, p44.



Formaldehyde — THE LUMMUS CO.

Application: A process for the production of commercial grade formaldehyde from liquid methanol.

Description: The process involves the vapor phase reaction of methanol and air in a fixed bed catalytic reactor. Liquid methanol is vaporized using the reactor effluent as heating medium, is mixed with air and the total stream is heated by the initial reactor effluent.

The feed then enters a fixed bed shell and tube catalytic reactor in which methanol and oxygen (from air) react to form formaldehyde, some carbon monoxide and water vapor. The catalyst contains oxides of molybdenum and iron.

Formaldehyde is recovered by absorption with demineralized water. Heat is removed from the absorber by circulating bottom and mid-column liquid streams through coolers. The absorber bottoms product consists of 37-50 wt. % formalin (formaldehyde-water). The methanol content in the final product is below 1.0 wt. %.

The scrubbed overhead off-gas is vented.

The formalin bottoms product, which contains 0.01 wt. % max. acidity as formic acid, can be passed to an ion exchanger where the acidity can be reduced to meet any product specifications.

Dowtherm A circulates by thermosyphon action through the reactor shell. The heat absorbed is used to generate steam at a pressure of up to 450 psig.

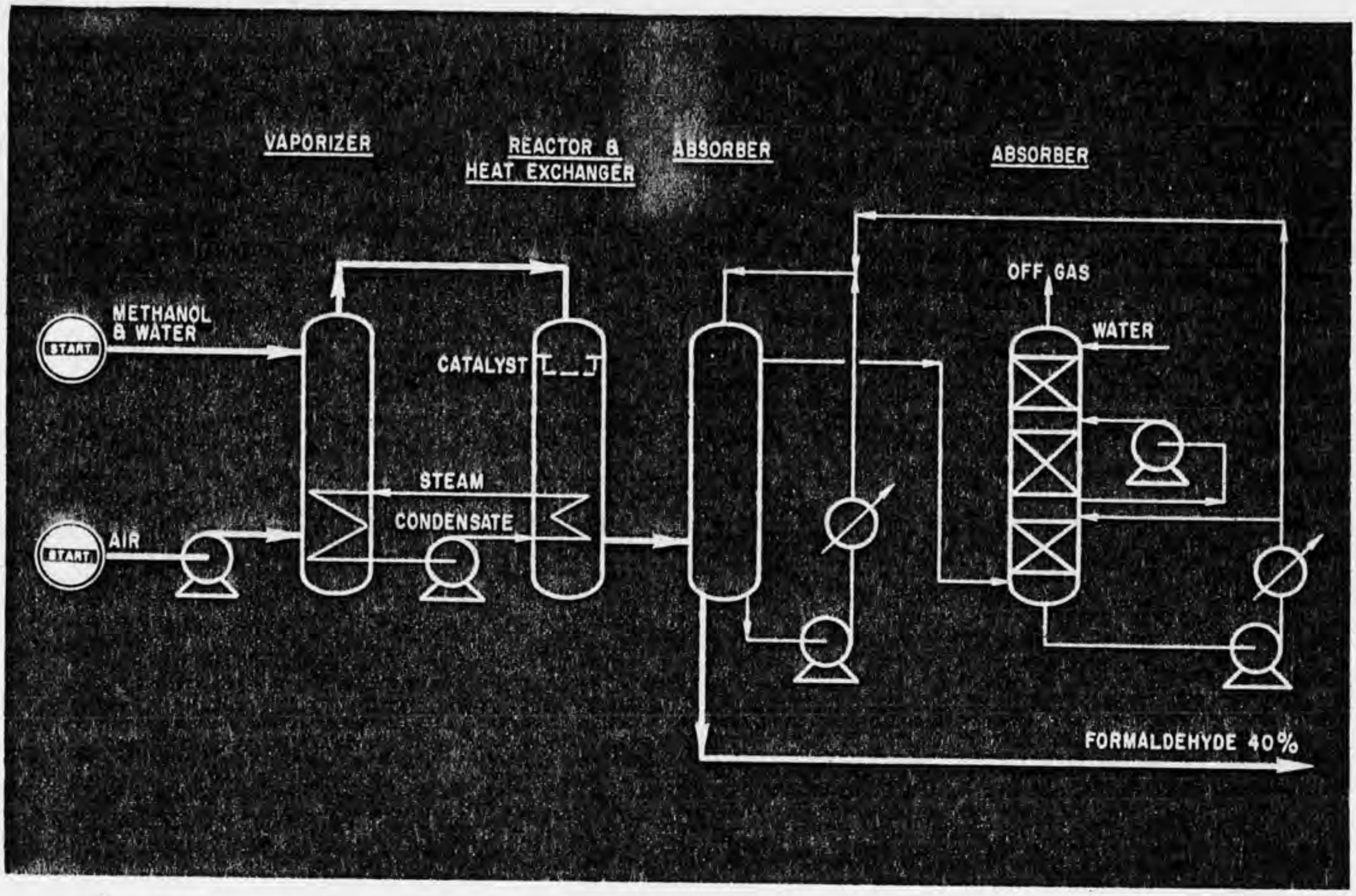
This steam may be used to supply part of the energy to drive the air compressor.

Typical Plant Requirements: (Per pound of 100% formaldehyde) (Equivalent to 2.7 pounds of 37 weight % solution or 2.0 pounds of 50 weight % solution.)

Raw Materials	
Methanol (100%) lbs.	1.17
Catalyst and Chemicals (Cost, U.S. Dollars)	0.0013
Utilities	
450-psig Steam (Generated)	(1.5 lbs.)
Cooling Water (85° F)	7.5 gal.
Boiler Feed Water	1.58 lbs.
Electric Power	0.10 Kwh

Demineralized Water: Total usage for both ion exchange and absorption: (1) When producing 37 wt. % product—0.273 gallons; (2) When producing 50 wt. % product—0.190 gallons.

Commercial Installations: One revamp for 18,200 MTA, one for 45,500, and one for 28,800 MTA now under construction in Japan.



Formaldehyde — BADISCHE ANILIN-& SODA-FABRIK AG

Application: A process for the production of formaldehyde from methanol.

Description: The process combines dehydrogenation and oxidation of methanol in contact with a silver catalyst. The over-all reaction is exothermic and proceeds adiabatically as follows:

$$CH_3OH \rightleftarrows CH_2O + H_2 \qquad -20\ \text{kcal/mole}$$
$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \qquad +58\ \text{kcal/mole}$$

A mixture of methanol and water is vaporized while supplying compressed reaction air. The vaporizer has also a rectifying effect. To prevent impurity build-up in the vaporizer bottoms, a constant slipstream is withdrawn. The reaction mixture, whose composition is above the upper ignition limit, flows through a thin layer of silver crystals where the reaction occurs at slight red heat. To achieve a good yield catalyst temperature is kept within ±5° C, by automatic control of air input. The hot reaction gas is cooled rapidly in a waste-heat boiler to prevent undesirable formation of carbon monoxide due to thermal decomposition of formaldehyde. Steam generated is sufficient to vaporize the methanol/water mixture. The cooled reaction gas is scrubbed countercurrently with steam condensate in a multi-stage absorber; more than 90% of the formaldehyde is absorbed in the first stage.

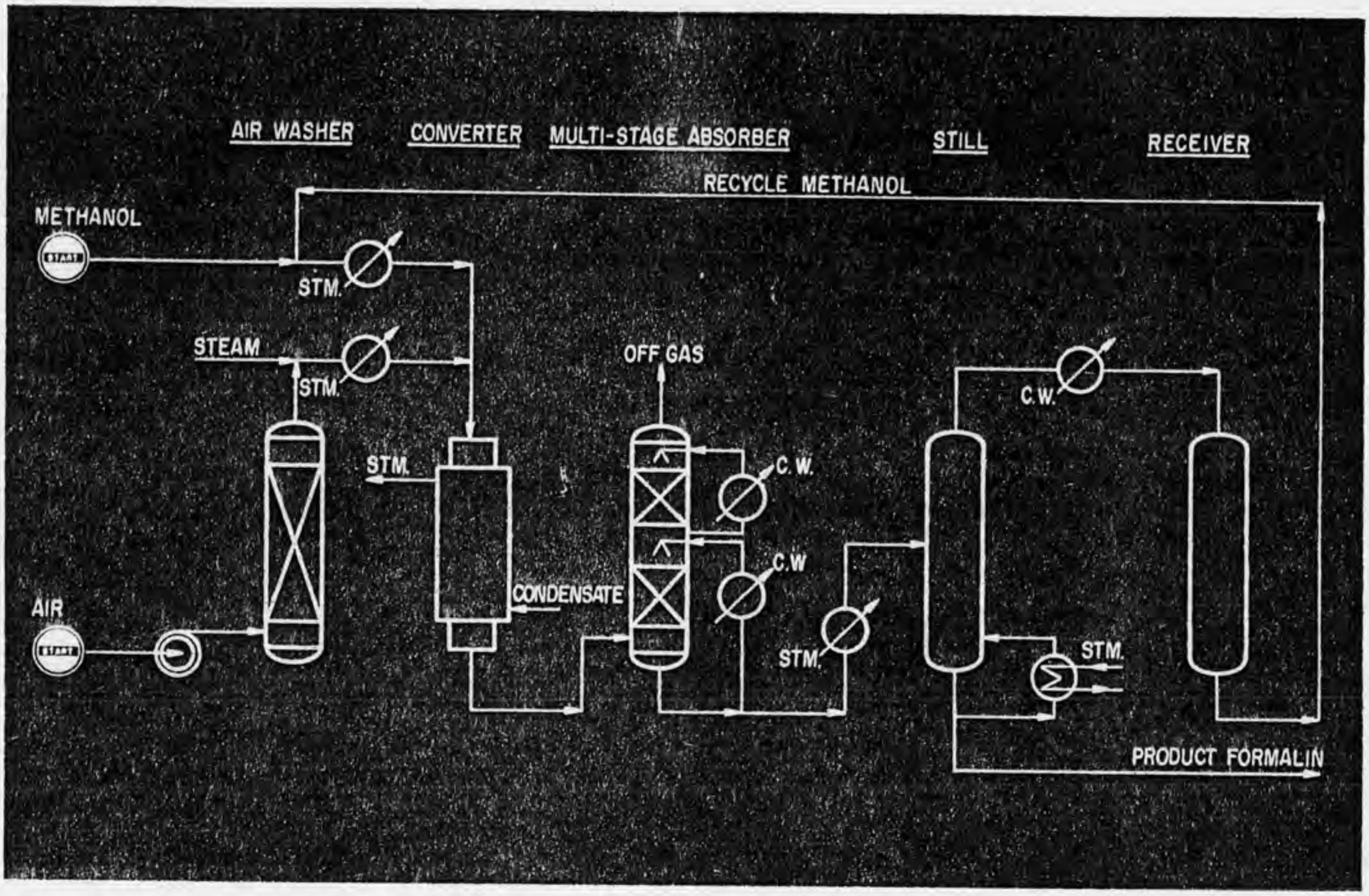
The absorption and condensation heat liberated is removed by means of heat exchangers in a product circulation system. Product concentration is adjusted by controlling the amount of water supplied to the last stage of the absorber.

Efficiency: The yield is 87.5% of theory based on methanol used and 91% based on methanol converted. Electricity and river water are the only utilities required. The economics of the process may be further improved by using crude methanol freed from disturbing contaminants instead of pure methanol.

Catalyst: Electrolytically purified silver crystals having a specific particle size are used as catalyst. The life of the catalyst is several months and depends on starting materials purity. The output is 12 to 15 metric tons of formaldehyde (calc. 100%) per pound of catalyst. Since the catalyst is very selective, one pass is sufficient to achieve almost complete conversion. Recovery of unreacted methanol by product distillation is unnecessary. The absence of a distillation unit ensures low formic acid content, so ion exchange deacidification is also unnecessary.

Commercial Installations: There are several units at BASF's Ludwigshafen works with a total annual capacity of 250,000 metric tons of formaldehyde (calc. 100%).

Reference: *Hydrocarbon Processing*, June 1967, pages 169-172.



Formaldehyde — MONSANTO CO.

Application: A process for manufacture of formaldehyde from methanol and air.

Description: Formalin is produced by dehydrogenation of methanol over a silver catalyst at elevated temperatures and essentially atmospheric pressure. A controlled mixture of purified methanol vapor, steam and air is passed over a granular silver catalyst bed. Most of the methanol is dehydrogenated as it contacts the high-temperature catalyst bed, producing one mole of formaldehyde and one mole of hydrogen. The reaction is endothermic, and system heat balance is maintained by burning a portion of the hydrogen released with the air provided.

Products of reaction are quickly cooled in the waste heat boiler section of the converter located just below the catalyst bed. Heat of reaction is recovered in this waste heat boiler, and a portion of the steam produced is used as process steam in the combined feed gas charged to the converter.

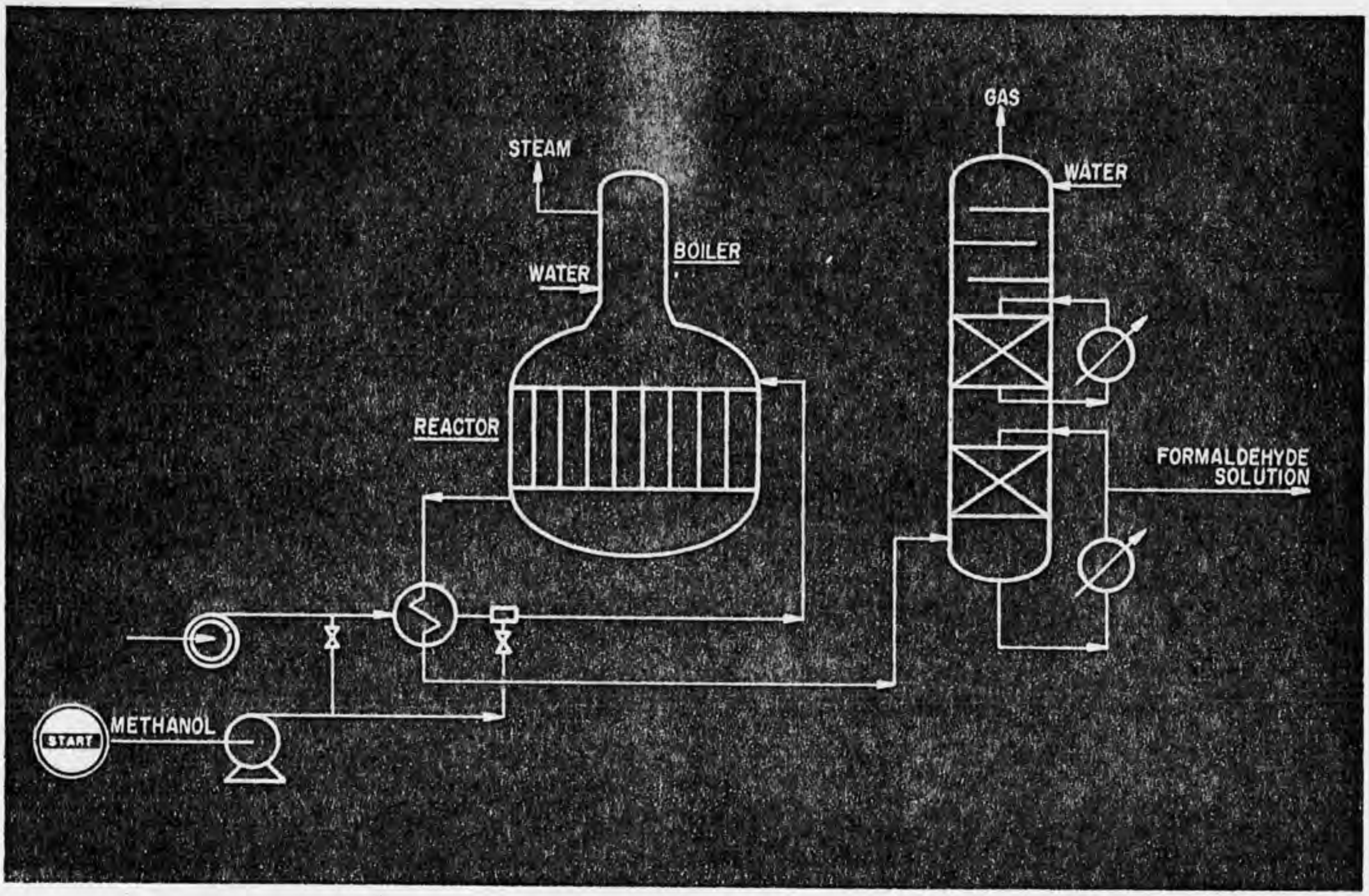
Converter effluent passes directly to an absorption train where the formaldehyde and other condensables are recovered by counter-current direct contact condensation and absorption in recirculating formalin streams. Heat of absorption is removed by heat exchangers in these recirculating intermediate reflux streams. Non-condensable gases pass out of the absorption train. Included in the absorption train is capability for meeting U.S. E.P.A. air emission standards.

Raw formalin is collected in the absorber sump and then passed to a distillation column where it is purified by stripping out the unconverted methanol. Methanol is recovered and recycled to the process. Purified product formalin is collected and sent to storage tanks. Formalin assay may be adjusted by regulating amounts of water added to the absorber column or by subsequently diluting 50% formalin to lower assays in storage tanks.

Appropriate temperature control in the total system and in storage tanks maintains paraform formation at a minimum and reduces the formic acid content of the formalin. A patented Monsanto inhibitor is added to retard the formation of paraform in storage.

Features distinguishing the Monsanto silver process from other processes include use of a single converter and catalyst bed to manufacture at rates up to 300 million pounds per year, on a 37% solution basis, minimum number and size of other equipment components, and long catalyst bed life. Economics of the Monsanto process favor plants of greater than 50 million pounds annual capacity.

Commercial experience: There are presently seven Monsanto-designed plants in the United States operated by Monsanto or by others having a total annual capacity of nearly one billion pounds.



Formaldehyde (CdF Chimie-IFP Process) — SOCIETE CHIMIQUE DES CHARBONNAGES

Application: A process for the manufacture of formaldehyde from methanol and air.

Description: A large excess of air is mixed with part of the methanol, exchanged with reactor effluent, and the remaining methanol added before going to the reactor. This air-methanol mixture is heated to reaction temperature in the upper part of the reactor by boiling heat transfer liquid. Excess heat in the transfer fluid is used to generate steam.

Reactor effluent is exchanged, cooled and sent to a three section absorption tower. Makeup water is added to the upper part to control tower bottom formaldehyde concentration.

The new type iron-molybdenum oxide catalyst has a life of more than one year.

Catalyst: The IFP-CdF Chimie catalyst is 3 mm x 3.8 mm cylinders. Rupture strength of about 70 kg/cm^2, specific area of $10/2m^2$ gram, specific gravity of 1.8 ± 0.1 g/cm^3, and a bulk density packed in the 16-mm ID reactor tubes of 1.05 ± 0.5 g/cm^3.

Investment: A 25,000-metric-ton/year pure formaldehyde plant has the following approximate economics:

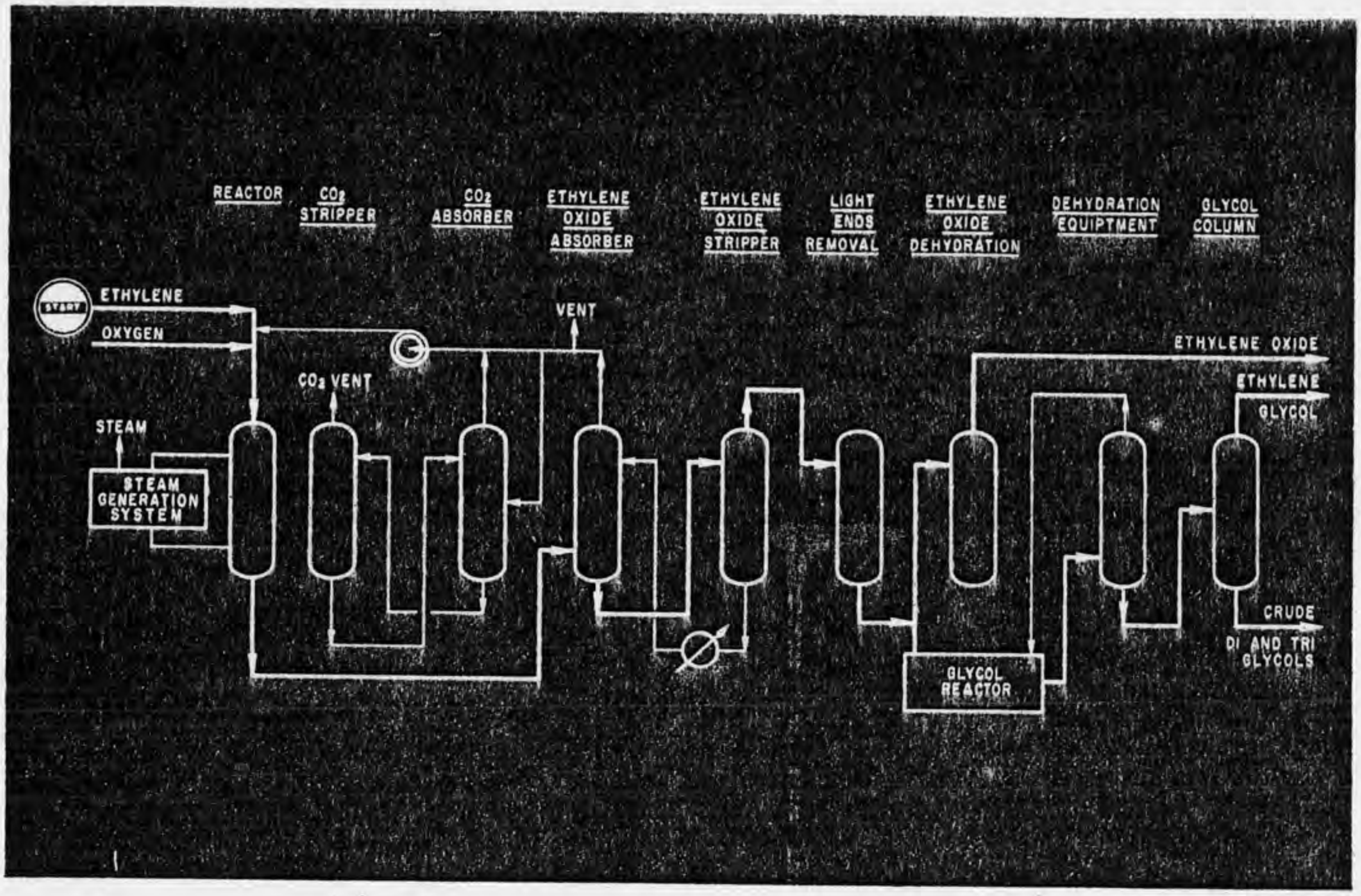
Investment, 10^6 French francs	
Battery limits investments	6.90
Off-sites (30%)	2.07
Total process, utilities, storage and general services investments	8.97
Engineering (12%)	1.08
Process data book	0.30
Fixed capital *	10.35
Initial catalyst load	0.44
Interest on construction loan (7%)	0.72
Startup costs (one month direct costs)	0.76
Depreciable capital	12.27
Working capital (2 months direct costs)	1.52

Operating costs, French francs per ton of pure formaldehyde

	Quantity per ton produced	Unit Cost French francs	Cost per ton produced
Methanol	1.15	280	322.0
Catalyst			17.6
Utilities			
Steam produced (20 bars)	1.58	12	(—) 19.0
Electricity, kWh	2.56	0.06	15.6
Cooling water, m^3	75	0.03	2.3
Boiler feedwater, m^3	3	0.08	0.2
Labor, 2 operators/shift + supervision			24.0
Total direct costs			362.7
Depreciation, 12.5% of capital; Interests 7% capital, 9% working capital; maintenance and overheads, 7% process, utilities; storage, and general services investments			126.3
Total operating costs			489.0

* Paid up royalties are not included

Reference: Chauvel, A. R., et al, *Hydrocarbon Processing*, Sept. 1973, p. 179-184.



Ethylene Oxide & Glycol — SHELL DEVELOPMENT CO.

Application: Processes for the production of ethylene oxide by direct oxidation of ethylene with oxygen and for the production of mono, di, and/or tri-ethylene glycols by reaction of ethylene oxide with water.

Description: Ethylene and oxygen feed are combined with recycle gas and fed to a large tubular isothermal catalytic reactor. The reaction is highly exothermic and temperature control is maintained through the use of a specially designed boiling coolant system which permits extremely close control and stable operation of the reactor. The supported silver catalyst of special composition is highly selective and long-lived. Commercial plants are in their 12th year of continuous operation with their original catalyst charges and have as yet experienced no measurable change in pressure drop, activity, or selectivity.

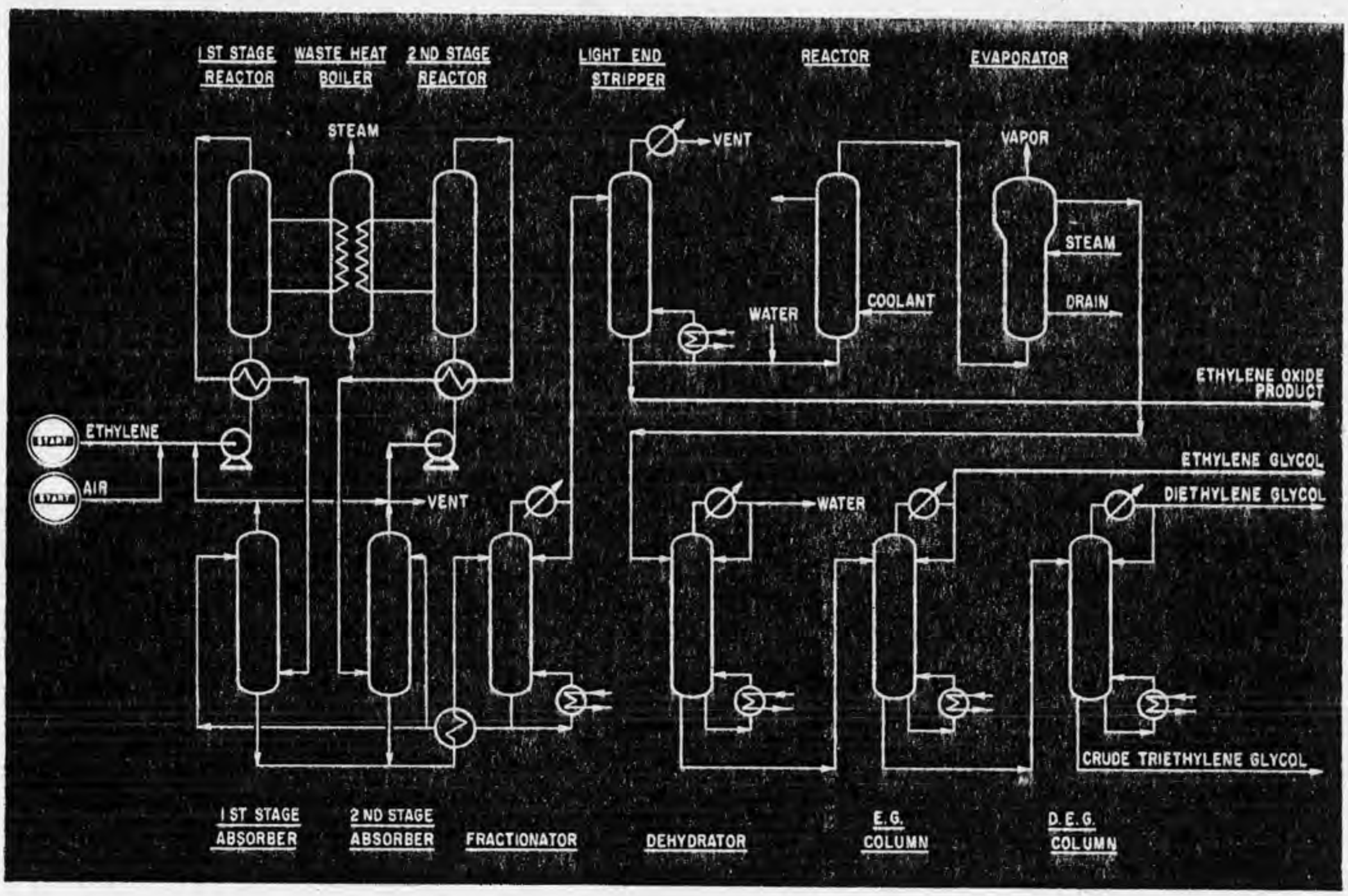
The reactor effluent gas containing the ethylene oxide product is first cooled by exchange and then passed into the ethylene oxide absorber in which the ethylene oxide is recovered by absorption in water. Except for a small vent, the residual gases are compressed and recycled. A side stream of the recycle gas is scrubbed with a suitable solvent for removal of excess CO_2 which is subsequently stripped and vented, or recovered if desired.

Ethylene oxide is stripped from the fat absorbent and distilled for removal of light ends. The lean absorbent (water) is cooled in a process cooling tower subsequent to its recycle to the absorber. A part or all of the ethylene oxide may be dehydrated to a finished high-purity product suitable for the manufacture of highest quality derivatives.

If glycols are to be produced, the ethylene oxide is transferred directly to the glycol reactor where, in an excess of water, the ethylene oxide is hydrated to glycol. It is possible to control the proportion of mono, di and triethylene glycols by a proper choice of reactor conditions.

The process design for each new plant is computer-optimized to give the lowest product cost consistent with specific plant conditions.

Commercial Status: There are 20 plants using this process and five plants under construction. The design capacity of the above plants plus others still to be announced is in excess of two billion pounds per year.



Ethylene Oxide & Glycols—NIPPON SHOKUBAI KAGAKU KOGYO CO., LTD.

Application: A process for the manufacture of ethylene oxide and glycols from ethylene, air and water.

Description: Ethylene oxide is produced by the vapor phase oxidation of ethylene with air in the presence of a silver based catalyst fixed in tubes of a shell-and-tube type reactor. The principal side reaction is a complete combustion of ethylene which is much more exothermic than the main reaction and prevails at higher temperatures. The control of the reaction temperature is a key factor for the successful operation of this process. The heat of reaction is removed by circulating an organic coolant in the shell side of the reactor, and this heat is then recovered as steam.

The reaction is carried out in two stages. In the first-stage reactor the conversion of ethylene is maintained relatively low in order to obtain a high selectivity of ethylene to ethylene oxide. Purging of the gas from the recycle system is needed to avoid accumulation of inert gas such as N_2 and CO_2. Ethylene in the purge stream is oxidized in the second-stage reactor at a higher conversion. Recycling is made also in the second stage for getting the maximum utilization of ethylene.

Ethylene oxide in the product gas is absorbed by water under pressure. The aqueous ethylene oxide solution from the bottom of the absorber is fed to a fractionator where ethylene oxide is stripped out and enriched. The distillate from the fractionator is charged to the top of the light ends stipper where light gases such as CO_2 and N_2 are stripped to get the final product of ethylene oxide.

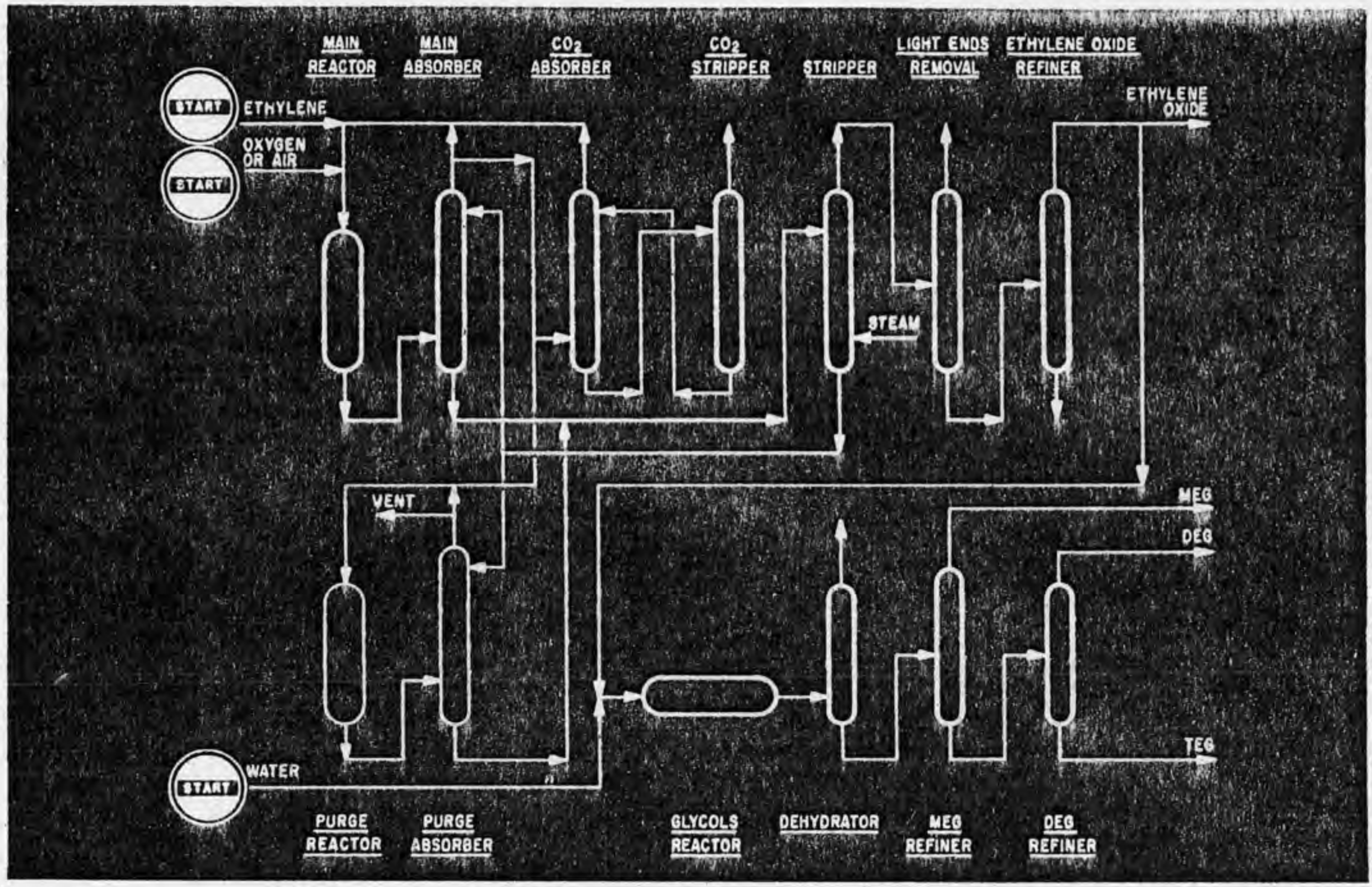
The catalyst is long lived and the utility cost can be maintained very low by efficiently utilizing heat and pressure energy of the reaction gas.

Ethylene glycol is made continuously by hydration of ethylene oxide. Di- and tri-ethylene glycols are produced simultaneously. The distribution of the products can be varied by changing the reaction conditions. The resulting aqueous solution is dehydrated and distilled under reduced pressure to yield respective glycols.

Yield: The yield of ethylene oxide from ethylene is well over 100 wt%. In glycols production, hydration of ethylene oxide is almost complete.

Commercial Installations: 120,000 tons/year (as ethylene oxide) at Nippon Shokubai's Kawasaki plant, Kawasaki, Japan and 60,000 tons/year at Kazan, U.S.S.R.

References: *Hydrocarbon Processing*, November 1967, Vol. 46, No. 11, p. 175.



Ethylene oxide and glycols — SNAM PROGETTI

Application: A process for the manufacture of ethylene oxide and glycols from ethylene using either air or oxygen as the oxidizing agent.

Description: Ethylene in the vapor phase is converted into ethylene oxide in presence of a silver based catalyst in the tubes of shell-and-tube type reactors. The reaction is highly exothermic and the reaction heat is removed by shell-side circulation in the reactor of a suitable coolant to insure a thorough control on the reaction. The reaction heat is then used to produce medium pressure steam.

The reactor effluent is conveyed into an absorber where ethylene oxide is separated from the effluent gases by water. Most of the unabsorbed gases are recycled back directly to the reactor and a side stream is diverted through a CO_2 removal system if oxygen is used, or fed to the secondary reaction system if air is used.

The ethylene oxide rich water stream out of the absorber is fed to a stripper where ethylene oxide is recovered. The water out of the stripper is cooled and recycled back to the absorber.

The stripper overhead effluent is fed to a light ends fractionator followed by a refiner to obtain ethylene oxide of the desired purity.

If glycols are to be produced the ethylene oxide is conveyed directly to the glycol reactor with the required amount of water. The reactor effluent is then fed to a separating and purifying system to yield mono-, di- and triethylene glycols in the desired distribution.

The process design for each new plant is computer optimized to give the lowest product cost consistent with specific plant conditions.

Commercial status: SNAM PROGETTI has built two plants using the air process. A number of plants using the oxygen process are currently in the design stage.

Economics: The following data apply to 1 ton EO based on O_2 process.

Ethylene, ton	0.91
Oxygen, ton	1.2
Electricity, kwh	470
Boiler feed water, m^3	5
Cooling water, m^3	240
Recovered MP steam, ton	2.3

PROYECTOS DE INVERSION GRANDE

TECNOLOGIA DE OPERACION

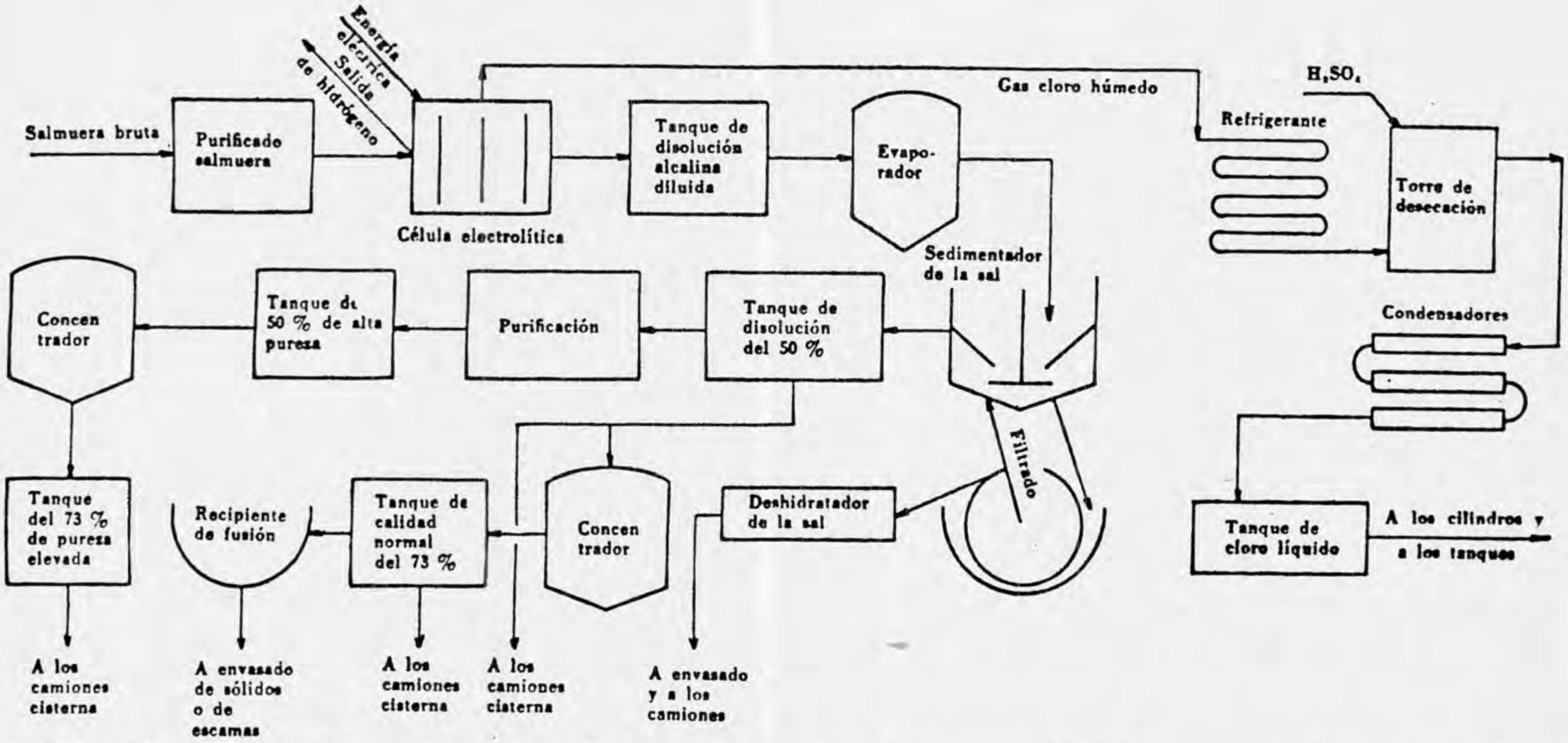
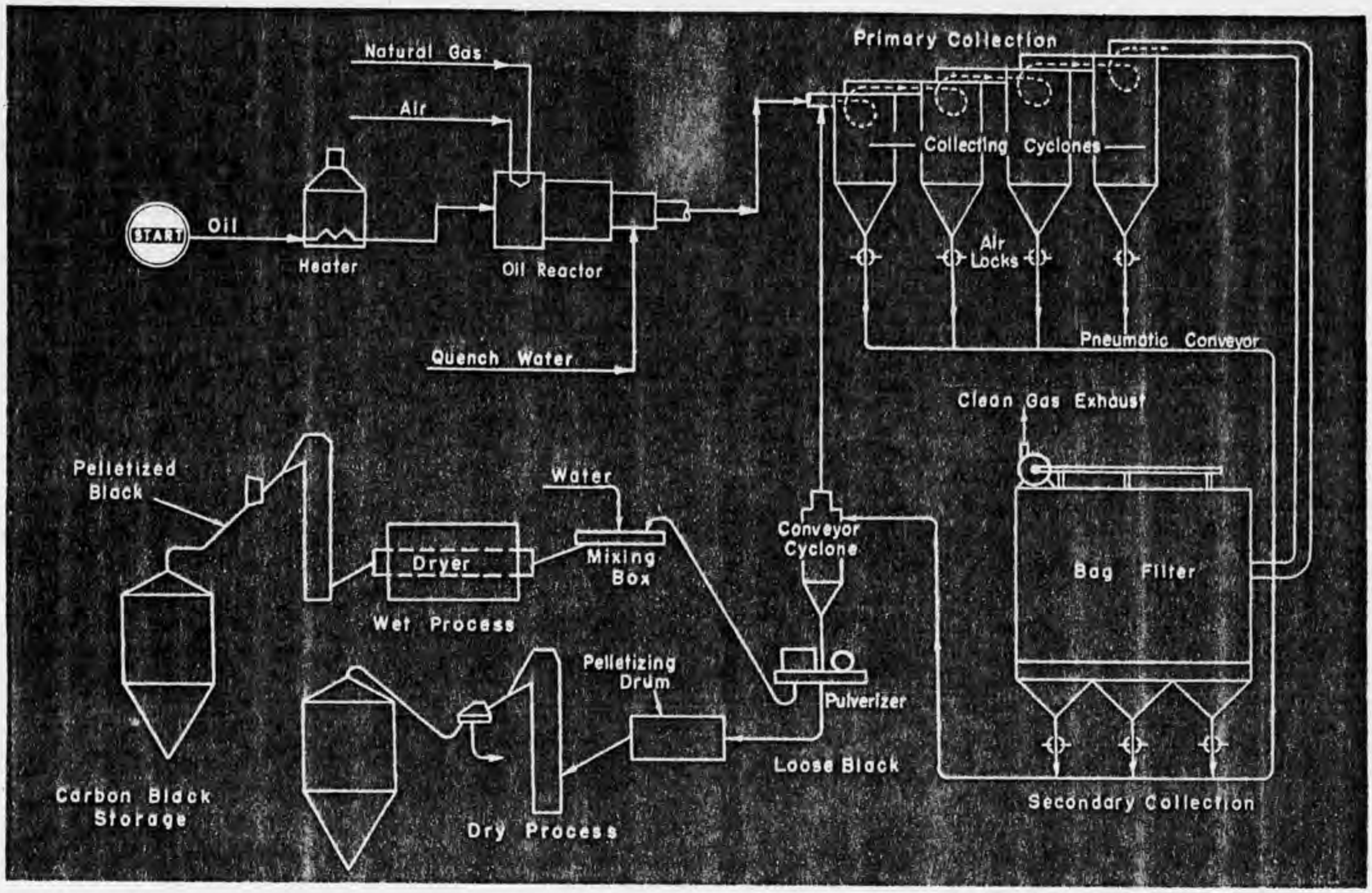


FIG. 6.17. Diagrama completo para la fabricación de sosa cáustica y cloro. (Cortesía de *Columbia-Southern Chemical Corp.*)



Carbon Black (Oil Black)— CONTINENTAL CARBON COMPANY

Application: A process for manufacturing highly re-inforcing furnace blacks from heavy residual oils.

Charge: Heavy residual oil, natural gas, air.

Products: HAF, ISAF, and SAF carbon blacks, pelletized, bulk density 20 to 24 pounds per cubic foot.

Description: Oil is preheated in a direct-fired or molten salt type heater and atomized into a reactor in which gas and air are burned to provide the heat necessary to crack the oil. The furnace used may be one of several variations. An example is the Phillips type (Krejci, J. C. to Phillips Petroleum Company, U.S. 2,526,700, August 21, 1951) now being used under a licensing agreement. Air for the reactor is furnished by centrifugal blowers. The temperature in the oil reactor is maintained in the range of from 2,500° to 2,600° F, by controlling the oil flow rate. The oil is cracked to carbon and hydrogen with side reactions producing carbon dioxide, carbon monoxide, and water. Trace amounts of acetylene and methane are also produced

In the quench section of the reactor, direct water sprays cool the carbon laden gases to about 1000° F. The mixture is further air cooled in a long duct to about 550° F, before entering a header leading to the collection system.

The cooled reaction mixture passes from the header into a series of four cyclones which remove 70 to 80 percent of the black then into the final cleaning step in which silicone coated glass fabric bags remove essentially 100 percent of the black. Alternatively, an electrostatic precipitator, cyclone, wet-scrubber combination may be used with the resultant slurry re-cycled to the quench for recovery.

Carbon black is continually discharged from the collection equipment by rotary valves and picked up by a pneumatic conveyor. The black is collected in a smaller diameter collecting cyclone and discharged through a high speed hammer mill to break up and disperse the very small quantities of hard agglomerates that may be present.

The pulverized carbon black is then conveyed by screw conveyor to the pelletizing system. Two methods of pelletizing are used, dry process and wet process. The dry process consists of a continuous feed of loose black into a rotating drum and a continuous discharge of pellets. In the wet process, the black is mixed with about an equal weight of water, the mixture agitated and the resultant pellets dried.

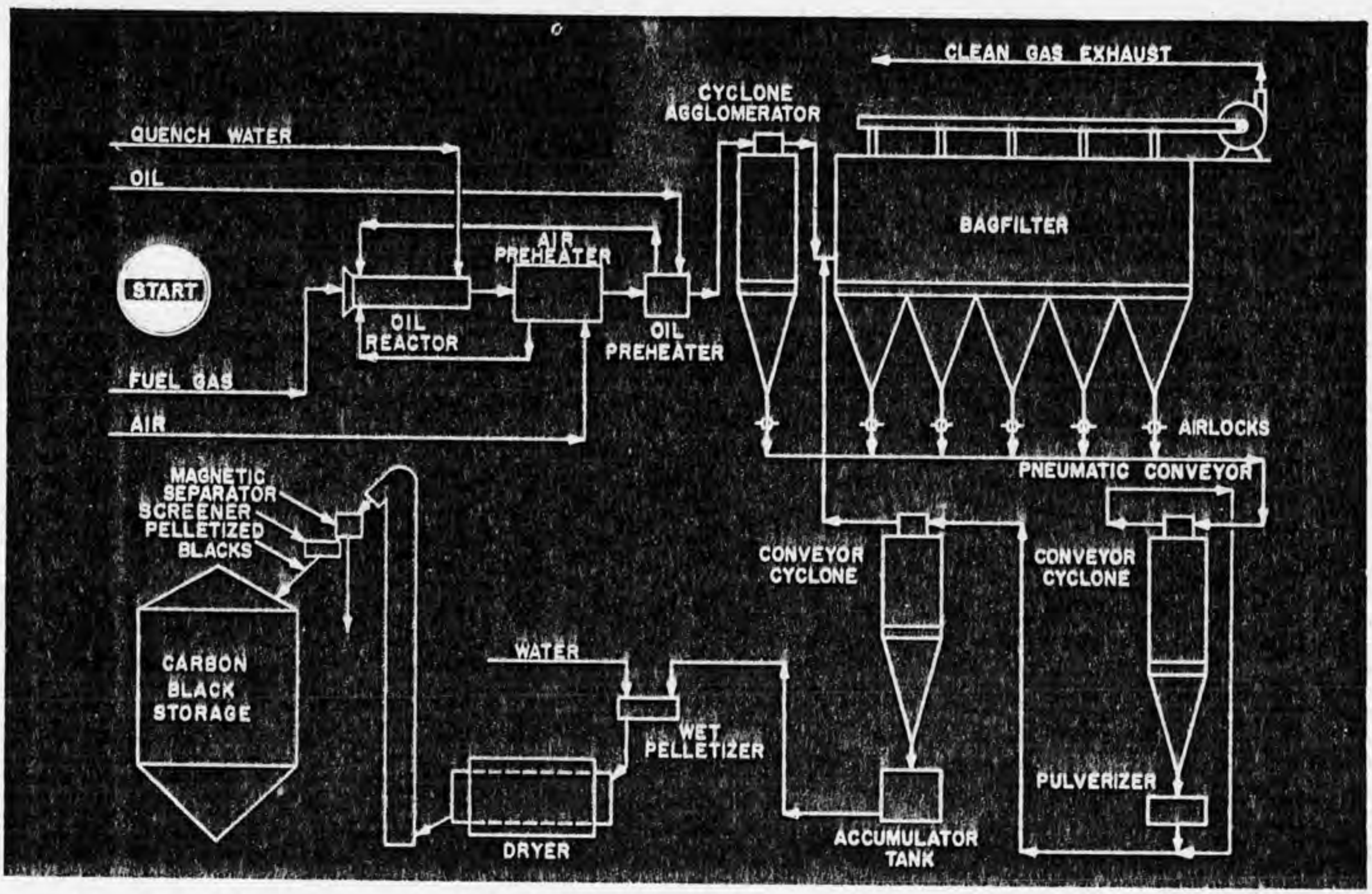
Pelletized black is shipped in bulk hopper cars or automatically packed in 50 pound three ply kraft paper valve type bags.

Operating Conditions: Reactor design and flow rates are extremely critical in determining the quality and type of black.

Yields: The process yields up to 60 percent of the carbon content of the oil feed depending on the charge stock and the grade of black desired as the finished product.

Commercial Installations: All producers use variations of the process. Examples are Continental Carbon Company at Ponca City, Oklahoma; and Westlake, Louisiana; Phillips Chemical Company, Borger, Texas.

References: PETROLEUM REFINER, Nov '57,p227; *Industrial & Engineering Chemistry*, April '52,p685-694.



Carbon Black (Oil Black) — ASHLAND CHEMICAL CO.

Application: A process for manufacturing tread and carcass grades of furnace blacks from aromatic oils. Products include: N110(SAF), N220(ISAF), N285, N330-(HAF), N358(SPF), N550(FEF), N660(GPF), and N761(SRF) carbon-blacks, pelletized, bulk density 19-30 lbs./cu. ft.

Description: Oil is preheated in a direct-fired or heat exchange heater and atomized into a reactor in which fuel gas or oil are burned in air to provide the heat necessary to crack the aromatic oil. The furnaces used may be of several variations. Air for the reactors is usually furnished by centrifugal blowers. The temperature in the oil reactor is maintained in the range of 2,400 to 2,900° F by controlling the flow rates. The oil is cracked to carbon and hydrogen with side reactions producing carbon dioxide, carbon monoxide, and water. Trace amounts of acetylene and methane are also produced.

In the quench section of the reactor, direct water sprays cool the carbon-laden gases to about 1,000° F. The mixture is further cooled by heat exchange with the process air before entering the collection system.

The cooled reactor effluent passes through a header into a cyclonic collector-agglomerator and then to a bag filter in which treated glass fabric bags remove essentially 100 percent of the black. The gaseous effluent is either vented to the atmosphere or used as a low Btu fuel.

Carbon black is continually discharged from the collection equipment by rotary valves into a pneumatic conveyor and subsequently collected in a smaller diameter collecting cyclone. From the collecting cyclone the black is fed through a high speed hammer mill to break up and disperse the very small quantities of hard agglomerates that may be present.

The pulverized black is then conveyed to the pelletizing system where it is mixed with about an equal weight of water the mixture is agitated in pin mixers to form small round pellets. The pellets are then fed to a rotary dryer.

The product is shipped in bulk hopper cars and trucks or automatically packed in 50-pound, three-ply kraft paper, valve-type bags for shipment by boxcar or van.

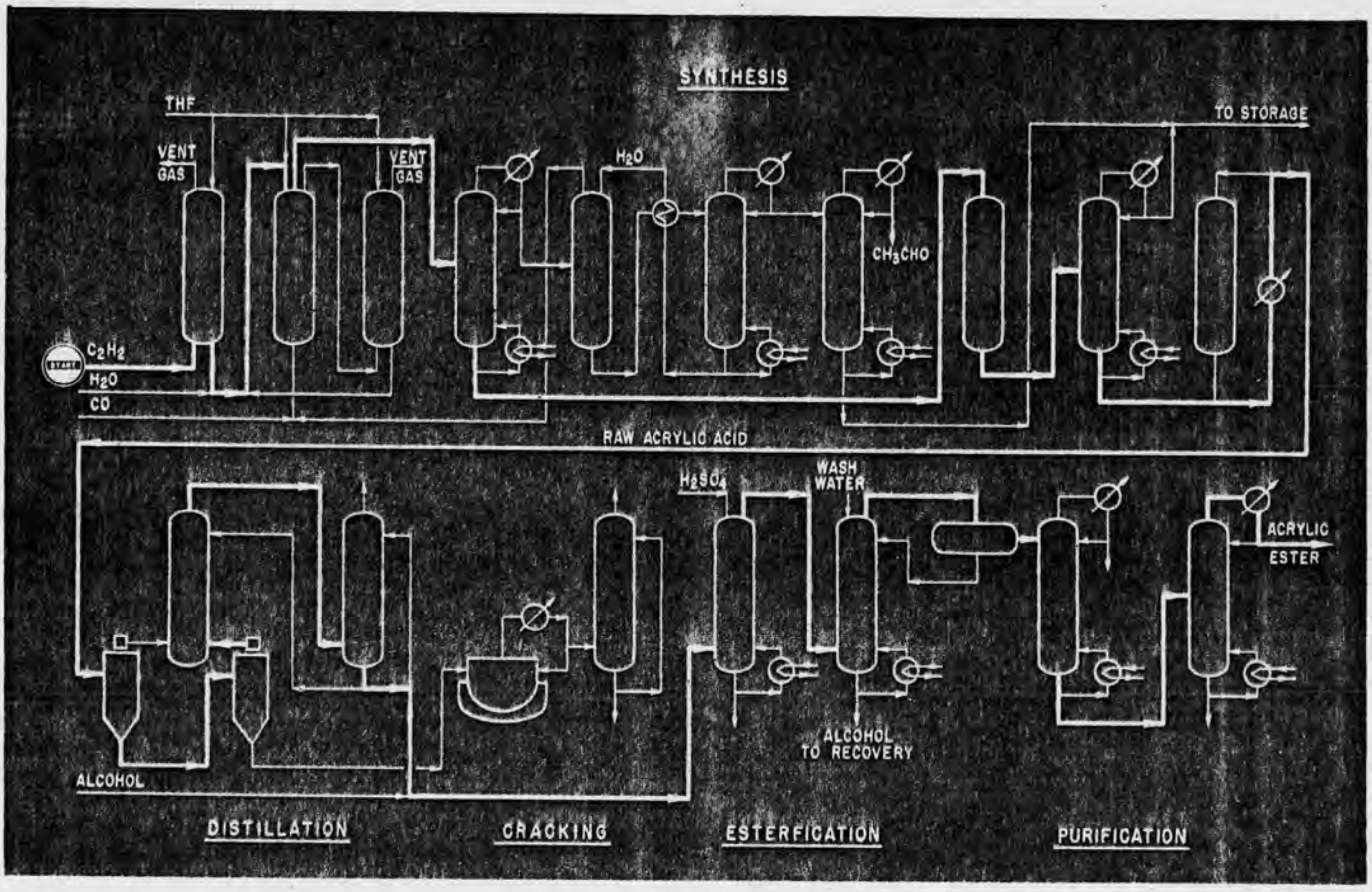
Operating Conditions: Reactor design, flow rates, and close control of all operating conditions are extremely critical in determining and maintaining constant the types and quality of black.

Yields: The process yields up to 60 percent of the carbon content of the oil feed, depending on the charge stock and the grade of black desired as the finished product.

Commercial Installation: Carbon Black & Synthetic Rubber Division of Ashland Chemical Co. plants at Aransas Pass, Texas, Eunice, N. M.; Ivanhoe, La.; Mojave, Calif.; Belpre, Ohio; and Shamrock, Texas. International installations in: France, India, Venezuela, Wales, Spain and Australia.

References: HYDROCARBON PROCESSING, Vol. 36, 11, Nov. 1957, p. 227; *I&EC*, April 1952, pp. 685-691; *Oil & Gas International*, Dec. 1964, pp. 62-64.

PROYECTOS DE INVERSION MEDIANA
TECNOLOGIA DE PROCESO



Acrylates (Reppe) — BADISCHE ANILIN-& SODA-FABRIK AG

Application: A process for the synthesis of acrylic acid. from acetylene, carbon monoxide, and water plus alcohol for production of acrylic esters.

Description: The synthesis proceeds on the basis of the following equation:

$$CH \equiv CH + CO + H_2O \rightarrow CH_2 = CHCOOH + 52.5 \text{ Kcal}$$

The reaction takes place in a liquid phase at 225° C and 100 atm. in the presence of contact salts. The solvent used is tetrahydrofuran. The heat insulated cylindrical reaction furnace has a small gas buffer at the top and contains a vertical, concentrically arranged tube by which an internal liquid circulation is effected. The components are fed to the contact furnace in two forms: in a gaseous form at the bottom and in solution at the top. The acetylene is, for reasons of safety, supplied to the reactor in the form of a gas solution in the tetrahydrofurane, which is produced in a saturator under pressure. The acetylene which is not converted in the synthesis, is recovered and after a water wash mixed with fresh carbon monoxide, again supplied to the synthesis in gaseous form. The catalyzer enters the furnace in solute form.

The inerts are cast off by continuously withdrawing some gas from overhead of the furnace, which is freed from nontransformed acetylene by means of a pressure wash in a separate high pressure vessel. The remainder of the gas is flared.

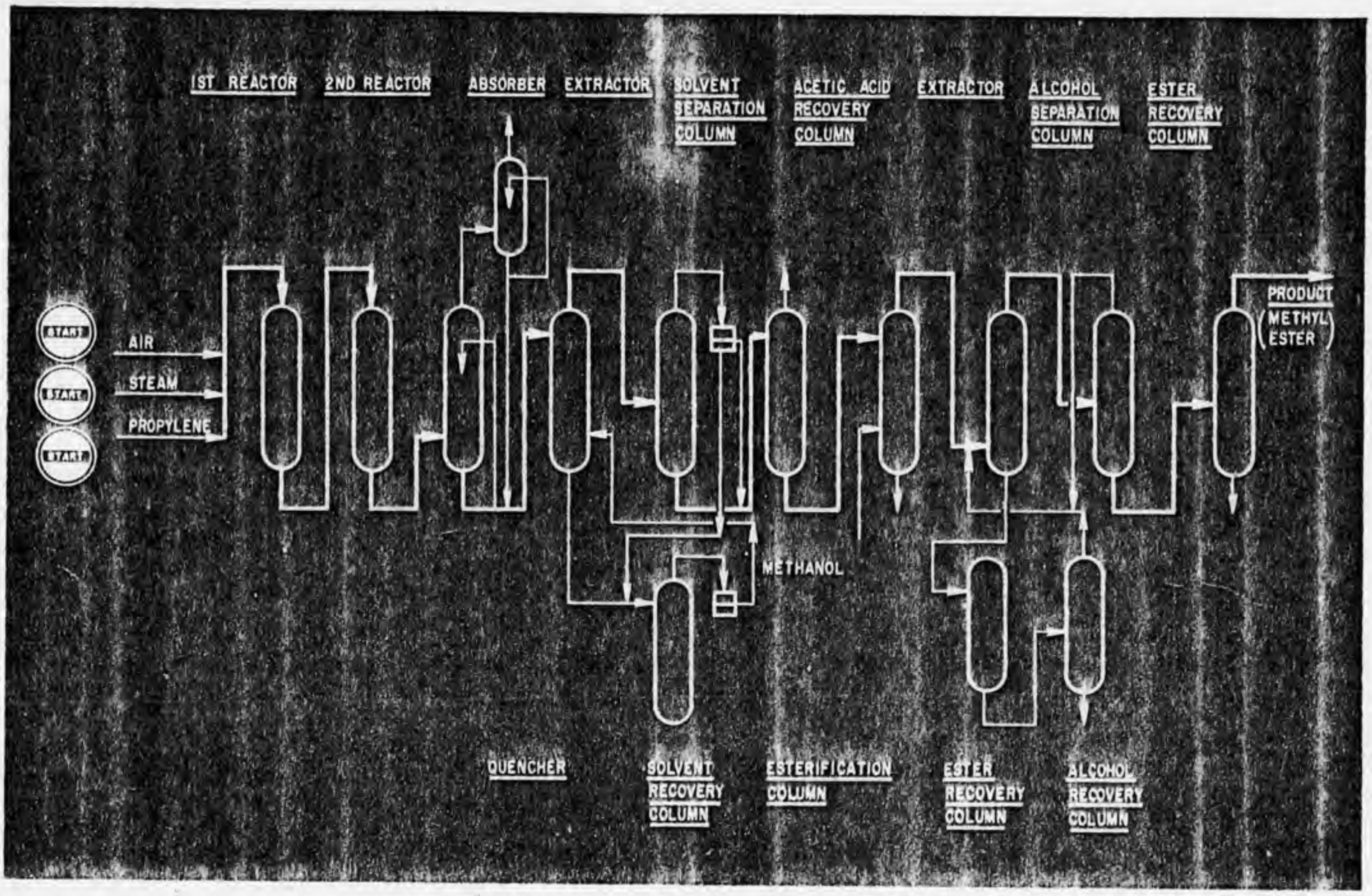
In this synthesis, an 18% solution of acrylic acid in tetrahydrofurane is produced. The furnace product is continuously drawn off the overflow pipe overhead and passed into a degasser column. The resulting degassed product is separated by distillation in tetrahydrofurane and acrylic acid.

The acrylic acid flows off at the sump of the column over a tube evaporator. Since the raw acrylic acid received in this process still contains some dimers, it is distilled. This acrylic acid received as a distillate flows directly to esterification, and the diacrylic acid that is recovered in the bottom is split thermally to acrylic acid.

A small quantity of acetaldehyde develops in the synthesis, which is concentrated in the return gas stream, where it is washed out with water, together with tetrahydrofurane. Tetrahydrofurane and acetaldehyde are separated in a small column.

The acrylic ester is produced in a continuous installation by means of esterification of acrylic acid with the respective alcohol. In the case of ethyl acrylate and methyl acrylate an alcohol surplus of about 100% is applied. For this reason, a separation of ester and unreacted alcohol is required, which takes place in a water wash column. In the case of butyl acrylate, only a slight excess of butanol is necessary. The alcohol/water mixtures that are formed in the wash column are separated by distillation. For stabilization of the acrylic acid and the acrylic ester during the synthesis and storage, stabilizers in solute form are added at various points.

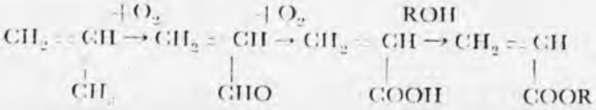
Operating Conditions: Major operating conditions are described above.



Acrylic Esters—TOYO SODA MANUFACTURING CO., LTD.

Application: A process for the manufacture of acrylic acid and/or acrylic esters from propylene, air and steam plus alcohol for esters.

Description: The synthesis proceeds on the basis of the following equations:


$$CH_2=CH-CH_3 \xrightarrow{+O_2} CH_2=CH-CHO \xrightarrow{+O_2} CH_2=CH-COOH \xrightarrow{ROH} CH_2=CH-COOR$$

Propylene, steam and preheated air are fed to the first reactor filled with the first oxidation catalyst. The reaction temperature is kept at 350° C in the catalyst bed by circulation of cooling medium. The oxidation products are fed directly to the second reactor filled with the second oxidation catalyst. The reaction temperature is kept at 300° C in the catalyst bed.

The oxidation product in which carbon monoxide, carbon dioxide, acetic acid, acetone, etc. besides acrylic acid and acrolein are contained, is cooled, and the by-products are removed from the main product. The acrylic acid solution is enriched and then distilled to provide acrylic acid at recovery column.

The acrylic acid, alcohol and conc. sulfuric acid are fed to the esterification reactor. The esterification is carried out at 80° C. The reaction product is sent to settler and then distilled to provide high-purity acrylate at acrylate recovery column.

Operating Conditions: The essential operating conditions are set forth in the above description.

Economics: The yield of acrylic acid and ethyl acrylate from propylene is about 67% and 60%, respectively.

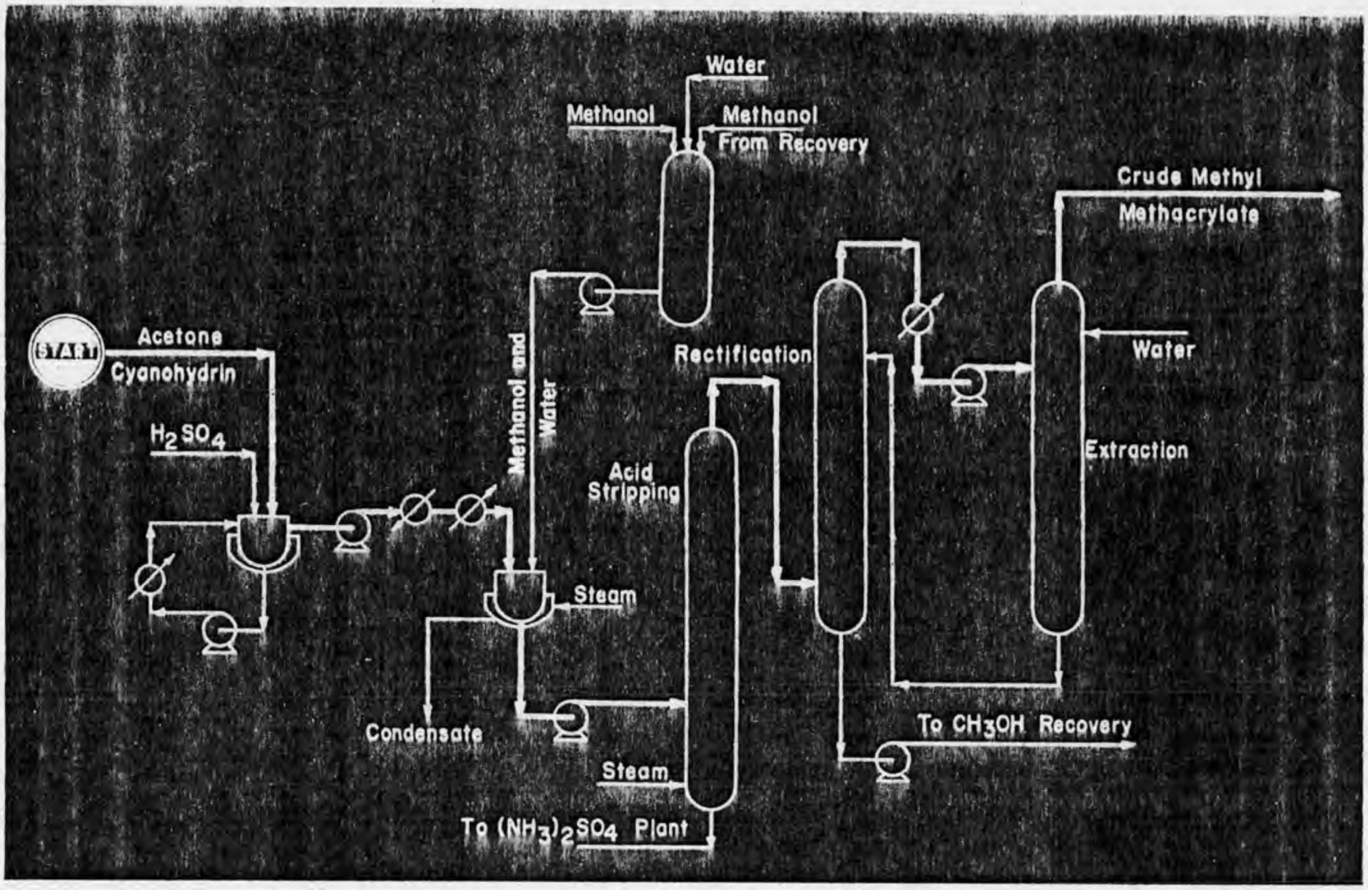
Unit consumptions of the process per pound of acrylic acid and ethyl acrylate are about as follows:

	Acrylic Acid	Ethyl Acrylate
Propylene	0.88 lbs	0.70 lbs
Catalyst & Chemicals	0.6¢	0.8¢
Ethanol	—	0.52 lbs
Steam	1 lb	14 lbs
Water	50 lbs	60 lbs
Power	0.5 kwh	0.62 kwh

Our estimate shows that the investment cost of the plant at a capacity of 25,000,000 lbs/yr of ethyl acrylate is about U.S. $1,500,000.

Commercial Installation: Pilot plant work has been completed and a commercial plant is planned for 1972 at the Shin Daikyowa petrochemical complex.

Reference: Hydrocarbon Processing, May 1969 p. 152-154.



Methyl Methacrylate Monomer — ROHM & HAAS COMPANY

Application: This is a process for the manufacture of methyl methacrylate monomer.

Charge: The raw materials for this process consist of acetone cyanohydrin, sulfuric acid and methanol.

Products: The product is methyl methacrylate monomer.

Description: The process represents the method used for the manufacture of methyl methacrylate, starting with acetone cyanohydrin (prepared by the reaction of hydrogen cyanide and acetone). The acetone cyanohydrin and 99 percent sulfuric acid are reacted to form a methylacrylamide sulfate intermediate. This intermediate is not isolated but is reacted with dilute methanol solution to produce the methyl methacrylate monomer in a continuous manner. The acetone cyanohydrin and concentrated sulfuric acid are pumped into a cooled reaction kettle to form the intermediate. The stream leaving this reaction kettle is dehydrated by heating it in exchangers to an elevated temperature. The stream is then cooled and passed into a series of esterification kettles. In the esterification kettles dilute methanol is added and the methyl methacrylate is formed. In order to prevent polymerization, inhibitors are added at various points in the process. The esterified stream is then pumped to the acid stripping column where methyl methacrylate, methanol and some water are taken off overhead, and the residue, consisting of excess sulfuric acid, ammonium bisulfate and water, is sent to the ammonium sulfate plant. The overhead stream from the acid stripping column enters the rectifier column where the methyl methacrylate and some methanol are removed at the top. This material is condensed and sent to the wash column where the methyl methacrylate is separated from the methanol. The water solution from the bottom of the wash column is returned to the rectifier column, and the bottoms from the rectifier column, consisting essentially of water and methanol, are sent to the methanol recovery column. Recovered methanol is recycled to the esterification kettle and the water is sent to waste. The crude methyl methacrylate, free of methanol, comes from the top of the wash column. The methyl methacrylate is further purified by distillation in a three-stage column system similar to that used for the preparation of the methyl and ethyl acrylate (see p. 269).

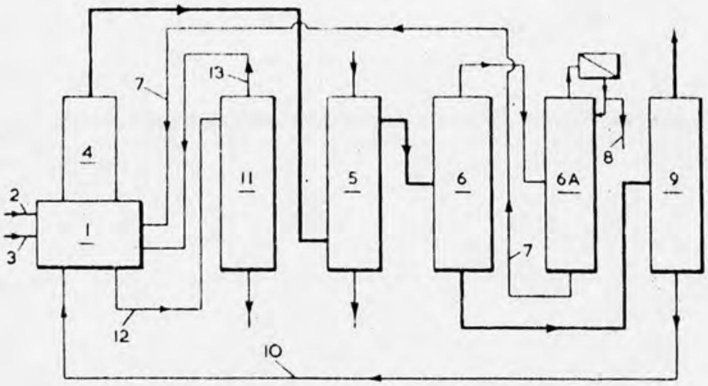
Operating Conditions: The principal operating conditions have been mentioned in the description above.

Commercial Installations: The Rohm & Haas Company has constructed two units at Houston, Texas, one unit at Bristol, Pa., and one unit at Louisville, Kentucky, employing this process.

Reference: *Ind. Eng. Chem.*, 51, 1232, 1328 (1959).

ETHYL ACRYLATE FROM ACRYLIC ACID

Reaction: $CH_2{=}CHCOOH + C_2H_5OH \longrightarrow CH_2{=}CHCOOC_2H_5 + H_2O$



1 - Reactor
2 - Ethanol Feed
3 - Acrylic Acid Feed
4 - Distillation Column
5 - Extraction Column
6, 6A - Topping Columns
7 - Ethyl Acetate Recycle
8 - Diethyl Ether and Ethyl Formate
9 - Product Column
10 - Heavy Recycle
11 - Evaporator
12 - Heavy Ends
13 - Light Recycle to Reactor

Feed Materials:
Acrylic Acid
Ethanol

Coproducts:

Catalyst: Sulfuric Acid
Phase: Liquid
Reactor type: Still Column
Solvent used: Ethyl Acetate
Temperature, °C: 80-90
Pressure psi: Atmospheric
Reaction time:
Heat Required: -
Heat evolved: -
Product yield:
Product purity:
Materials of Construction:

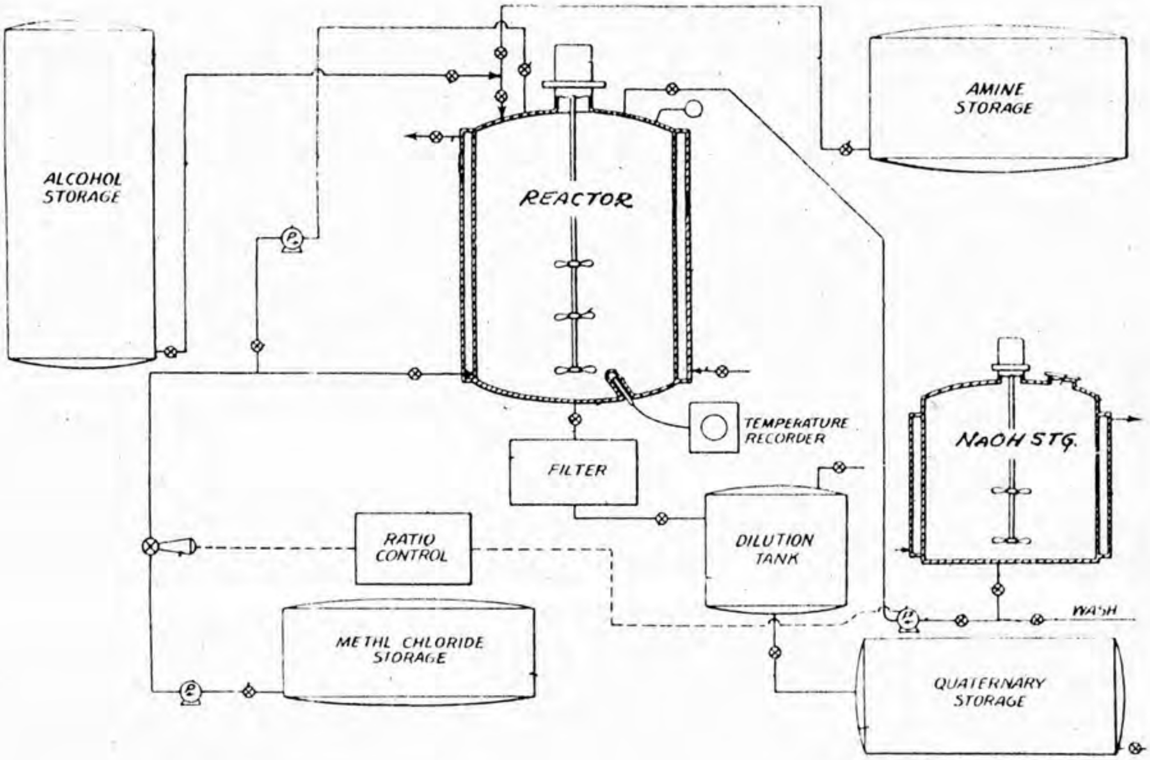
Major Product Uses: In acrylic paints and acrylate polymer manufacture.

Reference: U.S. Patent 3,354,199 by S.K. Lachowicz et al (to Distillers Co., Ltd.) (November 21, 1967)

QUATERNARY AMMONIUM COMPOUNDS

Reaction:

$$RNH_2 + 3CH_3Cl + 2NaOH \longrightarrow R(CH_3)_3NCl + 2NaCl + 2H_2O$$



Feed Materials:
- Long-Chain Alkyl Amine (RNH_2)
- Methyl Chloride
- Sodium Hydroxide

Coproducts:
- Sodium Chloride
- Water

Catalyst: None
Phase: Liquid
Reactor type: Stirred, Jacketed Kettle
Solvent used: Isopropyl Alcohol
Temperature, °C: 95-105
Pressure psi: 30-60
Reaction time: 2-6 hours
Heat Required: -
Heat evolved: Yes
Product yield:
Product purity:
Materials of Construction:

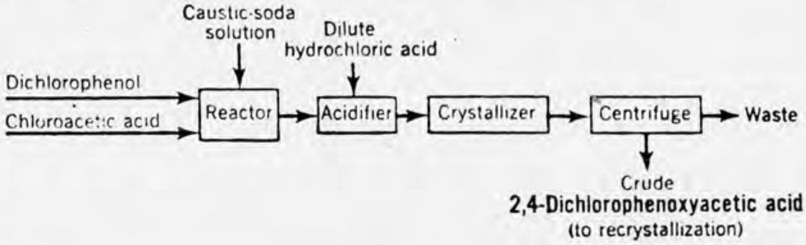
Major Product Uses: Cationic surface-active agents with high antibacterial effectiveness.

Reference: U.S. Patent 2,950,318 by S.H. Shapiro (to Armour & Co.) (August 23, 1960)

2,4-DICHLOROPHENOXYACETIC ACID (2,4-D)

$Cl_2C_6H_3—O—CH_2COOH$

From Dichlorophenol and Monochloroacetic Acid



Reaction

$$Cl_2C_6H_3OH + ClCH_2COOH + NaOH \rightarrow$$

$$Cl_2C_6H_3—O—CH_2COOH + NaCl + H_2O$$

80–85% yield

Material Requirements

Basis—1 ton 2,4-dichlorophenoxyacetic acid

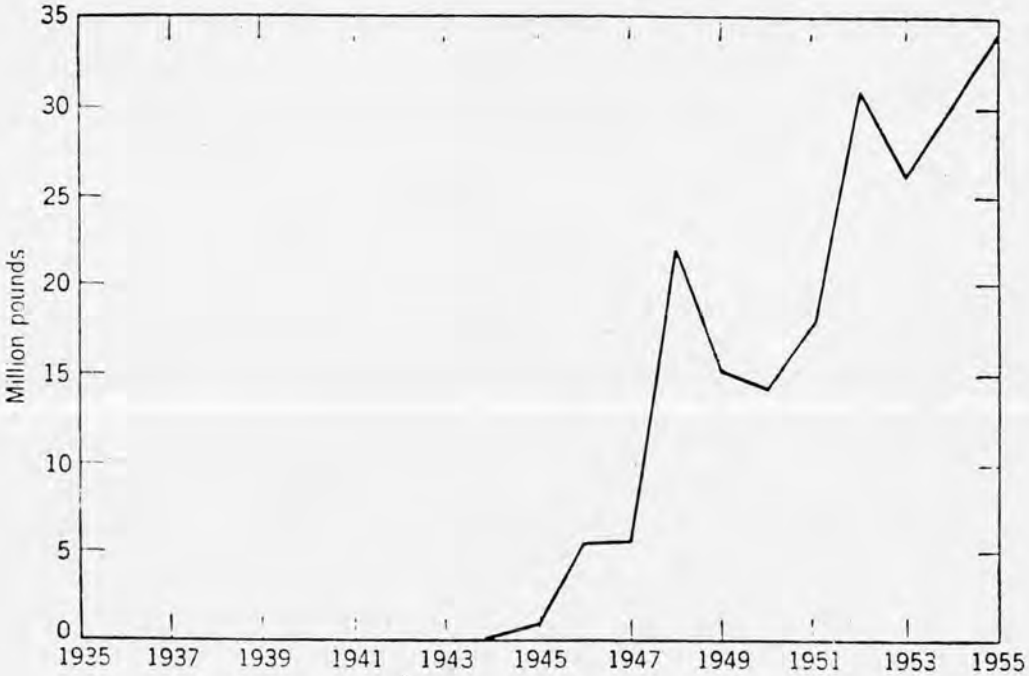
2,4-dichlorophenol	1,830 lb	Sodium hydroxide	990 lb
Monochloroacetic acid	970 lb	Hydrochloric acid (18°Bé)	1,750 lb

Process

Equimolecular quantities of 2,4-dichlorophenol and monochloroacetic acid are charged to a steam-heated closed kettle along with 2.2 moles of sodium hydroxide as a 15 per cent water solution. Reaction is carried on for several hours under reflux conditions, after which time the reaction mass is acidified (to 1.0 *p*H) with dilute hydrochloric acid. The acidified liquor is sent to a crystallizer and thence to a centrifuge. The crude crystals must then be recrystallized from a suitable solvent, for example benzene, and washed and dried. The reaction must be carried out under optimum conditions of time, temperature, and rate of addition of reactants to prevent hydrolysis of unconverted chloroacetic acid to glycolic acid. In one process variation, unreacted dichlorophenol is removed by distillation prior to acidification.

Better yields (90–92%) are claimed for carrying out the reaction in the presence of anhydrous monochlorobenzene. The reaction is carried out at the boiling point of the solvent; water is removed azeotropically. The insoluble product is separated from the solvent by filtration.

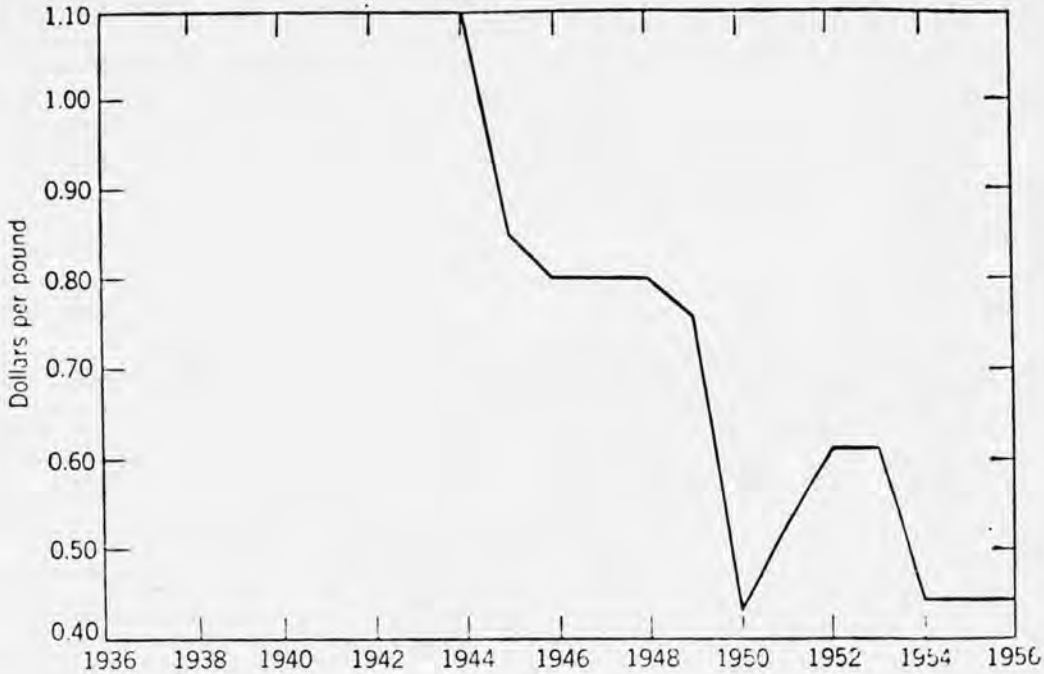
A 2-ton-per-day plant costs $180,000 exclusive of building and site.



Production—2,4-Dichlorophenoxyacetic Acid

Use Pattern

	Per cent
Weed killer	95
Other agricultural uses	5
	100



Price—2,4-Dichlorophenoxyacetic Acid

Miscellaneous

Properties. Colorless, odorless crystals.

Mol. wt. 221.05 M.P. 138°C

Very slightly soluble in water (0.4 g per 100 g at 25°C). Soluble in 50 per cent ethanol (10.3 g per 100 g at 25°C).

Grades. Technical (99 per cent).

Containers and Regulations. Fiber drums (100 lb). No ICC shipping label required.

Economic Aspects

The rapid increase in production and consumption of 2,4-dichlorophenoxyacetic acid (2,4-D) and its salts and esters since World War II is another example of the strides made by the agricultural chemicals industry in the postwar period (see *DDT*). The manufacture of organic herbicides is currently a 60,000,000-lb-per-year business, and appears destined to increase substantially for many years. It is estimated that annual crop losses due to weeds amount to $5,000,000,000.

2,4-D is still the most important of the herbicides and is used effectively in the control of broad-leaved annual weeds in grain fields and of herbaceous weeds in pasture lands. It is also used as a general herbicide in maintaining various rights-of-way, such as along highways.

Next in importance to 2,4-D is 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) which is used against brush and woody plants, particularly mesquite. It is also useful against weeds that have developed resistance to 2,4-D.

Among the other organic herbicides that show promise are dichloropropionic acid and trichloroacetic acid; chemicals for the pre-emergence treatment of soils (prevent germination of weed seeds), such as 2,4-dichlorophenoxyethyl sulfate, and dinitro-*o-sec*-butylphenol; soil sterilants, e.g., 3-(*p*-chlorophenyl)-1,1-dimethylurea (CMU); and the herbicides developed to control grassy weeds, e.g., isopropyl *n*-(3-chlorophenylcarbamate (CIPC).

The most important derivatives of 2,4-D at present are the amine salts and alkyl esters. In fact, several formulators buy the basic acid from manufacturers and make the derivative they prefer in their own plants. Most of the acid is used in these forms.

Like most other agricultural chemicals, however, weed-killer manufacturers are plagued from time to time with overproduction and price cutting. As in any other new field, the competition of newly developed herbicides presents a threat to established products. On the other hand, with increasing demands on the world's food supply, chemical weed control has become a necessity, and the sale of herbicides should increase for many years. The characteristics of 2,4-D are such that it will certainly supply a goodly portion of this demand. Larger quantities will also be used as a plant hormone, as further applications are developed.

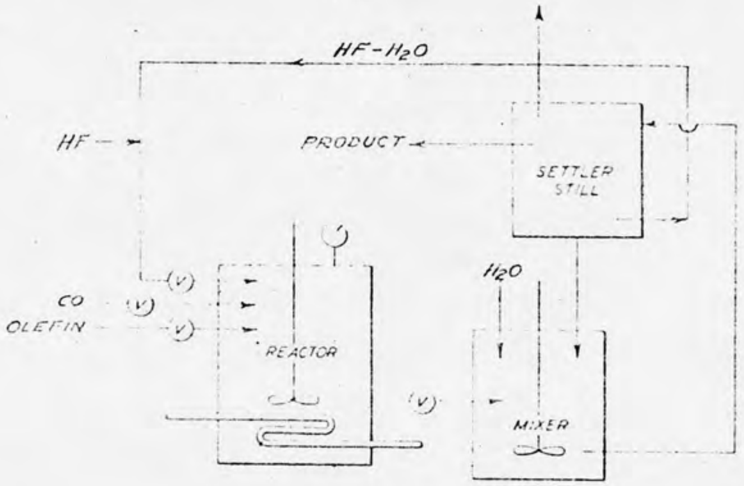
Of course for some uses, 2,4-D may be partially replaced with related compounds, such as its butyric acid homolog or by mixtures of herbicides.

Manufacturing plant requirements are comparatively simple, but production will probably be limited to those companies with a good raw material position and experience in agricultural chemical sales.

Manufacturers and Plant Sites

Chipman Chemical Co., Portland, Ore.
Diamond Alkali Chlorinated Products Div., Houston, Texas; Newark, N. J.; Des Moines, Iowa
Dow Chemical Co., Midland, Mich.
Monsanto Chemical Co., Monsanto, Ill.
Pittsburgh Plate Glass Co., New Martinsville, W. Va.
Pennsylvania Coke and Chemical Co., Neville Island, Pa.
Rohm and Haas Co., Bristol, Pa.

Reaction: $RCH=CH_2 + CO + H_2O \longrightarrow RCH_2CH_2COOH$



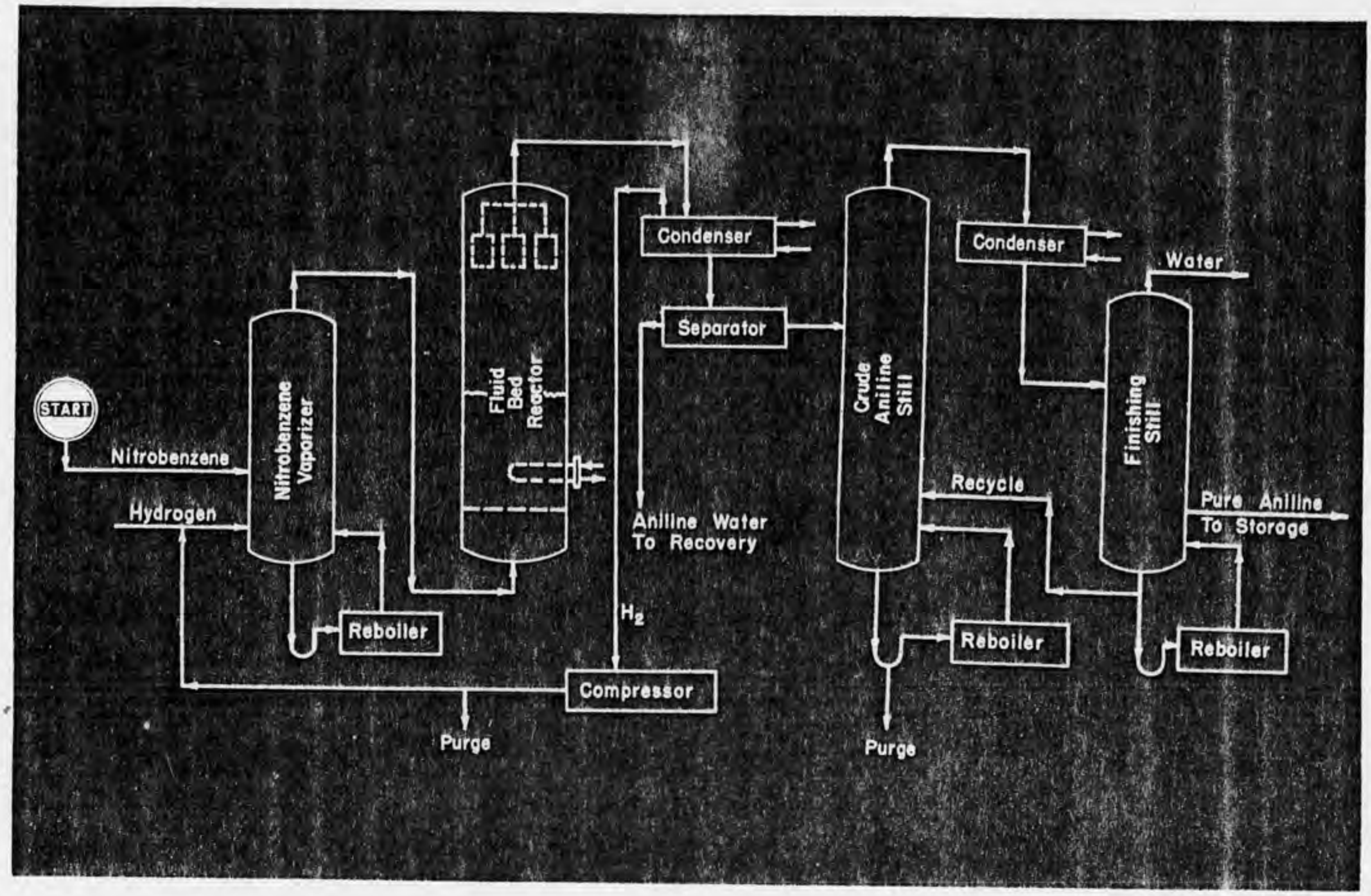
Feed Materials:
Diisobutylene
Carbon Monoxide
Water

Coproducts:

Catalyst: Hydrogen Fluoride
Phase: Liquid
Reactor type: Stirred, Jacketed Kettle
Solvent used: Water
Temperature, °C: 0-95
Pressure psi: 150-500
Reaction time: 1 minute to 1 hour
Heat Required: -
Heat evolved: Yes
Product yield: 90%
Product purity:
Materials of Construction:

Major Product Uses: In the manufacture of paint driers and in the formulation of alkyd resins.

Reference: U.S. Patent 3,005,846 by B.S. Friedman et al (to Sinclair Refining Co.) (Oct. 24, 1961)



Aniline—AMERICAN CYANAMID COMPANY

Application: A vapor-phase fluid-bed catalytic process for reduction of nitrobenzene to aniline.

Charge: Nitrobenzene containing less than 10 ppm nitrothiophene and hydrogen.

Product: Aniline—Freezing point —6.2° C minimum.

Description: Mononitrobenzene prepared from benzene by standard nitration processes, is fed to a lower tray of a bubble-tray tower. Heat supplied by a reboiler vaporizes the nitrobenzene into a stream of hydrogen which is fed up the tower. The mixture of nitrobenzene and hydrogen containing approximately three times the theoretical amount of hydrogen required for the reduction is passed through a porous distributor plate into a reduction chamber containing a fluidized bed of copper catalyst. Excess heat of reaction is removed by circulation of a heat-transfer liquid through tube bundles suspended in the catalyst bed. The upper portion of the reactor, essentially empty, acts as a disengaging zone and permits a major portion of the catalyst particles entrained in the gas stream to fall back into the catalyst bed. The exit gases are filtered free of catalyst on porous stainless steel filters.

The filtered gases are cooled in a condenser to separate aniline and water from the excess hydrogen which is recycled except for a small purge. The aniline is separated from water in a decanter. The crude aniline containing less than 0.5 percent unreacted nitrobenzene and about 5 percent water is distilled to remove high boilers. The water and aniline which pass overhead are condensed and redistilled in a finishing tower.

The catalyst is prepared by the adsorption of cuprammonium nitrate on silica hydrogel followed by spray drying to yield a fluidizable powder with a particle diameter of 20 to 150 microns. The catalyst is activated in place in the converter by reduction with hydrogen at a temperature of about 250° C. Careful control of the quality of nitrobenzene will give long active life catalyst (1,500 units of aniline per unit of catalyst) before regeneration is required. Regeneration may be accomplished in place by stopping the nitrobenzene feed, flushing the system with inert gas and passing air through the catalyst at 250° C — 350° C to burn off organic deposits.

The reaction is as follows:

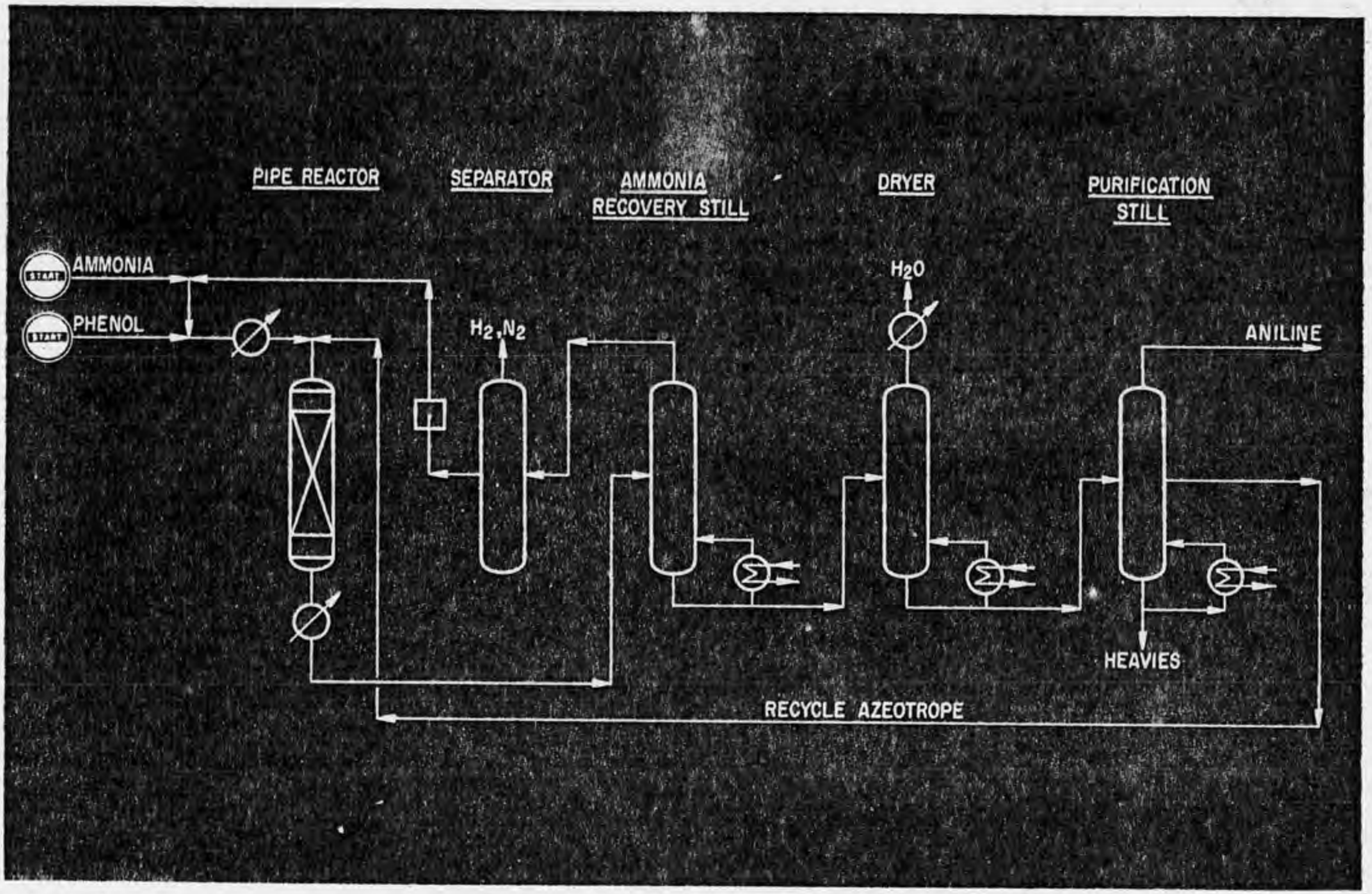
$$C_6H_5NO_2 + 3H_2 = C_6H_5NH_2 + 2H_2O$$

Operating Conditions: The reduction is carried out at 270° C and 20 psig.

Yield: The yield of aniline from nitrobenzene is approximately 98 percent of theory.

Commercial Installation: American Cyanamid Company, Willow Island, W. Va.

References: O. C. Karkalits, Jr., C. M. Vanderwaart and F. H. Megson (to American Cyanamid Company) U.S. 2,891,094.



Aniline — SCIENTIFIC DESIGN CO., INC.

Application: A process for the manufacture of aniline from pure or impure phenol.

Description: Reactor feed is prepared by combining phenol and ammonia. The preheated vapor feed mixture enters a fixed bed catalytic reactor, and aniline and water are produced by the ammonolysis reaction. Reactor effluent is partially condensed and unconverted ammonia is compressed and recycled. Water of reaction is removed from the crude aniline stream by distillation. High purity aniline product is recovered by distillation from heavies.

The key feature of the process is the unique Halcon-developed catalyst which attains nearly quantitative yields on phenol and ammonia so that the purification train is simple and the aniline product is of unusually high purity. Because of the long life of the catalyst no regeneration facilities are required.

Economic factors: Capital costs are a small fraction of those of equivalent capacity via nitrobenzene reduction technology: a 100 MM lb./yr. plant would cost $3.5 MM. Production of aniline from phenol is raw materials intensive, because the process itself is extremely simple. Where large quantities of low cost phenol are available, extremely high purity aniline is required, or minimum capital expenditure is desired, this process is favored.

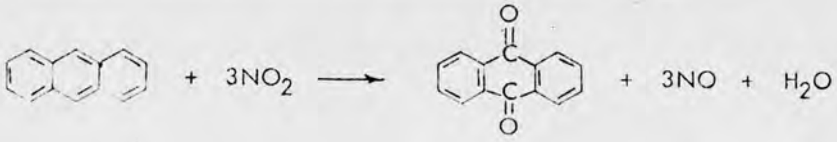
The process presents advantages over the classical technology by avoiding the hazardous nitration step and eliminating acidic purge streams. Waste disposal problems are minimal.

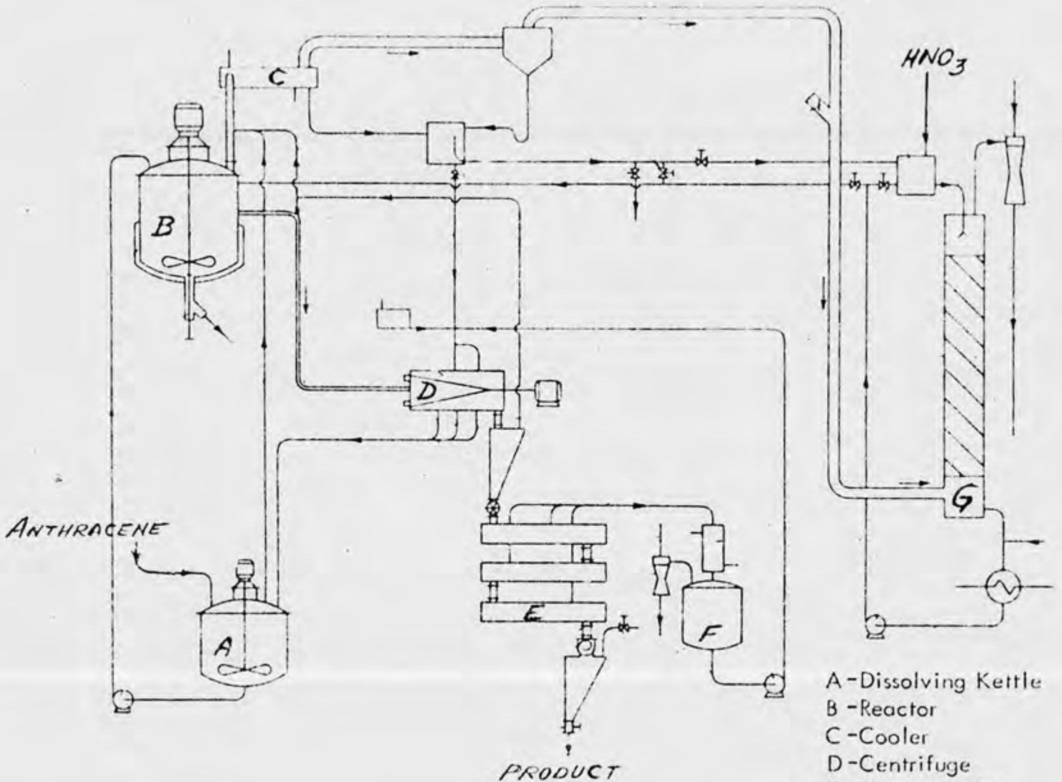
Commercial installations: A 20,000 metric ton/year plant has been in satisfactory operation since August 1970 for Mitsui Petrochemical Industries, Ltd., Japan.

Reference: *Chemical Engineering,* April 2, 1973.

ANTHRAQUINONE FROM ANTHRACENE AND NITRIC ACID

Reaction:





A - Dissolving Kettle
B - Reactor
C - Cooler
D - Centrifuge
E - Vacuum Drier
F - Diluent Tank
G - Nitric Recovery Tower

Feed Materials:
- Anthracene
- Nitric Acid

Coproducts:
- Water
- Nitric Oxide

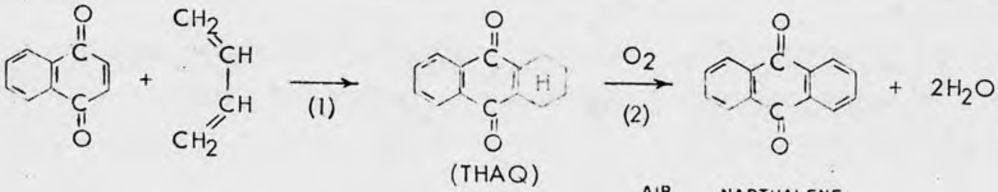
Catalyst:	None
Phase:	Liquid
Reactor type:	Stirred, Jacketed Kettle
Solvent used:	Trichlorobenzene
Temperature, °C:	105-110
Pressure psi:	Atmospheric
Reaction time:	
Heat Required:	-
Heat evolved:	Yes
Product yield:	95%
Product purity:	
Materials of Construction:	Stainless Steel

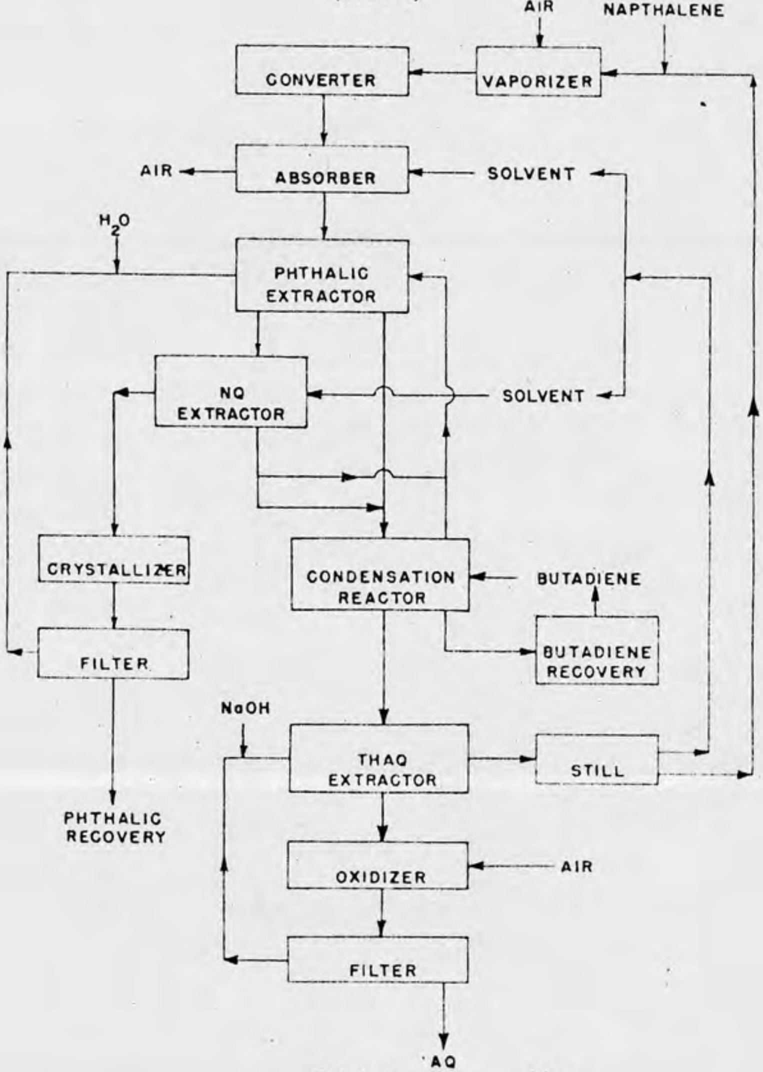
Major Product Uses: Used in the manufacture of anthraquinone vat dyes.

Reference: U.S. Patent 2,821,534 by W. N. Alexander (to General Aniline & Film Corp.) (Jan. 28, 1958)

ANTHRAQUINONE FROM NAPHTHOQUINONE AND BUTADIENE

action:





d Materials:

1,4-Naphthoquinone
Butadiene
Air

roducts:

Water

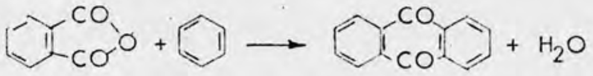
Catalyst:	None
Phase:	Liquid
Reactor type:	Pipeline
Solvent used:	Alpha Chloro Naphthalene
Temperature, °C:	100 (1); 140-150 (2)
Pressure psi:	60 (1); 70 (2)
Reaction time:	5 hrs. (1)
Heat Required:	-
Heat evolved:	-
Product yield:	85-90% Overall
Product purity:	
Materials of Construction:	

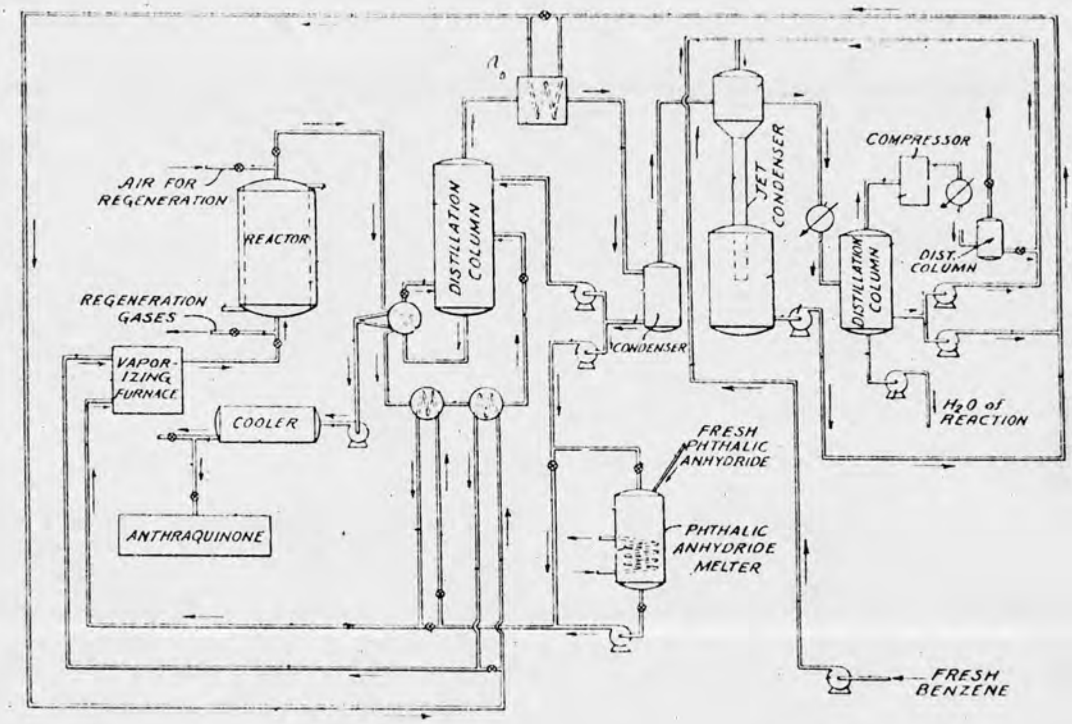
jor Product Uses: Used in the manufacture of anthraquinone vat dyes.

erence: U.S. Patent 2,938,913 by R.G. Weyker et al (to American Cyanamid Co.) (May 31, 1960)

ANTHRAQUINONE FROM PHTHALIC ANHYDRIDE

Reaction:





Feed Materials:

Phthalic Anhydride
Benzene

Coproducts:

Water

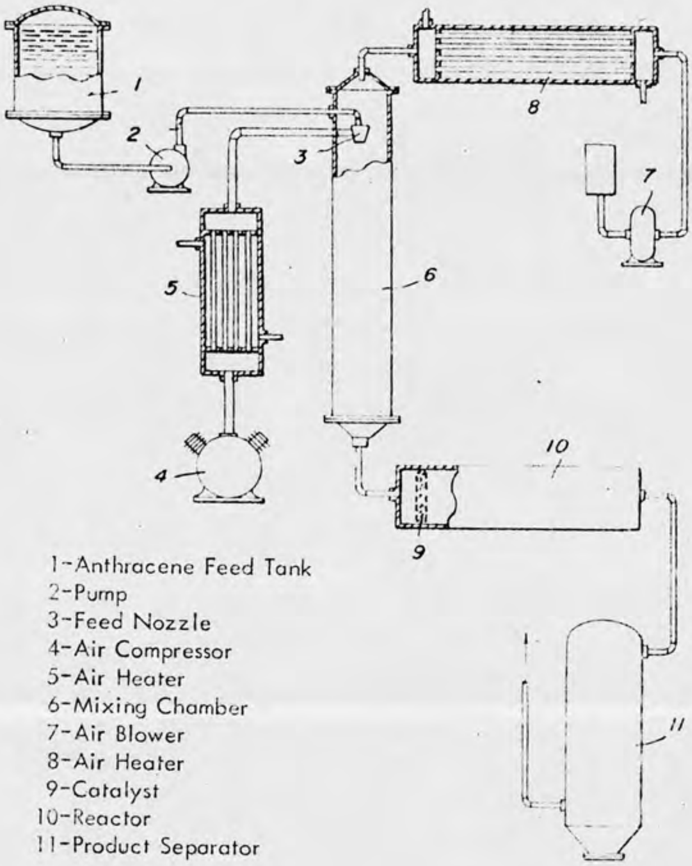
Catalyst: Silica-Alumina
Phase: Vapor
Reactor type: Fixed-Bed
Solvent used: None
Temperature, °C: 370-470
Pressure psi: Atmospheric
Reaction time: 0.25-0.5 seconds
Heat Required: -
Heat evolved: -
Product yield: 80%
Product purity:
Materials of Construction: Steel

Major Product Uses: Used in the manufacture of anthraquinone vat dyes.

Reference: U.S. Patent 2,401,225 by P.D. Caesar et al (to Socony-Vacuum Oil Co.)(May 28, 1946)

ANTHRAQUINONE FROM ANTHRACENE AND AIR

Reaction:



1-Anthracene Feed Tank
2-Pump
3-Feed Nozzle
4-Air Compressor
5-Air Heater
6-Mixing Chamber
7-Air Blower
8-Air Heater
9-Catalyst
10-Reactor
11-Product Separator

Feed Materials:
Anthracene
Air

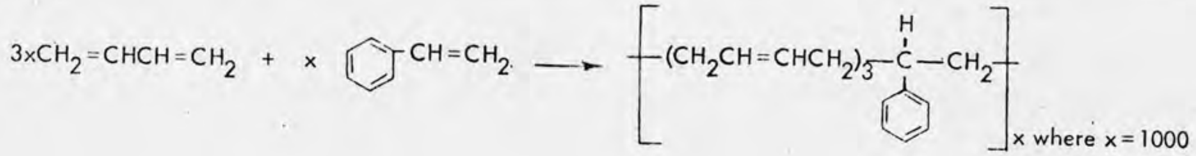
Coproducts:
Water

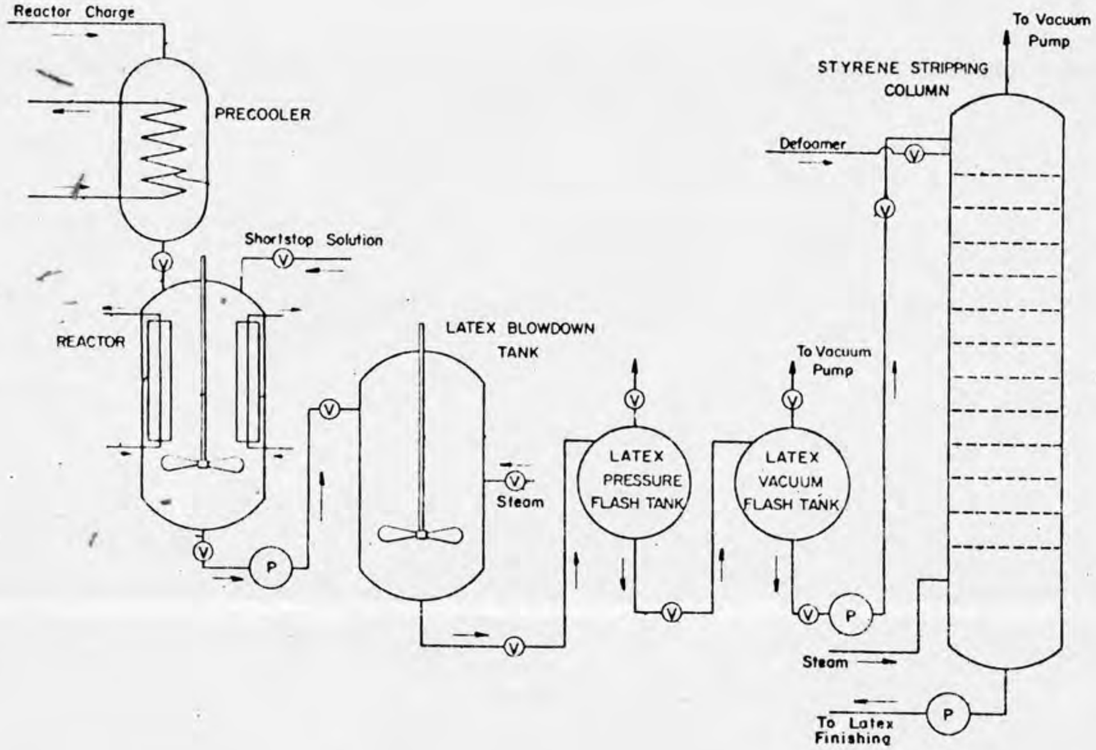
Catalyst:	Vanadium Pentoxide
Phase:	Vapor
Reactor type:	Horizontal Drum
Solvent used:	None
Temperature, C:	300-400
Pressure psi:	Atmospheric
Reaction time:	0.4-4.0 seconds
Heat Required:	-
Heat evolved:	Yes
Product yield:	90%
Product purity:	
Materials of Construction:	Steel

Major Product Uses: Used in the manufacture of anthraquinone vat dyes.

Reference: U.S. Patent 3,062,842 by G. Gross (to Ciba Ltd.) (Nov. 6, 1962)

Reaction:





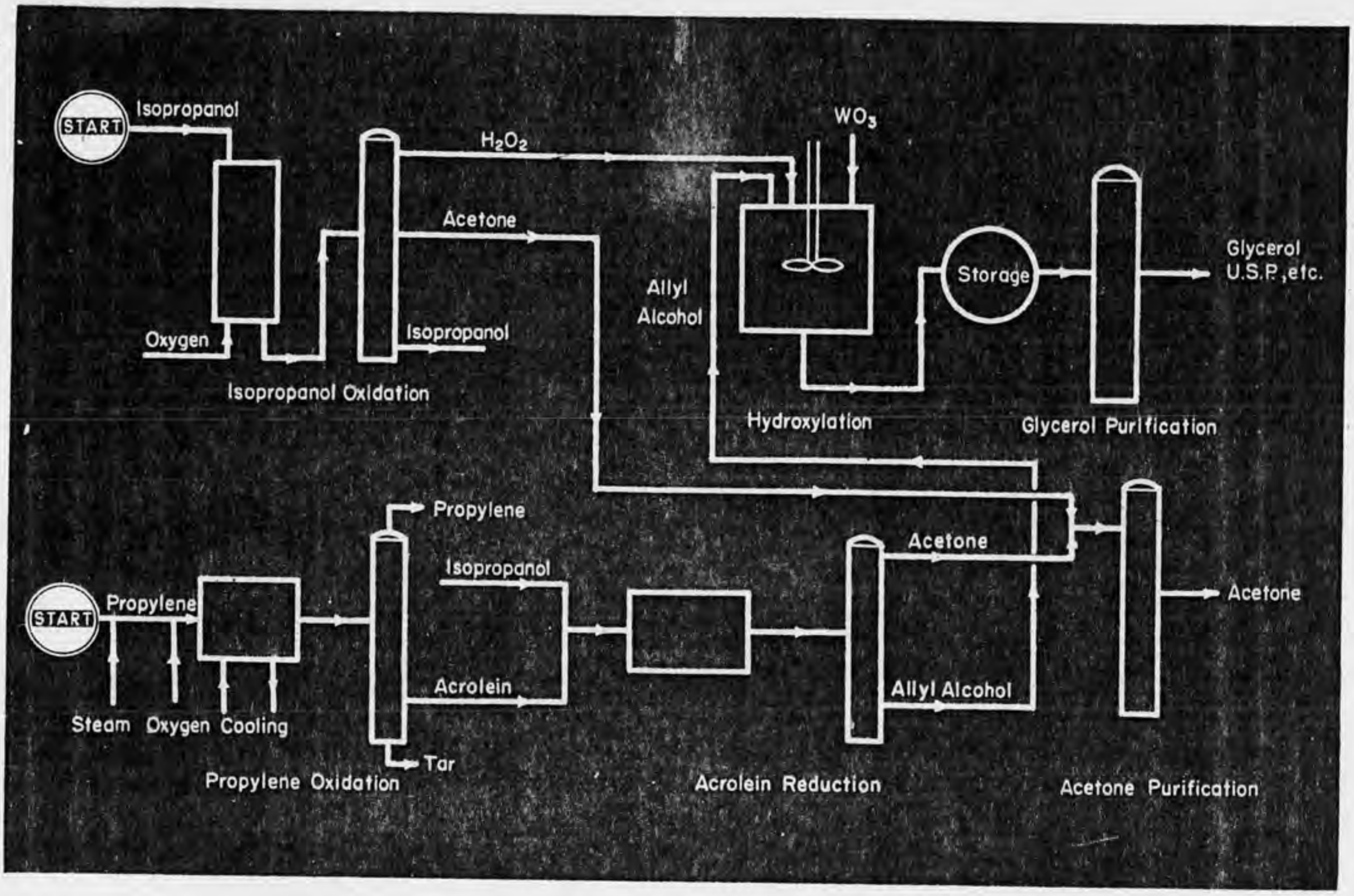
Feed Materials:
Butadiene
Styrene

Coproducts:

Catalyst:	Cumene Hydroperoxide
Phase:	Liquid (Emulsion)
Reactor type:	Jacketed, Stirred Kettle
Solvent used:	Water
Temperature, °C:	5
Pressure psi:	Atmospheric
Reaction time:	14 hours
Heat Required:	–
Heat evolved:	Yes
Product yield:	98-99% (70% Conversion)
Product purity:	
Materials of Construction:	Glass-Lined Steel

Major Product Uses: As general purpose elastomers for automotive tires and industrial uses.

Reference: U.S. Patent 3,052,645 by W.P. Denson (to Copolymer Rubber & Chemical Corp.) (Sept. 4, 1962)



Glycerol (Acrolein and Hydrogen Peroxide)

Application: This is a process for the manufacture of glycerol with large amounts of acetone as a coproduct.

Charge: Propylene, Oxygen.

Description: Propylene is first hydrated to isopropanol using a standard process. (See Page 264). The isopropanol is oxidized in the liquid phase by bubbling pure oxygen through a liquid mixture of isopropanol and H_2O_2 at a pressure of about 2.5 atmospheres and at temperatures between 90° and 140° C. The reaction mixture is diluted with water, stabilized, and fractionated to yield hydrogen peroxide solution, acetone and unreacted isopropanol, which can be recycled.

A mixture of propylene with slightly more than an equal amount of steam is reacted with 25 percent oxygen based on the weight of the propylene. The reaction is carried out over a fixed bed of catalyst based on cuprous oxide, supported on SiC or some other high thermal conductivity support. Close control of reaction temperature is necessary. The reaction pressure may be from 1 to 10 atmospheres and the temperature between 300° and 400° C. The reaction mixture is cooled and fractionated to give acrolein, unreacted proplyene, and tarry by-products. The yield of acrolein is near 86 percent of the propylene consumed.

The purified acrolein is mixed with pure isopropanol from the propylene hydration step and the mixture vaporized. The mixed vapors containing 2-3 moles of alcohol per mole of acrolein are passed through a catalyst bed containing both uncalcined magnesium oxide and zinc oxide, with the magnesia predominating. The reaction takes place at about 400° C and yields about 77 percent allyl alcohol (based on acrolein charged) and an additional quantity of acetone which is added to that formed in the isopropanol oxidation step.

Purified ally alcohol is agitated with a water solution of hydrogen peroxide containing a small amount of tungsten trioxide in solution. The effective catalyst is a 0.2 percent pertungstic acid solution in 2 molar aqueous hydrogen peroxide. The reaction temperature is 60°-70° C, reaction time is about two hours, producing glycerol in water solution.

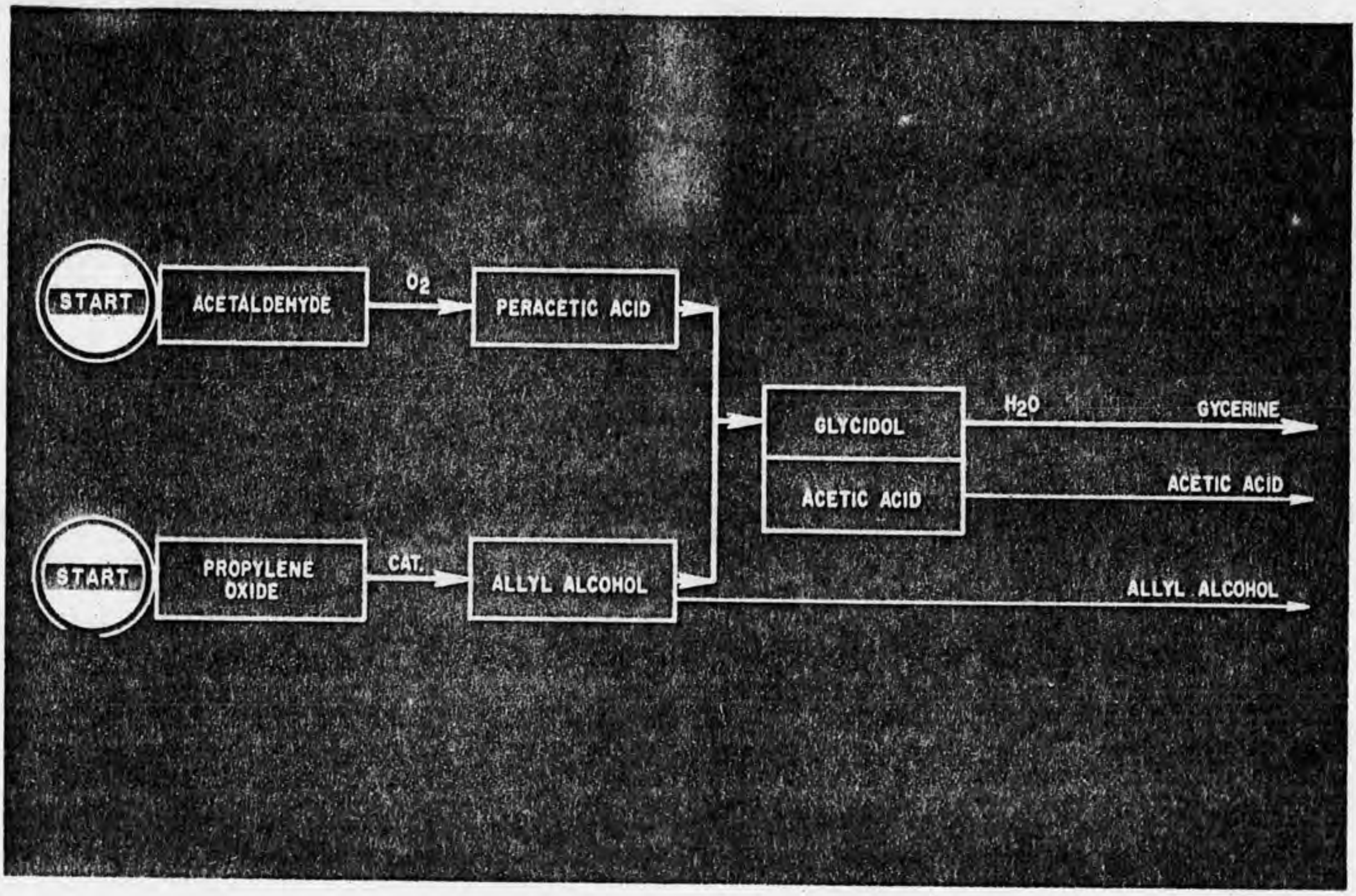
The reaction mixture is dumped to receivers and distilled to yield high-purity glycerol. The recovered catalyst solution is recycled. The yield of the final step 80-90 percent based on the allyl alcohol charged.

Operating Conditions: The control of both the propylene oxidation step and the hydroxylation step must be exceptionally good for acceptable yields. The conditions quoted are approximate, and the practical operating limits are doubtless much less broad.

Yields: The over-all yield of useful products (glycerol and acetone) is not known. The over-all glycerol yield on propylene charged to the oxidation is in the range of 50-60 percent.

Commercial Installations: This process is now in large-scale commercial use by Shell Chemical Co. at Norco, La.

References: Glycerol Payoff in Propylene Parlay, *Chemical Week*. May7,'55,p72-77; S. A. Ballard, H. deV. Finch and E. A. Peterson (to N. V. Bataafsche Petroleum Maatschappij), British Patent 619,014, Mar.2,'49; M. Mugdan and D. P. Young, *J. Chem Soc.*, 49,2988-3000,CA:43-5269h.



Glycerine — FMC CORP.

Application: A process for making glycerine from acetaldehyde and propylene oxide.

Description: Synthetic glycerine is made by a new peracetic acid-glycidol route and is the first such process to produce glycidol and acetic acid from allyl alcohol and peracetic aid.

The FMC process is also employed to make allyl alcohol and acetic acid.

Basic steps in the process are as follows:

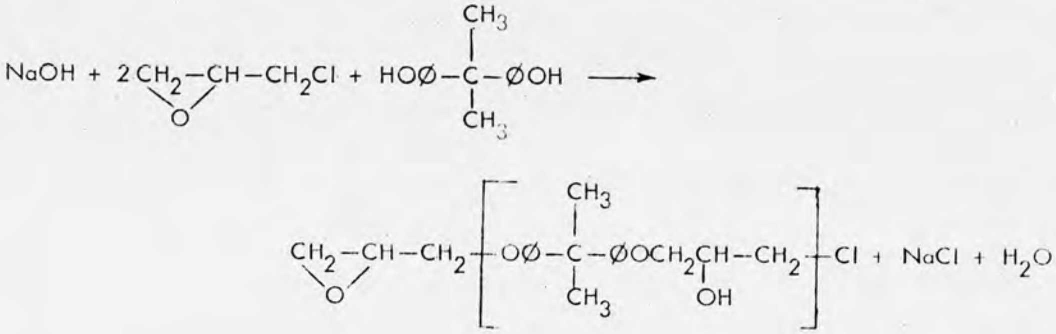
1. Propylene oxide is converted to allyl alcohol with the use of a catalyst.
2. Acetaldehyde is oxidized to peracetic acid, which is reacted with allyl alcohol to form glycidol and acetic acid.
3. Glycidol is then hydrolyzed to glycerine.

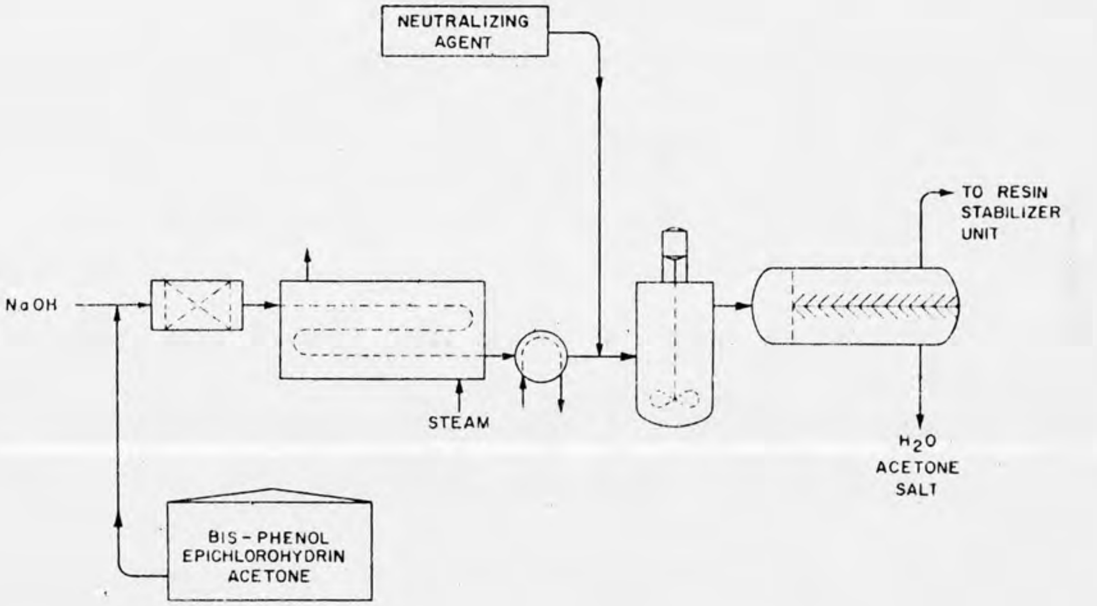
The peracetic acid made in the process can be used for other epoxidization reactions.

Commercial Installations: FMC Corp. operates the first plant using this process at Bayport, Texas.

EPOXY RESINS FROM EPICHLOROHYDRIN

Reaction:





Feed Materials:
- Bisphenol A
- Epichlorohydrin
- Sodium Hydroxide

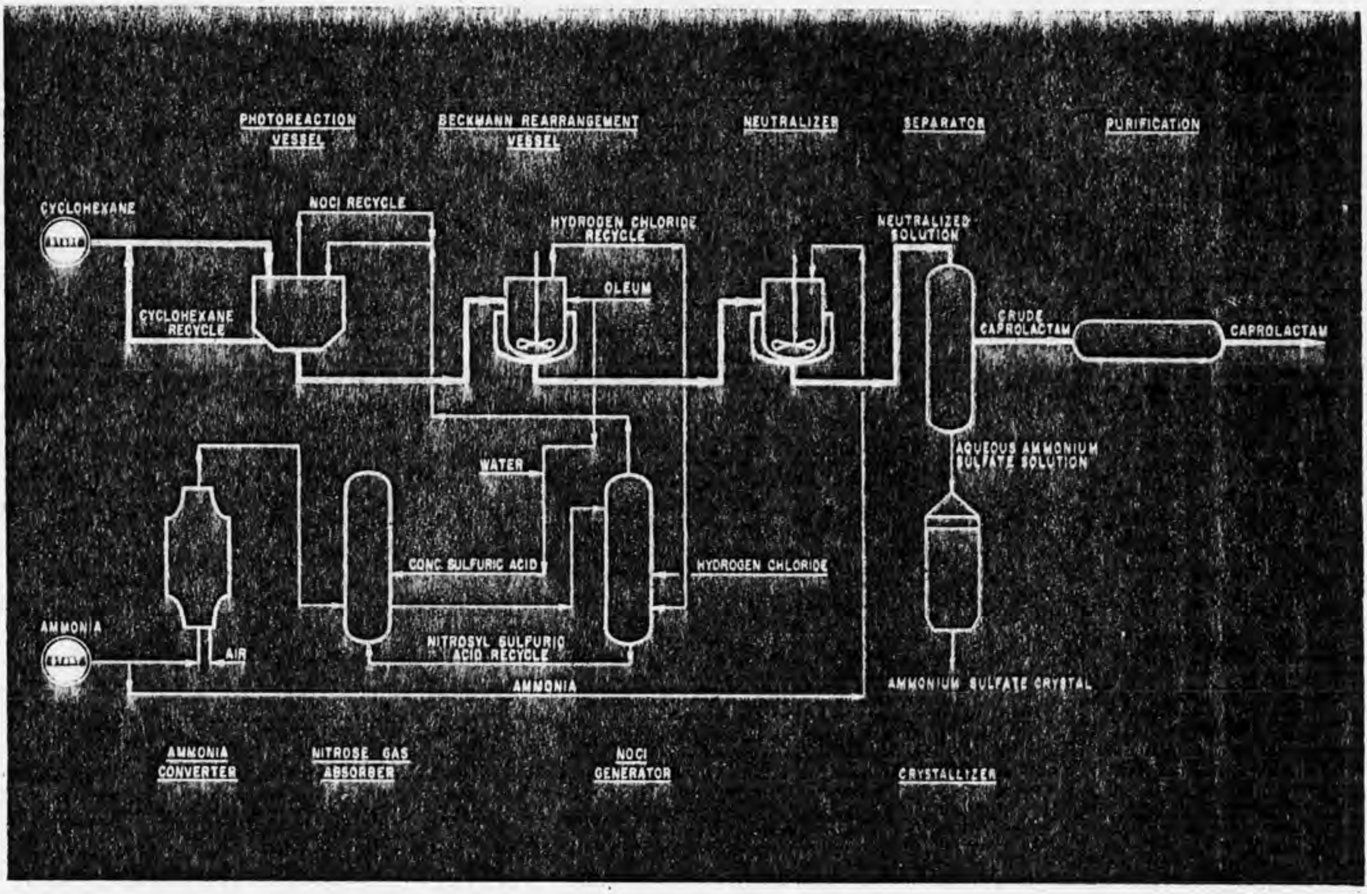
Coproducts:
- Sodium Chloride
- Water

Catalyst:	None
Phase:	Liquid
Reactor type:	Pipe Coil
Solvent used:	Acetone
Temperature, °C:	100-180
Pressure psi:	100
Reaction time:	5-20 minutes
Heat Required:	Yes
Heat evolved:	-
Product yield:	99%
Product purity:	
Materials of Construction:	Stainless Steel

Major Product Uses: In the formulation of surface coatings and as casting resins.

Reference: U.S. Patent 2,986,552 by A.J. Landua et al (to Shell Oil Co.) (May 30, 1961)

PROYECTOS DE INVERSION MEDIANA
TECNOLOGIA DE OPERACION



Caprolactam — TOYO RAYON CO., LTD.

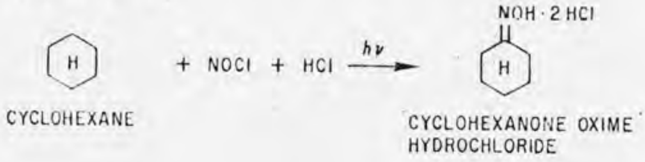
Application: A photochemical process for the manufacture of caprolactam from cyclohexane, ammonia, oleum and hydrogen chloride. The products are fiber-grade caprolactam and fertilizer-grade ammonium sulfate crystal.

Description: This is called PNC process which has come from "Photo-Nitrosation of Cyclohexane."

Nitrosyl Chloride. According to following equations, nitrosyl chloride is produced from ammonia.

$$2NH_3 + 3O_2 \rightarrow N_2O_3 + 3H_2O$$
$$2H_2SO_4 + N_2O_3 \rightarrow 2HNOSO_4 + H_2O$$
$$HNOSO_4 + HCl \rightarrow NOCl + H_2SO_4$$

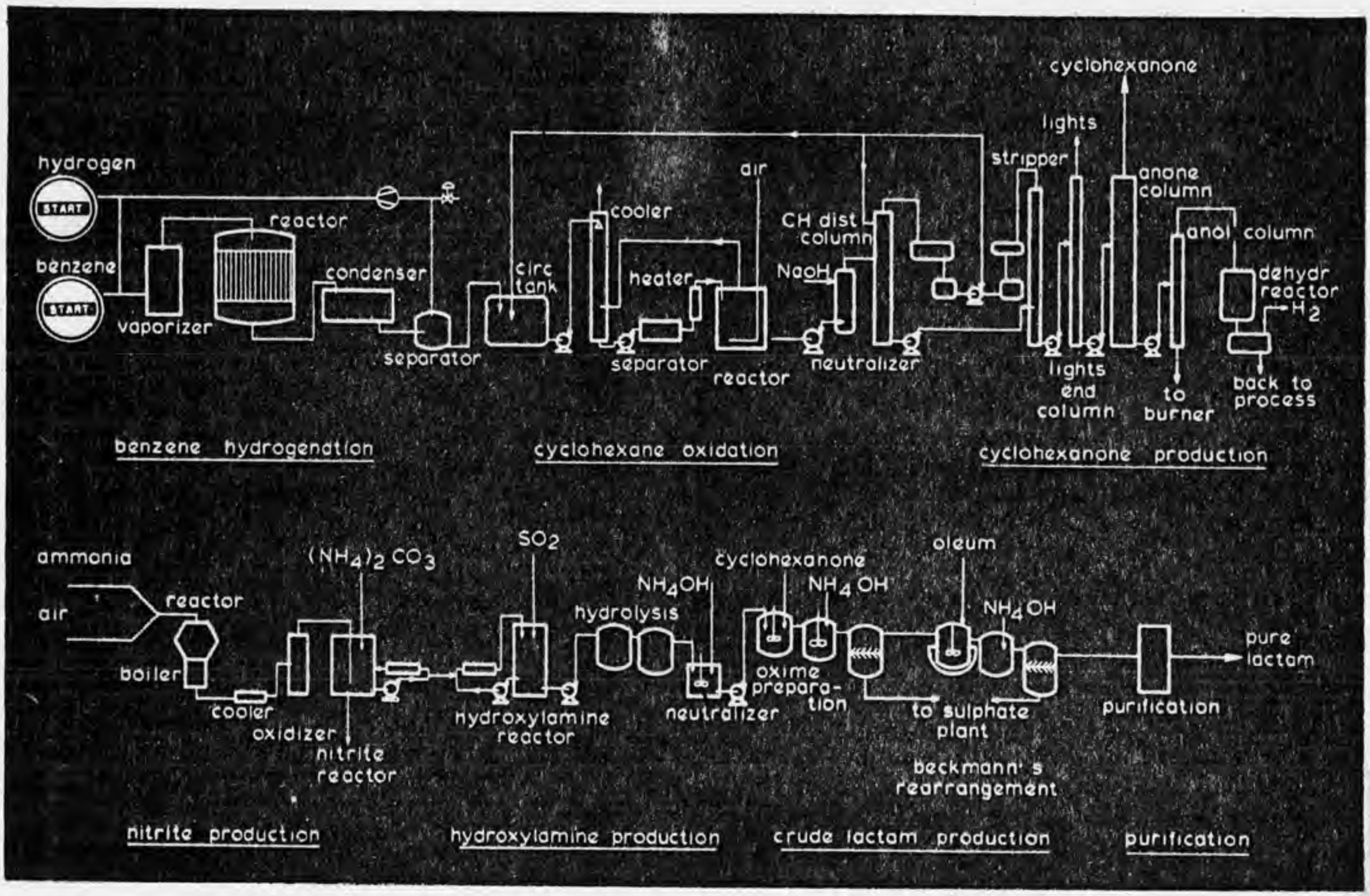
Cyclohexanone Oxime Hydrochloride. Special corrosion-resistant materials are employed for the hydrogen chloride and nitrosyl chloride gas circulation system including the photoreaction vessels. A large number of mercury lamps having 60 kw of capacity are immersed in the reaction mixture of photoreaction vessels. The electric power required for the photo reaction has been reduced to less than 1.4 kwh per pound of the oxime produced. Cyclohexanone oxime hydrochloride obtained by the photochemical reaction from cyclohexane is separated as a heavy oil at the bottom of the reaction vessel. Then it is directly supplied to the Beckmann rearrangement step.



The crude lactam solution in sulfuric acid after the rearrangement is continuously fed to neutralizer where the aqueous solution containing caprolactam and ammonium sulfate is obtained by ammonia neutralization. Through several purification steps including vacuum distillation, fibre-grade purified caprolactam is produced. Less than 0.92 pound of cyclohexane is consumed per pound of caprolactam produced. On the other hand, fertilizer-grade ammonium sulfate crystal is recovered from the ammonium sulfate aqueous solution. Less than 2.3 pounds of ammonium sulfate is recovered per pound of caprolactam produced.

Commercial Installation: As of July 1969, one is onstream (annual capacity 200 million pounds) and one under construction (110 million pounds).

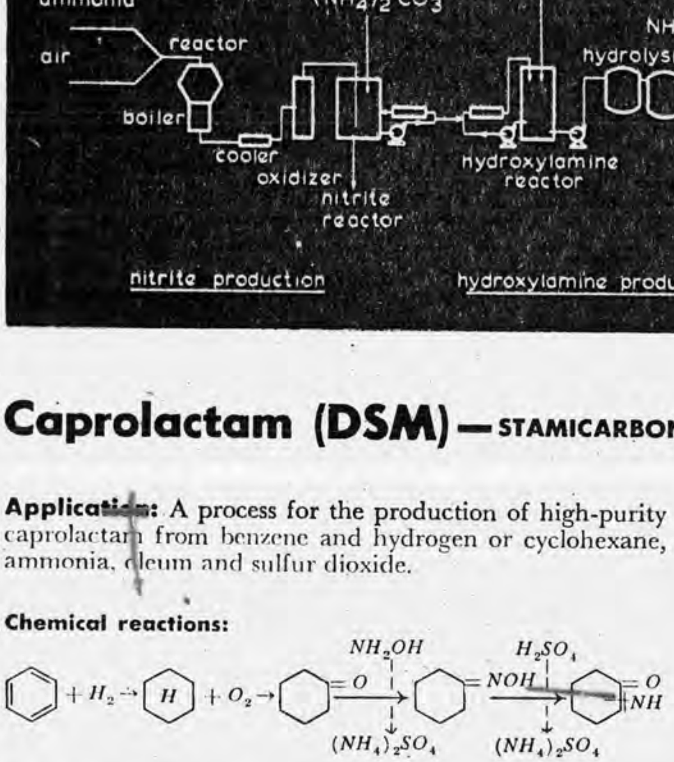
References: *European Chemical News, Caprolactam Supplement*, May 2, 1969, p. 32; P. Turner, *Chemical Processing*, January 1969, p. 1; P. Hulme and P. E. Turner, *Chemical & Process Engineering*, November 1967, p. 96; Hydrocarbon Processing, November 1967 p. 157.



Caprolactam (DSM) — STAMICARBON N.V.

Application: A process for the production of high-purity caprolactam from benzene and hydrogen or cyclohexane, ammonia, oleum and sulfur dioxide.

Chemical reactions:



Description: In a one-step vapor-phase hydrogenation benzene is hydrogenated to cyclohexane. The cyclohexane is oxidized with air-oxygen in the liquid phase at 150-160° C and 8-9 atmospheres pressure in the presence of a cobalt catalyst. Reaction products obtained: cyclohexanol, cyclohexanone, acids, esters and carbon oxide gases. Due to chosen reaction conditions the efficiency to cyclohexanol and cyclohexanone is in the 76% range. A caustic soda wash neutralizes all acids and saponifies most of the esters. The unreacted cyclohexane is distilled off and recycled; pure cyclohexanone is produced from the crude oxidation oil. The remainder, mainly cyclohexanol, is fed through a vapor phase dehydrogenation, thus producing cyclohexanone. The reaction mixture is recycled into the distillation section.

Hydroxylamine sulfate is produced from ammonium nitrite and sulfur dioxide. The cyclohexanone is reacted with hydroxylamine-sulfate to cyclohexanone-oxime and ammonium-sulfate byproduct. The oxime is rearranged in oleum to caprolactam according to Beckmann's reaction. Both the oximation and rearrangement steps proceed at efficiencies close to 100%. The aqueous crude lactam solution is neutralized and ammonium sulfate separated. Both ammonium sulfate streams are processed to fertilizer-grade crystals.

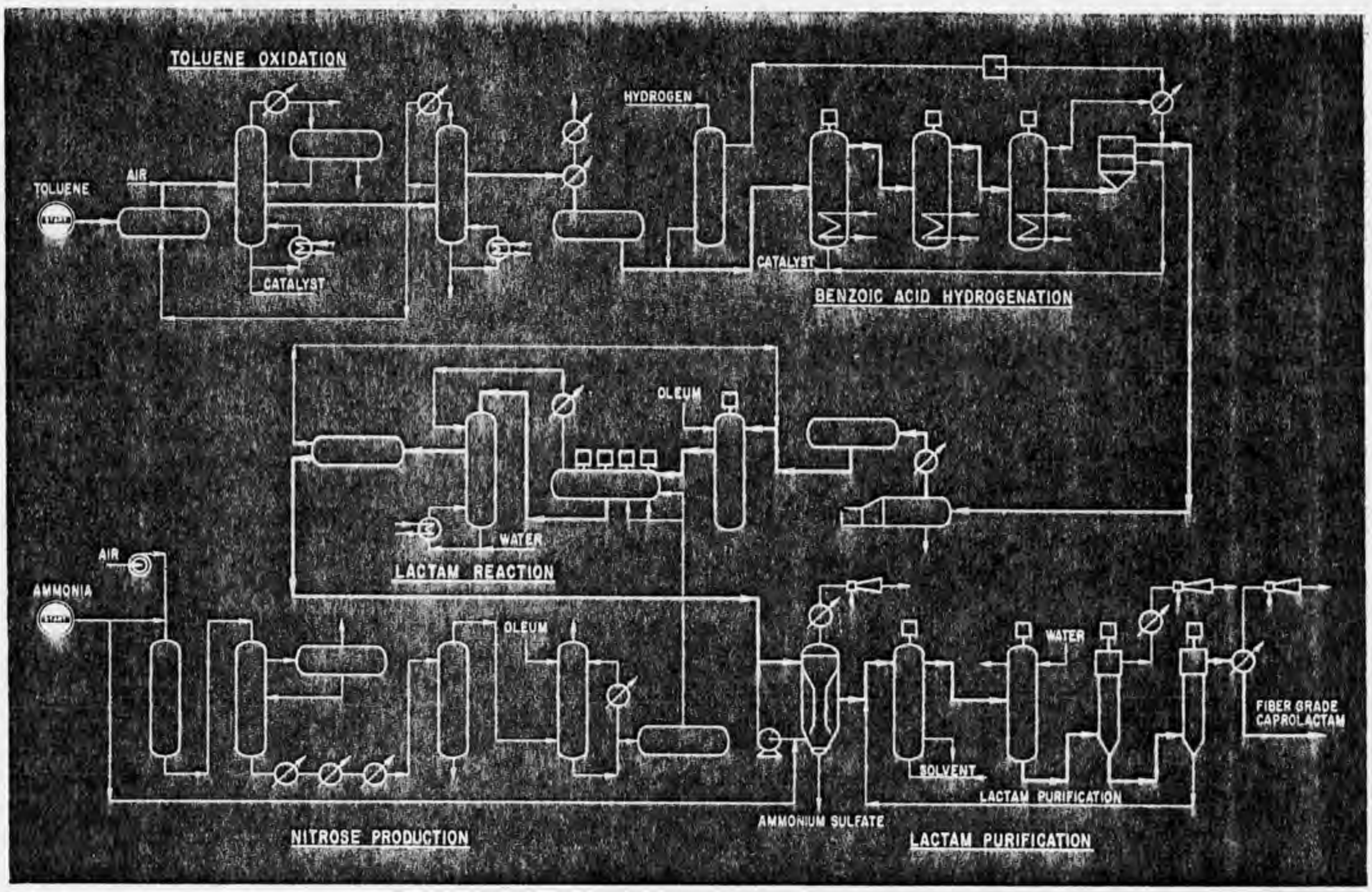
Several extensive purification steps including extractions and final vacuum distillation are used to purify the crude lactam thus producing extremely pure caprolactam at a constant quality level. In the purification section only minor mechanical losses occur.

Special Features: Process is extremely simple to operate and requires 2 shift foremen and 3 shift operaters for the complete plant. Use of regular chemical equipment ensures low capital investment and guarantees low maintenance cost. The process is continuous and in one stream up to high capacities.

Consumption figures per ton of caprolactam

Benzene	kg	1,018
Hydrogen	kg	85
Sulfur dioxide	kg	1,350
Ammonia	kg	1,510
Oleum	kg	1,310
Steam	kg	14,200
Electric power	kwh	465
Export sulfate	kg	4,450

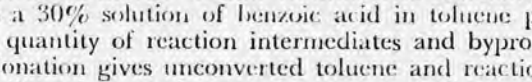
Commercial Installations: In Geleen, Holland, DSM operates a 100,000 metric ton-per-year plant. Two 20,000 metric ton-per-year plants are operated in Augusta, Ga., and Flixborough, U.K. Two 50,000-ton-per-year plants are under construction in Russia.



Caprolactam — SNIA VISCOSA

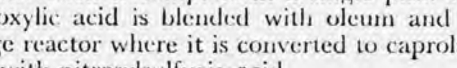
Application: A process to manufacture caprolactam from nitration-grade toluene, hydrogen, ammonia and oleum. Fiber-grade flaked or molten caprolactam and white ammonium sulfate crystals are produced.

Description: Toluene and air are fed to the reactor in which the oxidation



is carried out at 160° C and 10 atm. The reaction product is a 30% solution of benzoic acid in toluene plus a small quantity of reaction intermediates and byproducts. Fractionation gives unconverted toluene and reaction intermediates for recycle, pure benzoic and a bottom fraction of heavy byproducts.

Benzoic is hydrogenated under pressure in presence of palladium catalyst in a series of continuous tank reactors at 170° C and 10 atm.

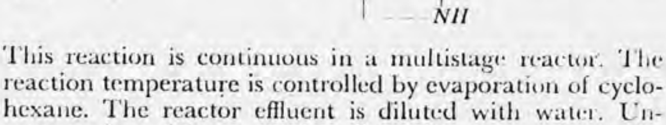


The conversion is complete in a single pass. Cyclohexane-carboxylic acid is blended with oleum and fed to a multistage reactor where it is converted to caprolactam by reaction with nitrosylsulfuric acid.

This acid is produced in a conventional ammonia oxidation plant, where the nitrogen oxides are absorbed in oleum.

$$N_2O_3 + H_2SO_4 + SO_3 \rightarrow 2\,NOHSO_4$$

The basic process reaction is the following:

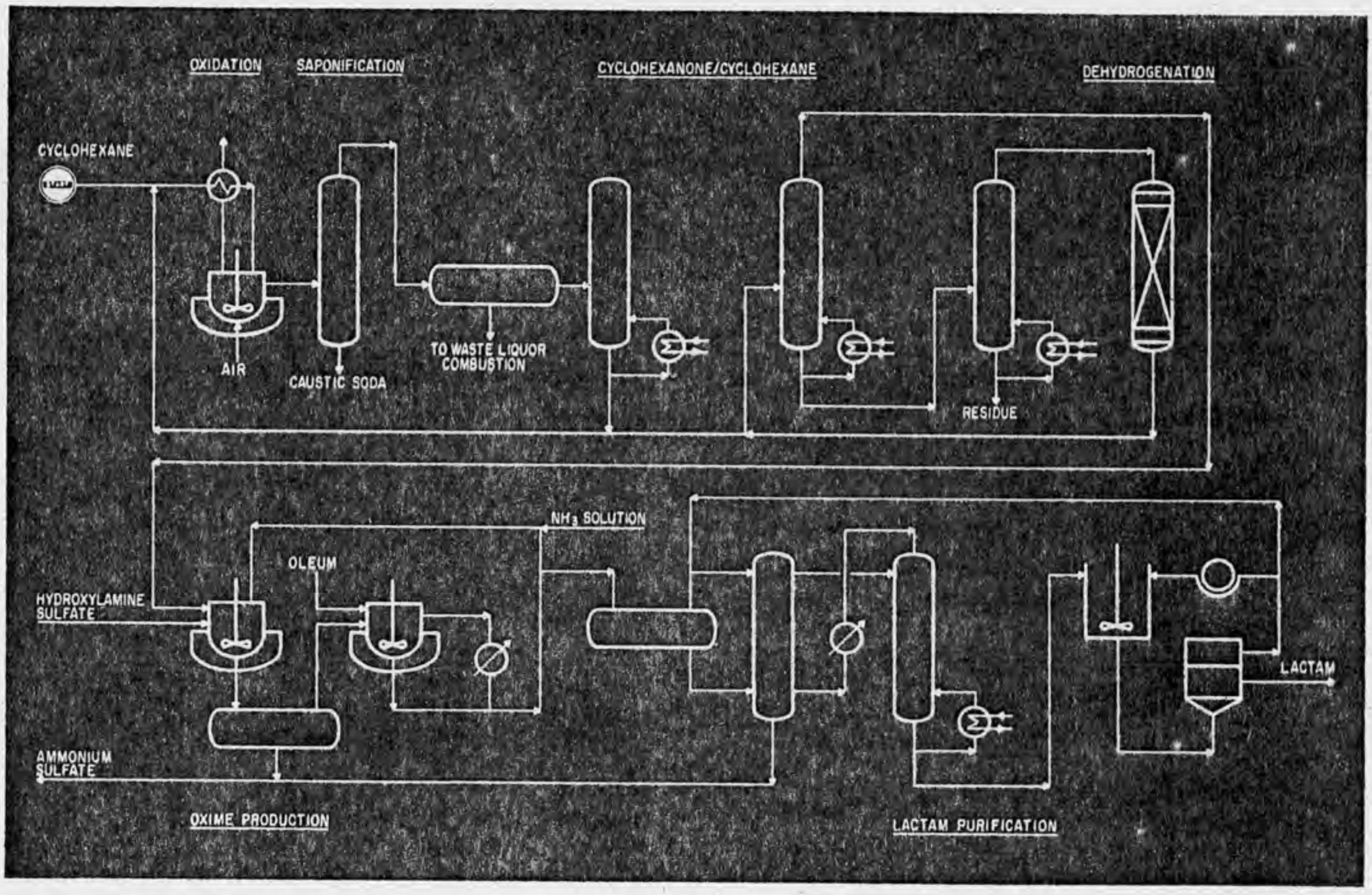


$$\text{(H)}-COOH + NOHSO_4 \rightarrow (CH_2)_5\left|\begin{array}{l} CO \\ \\ NH \end{array}\right. + CO_2 + H_2SO_4$$

This reaction is continuous in a multistage reactor. The reaction temperature is controlled by evaporation of cyclohexane. The reactor effluent is diluted with water. Unconverted cyclohexanecarboxylic acid passes from the acidic to the top cyclohexane phase and is recycled to the process. The acid solution flows to the crystallization plant where it is neutralized with ammonia; ammonium sulfate crystallizes at bottom, while the top organic layer of caprolactam is recovered and purified through a two-solvent (toluene and water) extraction and a continuous fractionation procedure. Fiber grade caprolactam of 10,000 sec. min. permanganate number is obtained. 1.06 Kg of toluene, 1.3 Kg of ammonia, 3 Kg of oleum, 0.8 ncm of hydrogen are consumed and 4.2 Kg of ammonium sulfate are recovered per Kg of caprolactam.

Commercial Installation: In Torviscosa, Italy, SNIA operates a 16,000 metric tons per year plant.

References: Snia Viscosa, Italian Patents 604.795, 603.606, 608.873, 666.827, 653.845, 653.848, 659.858, 661.532; Donati, I; Sioli, G.; Taverna, M. *La Chimica e l'Industria,* Vol. 50, n. 9 (September 1968), 997 Taverna, M. *La Rivista dei Combustibili,* Vol. XXII, n. 4 (April 1968), 203.



Caprolactam — INVENTA AG

Application: A process for the production of caprolactam starting from cyclohexane (or, alternatively, benzene or phenol).

Description: Cyclohexane is oxidized in liquid phase under elevated pressure and temperature. The oxidation product—a mixture of cyclohexanone, cyclohexanol, some byproducts and unreacted cyclohexane—undergoes a saponification process. The neutralized byproducts are removed for combustion or further processing to synthetic oils, while the remaining mixture is split off. Unreacted cyclohexane is recycled to the oxidation and cyclohexanol is dehydrogenated to cyclohexanone which is purified.

For the hydroxylamine sulfate production a new technology (NO-reduction) is used which reduces the ammonium sulfate byproduct considerably. Ammonia is oxidized to nitrogen oxide which reacts with hydrogen and sulfuric acid in the presence of a catalyst to hydroxylamine sulfate.

In the caprolactam synthesis, pure cyclohexanone with hydroxylamine sulfate forms cyclohexanone oxime. By Beckmann rearrangement the cyclohexanone oxime is transformed into caprolactam in presence of oleum. The product is then neutralized, passed through several purification steps, the last of which is crystallization.

Byproduct ammonium sulfate is crystallized from the aqueous solution by multiple evaporation.

Economics: The total erected costs of a 50,000-t/yr. caprolactam battery limit plant is approximately 110 million Swiss francs.

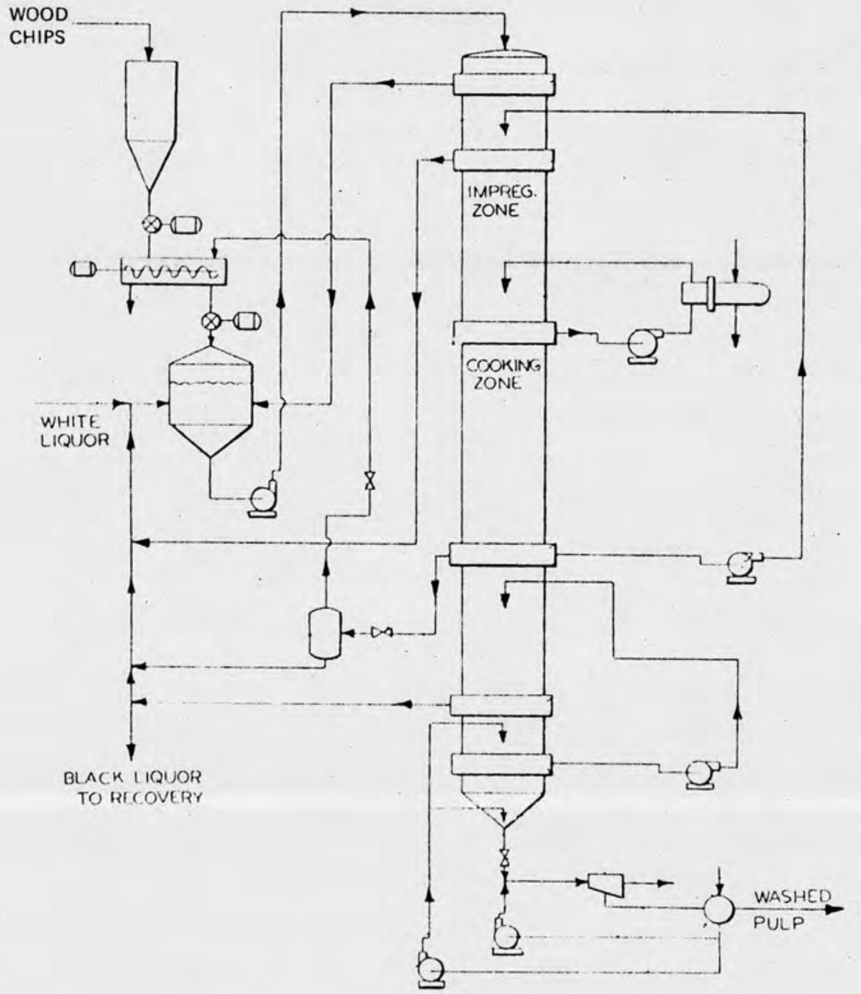
Unit consumption (per ton of caprolactam)

Cyclohexane, tons	1.01
Oleum (SO_3 100%), tons	1.1
NH_3, tons	0.96
H_2SO_4, tons	0.7
H_2 Nm^3	470
O_2 Nm^3	380
Catalyst, Swiss francs	32
Utilities, Swiss francs	200

Commercial installations: Plants using the Inventa caprolactam process are in operation or under construction in Japan, India, Poland, Spain, Switzerland and Turkey. Inventa's total licensed production capacity for caprolactam exceeds 320,000 tons per year.

CELLULOSE FROM WOOD

Reaction: Wood Chips + NaOH ⟶ Cellulose + Sodium Salts of Lignin



Feed Materials:

- Wood Chips
- Caustic Soda

Coproducts:

- Sodium Salts of Lignin

Catalyst:	None
Phase:	Liquid
Reactor type:	Vertical Digester
Solvent used:	Water
Temperature, °C:	170-180
Pressure psi:	15
Reaction time:	20-25 minutes
Heat Required:	Yes
Heat evolved:	-
Product yield:	
Product purity:	
Materials of Construction:	

Major Product Uses: Paper and rayon manufacture.

Reference: U.S. Patent 3,303,088 by A.W. Gessner (to The Lummus Co.) (February 7, 1967)

Nuevo proceso para la industrialización del Guayule

Ing. Sergio Autrey Maza
Ing. Carlos Michan Sidauy

INTRODUCCION

El presente reporte resultó de una investigación exhaustiva sobre los procesos anteriormente reportados para industrializar el Guayule. En base a estos procesos, se propusieron unos nuevos y utilizando el método de Síntesis de Procesos propuesto por Rudd y coautores(1) se determinó cuál de los procesos examinados era el más conveniente para lograr la industrialización de este recurso. El proceso resultó ser uno de los propuestos, y el hule obtenido por este método se probó a escala laboratorio resultando ser de una calidad comparable al de Hevea.

ANTECEDENTES

El estímulo a la producción de hule natural en México comenzó en 1971 cuando el gobierno actual creó la Comisión Nacional de las Zonas Aridas (CONAZA), y esta realizó los estudios referentes a los recursos del desierto del norte de México, encontrándose entre ellos el Guayule.

El Guayule había sido industrializado por medio de compañías norteamericanas con el objeto de suministrar hule natural a los Estados Unidos en tiempos de la Segunda Guerra Mundial. El hule obtenido en esta época era de una calidad muy pobre debido al alto contenido de resinas (22%) y de materiales deletéros como el cobre y el manganeso que le ocasionaban un rápido envejecimiento. Después de la Segunda Guerra Mundial se dejó de explotar el Guayule debido a que el suministro de hule natural por parte de los países del sureste de Asia se reinstaló.

El proyecto de industrialización del Guayule obedece a un programa de desarrollo nacional e integración de las zonas desérticas en la actividad productiva del país, creando empleos y distribución de riquezas entre los campesinos que habitan en estas zonas. Además, el abastecimiento de hule natural obtenido a partir del Guayule sustituirá las cuantiosas importaciones que en la actualidad ascienden a más de 250 millones de pesos al año.

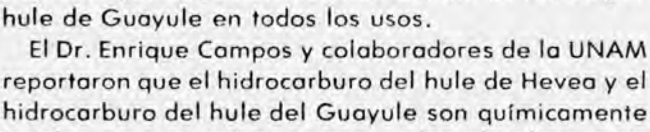
El Guayule es un arbusto del género "Parthenium

Argentatum Gray"; su altura oscila alrededor de 60 centímetros y abunda en las regiones desérticas del norte de México. El Guayule contiene un hule de tipo poli-isoprénico distribuido a través de la raíz, el tallo y las ramas. El contenido de hule varía de 10 a 14% dependiendo de la región, humedad de la planta, elevación, etc. Además el Guayule contiene una elevada cantidad de resinas que afectan la calidad del hule.

La Subsecretaría Forestal y de la Fauna, dependiente de la Secretaría de Agricultura y Ganadería realizó estudios sobre la abundancia actual del Guayule y se llegó a la conclusión de que existen 3 millones de toneladas de arbusto que son suficientes para abastecer la demanda nacional de hule natural que en la actualidad es de 30,000 toneladas anuales.

Ante la perspectiva de obtener hule natural de buena calidad —comparable al de Hevea—, se realizaron investigaciones(2) con el propósito de reducir el contenido de resinas y deletéreos en el Guayule. Estas investigaciones muestran satisfactoriamente que es posible sustituir al hule de Hevea por hule de Guayule en todos los usos.

El Dr. Enrique Campos y colaboradores de la UNAM reportaron que el hidrocarburo del hule de Hevea y el hidrocarburo del hule del Guayule son químicamente iguales, ya que ambos corresponden al polímero cis 1-4 de isopreno. Esta estructura la determinaron por los espectros de infrarrojo y resonancia magnética nuclear, predominando la configuración siguiente:



Polímero cis 1-4 de isopreno

El comportamiento fisicoquímico del hule de Guayule es idéntico al de Hevea excepto en el contenido del Gel como se muestra en la tabla 1 reportada por los mismos investigadores.

PRINCIPALES PROCESOS REPORTADOS

La Comisión Nacional de Ciencia y Tecnologia (CONACyT) ha elaborado dos procesos para obtener hule desresinado a partir de Guayule.

El primero de ellos consiste en desfoliar la planta, molerla y efectuar la extracción de hule por medio de hexano sin previa flotación. La solución que contiene al hule se filtra y se lleva al coagulador donde se pasa un coagulante a contracorriente para conglomerar las moléculas del hule. El hule coagulado se prensa y se le agrega antioxidante. El antioxidante se puede agregar en el coagulador si se juzga conveniente. La etapa final consiste en pasar al hule por un secador contínuo a vacío. Este proceso tiene una gran recuperación de los solventes empleados.

El segundo proceso consiste en desfoliar el arbusto, molerlo y efectuar una flotación para separar el material celulósico. Posteriormente el flotado se trata con acetona para eliminar las resinas. El hule desresinado se extrae con hexano para eliminar los finos y el corcho de tal forma que se obtiene un hule puro.

En vista de que el desarrollo de los procesos se encuentra en su etapa de ingenieria básica, hemos propuesto algunas innovaciones y nuevos procesos que analizamos conjuntamente con los procesos desarrollados por la CONACyT.

El método de análisis se basó en el procedimiento descrito por Rudd, D. y coautores(1) para síntesis de procesos, que se basa en las propiedades de las sustancias involucradas en la cual se utilizan algunas reglas heurísticas para la evaluación de los procesos apriori a las investigaciones en el laboratorio.

El proceso que obtuvo el mejor resultado por medio de este análisis fue una innovación propuesta sobre el primer proceso de la CONACyT, el cual se describe a continuación.

TABLA 1

COMPORTAMIENTO FISICOQUIMICO DEL HULE DE HEVEA Y EL HULE DE GUAYULE

PROPIEDAD	HULE HEVEA	HULE GUAYULE	METODO DE DETERMINACION
Estructura Química	Poli-isopreno cis 1-4 98%	Poliisopreno cis 1-4 98%	Infrarrojo y Resonancia Magnética Nuclear.
Peso Molecular	1.0 - 1.5X106	1.0 - 1.5X106	Osmometria y Cromatografía en Gel.
Temperatura de Transición Vitrea	-75ºC	-74ºC	Calorimetría Diferencial de Barrido.
Contenido de Gel	Variable	No tiene	Solubilidad

Fuente: "El Hule del Guayule", Propiedades Fisicoquimicas y Mecánicas.
E. Campos López, M.A. Ponce, H. Flores y J.L. Angulo.
Facultad de Química, UNAM, México, D.F.

PROCESO PROPUESTO

Una vez desfoliada y molida la planta, se efectúa una flotación para separar el bagazo; posteriormente, el hule flotado se extrae con un solvente selectivo y la solución se coagula en un solvente de las resinas que tenga un punto de ebullición mayor que el del solvente del hule.

Este proceso realiza la coagulación evaporando el solvente del hule; en cambio, en el proceso de la CONACyT el coagulado se efectúa en un equipo a contracorriente sin utilizar calor. La figura 1 muestra el diagrama del proceso propuesto.

PRUEBAS A ESCALA LABORATORIO

Posteriormente se realizó un estudio a nivel laboratorio del proceso propuesto. Para este análisis propusimos tres sistemas de solvente de hule-solvente de resinas que cumplen con la condición mencionada.

Los sistemas fueron:

Hexano — Ac. Acético
Hexano — Metil etil cetona-Agua
Benceno — Ac. Acético

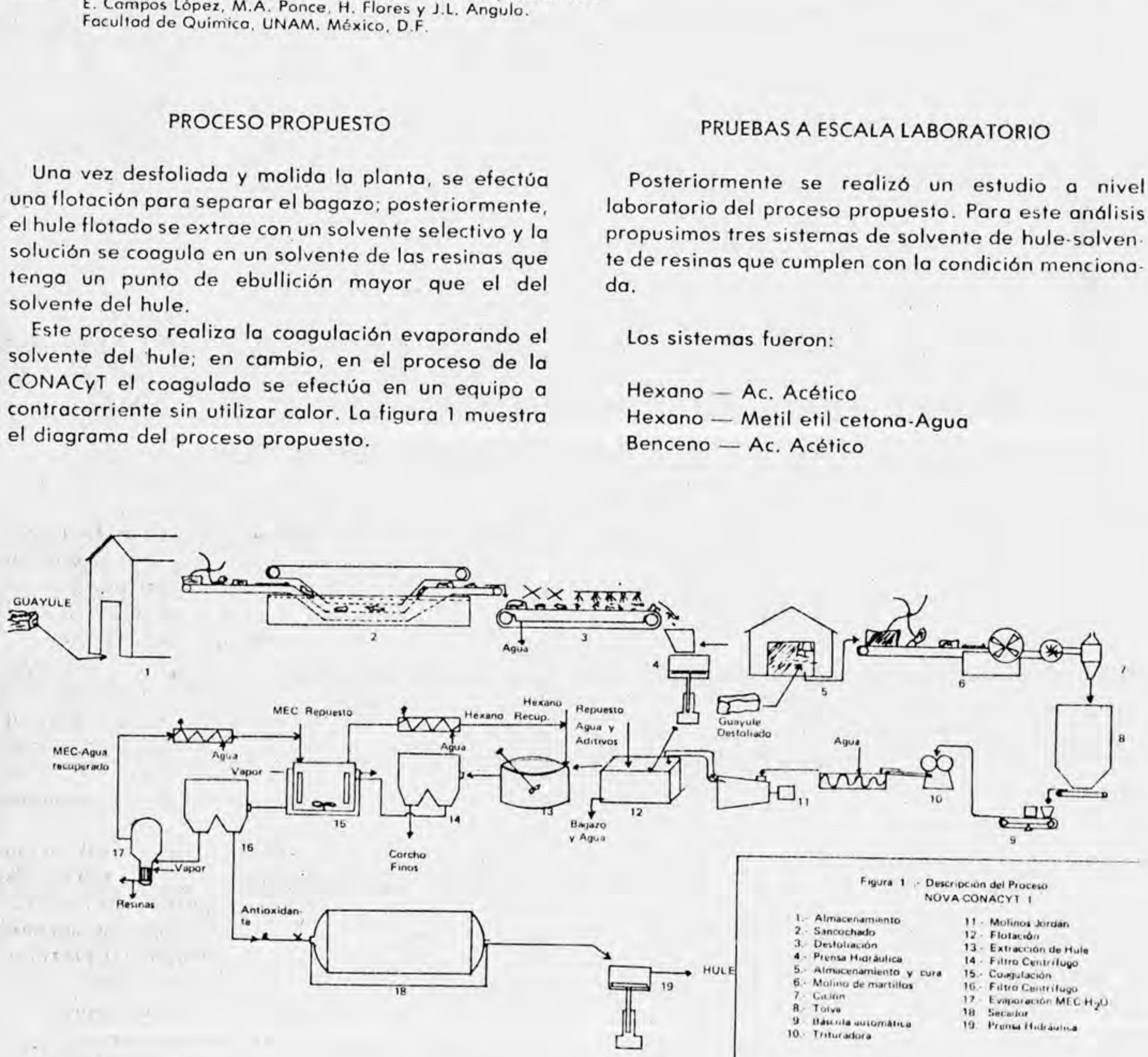


Figura 1 .- Descripción del Proceso NOVA CONACYT 1

1.- Almacenamiento	11.- Molinos Jordán
2.- Sancochado	12.- Flotación
3.- Desfoliación	13.- Extracción de Hule
4.- Prensa Hidráulica	14.- Filtro Centrífugo
5.- Almacenamiento y cura	15.- Coagulación
6.- Molino de martillos	16.- Filtro Centrífugo
7.- Ciclón	17.- Evaporación MEC H_2O
8.- Tolva	18.- Secador
9.- Báscula automática	19.- Prensa Hidráulica
10.- Trituradora	

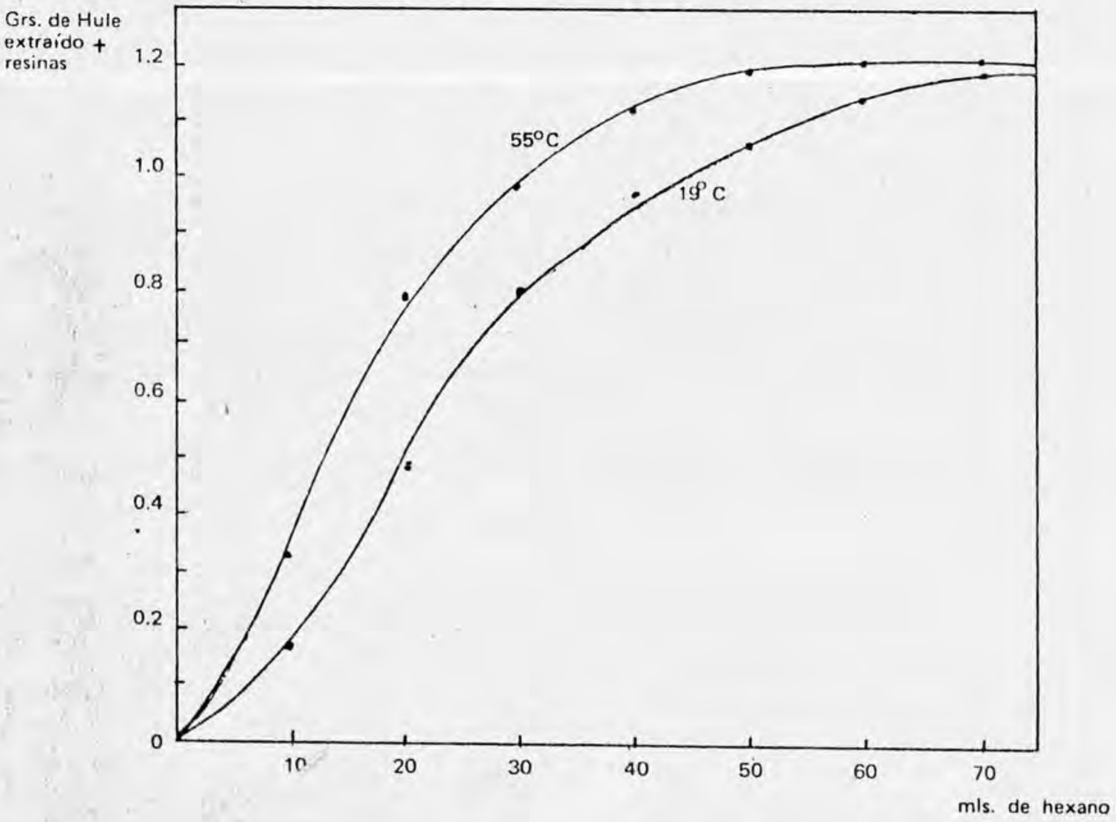
Los mejores resultados se obtuvieron con el sistema de hexano/MEC-Agua ya que mostraron las mejores propiedades físico-mecánicas en el hule y además porque presenta ciertas ventajas sobre los otros sistemas y estas son:

a) La mezcla MEC-Agua forma un azeótropo que tiene una composición de 11% agua y 89% MEC, siendo un excelente solvente de las resinas.
b) El azeótropo tiene un punto de ebullición de 73°C, lo que hace sencilla la recuperación de solvente, no siendo necesario separar el agua para purificar al solvente.
c) La MEC es un solvente parcialmente miscible en agua, lo que es muy importante para una buena extracción de las resinas y evitar que estas se vuelvan a precipitar como ocurre con los solventes que son totalmente miscibles en agua.(3).
d) El material a extraer posee cierta cantidad de agua que proviene de los molinos, y no es necesario un exprimido previo para efectuar las extracciones.
e) La extracción de resinas puede llevarse a cabo convenientemente a cualquier temperatura, desde la temperatura ambiente hasta la temperatura de ebullición.(3)

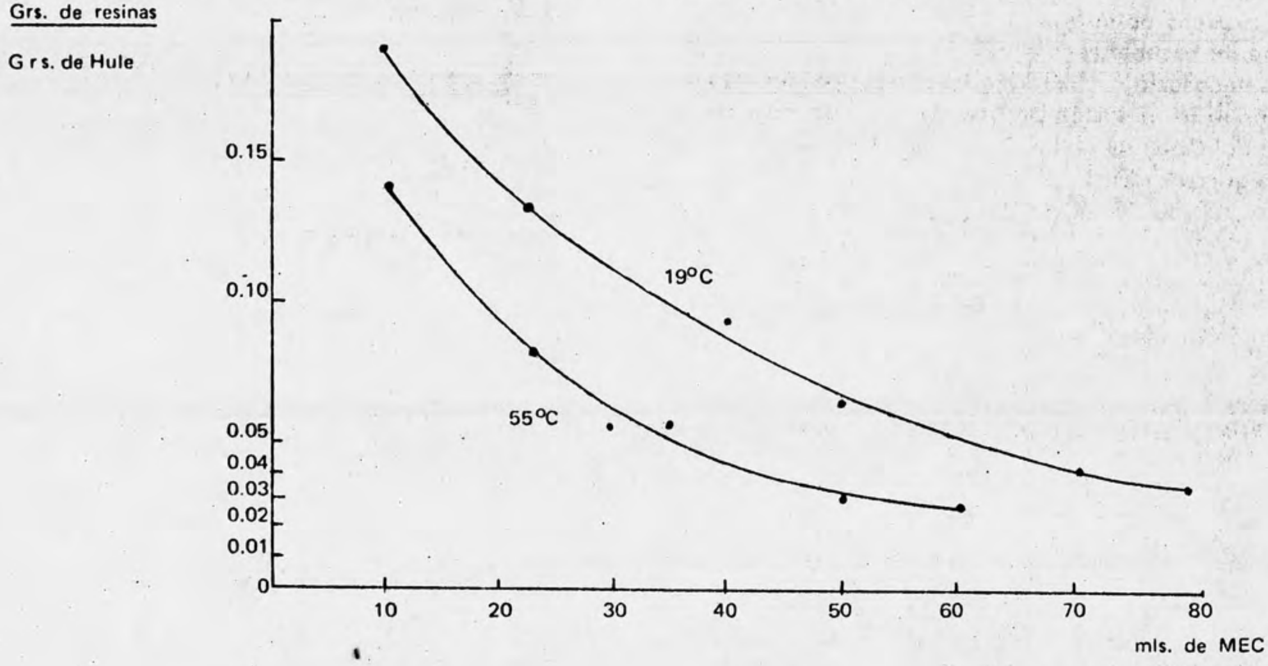
La determinación de las condiciones experimentales del sistema se llevaron a cabo en el laboratorio con el fin de establecer las variables de diseño para el proceso propuesto.

Los resultados se muestran en las gráficas 1, 2 y 3 en donde se determinan la cantidad de hexano requerida para extraer al hule a dos diferentes temperaturas; la cantidad de solvente de resinas necesaria para eliminarlas del hule y, por último el tiempo necesario de extracción de hule en un equipo con agitación.

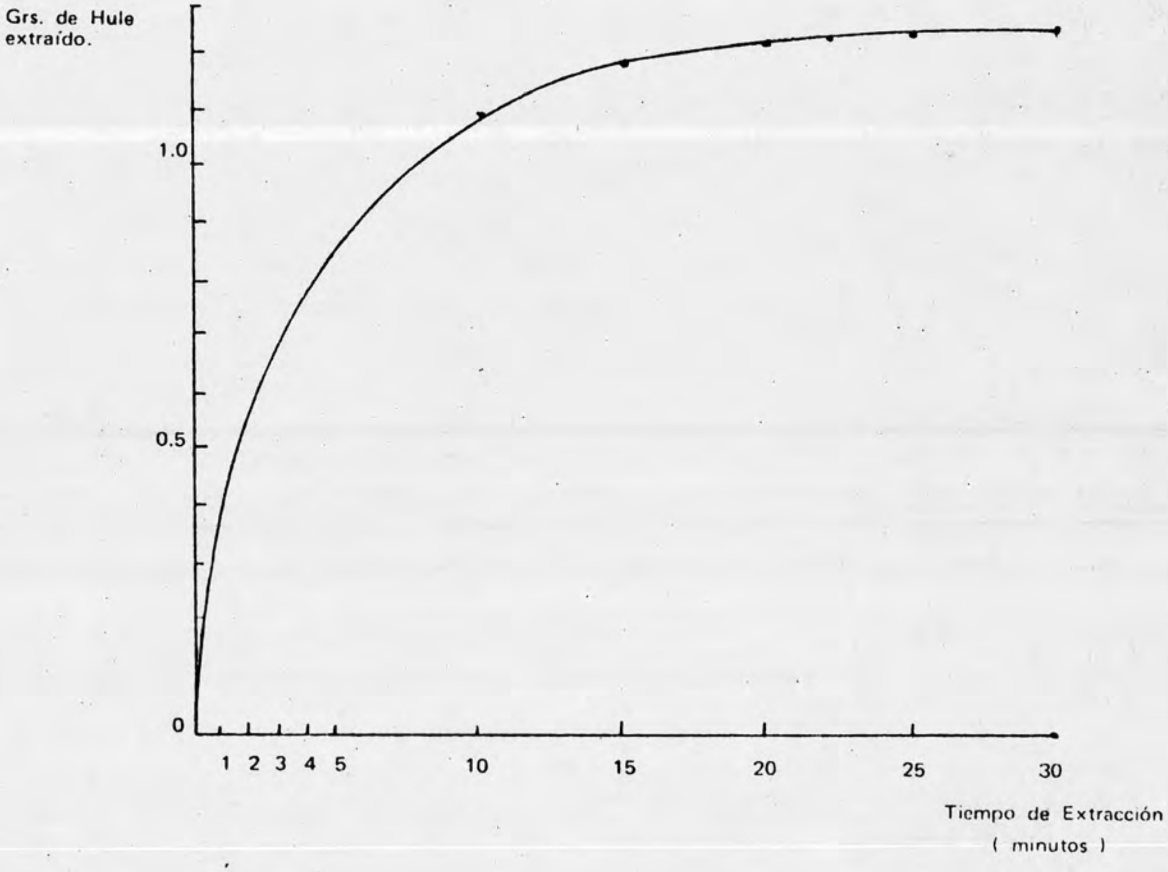
GRAFICA 1.- Gráfica de cantidad de hexano vs. cantidad de hule extraído (más las resinas).



GRAFICA 2.- Gráfica de cantidad de MEC-H_2O contra cantidad de resinas que permanecieron en el hule coagulado.



GRAFICA 3.- Tiempo necesario de extracción de hule (con agitación).



El hule obtenido de este proceso es de buena calidad en cuanto a sus propiedades físico-mecánicas, y el proceso optimizado ha demostrado ser económicamente factible.(4)

Es necesario realizar una investigación para determinar la formulación óptima de vulcanizado para el hule del Guayule en los usos específicos para los que se requiera.

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(2) CAMPOS, L.E., PONCE, M.A., FLORES, H., y ANGULO, J.L., "El Hule del Guayule", Propiedades Fisicoquímicas y Mecánicas. Facultad de Química, UNAM. México, D.F.

(3) CLARK, FREDERICK, E., U.S. Patent No. 2,618,670. Department of Agriculture. Noviembre 18, 1952.

(4) MICHAN, CARLOS S. y AUTREY, SERGIO, M., "Ingeniería de Procesos para la Industrialización del Guayule", Tesis Profesional, U.I.A. México D.F., 1976.

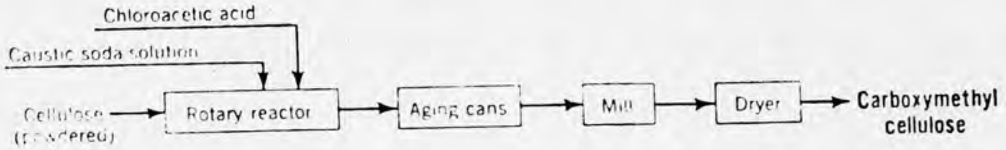
PROYECTOS DE INVERSION PEQUEÑA
TECNOLOGIA DE PROCESO

CARBOXYMETHYL CELLULOSE

(SODIUM SALT)

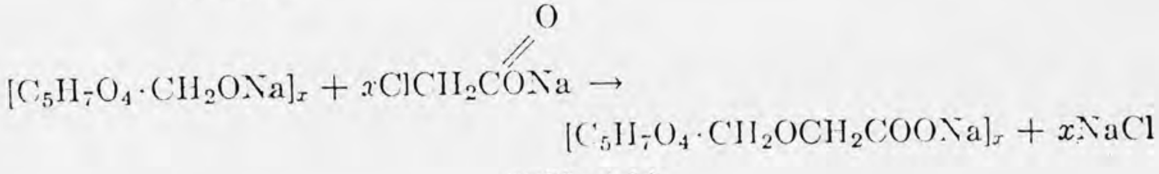
$[C_6H_9O_5 \cdot CH_2COONa]_x$

From Cellulose, Caustic Soda, and Sodium Chloroacetate



Reaction

$$\underset{\substack{\text{Cellulose}\\(C_6H_{10}O_5)}}{[C_5H_7O_4 \cdot CH_2OH]_x} + xNaOH \rightarrow [C_5H_7O_4 \cdot CH_2ONa]_x + xH_2O$$



$$[C_5H_7O_4 \cdot CH_2ONa]_x + xClCH_2\overset{\overset{\large O}{/\!/}}{C}ONa \rightarrow [C_5H_7O_4 \cdot CH_2OCH_2COONa]_x + xNaCl$$

99% yield

Material Requirements

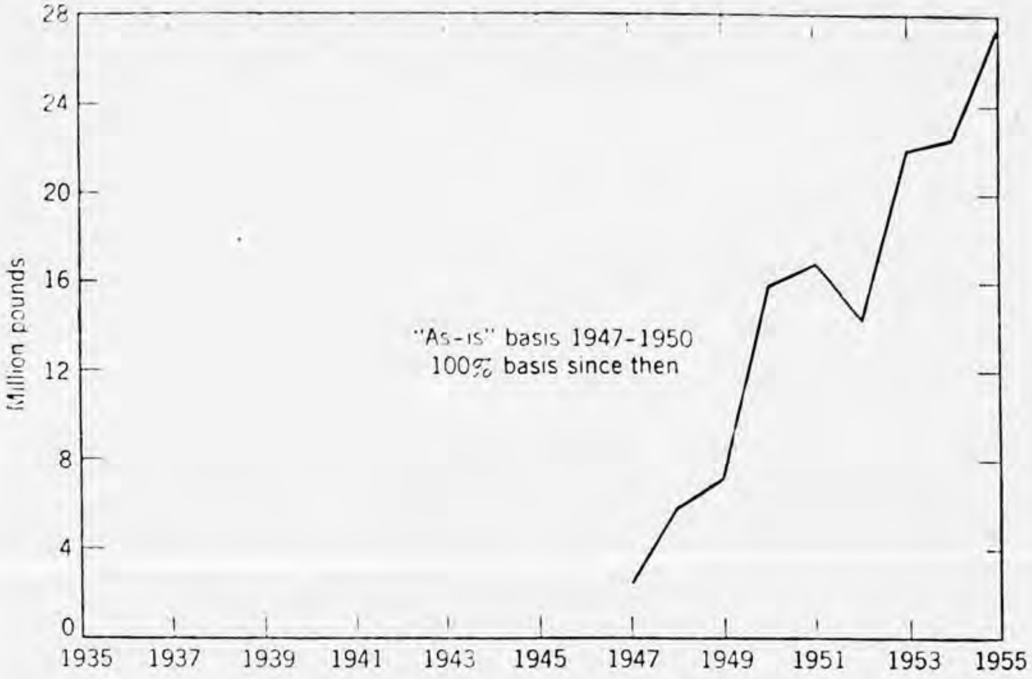
Basis—1 ton 68% carboxymethyl cellulose (5% moisture)

Cellulose (powdered) (5% moisture)	1,156 lb
Monochloroacetic acid (tech.) (anhydrous basis)	580 lb
Caustic soda (dry basis)	512 lb
Water	820 lb

Process

Carboxymethyl cellulose (CMC) is made by spraying powdered cellulose first with a caustic soda solution and then with chloroacetic acid. The resulting product is dried and packaged.

In a continuous process used by one manufacturer, the reactor is a rotating drum 20 ft long and 4 ft in diameter. Powdered cellulose is fed into the drum at a uniform rate (160 lb per hr) where it is sprayed with a 35 per cent solution of caustic soda in the front third of the reactor. In the middle third, the alkali cellulose is sprayed with a 78 per cent solution of chloroacetic acid. Reaction temperature is controlled at 35 to 40°C by blowing air through the reactor. The resulting dust loss is less than one per cent of the product. In the final third of the reactor (residence time is about one hour in each stage of the reactor) the reaction continues but is not completed. Product leaving the reactor at about 40 per cent moisture is discharged to fiber "aging" drums where the reaction goes to completion in 8 to 10 hours. The reaction temperature may rise in these drums to 50 to 55°C. After the "aging" is completed, the product is broken up and dried to 5 to 6 per cent moisture in a flash dryer. The resulting product contains sodium chloride formed during the reaction but is satisfactory for the technical grade. The purified grade required for food purposes must be washed to remove or reduce its sodium chloride content.



Production—Carboxymethyl Cellulose

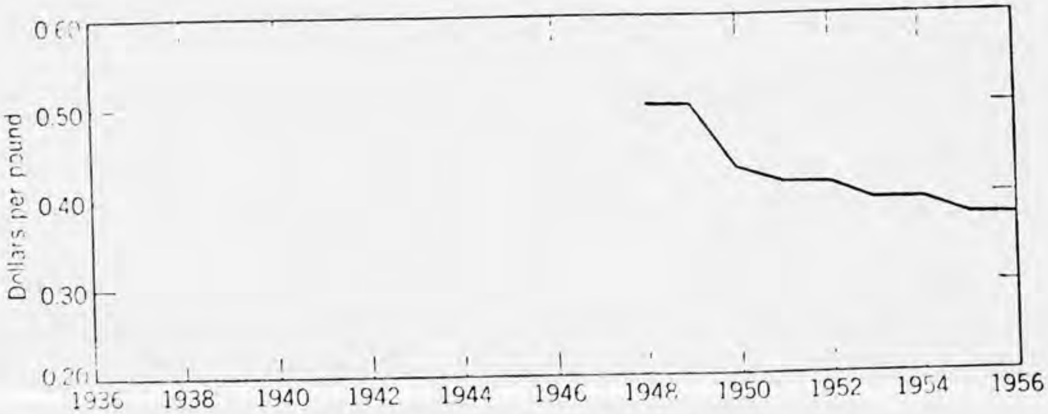
Most of the equipment is built of Type 316 stainless steel. An exception is the dilution tank for chloroacetic acid, which is made of Hastelloy C.

Several manufacturers make CMC by a batch process in which alkali cellulose "crumbs" are reacted with dry sodium chloroacetate in a kneader holding 1,200 lb cellulose.

Another manufacturer uses a continuous process in which cotton linters in continuous sheet form is treated with the necessary reactants. The final

Use Pattern

	1955 (est.), per cent
Detergents	37
Drilling muds	18
Food, principally ice cream	18
Paint	27
Paper sizing	
Textile sizing	
Pharmaceuticals	
Miscellaneous	
	100



Price—Carboxymethyl Cellulose

Miscellaneous

Properties. White to cream, odorless, tasteless, fibrous or granular powder.

Mol. wt. (Formula wt.)	242.18	M.P.	
Sp. gr.		B.P.	

Soluble in hot and cold water to produce viscous solutions at 1 to 6 per cent concentrations. Solubility increases with increased degree of substitution.

Grades. Technical (contains sodium chloride and sodium glycollate); low viscosity (36.5, 47.5, 58, and 62 per cent purity); high viscosity (58 per cent purity).

Purified (cellulose gum) 99 per cent. Various grades depending on degree of substitution, 0.3 to 1.20 (theoretically a completely substituted product would have a dS of 3.0), and viscosity of a 1 or 2 per cent solution at 25°C. Most common product has a dS of 0.70 (actually 0.65–0.85). Typical viscosities for this grade are: low, 25–50 (2 per cent conc.); medium, 300–600 (2 per cent conc.); high, 1,300–2,200 (1 per cent conc.).

Containers and Regulations. Drums and bags.

Economic Aspects

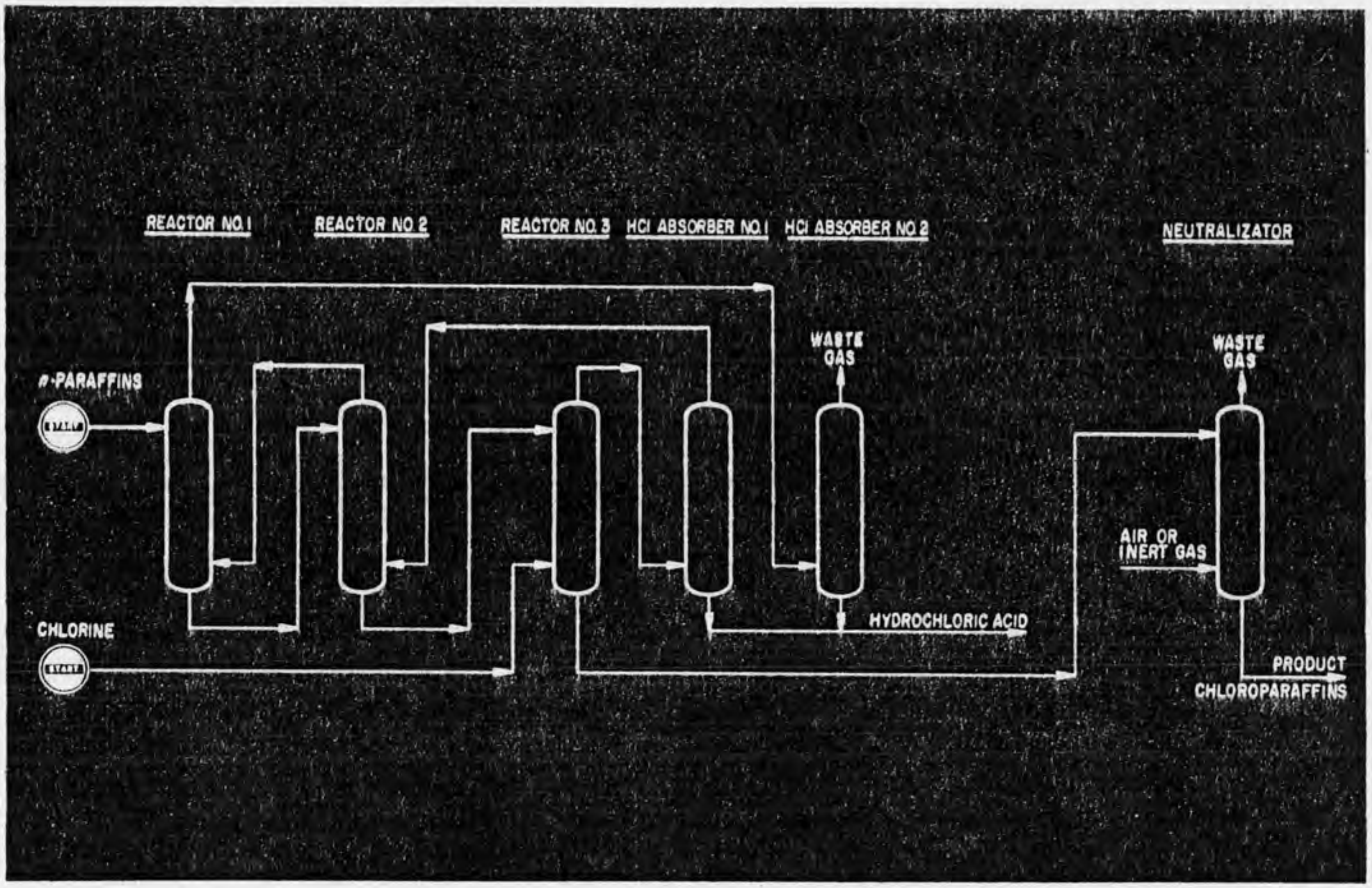
Carboxymethyl cellulose (CMC) (usually in the form of its sodium salt) entered the American chemical field only after World War II. It was originally developed in Germany during World War I, but did not reach commercial stature until World War II when it was used in large quantities as a detergent promoter.

The growth of CMC manufacture and use in the United States has resulted from its wide versatility as a thickener, stabilizer, and detergency-improver (see *Use Pattern*). Any one of its more promising fields of use, i.e., laundry starch replacement, soil conditioner, textile size, paper coating, latex paint stabilizer, or pharmaceutical (for reducing pills and laxatives), could increase almost overnight and overwhelm present production facilities. Relative cost of CMC and competing products appears to be the controlling factor. The greater effectiveness of CMC is still not sufficient to warrant widespread use at its present price.

Currently, plants as small as 350,000 lb per year are economic in some locations. The plants of the three major producers can probably make at least 5 million pounds annually. Plants of this size cost between $1,500,000 and $2,000,000.

Manufacturers and Plant Sites

Buckeye Cotton Oil Co., Memphis, Tenn.
E. I. du Pont de Nemours & Co., Inc., Carney's Point, N. J.
Hercules Powder Co., Hopewell, Va.; Radford, Va.
Wyandotte Chemicals Corp., Wyandotte, Mich.



Chloroparaffins — WINTERSHALL AG

Application: A continuous process for production of chlorinated paraffins from chlorine and liquid normal paraffins.

Description: Chlorinated paraffins are made by a new continuous route of thermal liquid phase chlorination. The process has been developed particularly for *n*-paraffins in the C_{20}-C_{24} range, but it is now available for *n*-paraffin fractions within the whole C_{10}-C_{30} range. It operates with chlorine conversion rates of nearly 100%.

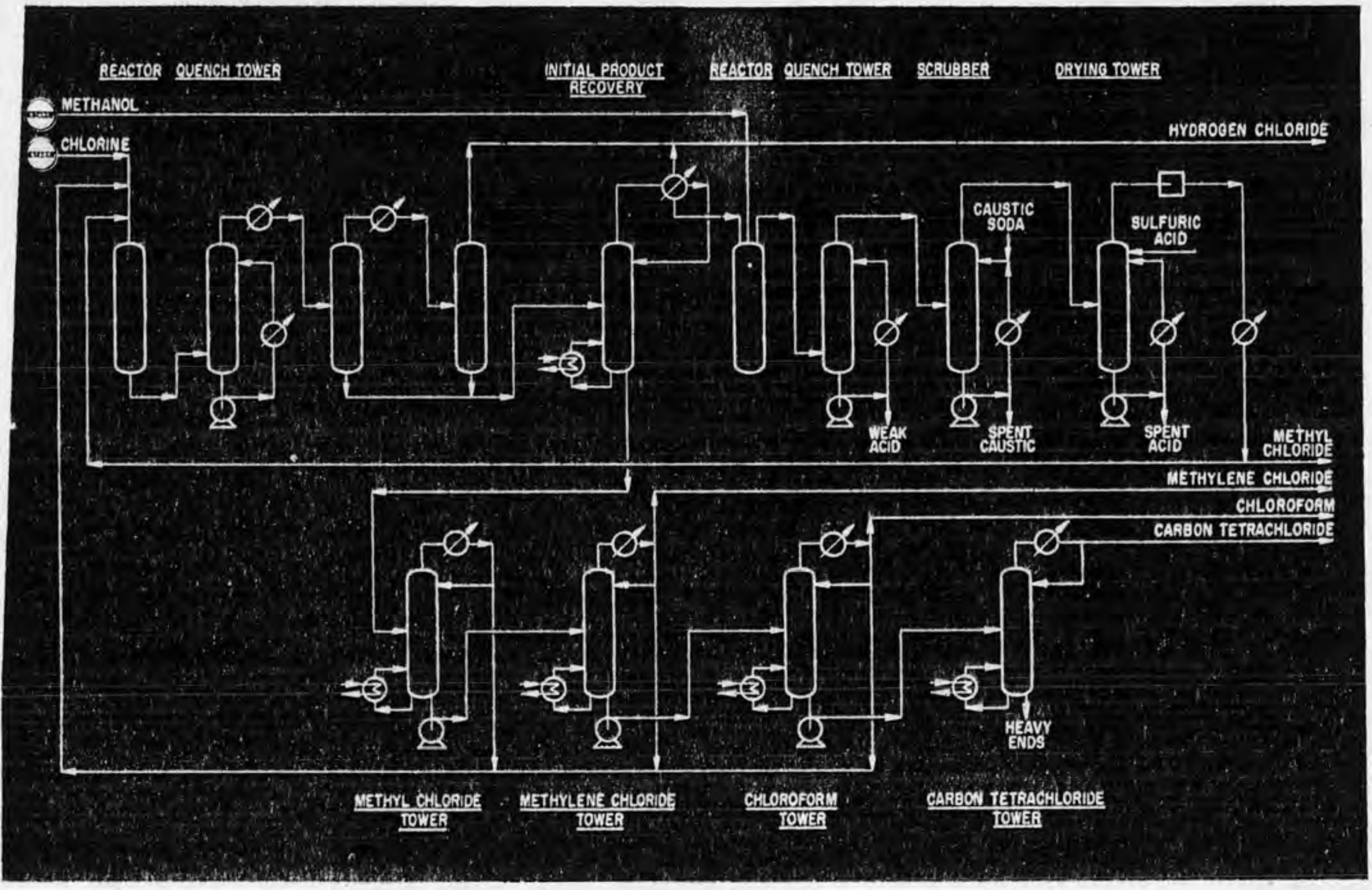
Chlorination takes place in three bubble column reactors (1, 2, 3) at atmospheric pressure between 80 and 120° C. Gas entering at the bottom of the columns is reacted with down-flowing hydrocarbon feed.

Fresh chlorine gas is only used in reactor 3 where it reacts with prechlorinated paraffins. The off-gas of reactor 3 passes through HCl-Absorber 1 for removing the excess of hydrogen chloride and converting it into a 30% technical hydrochloric acid before the gas enters the bottom of reactor 2 and reacts in reactor 2 with low chlorinated paraffins from reactor 1. The off-gas of reactor 2 is reacted with fresh hydrocarbon feed, entering the top of reactor 1. The off-gas of reactor 1 is converted into a 30% technical hydrochloric acid by the adiabatic HCl-Absorber 2.

Material: Borosilicate glass is used throughout the process plant for avoiding corrosion damages.

Commercial installations: Wintershall AG Kassel operates a commercial plant at their Salzbergen refinery since 1966. The plant was constructed by Jenaer Glaswerk Schott u. Gen., Mainz.

References: *European Chem. News,* Vol. 21, No. 532, May 12, 1972, p. 26. Further information is available from Proprietary Rights Service Corp., 180 East End Avenue, New York, N.Y. 10028 U. S. A. and "Ragged Hall," 33 Ragged Hall Lane, St. Albans/Hertfordshire, England.



Chloromethanes — VULCAN MATERIALS CO.

Application: A process for manufacture of chloromethanes (CH_3Cl, CH_2Cl_2, $CHCL_3$ and CCl_4) from methanol and chlorine.

Description: Hydrochlorination of methanol with HCl from the thermal chlorination reaction gives CH_3Cl which is thermally chlorinated with Cl_2 to produce the desired distribution among CH_2Cl_2, $CHCl_3$ and CCl_4. The hydrochlorination reaction is carried out in liquid phase with a catalyst. Sufficient CH_3Cl must be produced to balance the amount consumed by the thermal reaction. All or a portion of any excess HCl may be recovered as CH_3Cl or withdrawn as HCl. The process is straightforward utilizing standard practices and a minimum of exotic materials of construction is required. Liquid product from the thermal reactor is fractionated to recover chlorocarbons. HCl from the thermal reactor is combined with vaporized methanol and passed through the hydrochlorination reactor to produce CH_3Cl which in turn is fed to the thermal reactor.

Yields: Over-all yields of raw materials to desired products are chlorine, 95 wt % and methanol, 93-95 wt %. A stream factor of 350 days/year can be maintained.

Operating and maintenance requirement:

Utilities, per pound of product	
Steam, pounds at 75 psig	4
Cooling tower water, gals ($\triangle t = 15°$ F)	42
Power, kwh	0.16
Chemicals	
Sulfuric acid, pounds (98%)	0.17
Operating personnel, operators/shift	2
Operating supplies, % of labor	15
Annual maintenance, % BL investment	6.5

Commercial installations: A commercial plant using this technology was put into operation in Vulcan's N.J., plant in 1962; expanded in 1966 and doubled in capacity in 1968. The thermal chlorination system is based on technology developed for a methane chlorination plant which has been operated since 1957. Since then, two more plants have been built using this technology. The hydrochlorination portion of this process can be used to produce methyl chloride. Vulcan has designed and operated two such plants for methyl chloride.

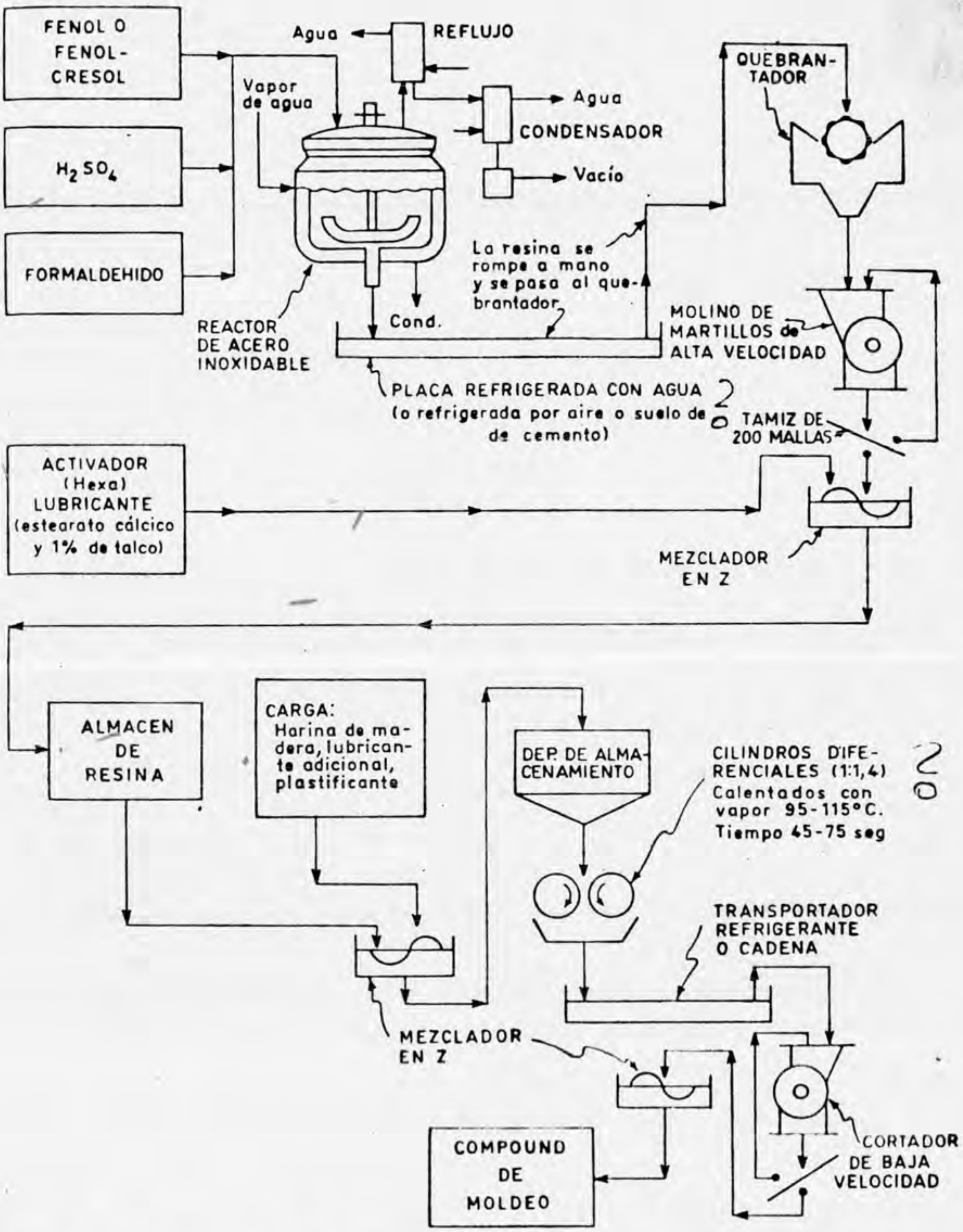
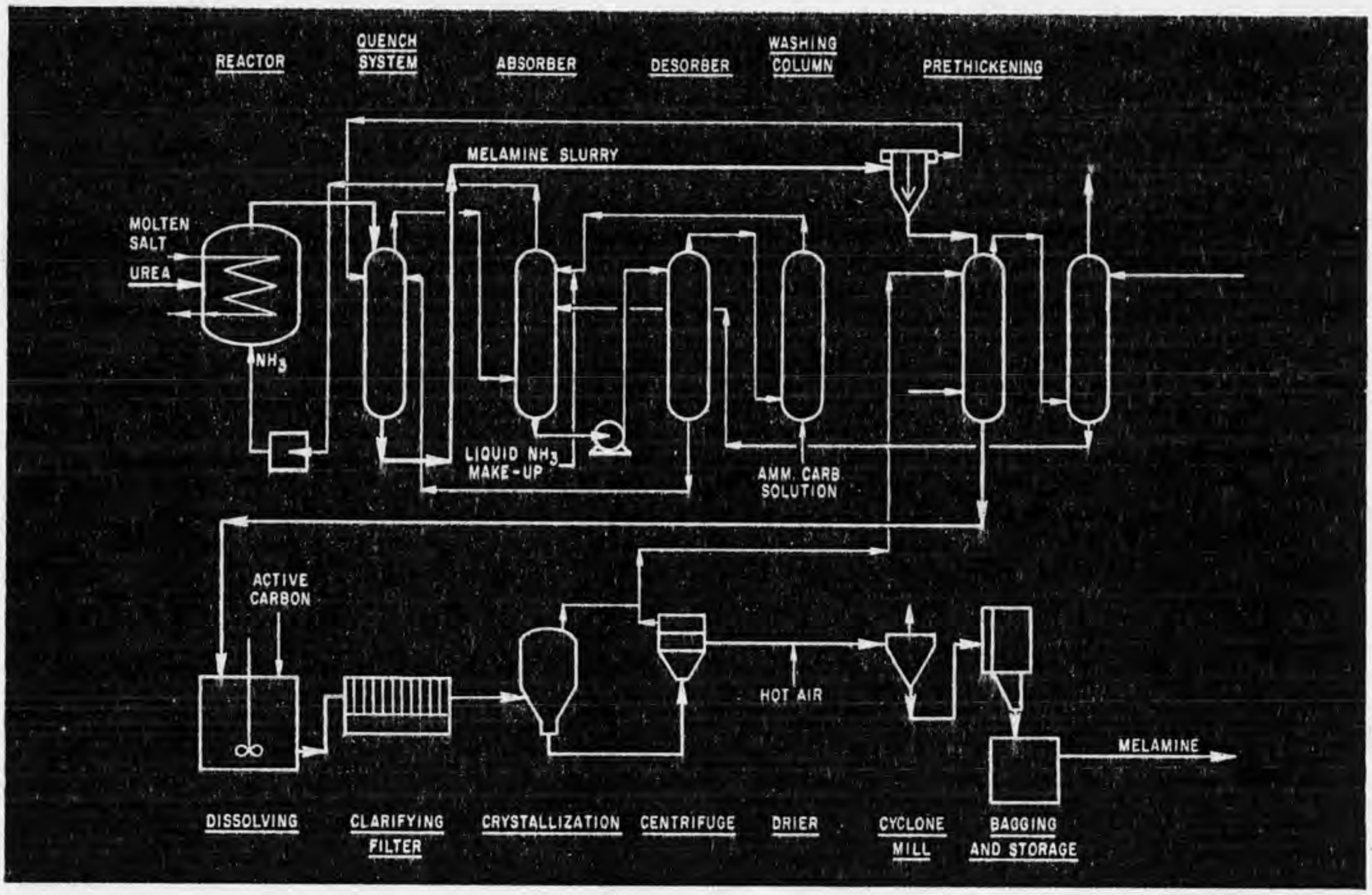


FIG. 10.14. Diagrama de la fabricación de polvos de moldeo de fenol-formaldehído. (C. C. Winding y R. L. Hasche, *Plastics, Theory and Practice*. Cortesía de McGraw-Hill Book Co.)

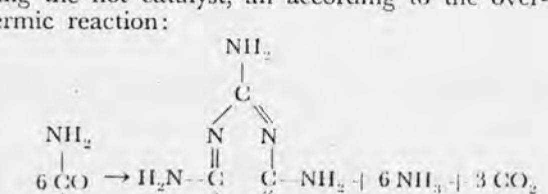


Melamine (DSM) — STAMICARBON N.V.

Application: A process for making high purity melamine from fertilizer grade urea at medium pressure (5-10 atm. abs.).

Description: A urea melt is supplied to a one-stage reactor, where it contacts a fluid bed catalyst. The reactor is heated internally by circulating molten salt.

The urea decomposes upon entering the reactor, the decomposition products being converted to melamine on contacting the hot catalyst, all according to the over-all endothermic reaction:



Hot gaseous ammonia is used as carrier gas and serves simultaneously as fluidizing agent.

The reactor effluent is rapidly quenched with aqueous mother liquor in specially designed equipment operating at pressures essentially equal to the reactor pressure. This operation yields a lean melamine-crystal slurry saturated with ammonia and CO_2 and an off-gas consisting of ammonia, CO_2 and water vapor. The lean slurry is sent to a hydroclone battery to obtain a concentrated crystal-slurry. The mother liquor overflow is returned to the quenching system. The concentrated slurry is redissolved in the mother liquor of the crystallization system, and the dissolved ammonia is stripped off simultaneously.

The off-gas leaving the quench system is treated at an elevated pressure in an absorber from which the bulk of the ammonia is withdrawn as a dry overhead gas stream, free of CO_2.

This ammonia is recycled to the reactor via a compressor and a heater. Liquid ammonia is used as reflux on the top of the absorber. The net amount of CO_2 formed in the reactor is removed as bottom product from the absorber in the form of a weak ammonium carbamate solution, which is concentrated in a desorber-washing column system. The bottom-product of this washing column, being a concentrated ammonium carbamate solution, is reprocessed in a urea plant. The top product, pure ammonia, is liquefied and used as reflux, as mentioned above, together with liquid make-up ammonia. The desorber bottom product, practically pure water, is used in the quench system in addition to the recycled mother liquor.

In order to upgrade the melamine to a high quality level, the solution, obtained after prethickening and stripping, is treated with activated carbon, passed over a clarifying filter and fed to a two-stage vacuum crystallization system.

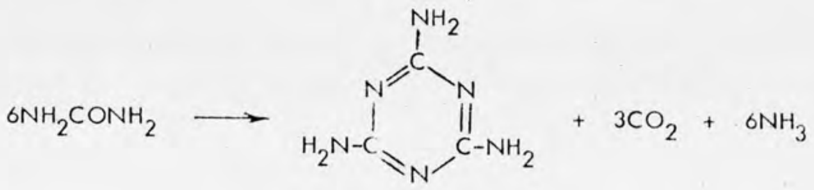
Recovery of the pure melamine product from the suspension is brought about in a continuous centrifuge.

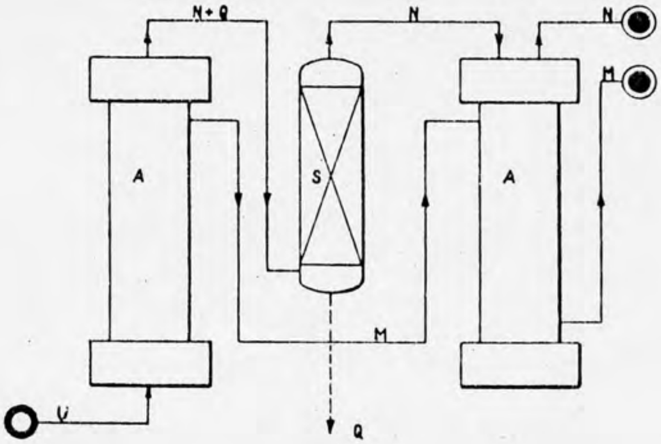
Stainless steel is used as construction material for nearly all parts of the equipment coming in contact with product streams.

Commercial Installations: A commercial 10,000 t/y plant for DSM was put onstream in the first quarter of 1967. Under construction a 30,000 t/y plant for DSM, a 9,000 t/y plant for Premier Petrochemical in Texas and for Milchem Inc., a 32,000 t/y plant in Louisiana.

MELAMINE FROM UREA

Reaction:





U-Urea Feed
A-Reactors
S-Separator
N-Ammonia
M-Melamine Product
Q-Carbon Dioxide

Feed Materials:
Urea

Coproducts:
Carbon Dioxide
Ammonia

Catalyst:	None
Phase:	Liquid Melt
Reactor type:	Tubular Autoclave
Solvent used:	None
Temperature, °C:	340-400
Pressure psi:	600-2250
Reaction time:	5 to 60 minutes
Heat Required:	-
Heat evolved:	-
Product yield:	99%
Product purity:	99%
Materials of Construction:	Silver-Lined Steel

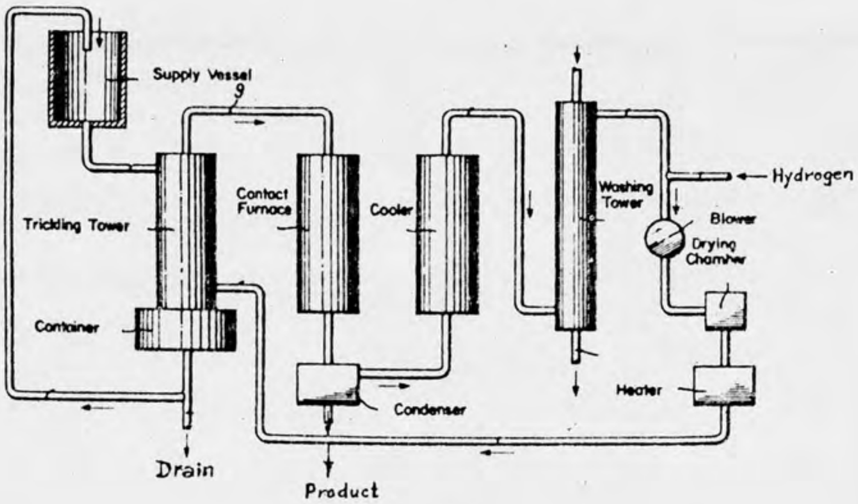
Major Product Uses: For the manufacture of melamine-formaldehyde resins.

Reference: U.S. Patent 3,116,294 by G. Marullo et al (to Montecatini) (Dec. 31, 1963)

PROYECTOS DE INVERSION PEQUEÑA
TECNOLOGIA DE PRODUCTO

CHLOROACETIC ACID

eaction: $Cl_2CHCOOH + CH_3COOH \longrightarrow 2ClCH_2COOH$



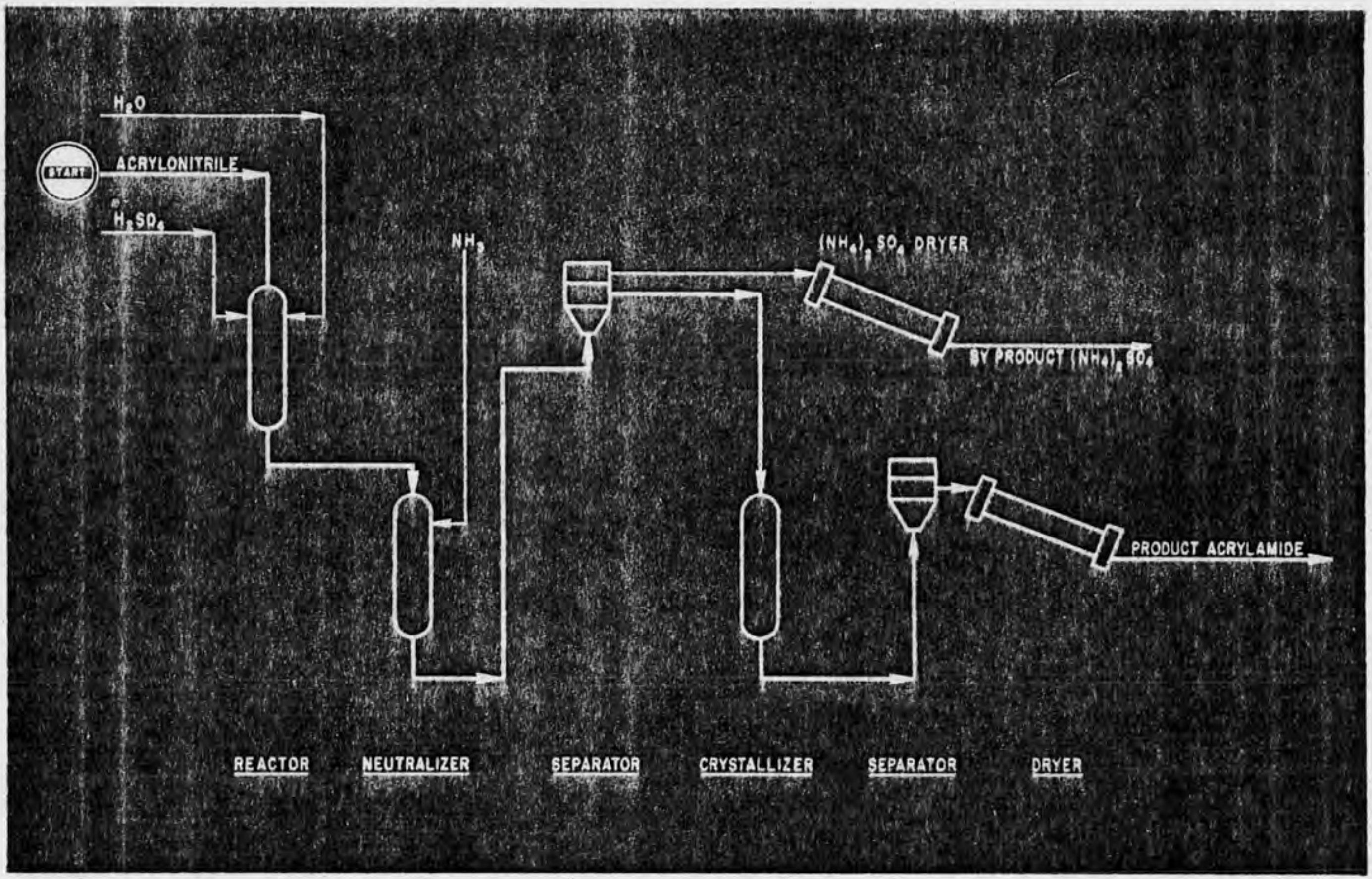
eed Materials:
Dichloroacetic Acid
Acetic Acid

oproducts:

Catalyst:	Platinum
Phase:	Vapor
Reactor type:	Packed Tower
Solvent used:	None
Temperature, °C:	110
Pressure psi:	Atmospheric
Reaction time:	
Heat Required:	-
Heat evolved:	-
Product yield:	97%
Product purity:	
Materials of Construction:	

ajor Product Uses: For carboxymethyl cellulose; 2,4-dichlorophenoxy acetic acid herbicides; and synthetic indigo.

eference: U.S. Patent 3,071,615 by W. Opitz et al (to Knapsack-Griesheim A.G.) (Jan. 1, 1963)



Acrylamide—MITSUBISHI CHEMICAL INDUSTRIES LTD.

Application: A process for the hydrolysis of acrylonitrile to produce high quality acrylamide from acrylonitrile, ammonia and sulfuric acid.

Product: Acrylamide of the following quality (typical analysis) is available.

Purity	99%
Water	0.5%
Iron	trace
Ammonium sulfate	0.5%
Color (at 10% aqueous)	APHA 5-10

Byproduct: Ammonium sulfate of the following quality

Purity	99%
Water	0.7%

Description: The process contains the following sections: hydrolysis, neutralization, ammonium sulfate separation, crystallization, acrylamide separation and product drying. Mitsubishi has developed a continuous and efficient process. Special features of the process are:

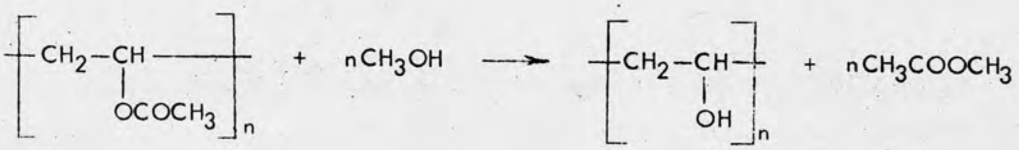
1. Production of high-purity product for versatile use at high yield.
2. Simpler and smoother operation.

Commercial Installation: A 3,600 tons/year plant is now being operated and two new plants are under construction, i.e., a 15 MM lbs./year plant in the United States and one plant for Mitsubishi in Japan.

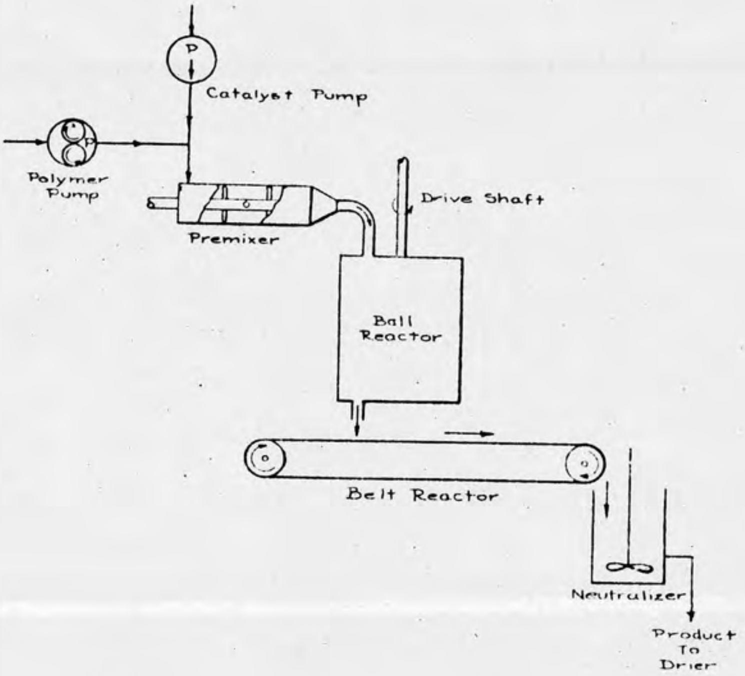
Reference: *Japan Chemical Quarterly,* July 1968, Vol. 4-No. 3, pp 54-56.

POLYVINYL ALCOHOL

action:



$$\left[-CH_2-\underset{\displaystyle OCOCH_3}{\underset{|}{CH}}-\right]_n + nCH_3OH \longrightarrow \left[-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-\right]_n + nCH_3COOCH_3$$



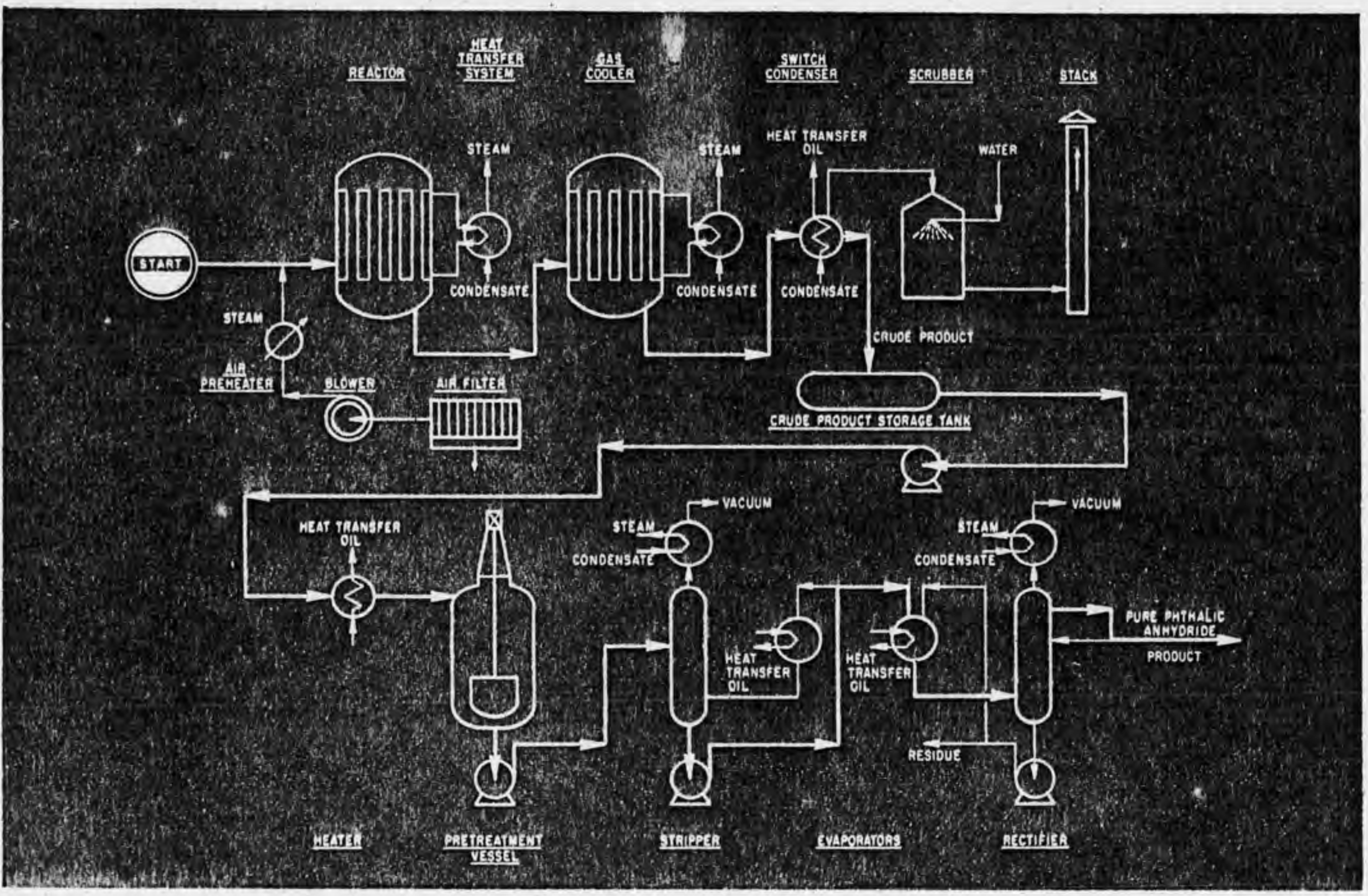
Feed Materials:
Polyvinyl Acetate
Methanol

Coproducts:
Methyl Acetate

Catalyst: Sodium Methoxide
Phase: Liquid
Reactor type: Stirred Tank then Conveyor Belt
Solvent used: Methanol
Temperature, °C: 65-85
Pressure psi: Atmospheric
Reaction time: 10-30 minutes
Heat Required: -
Heat evolved: -
Product yield: 85%
Product purity:
Materials of Construction: Stainless Steel

Major Product Uses: Binder and thickener for coatings, cosmetics, etc; water-soluble films; polyvinyl formal fiber.

Reference: U.S. Patent 2,779,752 by W.H. Vining (to Du Pont) (Jan. 29, 1957)



Phthalic Anhydride (BASF)— FOSTER WHEELER CORP.

Application: A process for the manufacture of phthalic anhydride from ortho-xylene and air.

Description: Hot air and ortho-xylene are mixed before entering the fixed-bed tubular reactor where the ortho-xylene is partially oxidized to phthalic anhydride; maleic anhydride, benzoic acid, CO and CO_2 being formed as byproducts.

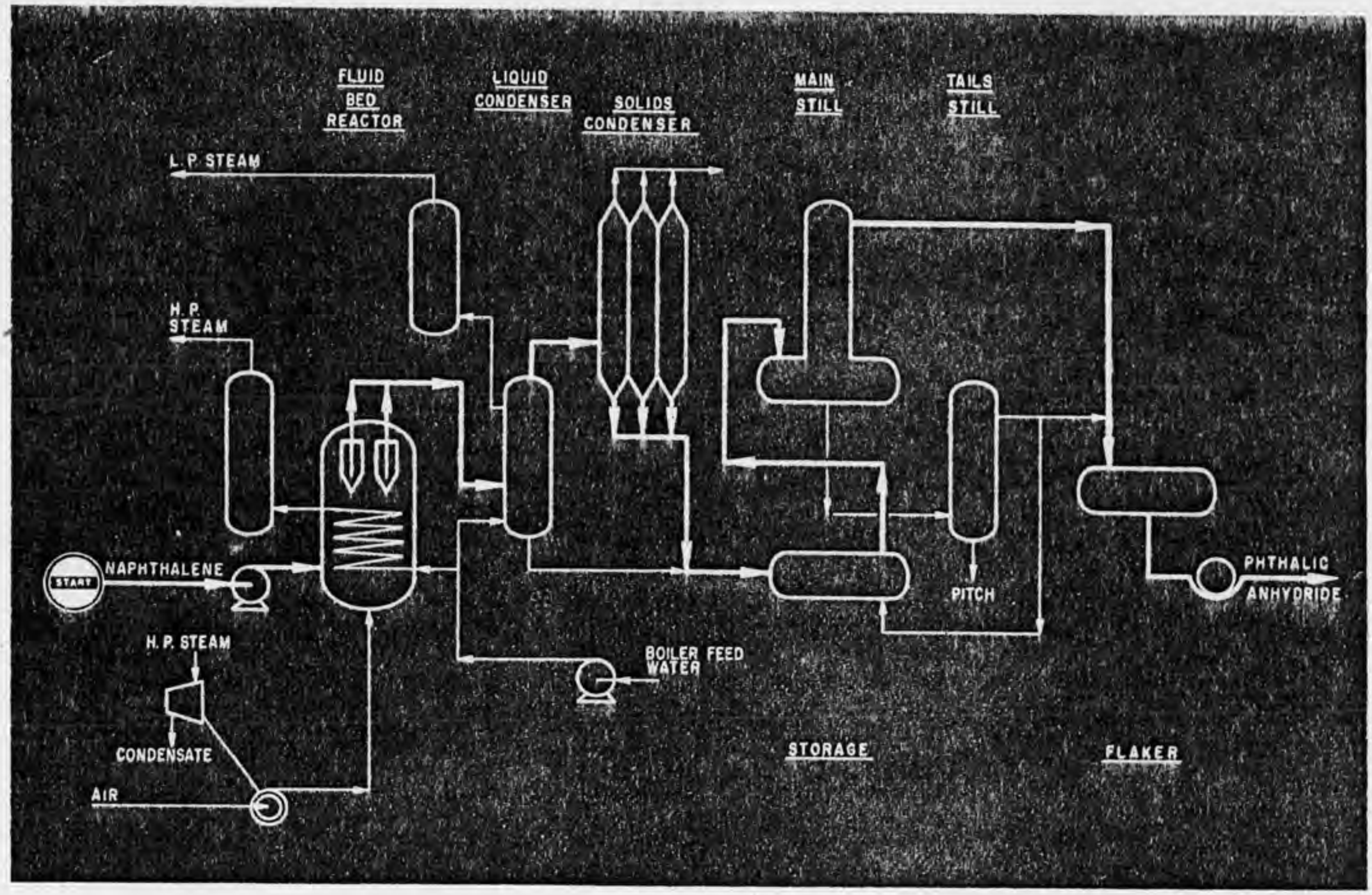
The heat of the exothermic reaction is removed from the reactor by a recirculated salt bath, which is cooled in an external cooler with water, thus generating high-pressure steam. The reactor product gases are passed through two waste heat boilers generating high and low-pressure steam respectively. The partially cooled gas is then sent through switch condensers where the phthalic anhydride is condensed to the solid state.

Off-gas leaving the condensers is scrubbed with water or incinerated before being discharged to the atmosphere. The crude phthalic anhydride is collected from the switch condensers by melting and then thermally pretreated and purified in a two-stage distillation unit in continuous operation.

Yields: Yield is in the order of 103 pounds phthalic anhydride for 100 pounds of ortho-xylene (95 percent purity) due to the use of a new, highly active vanadium-pentoxide catalyst. One reactor of standard size (approximately 10,000 tubes) has a capacity of 14,400 metric tons per year of pure phthalic anhydride.

General: Foster Wheeler Corp. is one of the engineering companies authorized by BASF to provide engineering and construction services for plants using the BASF phthalic anhydride process. Additional information may be obtained from Foster Wheeler Corp., 110 South Orange Ave., Livingston, N.J. Other companies authorized to provide engineering and construction services for plants using the BASF phthalic anhydride process include: The Badger Co., Cambridge, Mass.; Heinrich Koppers GmbH, Essen, Germany; Linde AG, Hollriegelskreuth, Germany, and The Lummus Co., Bloomfield, N.J.

As of Oct. 1, 1969, thirteen license agreements with independent or affiliated companies have been made.



Phthalic Anhydride—UNITED COKE & CHEMICALS LTD. FOSTER WHEELER CORP.

Application: A process for the manufacture of phthalic anhydride from naphthalene and air.

Description: Crude phthalic anhydride is produced by the partial oxidation of naphthalene. The main reaction, in the presence of a catalyst, is:

$$C_{10}H_8 + 4.5O_2 = C_8H_4O_3 + 2CO_2 + 2H_2O$$

The crude phthalic anhydride thus produced is then refined, in the distillation unit.

Air and naphthalene are fed to the fluidized reactor. Compressed air enters the reactor under the distribution plate. Naphthalene is pumped from the storage tank to spray nozzles in the side of the reactor above the perforated distribution plate.

In the fluidized bed process, the fluidized catalyst particles in the reactor render the vapor mixture in the reactor unexplosive.

The oxidation reaction takes place in the bed of fluidized catalyst. The reaction heat is removed in a cooler consisting of elements immersed in the catalyst. Boiler feedwater is fed to the tubes and is converted to high pressure superheated steam. The reaction temperature is controlled by metering the boiler feedwater.

For startup an in-line air preheater brings the combustion products to a controlled temperature and the catalyst in the reactor is brought to reaction temperature within a few hours. When normal operation is under way, the fuel to the air preheater is shut off.

A catalyst storage vessel and eductor for loading and unloading the catalyst permit the catalyst to be loaded without shutting down the unit. One complete reactor charge can be stored in the catalyst storage vessel.

The mixed vapors leaving the reactor pass to a group of filter vessels. By a time-cycle mechanism, one vessel at a time may be blown back by a stream of air, freeing the filter surface of catalyst. The fines are blown back to the dense phase catalyst bed inside the reactor.

Crude phthalic anhydride leaves the filter vessels as vapor which includes nitrogen, oxygen, carbon dioxide, water vapor and byproducts. This stream flows to a condenser where a large portion of the phthalic anhydride is recovered in liquid form. Final recovery of crude product as a solid is in parallel condensers run on a condensing melting cycle. Spent gas containing traces of odoriferous organics is treated with either scrubbing or combustion apparatus for pollution abatement.

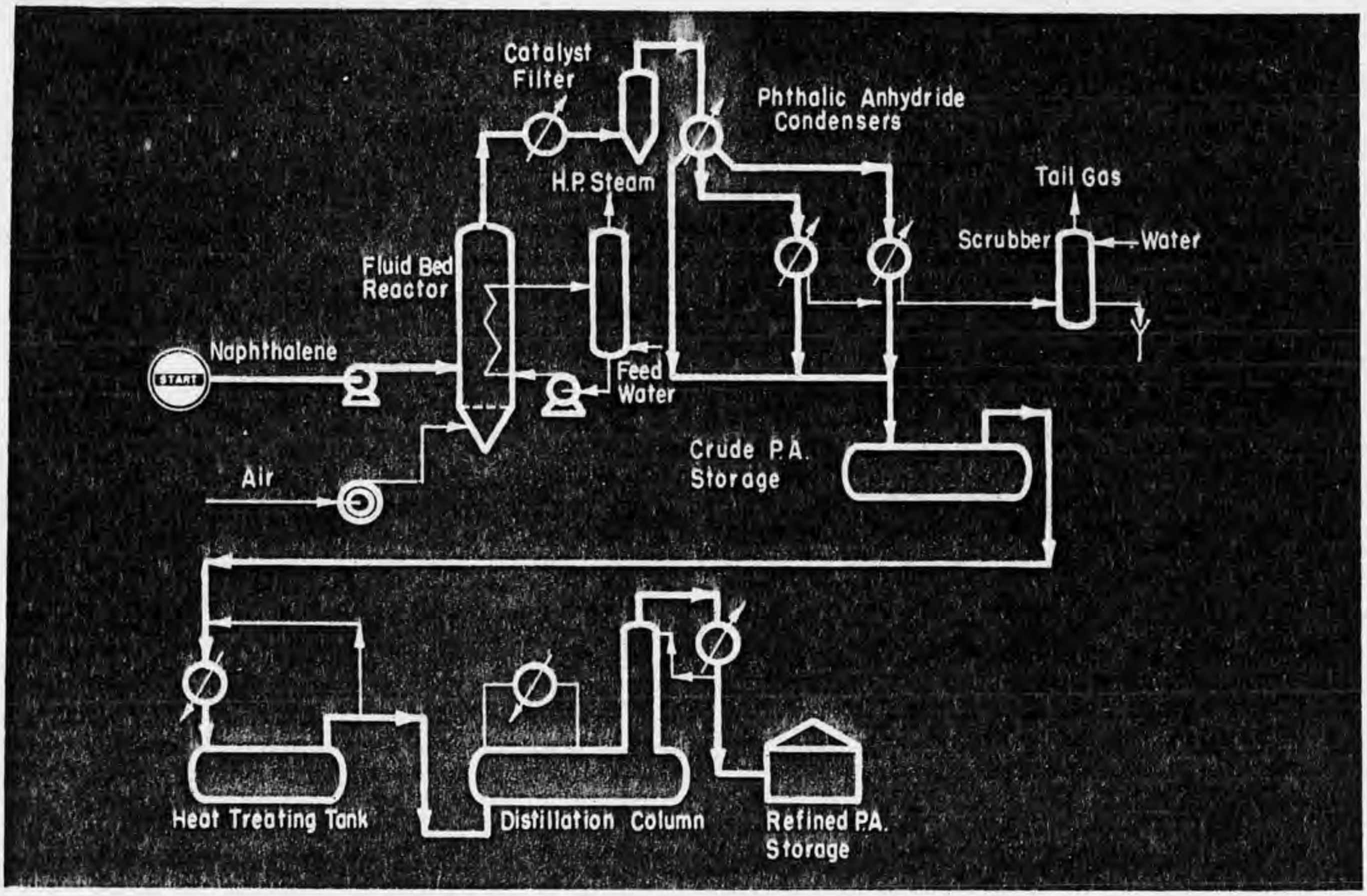
Molten crude phthalic is thermally treated prior to vacuum batch distillation.

During the first few hours of distillation a forecut is taken to remove light ends. This forecut returns by gravity to the synthesis unit.

After removal of the light ends the distillation continues. During this time the product is withdrawn from the reflux divider and passed to the pure anhydride receiver where it may be withdrawn as a liquid or it may be flaked.

The residual material left in the main still is treated in a tails still from which an overhead cut is recycled and pitch discharged to waste.

Installed Capacity: Three plants using this process have been built.



Phthalic Anhydride (Sherwin-Williams/Badger) — THE BADGER COMPANY INC.

Application: A fluid bed process for the production of high purity phthalic anhydride from naphthalene.

Description: Liquid naphthalene is introduced directly into the reactor at the bottom of the catalyst bed. It is immediately vaporized and dispersed throughout the bed upon contact with hot catalyst and the reaction air which is introduced below the reactor distribution grid. Here in the presence of reaction air and a fluidized vanadium-oxide catalyst, the vaporization and oxidation of naphthalene to phthalic anhydride takes place. Because of the high degree of agitation and mixing within the fluid bed, a uniform temperature is maintained throughout the reaction zone. The bed temperature is controlled within narrow limits in the range of 650° F to 725° F.

Heat from the highly exothermic reaction is removed by cooling tubes located in the catalyst bed and high pressure steam is generated without the need of a secondary heat transfer agent.

Entrained catalyst is removed from the reaction gases in specially constructed ceramic filter elements, and the recovered catalyst is blown back to the reactor. Several filters are provided and one filter vessel at a time is blown back by a stream of air which frees the filter surface of catalyst. Phthalic anhydride product is condensed both as a liquid and a solid from the effluent gases.

The required air to feed ratio in a fluid bed reactor is significantly lower than conventional fixed bed units by a factor of two or three. At this low air ratio, 40 to 60 wt. percent of the crude product can be condensed directly as liquid phthalic anhydride. This fact plus the much lower air rate greatly reduces the load on the solid product condensers with a proportional decrease in plant cost as compared to fixed bed units.

Crude phthalic anhydride is sent to a purification system where simple batch heat treatment and vacuum distillation produce high purity phthalic anhydride. Facilities may be provided to produce a flaked product; however, in modern practice, much is shipped in molten form.

Economics: The development of large capacity fluid bed units has substantially improved the economics of phthalic anhydride production. Plants with capacities of 125-150 MM lb./yr. of product in a single train are now in operation.

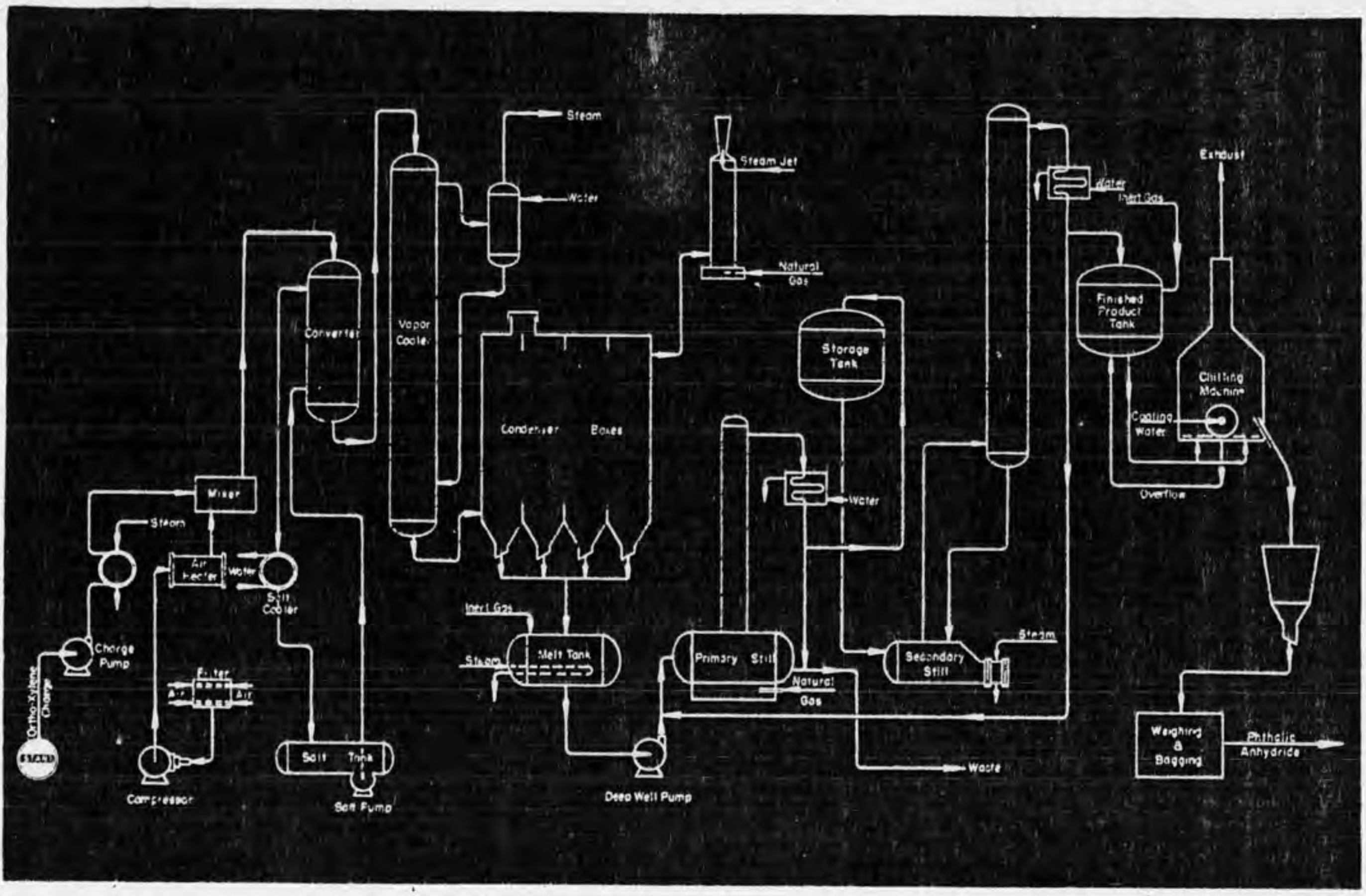
Yields: Yields are in the order of 98 lbs. phthalic anhydride for 100 lbs. feed.

Operating Costs: (For a plant rated @ 100 MM lb./yr.)

Utilities (current U. S. Gulf Coast Costs)	0.15¢/lb. product
Catalyst Makeup	0.10¢/lb. product
Maintenance Charges	2.5-3% of plant investment
Labor Requirements	2-3 men per shift plus one supervisor day shift only

Commercial Installations: Fourteen plants have been built having an aggregate capacity of about 630,000,000 pounds per year of refined phthalic anhydride.

Reference: *Chemical Engineering Progress* Vol. 58, No. 1; *Chemical Engineering,* Jan. 22, 1962; *European Chemical News,* Sept. 30, 1966.



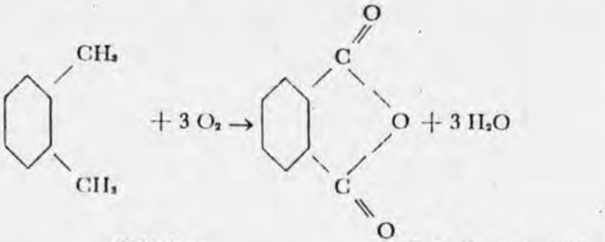
Phthalic Anhydride—CALIFORNIA RESEARCH CORPORATION

Application: This process is applied to the manufacture of phthalic anhydride.

Charge: The charge is ortho-xylene.

Product: The product is solid phthalic anhydride.

Description: The liquid ortho-xylene feed is pumped at controlled rates into vaporizers. The vaporized xylene is fed to a mixer where it is contacted with heated air. This mixture then goes to salt-cooled converter units where the following reaction occurs:



O-Xylene Phthalic Anhydride

This direct oxidation of the xylene to phthalic anhydride is promoted by the catalyst in the converter tubes which is based on vanadium pentoxide (V_3O_5). This catalyst must be carefully prepared for proper catalyst activity.

The reaction gases leaving the bottom of the converters are cooled to condense crude phthalic anhydride. The spent gases pass into catalytic incinerating furnaces to eliminate fume nuisance.

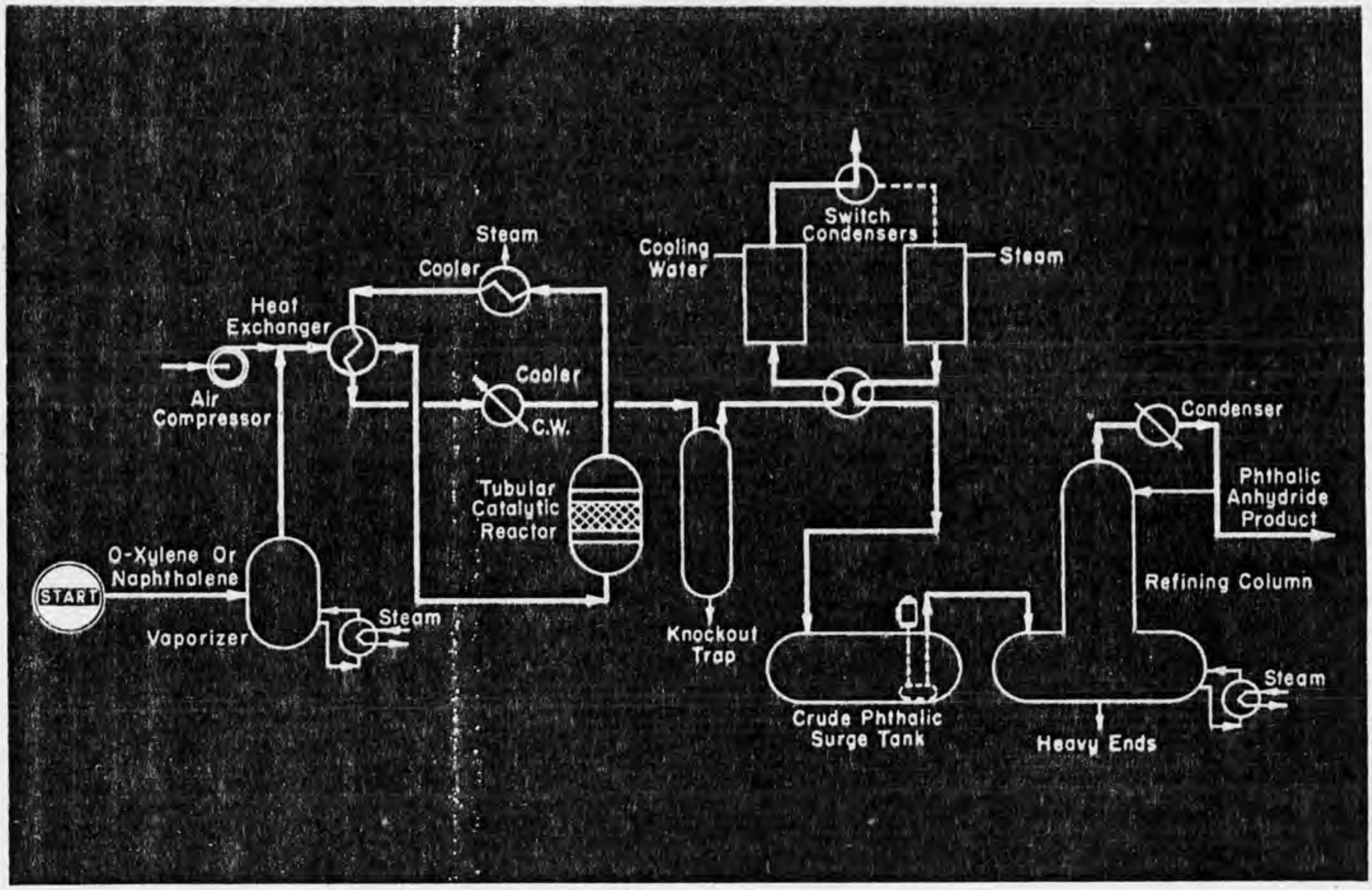
The crude phthalic anhydride goes to melt tanks for storage. The molten anhydride is distilled batchwise in two distillation stills in series. Light boilers such as benzoic acid are taken off under vacuum as a heads cut. The purified phthalic anhydride is removed as a heart cut from the second still which also operates under vacuum. The product goes from the secondary still to an aluminum storage tank. From this tank it is fed to a stainless-steel water-cooled surface for solidification. The final product in the form of chips is weighed and packed in paper bags. Molten anhydride also is shipped in steam-heated tank cars.

Operating Conditions: The most important operating conditions are the air/hydrocarbon ratio, the temperature in the converter and the contact time. Typical operating ranges for these variables are given below:

Air/Hydrocarbon Ratio	18-20
Temperature, F.	900-1150
Contact Time, Seconds	0.1-0.15

Commercial Installation: Oronite Chemical Company, Richmond, Calif.

Reference: PETROLEUM REFINER, Oct.'53,p113; *Chemical Engineering Progress,* Apr.'47,p167.



Phthalic Anhydride — SCIENTIFIC DESIGN COMPANY, INC.

Application: A process for the manufacture of phthalic anhydride.

Charge: Naphthalene and/or ortho-xylene.

Product: High purity phthalic anhydride.

Description: Phthalic anhydride is best produced from naphthalene in a fixed-bed catalytic vapor phase reaction. In sequence, the feedstock, comprising naphthalene, *o*-xylene, or mixtures thereof, is vaporized, mixed with air, preheated by exchange with effluent gases, and fed to the reactor. The reactor cooling system (not shown) consists of molten salt circulating outside the tubes of the reactor.

Reaction effluent gases containing phthalic anhydride vapor are first cooled by a waste heat boiler generating steam, then used to preheat the feed mixture, and finally are cooled with cooling water to a temperature a few degrees above the dew point of phthalic anhydride. After leaving this cooler, the gases are passed through one of a pair of highly efficient switch condensers of novel design which condense solid crystals of phthalic anhydride. The condenser effluent gases, which may contain traces of by-products, are burned or water-scrubbed before release to the atmosphere. Meantime, in the alternate switch condenser, phthalic anhydride from the previous cycle is being melted out. The crude phthalic anhydride is treated to destroy contaminants and is then distilled under vacuum. The refined product may be flaked, pelletized, or packaged for shipment in liquid-full steel drums or tank cars. Fumaric acid may be recovered from the maleic anhydride content of the off-gas scrubber liquor.

Chemical Reactions.

Main Reaction—

a) $C_{10}H_8 + 4\frac{1}{2} O_2$ (air) $\rightarrow C_8H_4O_3 + 2 CO_2 + 2 H_2O$

b) $C_8H_{10} + 3 O_2$ (air) $\rightarrow C_8H_4O_3 + 3 H_2O$

Principal Side Reaction—

a) $C_{10}H_8 + 12 O_2$ (air) $\rightarrow 10 CO_2 + 4 H_2O$

b) $C_8H_{10} + 10\frac{1}{2} O_2$ (air) $\rightarrow 8 CO_2 + 5 H_2O$

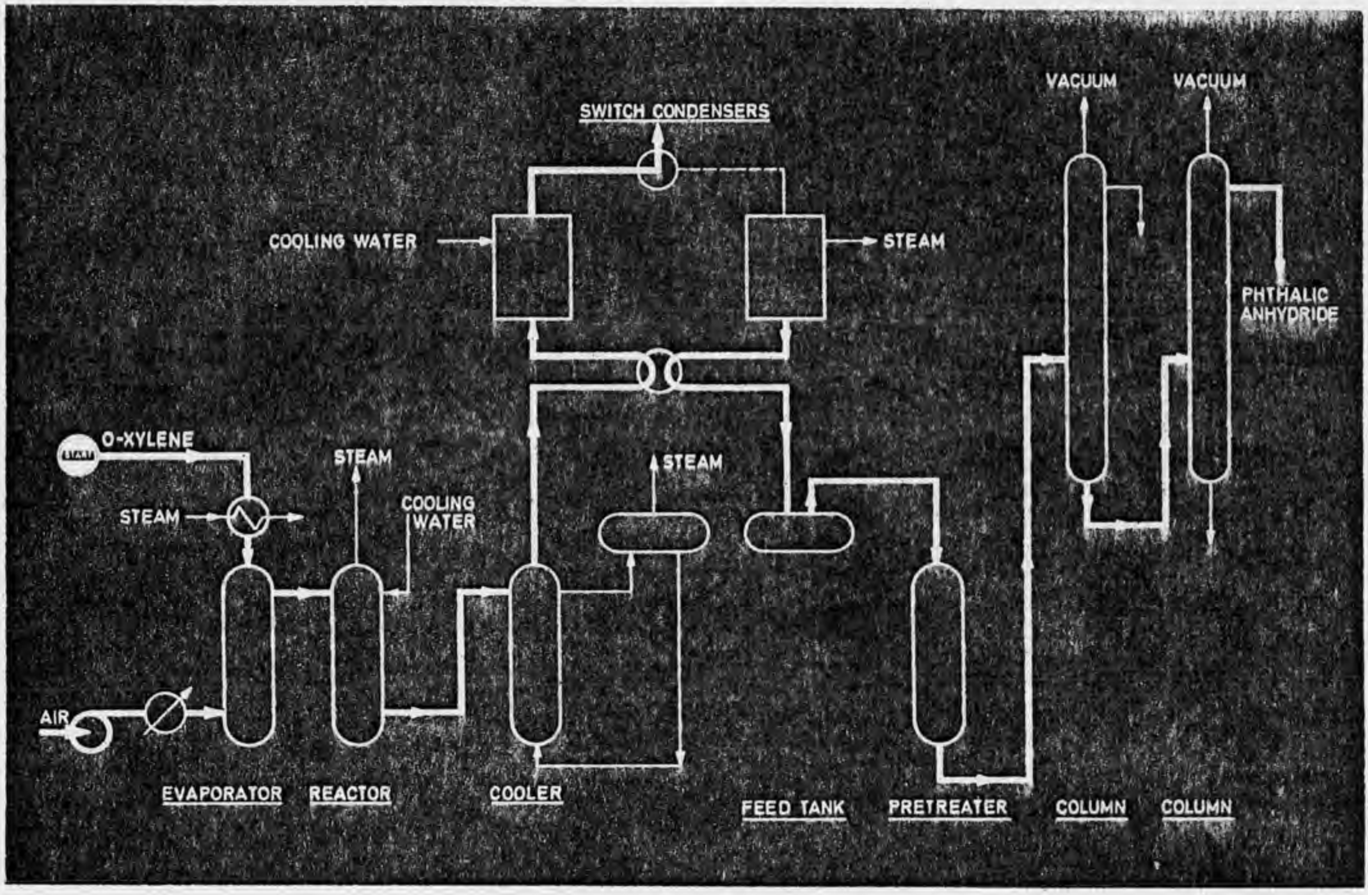
Minor Side Reaction—

a) $C_{10}H_8 + 9 O_2$ (air) $\rightarrow C_4H_2O_3$ (Maleic) $+ 6 CO_2 + 3 H_2O$
(Anhydride)

b) $C_8H_{10} + 7\frac{1}{2} O_2$ (air) $\rightarrow C_4H_2O_3$ (Maleic) $+ 4 CO_2 + 4 H_2O$
(Anhydride)

Note that almost all side reactions are much more exothermic than the desired main reaction. SD's highly selective oxidation catalyst thus aids temperature control and permits higher thruput rates in the reactor.

Commercial Installations: Witco Chemical Co., Chicago, Ill.; Compagnie Francaise des Matieres Colorantes, Villers-St. Paul, France; Staatsmijnen in Limburg, Geleen, Holland; and Witco Chemical Co., Perth Amboy, N. J.



Phthalic anhydride — CHEMISCHE FABRIK VON HEYDEN GMBH

Application: Production of phthalic anhydride from *o*-xylene or naphthalene by choice of catalyst or a special catalyst for both feedstocks.

Product: Phthalic anhydride (PA) content 99.9%; maleic anhydride max. 0.05%; benzoic acid max. 0.05%; Color: 5-10 Hazen (APHA); Heat Test: 10-20 Hazen; Solidification Point: 131° C.

Description: Filtered and compressed oxidation air of 7-10 psig is heated to 140-160° C and loaded with evaporated naphthalene or *o*-xylene in an air-hydrocarbon ratio below the explosive limit.

The mixture of naphthalene or *o*-xylene enters a reactor with vertical tubes holding the granular catalyst. A salt melt circulating around the tubes removes the heat of reaction and maintains constant temperature conditions. The reaction heat is utilized for the generation of high pressure steam.

The reactor effluent containing PA vapors is precooled in a waste heat boiler generating steam. By further cooling PA is then sublimated in specially designed finned tube switch condensers with optimal efficiency and safety. The crude PA deposited on the condensing surfaces is periodically melted and discharged into a tank. The effluent gas is discharged to atmosphere after water scrubbing or incineration. The crude PA is pretreated thermally under atmospheric or reduced pressure, from where it is supplied to either a batchwise or a continuous vacuum distillation system. Low and high boiling impurities are removed and the pure PA is obtained as a distillate which can be stored either in the molten state or flaked and bagged.

Yields: 102-105 lbs. PA from 100 lbs. technical grade *o*-xylene (min. 96%) depending on *o*-xylene quality. 94-98 lbs. PA from 100 lbs. naphthalene depending on naphthalene quality.

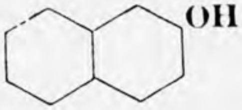
Economics: Life time of the catalyst is at least 3 years. Experienced maintenance charges are in the range of 1.5 to 2% of plant equipment investment. Capacity of single reactor: up to 80 million lbs./year. Onstream factor: 98-99%.

Commercial installations: Up to the present time, 65 commercial plants with an installed capacity of more than 800,000 metric tons per year using the von Heyden process have been erected or are under construction. Forty-one of these operate on *o*-xylene basis.

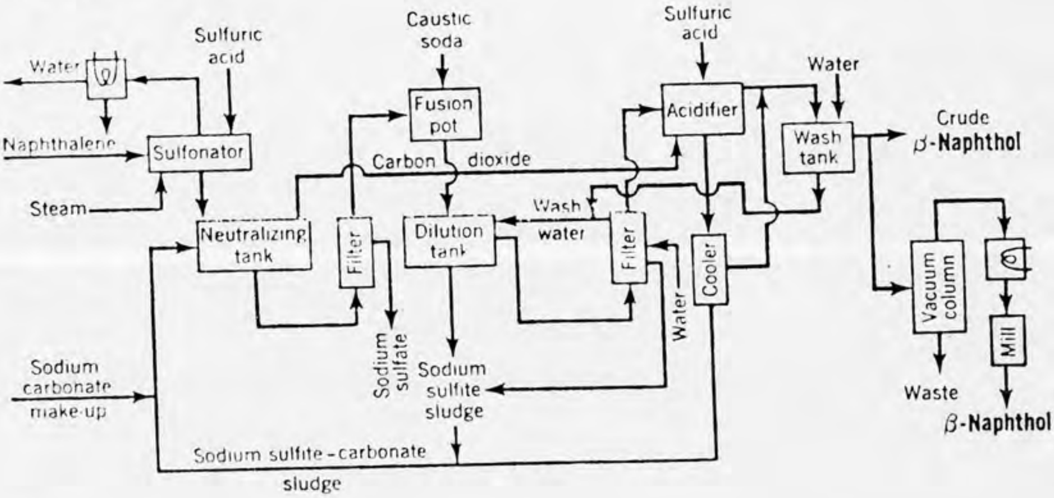
The licensees of the von Heyden process for the world are: DAVY POWERGAS GmbH, 5000 Köln-Braunsfeld, Aachener Strasse 958, W. Germany, and LURGI Gesellschaft für Mineralöltechnik m.b.H, 6000 Frankfurt/Main Bockenheimer Landstrasse 8, W. Germany.

BETA-NAPHTHOL

(2-NAPHTHOL)



From Naphthalene



Reaction

$$C_{10}H_8 + H_2SO_4 \rightarrow C_{10}H_7SO_3H + H_2O$$

$$2C_{10}H_7SO_3H + Na_2CO_3 \rightarrow 2C_{10}H_7SO_3Na + CO_2 + H_2O$$

$$C_{10}H_7SO_3Na + 2NaOH \rightarrow C_{10}H_7ONa + Na_2SO_3 + H_2O$$

$$2C_{10}H_7ONa + CO_2 + H_2O \rightarrow 2C_{10}H_7OH + Na_2CO_3$$

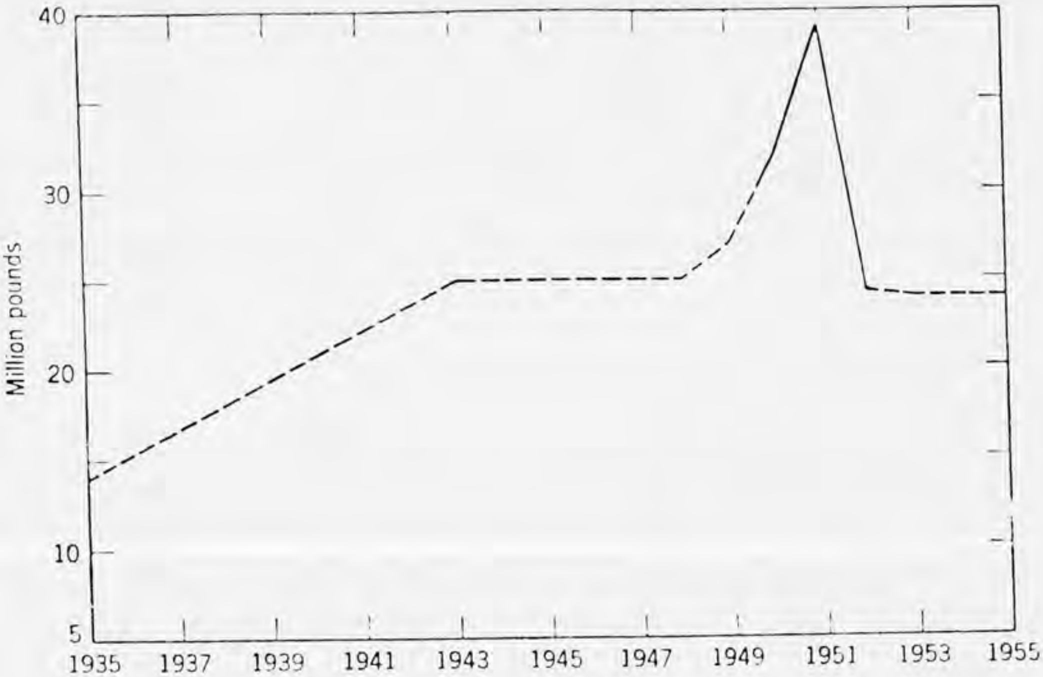
75–80% yield

A third method consists of treating the dilute naphthalene-β-sulfonic acid solution with the alkali fusion mass from the preceding batch. The following reactions illustrate the procedure:

$$C_{10}H_7SO_3Na + 2NaOH\ (\text{fusion}) \rightarrow C_{10}H_7ONa + Na_2SO_3 + H_2O$$

$$C_{10}H_7ONa + C_{10}H_7SO_3H \rightarrow C_{10}H_7OH + C_{10}H_7SO_3Na$$

A method that competes favorably with the sodium sulfite–sulfur dioxide procedure uses sodium carbonate. The evolved carbon dioxide may be utilized in the ensuing acidification and yet offers none of the disagreeable qualities exhibited by sulfur dioxide. The dilute sulfonation product is neutralized with sodium carbonate. Carbon dioxide is liberated and is piped to the acidifiers. The resulting sodium naphthalene-β-sulfonate–sodium sulfate–sodium carbonate mixture is filtered at the boiling temperature. Most of the sodium sulfate remains on the filter. The filtrate may be cooled to precipitate the β-sulfonate or charged into the fusion kettle *per se*. The fusion pot is charged with fused sodium hydroxide (caustic soda) and heated to 305°C. The sodium naphthalene-β-sulfonate is added to the melt, maintaining the temperature between 295 and 305°C. Generally about 2.8 lb of sulfonate is added per lb of caustic. The fusion is maintained at about 300°C for 6 hr and is then discharged into water or the weak β-naphthol wash water from the previous charge. The resulting hot solution is filtered, and the washed cake is added to the dilution-tank residue (sodium sulfate). The clear mother liquor is charged into the acidifiers.



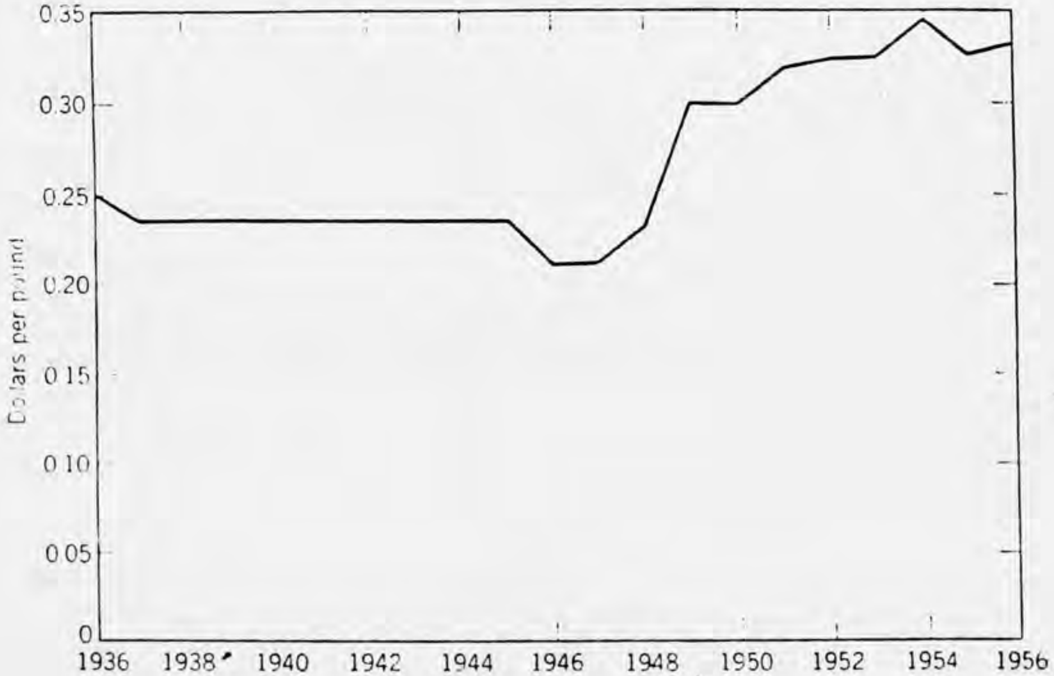
Production—β-Naphthol

Carbon dioxide from the neutralization tank is employed to acidify the diluted caustic fusion melt. A small amount of sulfuric acid is generally added to complete the acidification. Crude β-naphthol separates out as the top layer and is decanted. The bottom layer, consisting of a mixture of sodium sulfite, sodium sulfate, and sodium carbonate, is cooled to recover the 10 per cent β-naphthol contained in it. The solution of salts may be fortified with sodium carbonate and re-used in the neutralization step.

The crude β-naphthol is passed into a tank and thoroughly washed until the water shows a specific gravity of 1.0. These washings may be used to dilute the subsequent fusion melt. The washed product is charged into a vacuum still where the main distillation is carried out at about 28 in. of vacuum and 248°C. Refined β-naphthol is collected in zinc-lined boxes where it solidifies on cooling. The product is broken up and ground to a fine powder. A yield of about 84 per cent is realized based on sodium naphthalene β-sulfonate, and an over-all yield of about 74 per cent is obtained based on the naphthalene used.

Use Pattern

	Per cent
Dyes	60
Rubber	30
Miscellaneous	10
	100



Price—β-Naphthol

Miscellaneous

Properties. White, lustrous, bulky leaflets or white powder.

Mol. wt.	144.16	M.P.	123°C
Sp. gr.	1.217 4°C	B.P.	286°C

Soluble in alcohol, ether, benzene, chloroform, and glycerine. Slightly soluble in water (0.1 per cent cold, 1.25 per cent hot).

Flash point (closed cup)	310°F
Vapor density	4.97

Grades. Technical, and USP (resublimed).

Containers and Regulations. Wooden barrels, cartons, and bottles. No ICC shipping label required.

Economic Aspects

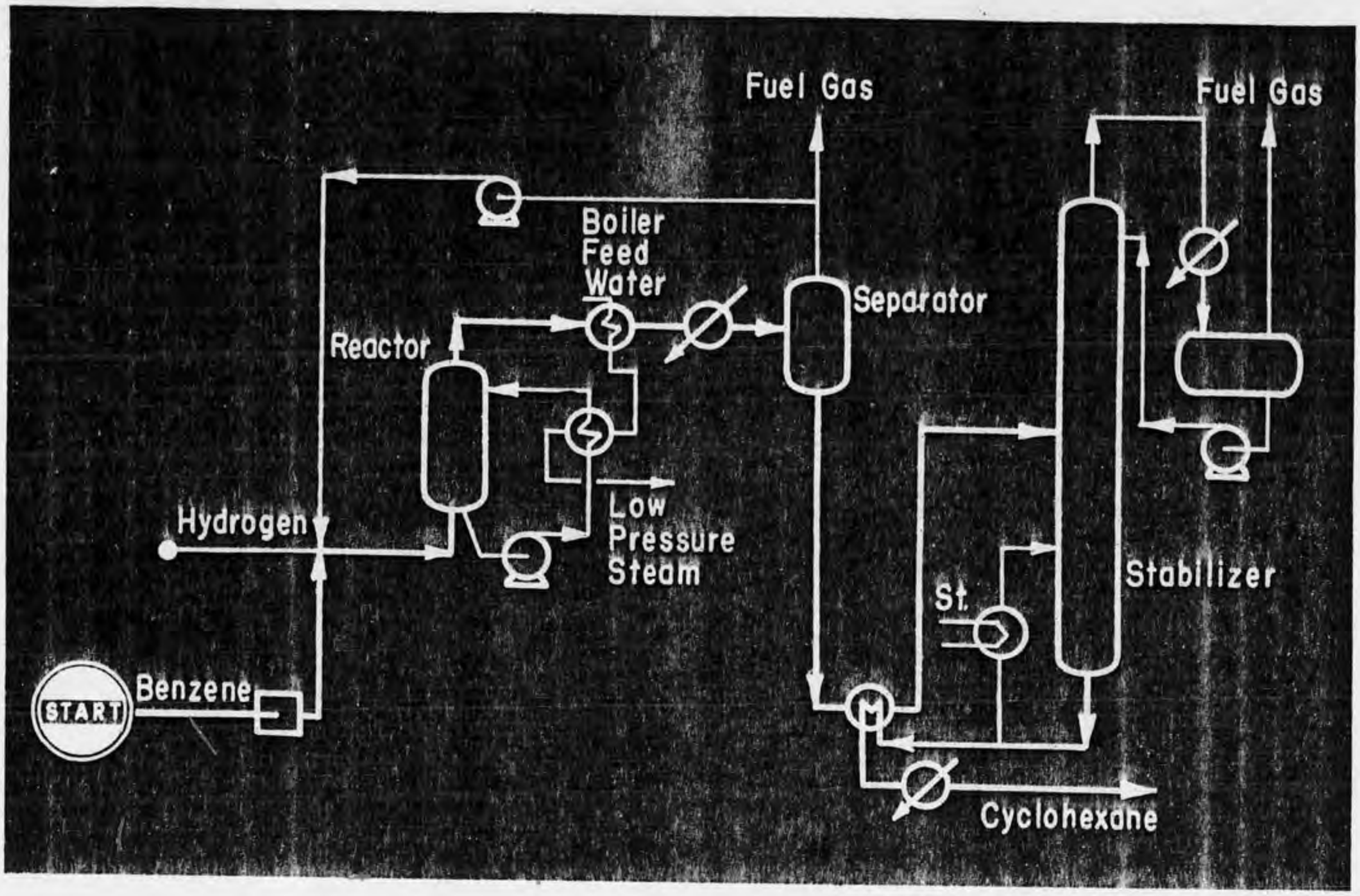
β-Naphthol is one of the chief intermediates in the coal-tar dye industry, and accordingly its production is linked closely to variations in dye manufacture. During World War II, however, large quantities of β-naphthol were required in the manufacture of synthetic-rubber anti-oxidants and stabilizers. This market has continued since that time.

The manufacturing process is similar to the sulfonation process for phenol production but is considerably more difficult because of the production of α- and β-naphthylsulfonic acids, which must be separated by chemical means before alkali fusion. Plants probably vary in size from 1,000,000 to 10,000,000 lb annual capacity. The larger plants require an initial investment of 10 to 12 cents per annual pound.

β-Naphthol can also be made by boiling naphthalene-2-diazonium chloride with dilute sulfuric acid or by hydrolysis of 2-naphthylamine with dilute acid under pressure. It is doubtful if either of these will ever replace the sulfonation process.

Manufacturers and Plant Sites

American Cyanamid Co., Organic Chemicals Div., Bound Brook, N. J.
National Aniline Div., Allied Chemical and Dye Corp., Buffalo, N. Y.
Sherwin-Williams Co., Chicago, Ill.



Cyclohexane — INSTITUT FRANCAIS DU PETROLE

Application: A process for the liquid-phase catalytic hydrogenation of benzene to produce high-purity cyclohexane.

Charge: Benzene and a hydrogen-rich gas.

Product: When processing high grade benzene (5.4° C solidification point), a product containing 99.8 + wt. percent cyclohexane with less than 0.1 wt. percent benzene and having a freezing point of 6.0° C is obtained. Lower purity benzene feed will lower the cyclohexane product freezing point.

Process Description: Fresh and recycle hydrogen-rich gas, together with benzene feed are introduced into the reactor where the conversion of benzene to cyclohexane is virtually complete. Agitation of the reacting phase is assured by external circulation of the liquid through a steam generator.

Reactor effluent is condensed and the liquid separated in a flash drum. Most of the flashed gas is recycled, a small amount being bled from the system to avoid light HC build up.

The liquid effluent passes to the stabilizer which removes light dissolved gases overhead.

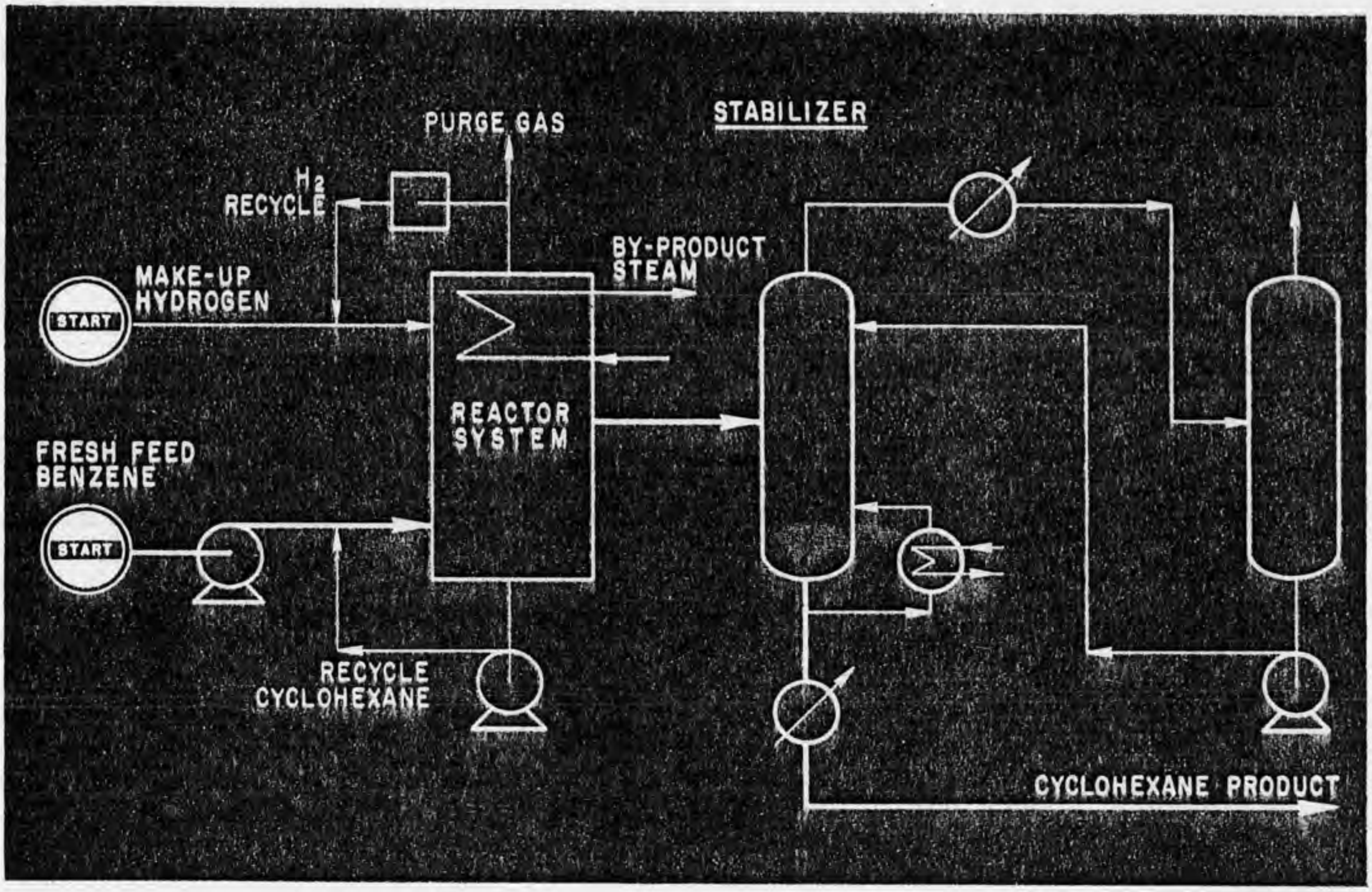
Operating Conditions: One of the features of the process is to operate in the liquid phase with consequent mildness of operating conditions resulting in minimum capital investment and reduced operating costs.

Yield: Virtually stoichiometric yields of cyclohexane from benzene are obtained.

Economics: The study presented hereunder corresponds to a 10,000 t/yr unit under French conditions and assumes a H_2 gas containing 95 percent vol. H_2 and available at 40 atm. Offsites and storage facilities are not included. Contractor's costs are included in the investment.

Investments (delivered and erected in France)	$200,000
Initial catalyst load + paid up royalty	11,000
Estimated Operating Costs	$/year
Labor (incl. sup. & adm. ovh.)	26,000
Utilities (no credit given to LP steam produced)	8,000
Catalyst & Chemicals	4,000
Maintenance	8,400
Local Taxes & Insurance (2% of investment)	4,220
Depreciation Allowance (10% of investment	21,100
Interest on loans (8% on avg. investment)	8,440
Total Operating Cost	$ 80,160/year
	or 2.34¢ gal. cyclohexane

Commercial Installations: The first commercial unit has been engineered and others are at the design stage.



Cyclohexane (Arosat) — THE LUMMUS CO.

Application: Catalytic hydrogenation process to produce high-purity cyclohexane from benzene and hydrogen-rich gas.

Description: Fresh feed benzene (IBP, 79.9° C; dry point, 80.4° C; freezing point, 5.44° C; thiophene content < 1 ppm) is mixed with recycle cyclohexene, make-up hydrogen (sulfur < 1 ppm; chlorine < 1 ppm; carbon monoxide < 4 ppm; carbon dioxide < 8 ppm) and recycle hydrogen and charged to the reactor system.

Essentially stoichiometric conversion of benzene to cyclohexane is obtained with minimum production of undesirable isomerization products.

A substantial fraction of the heat of reaction is recovered as low pressure steam. The product cyclohexane is stabilized to eliminate dissolved light hydrocarbon gases introduced into the system with the make-up hydrogen cooled and sent to storage. A purge gas is taken from the reactor system to regulate the build up of inerts introduced with the make-up hydrogen.

Parameters which set the unit design can be selected over a broad range in order to take maximum advantage of conditions in the refinery or petrochemicals complex and minimize production costs chargeable to the cyclohexane product.

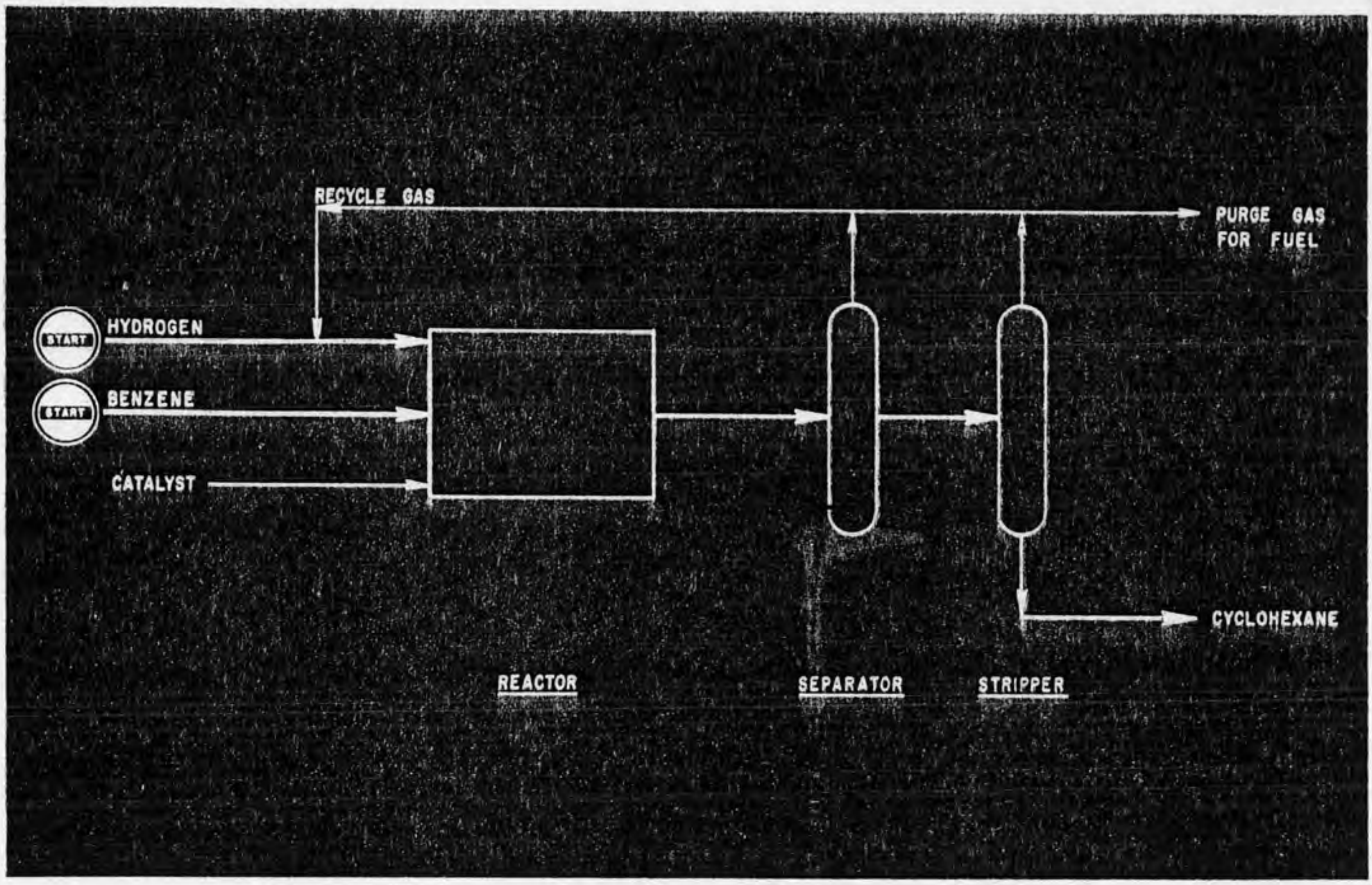
High purity cyclohexane—IBP 80.6° C; freezing point 6.34° C; dry point, 80.9° C; benzene content < 50 ppm is obtained.

Economic Data: A 2,424-bpsd cyclohexane unit required an investment of approximately $430 per bpsd of product capacity. This includes hydrogen make-up compressor with hydrogen available at 90% purity and 300 psia.

Typical requirements per bbl. of product:

Steam, 50 psig	lbs. (158) credit
Cooling Water (Δ 25° F)	550 gals.
Power	5.4 Kwh
Hydrogen (90%)	4272 scf
Fuel	1,000 Btu (442) credit

Reference: U.S. Patent #3,450,784.



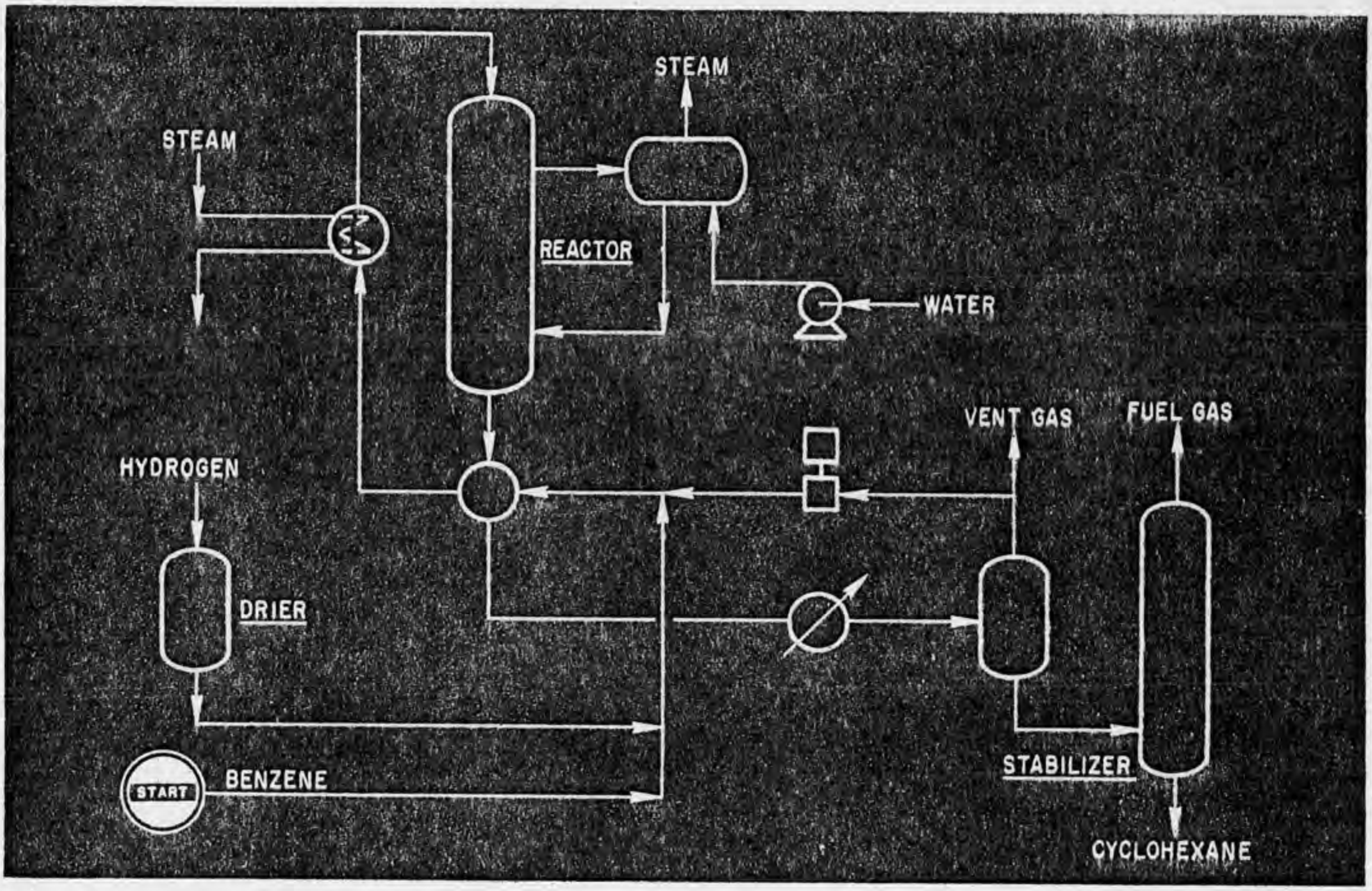
Cyclohexane — MITSUBISHI CHEMICAL INDUSTRIES LTD.

Application: A process for the liquid phase catalytic hydrogenation of benzene to produce high-purity cyclohexane.

Description: By adopting a liquid phase reaction and by selecting a suitable catalyst, uniform stable distribution can be successfully maintained throughout the reaction. It is very important with this process that operation be uniform and stable. Since the process is very simple, the plant layout can be very compact and result in very low construction costs. The process has been successfully operated without any difficulty for more than two years of continuous operation. Product cyclohexane is very pure with almost complete conversion of benzene in the feed.

Yields: Depending upon the purity of the raw material benzene, yields can approach 100% based on feed. With very high purity benzene feed, almost complete conversion of the benzene occurs with very little side reactions. Therefore, a special purification unit is not necessary to produce finished high purity product.

Commercial Installation: This process was developed by Mitsubishi Chemical Industries Ltd. in 1966 and the first commercial plant went on stream in 1967 with a capacity of 70,000 tons/year.



Cyclohexane — ATLANTIC RICHFIELD CO.

Application: A process for producing high purity cyclohexane by catalytic hydrogenation of benzene using precious metal Engelhard catalyst.

Description: Fresh feed benzene is combined with makeup hydrogen and recycle hydrogen and exchanged against reactor effluent and preheated to reaction temperature before entering the reactor. The vaporization of water to produce steam removes the heat of reaction and assists in control of peak and outlet temperatures. It is not necessary to recycle cyclohexane for temperature control.

After exchange with feed, th reactor effluent is cooled and flashed. Part of the vapor is used as recycle hydrogen, forward vent gas is chilled by refrigeration to minimize cyclohexane losses and is available as high pressure fuel gas. There is usually no requirement for hydrogen purification of the vent gas. Separator liquids and condensate from the vent chilling are stabilized with light ends going overhead and high purity cyclohexane as product.

Product:

	Composition, wt. %	
	Charge benzene	Cyclohexane product
C_6 paraffins	0.0150	0.0150
Methyl-cyclopentane	0.0100	0.0100
Benzene	99.9500	0.0010
Cyclohexane	0.0150	99.9640
n-heptane	0.0020	0.0020
Methyl-cyclohexane	0.0030	0.0080
Toluene	0.0050	0.0000
Solidification point, °C	5.50	6.46

Process requirements: For 100 million lbs./yr. cyclohexane, 350 days/year

Utilities	
Electricity, kW	250
Steam, lbs./hr.	
Consumed (600 psig)	11,000
Generated (170 psig)	14,000
Cooling water, gpm ($\Delta T = 20°F$)	800
Catalyst life	5 years plus
Operating labor, men/shift	1

Investment: U.S. Gulf Coast, 100 million lbs./yr. cyclohexane, ISBL including hydrogen makeup compressor—$700,000. Initial catalyst charge about $75,000.

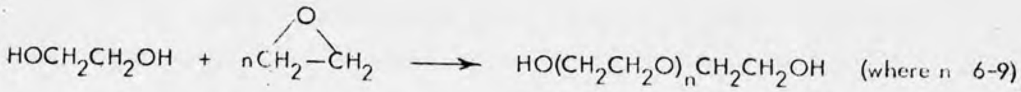
Commercial installations: Atlantic Richfield, Los Angeles, 100 million lbs./yr. since 1964.

A 43-million-pound/year plant is in construction in Argentina for PGM.

Reference: *Hydrocarbon Processing,* May 1967, p. 169-174.

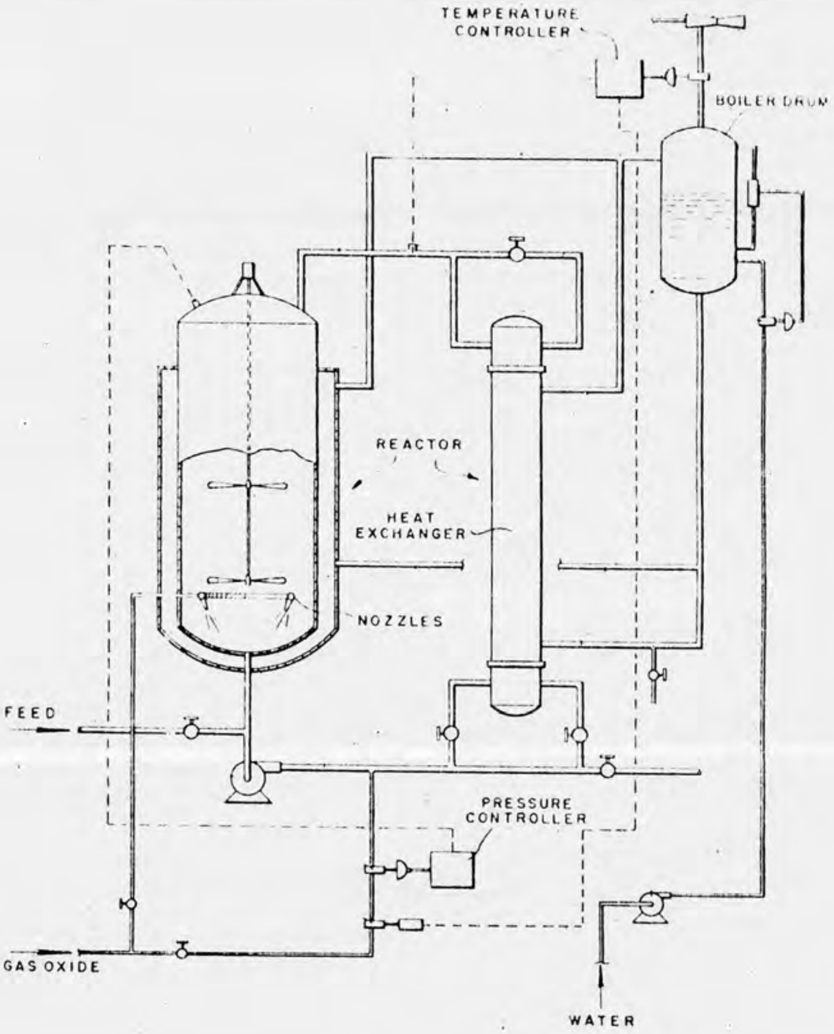
POLYETHYLENE GLYCOL

Reaction:



$$HOCH_2CH_2OH + nCH_2\text{—}CH_2 \text{ (with O bridging) } \longrightarrow HO(CH_2CH_2O)_nCH_2CH_2OH$$

(where n 6-9)



Feed Materials:
- Ethylene Glycol
- Ethylene Oxide

Coproducts:

Catalyst:	Sodium Hydroxide
Phase:	Liquid
Reactor type:	Kettle and Heat Exchanger
Solvent used:	None
Temperature, °C:	125–200
Pressure psi:	15–100
Reaction time:	
Heat Required:	–
Heat evolved:	Yes
Product yield:	
Product purity:	
Materials of Construction:	Steel

Major Product Uses: In the manufacture of stearate emulsifiers for the food, drug and cosmetic industries.

Reference: U.S. Patent 3,297,412 by C. Phillips, Jr. et al (to Esso Research & Eng. Co.) (Jan. 10, 1967)

PROYECTOS DE INVERSION PEQUEÑA
TECNOLOGIA DE OPERACION

Fertilizers Fertilizers are natural or manufactured materials containing plant nutrients in available form.[1,2,8] At least 16 elements* are essential to plant life. Carbon, hydrogen, oxygen, nitrogen, phosphorus, and potassium are needed in macro amounts. Calcium, magnesium, and sulfur are required in semimacro quantities, and the remainder — iron, manganese, silicon, cobalt, copper, and molybdenum — in trace amounts.[3-16] Carbon, hydrogen, and oxygen are obtained from ambient air and water, while a few plants, such as legumes, can use root bacteria to fix atmospheric nitrogen. Other elements are mostly assimilated from the soil via complex physicochemical root mechanisms.

To ensure repeated healthy crops, farmers must maintain adequate soil-nutrient levels by appropriate fertilizer additions. Traditional low-analysis materials, such as manure and other animal or vegetable wastes, are usually in limited supply on large modern farms and have to be supplemented or replaced by high-analysis chemical fertilizers formulated to specific soil and crop needs. While some people express a preference for "naturally" fertilized crops, no alternative to chemical fertilizers as a way of meeting current world food needs of 3.5 billion people (estimated to reach 7 billion by the year 2000) is known.

Nitrogen Fertilizers. Studies by nineteenth century scientists established nitrogen as a primary plant nutrient and one of the key elements in organic fertilizers.[1-5] The first chemical nitrogen fertilizers were Chilean saltpeter, $NaNO_3$, which today finds a limited use as a tobacco topdressing, and ammonium sulfate produced as a coal-gas by-product. Ammonium sulfate still is applied in considerable quantities outside the United States. Early twentieth-century attempts at fixing nitrogen via electric arc led to the production of calcium cyanamide, $CaCN_2$, in the United States, and calcium nitrate via HNO_3 in Norway. The last $CaCN_2$ plant in the Western world closed in June 1971, but large tonnages of $Ca(NO_3)_2$ still are made in Europe. Today, virtually all nitrogen fertilizers are based on NH_3 synthesized from atmospheric nitrogen plus hydrogen derived from natural gas, oil, coal, lignite, or electrolysis of water (in decreasing order of use). See also **Ammonia**.

Ammonium Sulfate: $(NH_4)_2SO_4$ contains approximately 21% N. Initially it was produced by scrubbing coal gas with H_2SO_4, followed by evaporation, crystallization, separation, and drying. This method is still used to a limited extent, as is reacting H_2SO_4 with anhydrous NH_3. A major current source is caprolactam manufacture, which gives several tons of by-product sulfate per ton of caprolactam. Outside the United States, several large producers use the Merseburg reaction, by which natural or by-product gypsum is reacted with ammonium carbonate to yield ammonium sulfate:

$$CaSO_4 \cdot 2H_2O + (NH_4)_2CO_3 \rightarrow \\ CaCO_3 + (NH_4)_2SO_4 + H_2O - 3.9\ \text{kcal}$$

When properly prepared, the product is in the form of free-flowing, stable crystals.

Calcium Nitrate: $Ca(NO_3)_2$ contains approximately 15% N. This material was made initially

*For example, the nutrients required to produce 150 bushels of corn, in pounds per acre required are N, 310; P, 120 as phosphate, 52 as phosphorus; Ca, 58, equivalent to 150 lb of agricultural limestone; Mg, 50, equivalent to 275 lb of epsom salt, or 550 lb of sulfate of potash magnesia; S, 33; Fe, 3, equivalent to 15 lb of iron sulfate; Mn, 0.15; B, 0.10; Zn, Cu, and Mo in trace amounts; O, 10,200; C, 7,800; and H_2O, 3,225–4,175 tons, equivalent to 29–36 in. of rain. The effect of most fertilizer addition is asymptotic. For example, the yield of corn on an irrigated test farm shows that increasing the nitrogen applied per acre from 40 to 80 lb increases corn yield by 30 bushels; increasing N to 120 lb further increases the yield by 20 bushels; increasing N to 160 lb further increases the yield by 15 bushels; a further increase of N to 200 lb increases the yield by only another 10 bushels.

by directly reacting limestone and HNO_3, a method still in limited use. $Ca(NO_3)_2$ currently is produced in large quantities as a by-product from nitrophosphate manufacture (described later). There are several commercial processes for air-prilled, oil-prilled, and crystalline products. $Ca(NO_3)_2$ is very hygroscopic, making suitable storage and shipping precautions imperative.

Ammonium Nitrate: NH_4NO_3 contains approximately 35% N. As shown in Fig. F-1, ammonium nitrate is produced by directly reacting NH_3 and HNO_3. Various commercial processes operating under vacuum and at atmospheric pressure or above are available: $NH_3 + HNO_3 \rightarrow NH_4NO_3 - 26\ \text{kcal}$. NH_4NO_3 also is made in large quantities by reacting calcium nitrate by-product from nitrophosphate plants with NH_3 and CO_2: $Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O \rightarrow 2NH_4NO_3 + CaCO_3$. It usually is produced as prills, granules, or solution, either alone or in conjunction with other nitrogen-containing liquids, e.g., urea and aqua NH_3. Solid and molten forms of NH_4NO_3 can be hazardous under certain conditions, e.g., when detonated and/or when organic matter is present. A popular explosive, ANFO, for example, is a mixture of NH_4NO_3 and fuel oil. Accordingly, suitable precautions are necessary in production, storage, and handling. One way of minimizing danger is to produce nitro chalk, a mixture of NH_4NO_3 and $CaCO_3$ with a maximum nitrogen content of about 26%.

Precautions must also be taken against spontaneous slow burning as well as physical breakdown caused by volume changes induced by crystal transitions between forms IV and III, when storage temperatures are allowed to fluctuate in the 30–35°C range.[5] Small amounts of urea help to suppress self-burning, and certain alkali salts plus low free-moisture improve particle stability.[6] As NH_3NO_3 is hygroscopic, clay coatings and moisture-proof bags are necessary safeguards against spoilage in storage and transportation.

With reference to Fig. F-1, aqueous HNO_3, gaseous NH_3, and a conditioner solution (magnesite dissolved in HNO_3) are fed into a reactor to form NH_4NO_3 solution. The pH of the final NH_4NO_3 solution is adjusted by addition of NH_3. From the final neutralizer, the solution is pumped to a falling-film evaporator, where the water content is reduced to a maximum of 0.5%, necessary for the subsequent prilling step. The concentrated NH_4NO_3 solution is sent to a prilling tower, where it is finely distributed through spraying roses. The droplets descending in the tower are cooled with

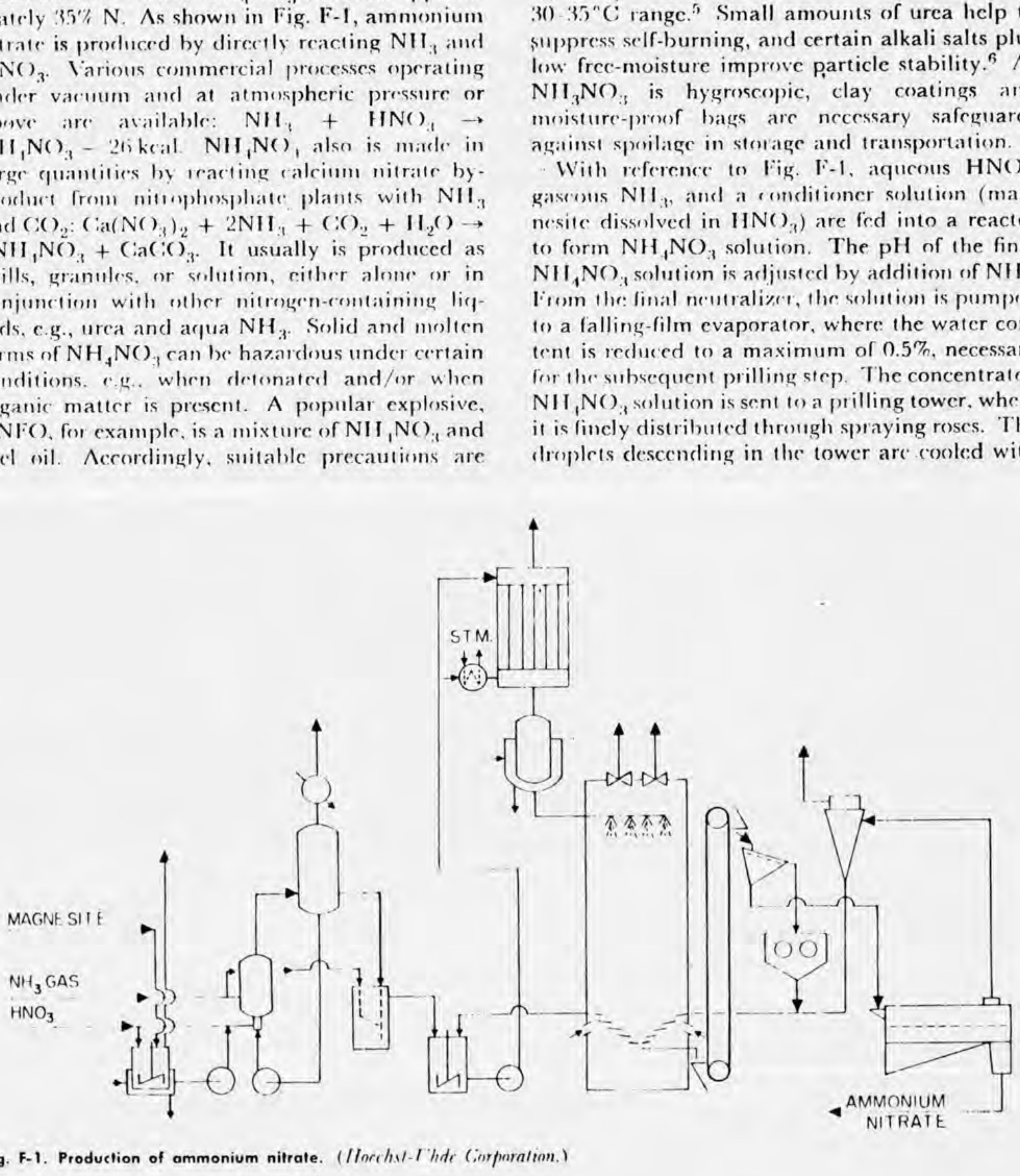


Fig. F-1. Production of ammonium nitrate. (*Hoechst-Uhde Corporation.*)

a countercurrent stream of air; the prills are withdrawn through an opening in the bottom of the tower for subsequent classifying. The oversize is crushed and dissolved in NH_4NO_3 solution together with the fines from the dust-collecting equipment. The normal-grain-size fraction is sent to a fluidized-bed cooler, where the product temperature is reduced by means of cold air to make the product suitable for storage.

Urea: $CO(NH_2)_2$ contains 16.65% N. First synthesized by Wöhler in 1828 from ammonium cyanate, urea has become the dominant nitrogen fertilizer in the last few years. Urea also is used increasingly as an animal feed and a raw material for melamine and urea-formaldehyde resins. The production of urea is described under **Urea.**

Trends in Nitrogen Fertilizers: In the United States, large quantities of liquid nitrogen fertilizers, such as anhydrous NH_3, aqua NH_3, ammonium salts, and many combinations, including some containing phosphate salts, are being used. Since all these materials are highly water-soluble, the possibility of ecological upset caused by nitrogen runoff has been raised. Fortunately, many soils rapidly fix ammonium ions, thereby checking waste and pollution. Controlled release of nitrogen can be obtained by reacting urea and formaldehyde to produce "ureaform" fertilizers, by coating urea with sulfur, or by using slowly soluble compounds containing nitrogen, such as isobutylidene diurea.[5,6] These materials are relatively costly and are sold principally to nonfarm markets.[15] Recent attempts to make controlled-release, high-analysis nitrogen fertilizers in combination with phosphorus show promise.[7]

Phosphate Fertilizers. In the mid-nineteenth century, Liebig and others showed that the traditional fertilizer properties of bones are due largely to a high phosphate content and that treatment with H_2SO_4 greatly increases effectiveness. Rapidly expanding fertilizer needs created a big demand for such chemical manures and led to an acute shortage of bones. This was overcome by the timely discovery of phosphate minerals in Florida and elsewhere, plus guano deposits in Peru. Today, bone and guano are mostly limited to special nonfarm uses and have been virtually replaced by fertilizers prepared from phosphate rock mined in many countries.[8,9]

An important property of phosphate fertilizers is *availability* to plants, which is largely a function of phosphate solubility in a specific soil. Many phosphate rocks consist of a clay-sand matrix bearing an apatite mineral, $Ca_5(PO_4)_3R$, where R is usually fluorine but may be OH, CO_3, or Cl. Washing followed by screening and beneficiation yields pebbles and sandy concentrates often having the general composition $3Ca_3(PO_4)_2 \cdot CaF_2$ (about 30–40% P_2O_5). In water and alkaline and neutral soils, apatites and tricalcium phosphate, $Ca_3(PO_4)_2$, are highly insoluble, but they are moderately soluble in acid soils. Dicalcium phosphate, $CaHPO_4$, is readily soluble in acid soils and moderately so in water and alkaline and neutral soils, whereas monocalcium phosphate, $Ca(H_2PO_4)_2$, is soluble in water and all moist soils. Also affecting availability is the presence of Fe and Al phosphates, which are insoluble in water but soluble in weak acids.

In some countries total water solubility is demanded or is at a premium, which means that monocalcium and ammonium phosphates must be used. In others, slight solubility in water or appreciable solubility in weak acids such as citric is adequate, thus permitting fertilizers to include large amounts of dicalcium phosphate as well as phosphates of Fe and Al. Several nitrophosphate fertilizers and steel slags are in this category. Some humic and acid soils are able to assimilate ground phosphate rock without prior chemical treatment.

Single Superphosphate: Approximately 20% P_2O_5,[2,8,10] this is the oldest water-soluble phosphate fertilizer, and it still is produced in large quantities. The material is made by reacting ground phosphate rock and 70% H_2SO_4 in a batch den or on a continuous belt. A solid mass of monocalcium phosphate and gypsum is formed, which is cured by storing for several weeks before grinding and shipping. Gaseous compounds of fluorine and silicon are evolved and removed by water scrubbing. The empirical reaction is $3Ca_3(PO_4)_2 \cdot CaF_2 + 7H_2SO_4 \rightarrow 3Ca(H_2PO_4)_2 + 7CaSO_4 + 2HF$.

Wet-Process Orthophosphoric Acid: This is commercially 30–54% P_2O_5. The addition of H_2SO_4 to phosphate rock in amounts greater than needed to make single superphosphate produces orthophosphoric acid, H_3PO_4. Several reactions occur. Monocalcium phosphate reacts with H_2SO_4 to yield phosphoric acid, part of which reacts with more rock to make additional monocalcium phosphate. Qualitatively this is $Ca(PO_4)_2 \cdot CaF_2 + H_2SO_4 + H_2O \rightarrow H_3PO_4 + CaSO_4 \cdot H_2O + HF$.

This acid is a fertilizer intermediate and also is used to make detergent phosphates after purification.[1] Commercial processes are all based on violent agitation of the rock-acid slurry, followed by removal of $CaSO_4$ via filtration and evaporation of H_2O to obtain the desired concentration, up to 54% P_2O_5. Traditional processes separate the sulfate as impure dihydrate (gypsum), which usually is discarded. Some polymorphic P_2O_5 invariably is trapped in the filter cake, and this loss can be largely overcome by precipitating the sulfate as the hemihydrate and recrystallizing in dihydrate form, as is done in some recent processes of Japanese origin.[11] In this way, a gypsum suitable for wallboard, plaster, and cement manufacture can be produced simultaneously.

Triple Superphosphate: This is approximately 46-48% P_2O_5.[2-8] Acidulating phosphate rock with phosphoric acid produces concentrated or triple superphosphate, which is essentially monocalcium phosphate containing very little gypsum. The reaction is $Ca(PO_4)_2 \cdot CaF_2 + H_3PO_4 + H_2O \rightarrow Ca(H_2PO_4)_2 \cdot H_2O + HF$. Continuous processes are available for making powdered (run-of-pile) and granulated products. Triple superphosphate is used mostly to furnish P_2O_5 in mixed fertilizers and is water-soluble. Its high analysis compared with single superphosphate offers savings in storage and shipping.

Ammonium Phosphates:[4-6] Several ammonium phosphates can be prepared, but only the mono and the di compounds are made for fertilizer purposes, alone or in combination with other salts. Numerous commercial processes are available whereby anhydrous NH_3 is reacted with H_3PO_4 and the resulting slurry is converted to solid form and dried. NH_3/H_3PO_4 ratios between 1 and 2 can be selected to produce various product grades. For example, for diammonium phosphate $2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4$.

Wet-process acid is commonly used, but minor quantities are made from acid of electric-furnace origin. Since impurities in wet-process acid make crystallization difficult, the corresponding products are granulated. Mono- and diammonium phosphates based on furnace acid can be crystallized easily. The general process for making granular ammonium phosphate fertilizer is shown in Fig. F-2. Typical analyses are tabulated below:

	Monoammonium Phosphate		Diammonium Phosphate	
Acid Used	N, %	P_2O_5, %	N, %	P_2O_5, %
Wet-process	11	48	18	46
Electric-furnace	12	61	21	53

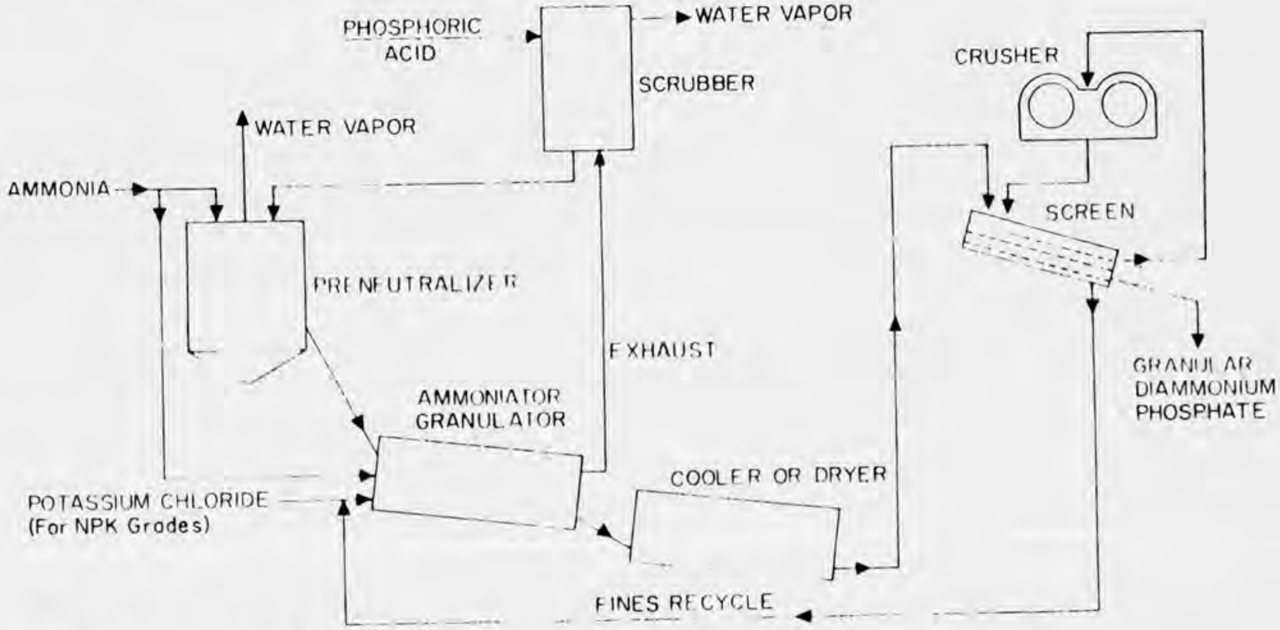


Fig. F-2. Granular ammonium phosphate fertilizer process.

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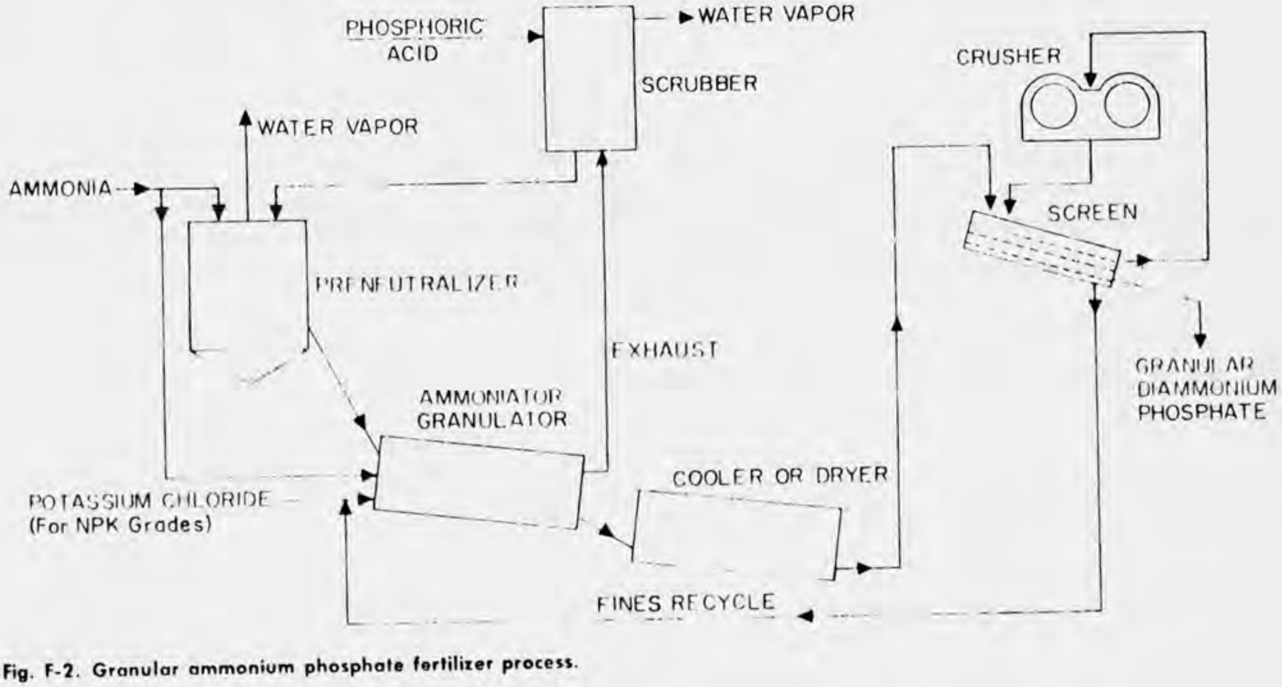

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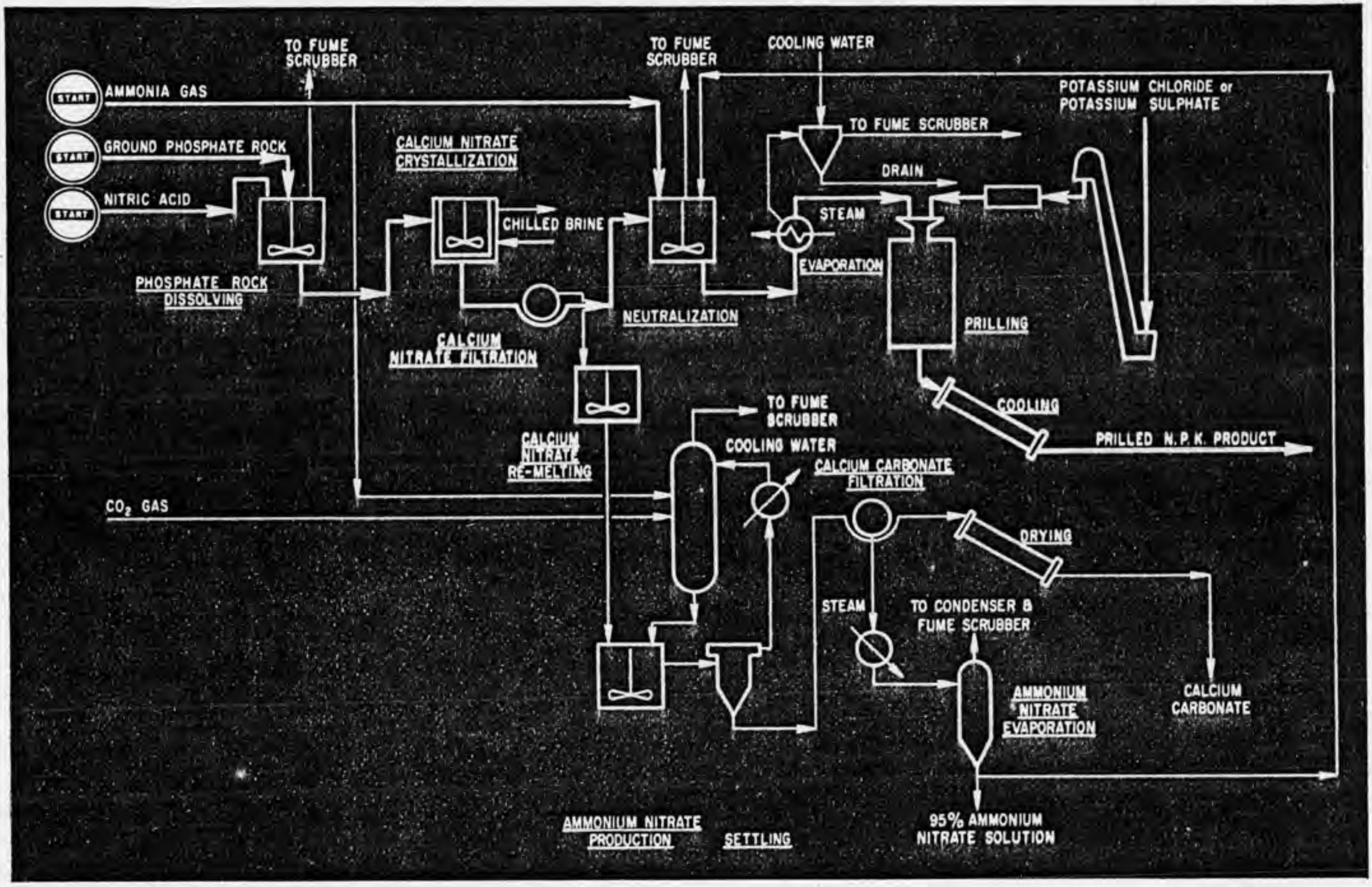

NPK Fertilizer (Norsk Hydro) — HUMPHREYS & GLASGOW LTD.

Application: A process for the manufacture of NP and NPK fertilizers from phosphate rock, potassium salt, nitric acid, ammonia and carbon dioxide. Products include NP or NPK fertilizers as prills (or granules); calcium nitrate solution or prills; or ammonium nitrate solution or prills plus calcium carbonate slurry, cake or dried solid.

Description: Phosphate rock is digested with excess 58—60% nitric acid to give phosphoric acid and calcium nitrate, represented by the reactions:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + (20 + x)\ HNO_3 = 6H_3PO_4 + 10\ Ca(NO_3)_2 + 2HF + xHNO_3$$

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + CO_2 + H_2O$$

The acid liquor at 60 to 80° C is passed to a series of batch crystallizers (operated in parallel for continuous production) where calcium nitrate is removed. The desired level of water soluble P_2O_5 in the product determines the temperature to which the solution must be cooled: $-5°$ C is required for 85% water solubility. By careful control of the crystallization conditions, crystals in the range 0.5 to 1.0 mm are produced which filter readily and permit easy drainage of the filtrate and hence recovery of acid solution. The filter is a continuous rotary vacuum design employing a stainless steel cloth with 0.5-mm mesh.

The filtrate is neutralized with gaseous ammonia in two stages to avoid the viscous solutions occurring at intermediate pH levels and to minimize loss of ammonia vapor. The $N:P_2O_5$ ratio is adjusted if necessary to the desired value by the addition of ammonium nitrate solution in a third stage. The neutralized NP solution is evaporated under vacuum to about 0.5% water. Potassium salt and micro nutrients are added before prilling (or granulation).

The calcium nitrate filter cake is melted and either neutralized, concentrated and prilled as calcium nitrate, or reacted with ammonia and carbon dioxide to give about 60% ammonium nitrate solution and calcium carbonate.

A P_2O_5 water solubility of 85% can be achieved with an over-all yield of 98-99% based on raw materials.

Raw Material and Utility Requirements:

Based on 330,000 t/a of 17:17:17 prills

	Quantity/ton product
Phosphate rock	0.43 ton
Nitric acid	0.66 ton
Ammonia	0.23 ton
Potash	0.28 ton
Carbon dioxide	0.16 ton
Ammonium nitrate byproduct	0.46 ton
Electricity	60 Kwh
Steam	0.9 ton
Process water	2.5 ton
Cooling water	22 ton

Commercial Installations: Three plants operated by Norsk Hydro with a combined capacity of 1,000,000 t/a; one plant in United States under construction.

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compuestos aromáticos, compuestos nitrogenados y oxigenados, compuestos de azufre y otras impurezas. El asfalto se encuentra solamente en el residuo, y por tanto únicamente éste requiere un tratamiento para separarlo.

Desasfaltado. — El residuo procedente de la destilación al vacío pasa a una torre en donde se pone en contacto con propano líquido, el cual disuelve todos sus componentes a excepción del asfalto que se recoge en la parte inferior de la columna. Se trabaja a una presión de hasta 35 Kg/cm^2 aproximadamente, con objeto de mantener el propano en estado líquido a las temperaturas de trabajo. Un hecho interesante es el de que la columna trabaja a una temperatura unos 30°C más elevada en las proximidades de la parte superior que en la parte inferior (93°C en la parte superior y 60°C en la inferior). Con esto se consigue disminuir la solubilidad de los hidrocarburos más pesados y permite además estrechar el intervalo de ebullición de la fracción tratada. El propano se recupera del aceite y del asfalto y vuelve a entrar en el ciclo. Este procedimiento ha adquirido importancia en la eliminación del carbón y en el desasfaltado de la materia prima a utilizar en el cracking catalítico (9).

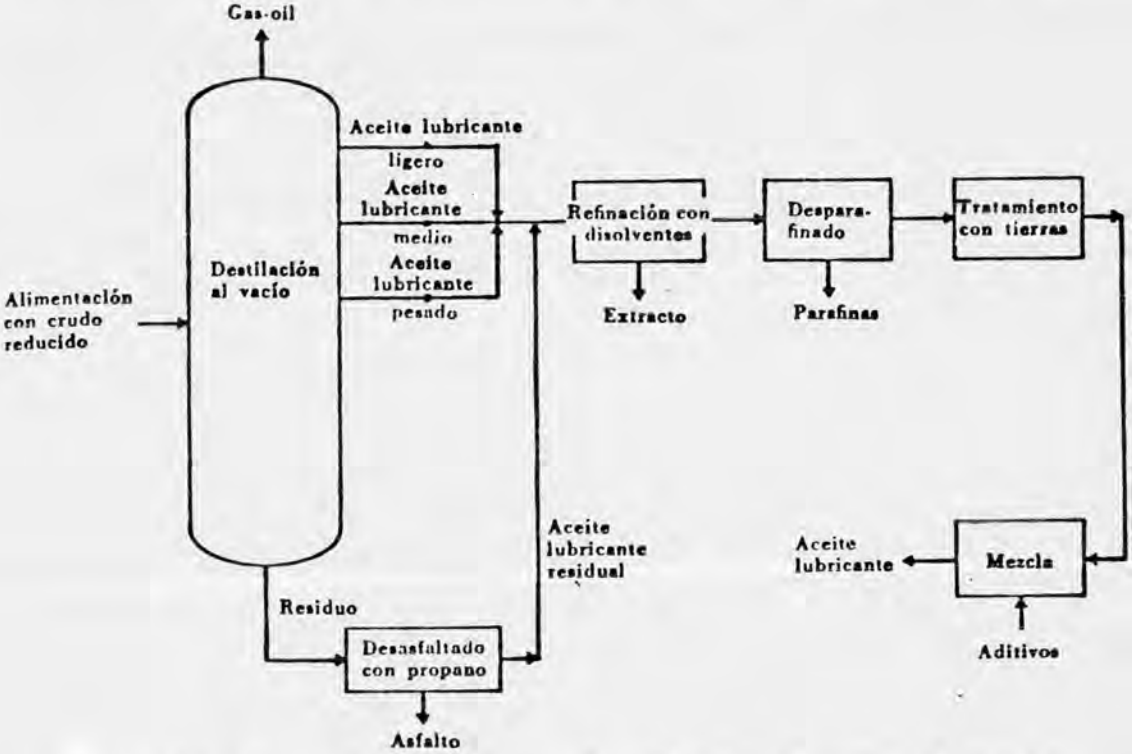

Fig. 14.14. Diagrama general para la refinación de aceites lubricantes.

El tratamiento posterior de la fracción que contiene el aceite es análogo al proceso a que se someten las otras fracciones procedentes de la

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