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Alkylbenzene, linear
 Alpha olefins, linear
 Ammonia
 Ammonia, KAAP plus
 Ammonia, KBR purifier
 Aromatics recovery—liquid-liquid extraction
 Aromatics—progressive extractive distillation
 Benzene
 Bisphenol-A
 BTX aromatics
 Butadiene
 Butadiene extraction
 Butanediol, 1, 4
 Butene-1
 Butyraldehyde, n and i
 Caprolactam
 Cumene
 Cyclohexane
 Dimethyl terephthalate
 Dimethylformamide
 EDC by direct chlorination—high temperature
 EDC via lean oxychlorination
 EDC via oxychlorination—single stage

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Ethanolamines
Ethyl acetate
Ethylbenzene
Ethylene
Ethylene feed pretreatment
Ethylene glycol
Ethylene oxide
Formaldehyde
Iso-octane
Maleic anhydride
Methanol
Methylamines
Mixed xylenes
Octenes
Olefins
Paraffins, normal
Paraxylene
Phenol
Phthalic anhydride
Polycaproamide
Polyethylene
Polyethylene (compact solution)
Polyethylene, HDPE

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Polyethylene LDPE-EVA
Polypropylene
Polystyrene
Propylene
PVC, suspension
Styrene
Terephthalic acid
Terephthalic acid (MTA)
Terephthalic acid (PTA)
Urea
Urea-formaldehyde
VCM removal
Vinyl chloride monomer (VCM)
Xylene isomerization
Xylene isomers

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ABB Lummus Global

Benzene
Butadiene
Cumene
Ethylbenzene
Ethylene
Maleic anhydride
Propylene
Styrene
Styrene

Basell Technology Co., BV

Polyethylene
Polyethylene, HDPE
Polypropylene

BOC Gases

Maleic anyhdride

Borealis A/S

Polyethylene
Polypropylene

BP

Butanediol, 1,4-
Polyethylene
Polypropylene

CDTECH

Cumene

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Chevron Phillips Chemical Co., LP

Polyethylene

Chisso Corp.

Polypropylene

PVC (suspension)

Vinyl chloride monomer (VCM)

Chiyoda Corp.

Bisphenol-A

Degussa AG

Dimethyl terephthalate

Terephthalic acid

Dow Chemical So.

Ethylene glycol

Ethylene oxide

Polypropylene

EniChem

Polyethylene, LDPE-EVA

ExxonMobil Chemical Co.

Mixed xylenes

Mixed xylenes

Paraxylene

Polyethylene

Xylene isomerization

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GTC Technology Corp.

BTX aromatics
Dimethyl terephthalate
Styrene

Haldor Topsøe A/S

Ammonia
Formaldehyde
Methanol

HYDRO

Olefins

IFP

Alpha olefins, linear
BTX aromatics
Butene-1
Cyclohexane
Ethylene feed pretreatment—mercury, arsenic and lead removal
Mixed xylenes
Mixed xylenes
Paraxylene
Paraxylene
Propylene
Xylene isomerization

IFPNA

Alpha olefins, linear
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IFPNA continued

Ethylene feed pretreatment—mercury, arsenic
and lead removal

Mixed xylenes

Paraxylene

Propylene

Inovyl B.V.

EDC by direct chlorination—high temperature

EDC via oxychlorination—single stage

PVC (suspension)

Vinyl chloride monomer (VCM)

INVENTA-FISCHER

Polycaproamide

Urea-formaldehyde

Kellogg Brown & Root, Inc.

Ammonia, KBR purifier

Bisphenol-A

Butadiene extraction

Ethylene

Paraffins, normal

Phenol

Propylene

Krupp Uhde GmbH

Ammonia

Aromatics—progressive extractive distillation

EDC via lean oxychlorination

Methanol

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Krupp Uhde GmbH continued

Polyethylene, HDPE

PVC (suspension)

Kvaerner Process Technologies

Butanediol, 1,4-

Butyraldehyde, n and i

Dimethylformamide

Ethanolamines

Ethyl acetate

Isooctane

Methanol

Methylamines

Linde AG

Ammonia

Ethylene

Lonza S.p.A.

Maleic anhydride

Lurgi Öl-Gas-Chemie GmbH

Butanediol, 1,4-

Methanol

Phthalic anhydride

Terephthalic acid (MTA)

Terephthalic acid (PTA)

Lyondell Chemical

Isooctane

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Mitsui Chemicals, Inc.
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[Polypropylene](#)
Nippon Kasei Chemical Co., Ltd.
[Formaldehyde](#)
Research Institute of Petroleum Processing
[Olefins](#)
Scientific Design Co., Inc.
[Ethylene glycols](#)
[Ethylene oxide](#)
Shell International Chemicals B.V.
[Ethylene glycols](#)
[Ethylene oxide](#)
Snamprogetti S.p.A.
[Polyethylene, LDPE-EVA](#)
[Urea](#)
SNIA BPD S.p.A.
[Caprolactam](#)
Stamicarbon bv.
[Polyethylene \(COMPACT solution process\)](#)
[Polypropylene](#)
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Stone & Webster Inc., a Shaw Group Co.
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Synetix

Ammonia
Methanol
Methanol, LPM

Technip

Ethylene
Ethylene

The Washington Group International, Inc.

Cumene
Ethylbenzene

Union Carbide Corp.

Butyraldehyde, n and i
Ethylene glycol
Ethylene oxide
Polypropylene

Univation Technologies

Polyethylene

UOP

Alkylbenzene, linear
BTX aromatics
Cumene
Ethylene
Olefins
Polystyrene
Propylene
Styrene

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UOP continued

Styrene

Xylene isomers

Vin Tec GmbH

EDC via lean oxychlorination

PVC (suspension)

Wacker Chemie GmbH

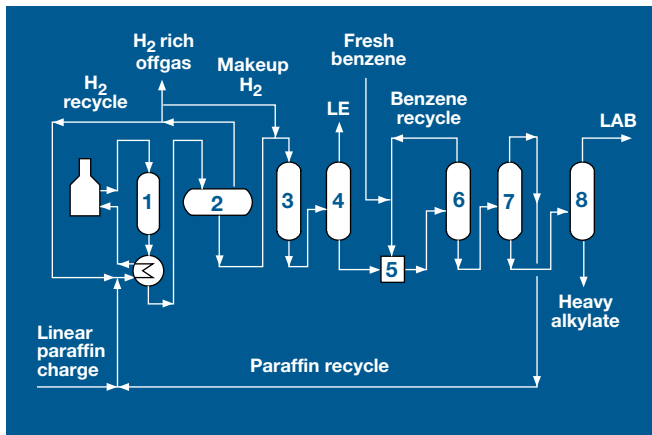
Phthalic anhydride

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Alkylbenzene, linear

Application: To produce linear alkylbenzene (LAB) from C_{10} to C_{14} linear paraffins by alkylating benzene with olefins made by the Pacol dehydrogenation and the DeFine selective hydrogenation processes. The alkylation reaction is carried out over a solid, heterogeneous catalyst in the Detal process unit.

Description: The Pacol reactor (1) dehydrogenates the feed into corresponding linear olefin. Reactor effluent is separated into gas and liquid phases in a separator (2). Diolefins in the Pacol separator liquid are selectively converted back to mono-olefins in the DeFine reactor (3). Light ends are removed from the reactor effluent in a stripper (4). The olefin-paraffin mixture is then alkylated with benzene

in the fixed-bed Detal reactor (5). Product from the reactor flows to the fractionation section (6) for separation and recycle of unreacted benzene to the reactor, and unreacted paraffins are separated (7) and recycled to the Pacol section. A rerun column (8) separates the LAB product from the heavy alkylate bottoms stream.

An existing LAB producer can increase production by using UOP's new Pacol catalyst and Molex adsorbent, adding a PEP unit to remove aromatics and increase the alkylation reaction efficiency, revamping the Pacol unit to apply TCR reactor technology, and/or revamping to add a Detal process unit.

The process is nonpolluting. No process waste streams are produced. The catalysts used are noncorrosive and require no special handling.

Yields: Based on 100 weight parts of LAB, 81 parts of linear paraffins and 34 parts of benzene are charged to process. The LAB product has a typical Bromine Index of less than 10 and is 99% sulfonable.

Economics: U.S. Gulf Coast battery limits for the production of 80,000 tpy of LAB:

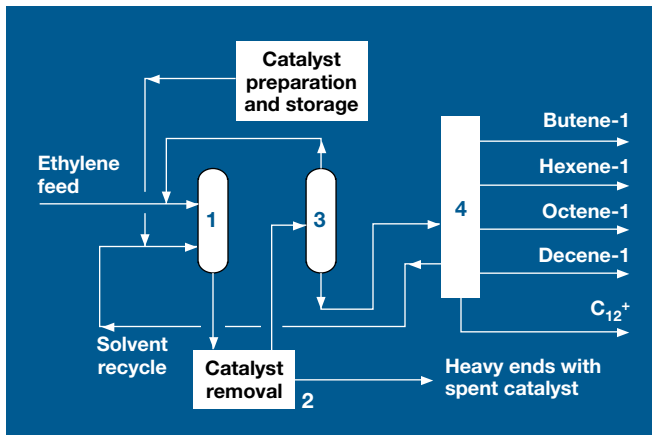
Investment, \$/tpy	585
Typical utilities consumption, per metric ton of LAB:	
Catalysts and chemicals, \$	44
Power, kWh	295
Water, cooling, m^3	7
Fuel fired, 10^6 kcal	4.6

Commercial plants: Twenty-five LAB complexes based on the Pacol process are in operation. Three of these complexes use the Detal process.

Reference: Banerji, A., et al., *Growth and Developments in LAB Technologies: 30 Years of Innovation and More to Come*, 1993 World Surfactant Congress, Montreaux, Switzerland, September 1993.

Licensor: UOP.

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Alpha olefins, linear

Application: To produce high purity alpha olefins (C_4 – C_{10}) suitable as copolymers for LLDPE production and as precursors for plasticizer alcohols and polyalphaolefins using the AlphaSelect process.

Description: Polymer-grade ethylene is oligomerized in the liquid-phase reactor (1) with a catalyst/solvent system designed for high activity and selectivity. Liquid effluent and spent catalyst are then separated (2); the liquid is distilled (3) for recycling unreacted ethylene to the reactor, then fractionated (4) into high-purity alpha-olefins. Spent catalyst is treated to remove volatile hydrocarbons and recovered. The table below illustrates the superior purities attainable (wt%) with the AlphaSelect process:

n-Butene-1	> 99.5
n-Hexene-1	> 98.5
n-Octene-1	> 96.5
n-Decene-1	> 94.0

The process is simple; it operates at mild operating temperatures and pressures and only carbon steel equipment is required. The catalyst is nontoxic and easily handled.

Yields: Yields are adjustable to meet market requirements and very little high boiling polymer is produced as illustrated:

Alpha-olefin product distribution, wt%

n-Butene-1	33-43
n-Hexene-1	30-32
n-Octene-1	17-21
n-Decene-1	9-14

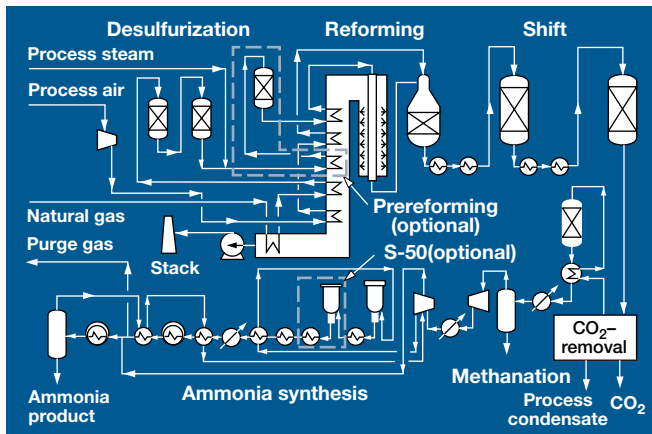
Economics: Typical case for a 2000 ISBL investment at a Gulf Coast location producing 65,000 tpa of C_4 – C_{10} alpha-olefins is:

Investment, million \$U.S.	34
Raw material	
Ethylene, tons per ton of product	1.15
Byproducts, ton/ton of main products	
C12+ olefins	0.1
Fuel gas	0.03
Heavy ends	0.02
Utilities cost, \$U.S./ton product	51
Catalyst + chemicals, \$U.S./ton product	22

Commercial plants: The AlphaSelect process is strongly backed by extensive IFP industrial experience in homogeneous catalysis, in particular, the Alhabutol process for producing butene-1 for which there are 20 units producing 318,000 tpy.

Licensor: IFP, IFPNA.

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Ammonia

Application: To produce ammonia from a variety of hydrocarbon feedstocks ranging from natural gas to heavy naphtha using Topsøe's low-energy ammonia technology.

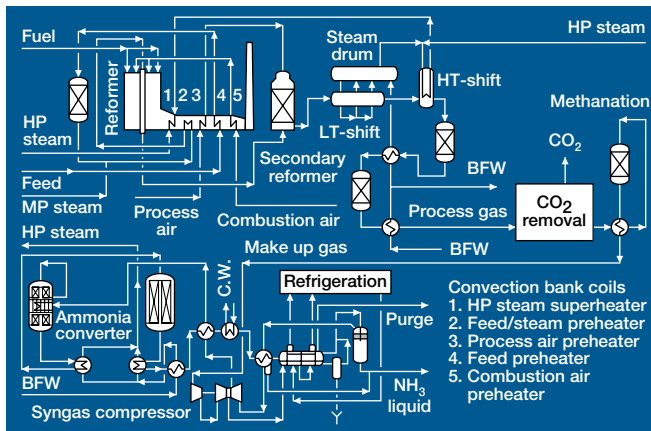
Description: Hydrocarbon feedstock is desulfurized, mixed with steam and then converted into synthesis gas in the steam reforming section. The reforming section comprises a prereformer (optional, but gives particular benefits when the feedstock is higher hydrocarbons or naphtha), a fired tubular reformer and a secondary reformer where process air is added. The tubular steam reformer is Topsøe's proprietary side wall fired design. After the reforming section, the synthesis gas undergoes high and low temperature shift conversion, carbon dioxide removal and methanation.

Synthesis gas is compressed to the synthesis pressure, typically ranging from 140 to 220 kg/cm²g, and converted into ammonia in a synthesis loop using radial flow synthesis converters, either the two-bed S-200, the three-bed S-300 or the S-250 concept using a S-200 converter followed by a boiler or steam superheater and a one-bed S-50 converter. Ammonia product is condensed and separated by refrigeration. All the catalysts used in the catalytic process steps for ammonia production are supplied by Topsøe.

Commercial plants: More than 60 plants use the Topsøe process concept. In addition, many plants based on other feedstocks use the Topsøe ammonia synthesis technology. Since 1988, 52% of all new ammonia production capacity has been based on Topsøe technology.

Licensor: Haldor Topsøe A/S.

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Ammonia

Application: To produce ammonia from natural gas, LNG, LPG or naphtha. Other hydrocarbons—coal, oil, residues or methanol pure gas—are possible feedstocks with an adapted front-end. The process uses conventional steam reforming synthesis gas generation (front-end) and a medium-pressure ammonia synthesis loop. It is optimized with respect to low energy consumption and maximum reliability. The largest single-train plant built by Uhde has a nameplate capacity of 1,800 metric tons per day (mtpd) and an energy consumption of 6.65 Gcal per metric ton (mt) of ammonia. Since a revamp, it is operating beyond 2,000 mtpd.

Description: The feedstock (natural gas as an example) is desulfurized, mixed with steam and converted into synthesis gas over nickel

catalyst at approximately 40 bar and 800°C to 850°C in the primary reformer. The Krupp Uhde steam reformer is a top-fired reformer with tubes made of centrifugal high alloy steel and a proprietary “cold outlet manifold” system, which enhances reliability.

In the secondary reformer, process air is admitted to the syngas via a special nozzle system that provides a perfect mixture of air and gas. Subsequent high-pressure steam generation and superheating guarantee maximum process heat usage to achieve an optimized energy efficient process.

CO is converted to CO₂ in the HT and LT shift over standard catalysts. CO₂ is removed in a scrubbing unit, which is normally either the BASF-aMDEA or the UOP-Benfield process. Remaining carbonoxides are reconverted to methane in the catalytic methanation to trace ppm levels.

The ammonia synthesis loop uses two ammonia converters with three catalytic beds. Waste heat is used for steam generation downstream the second and third bed. Waste-heat steam generators with integrated boiler feedwater preheater are supplied with a special cooled tube sheet to minimize skin temperatures and material stresses. The converters themselves have radial catalyst beds with standard small grain iron catalyst. The radial flow concept minimizes pressure drop in the synthesis loop and allows maximum ammonia conversion rates.

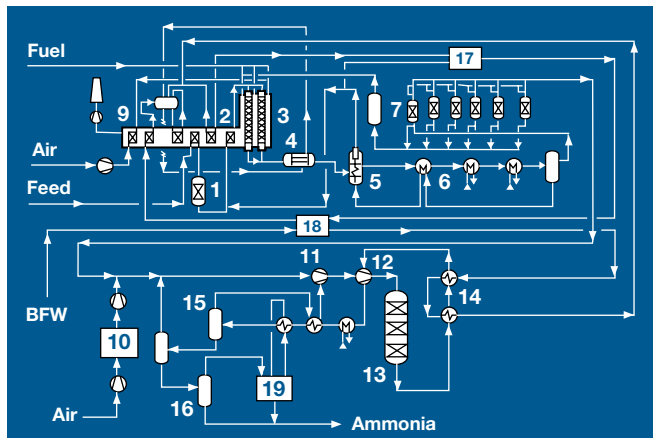
Liquid ammonia is separated by condensation from the synthesis loop and is either subcooled and routed to storage, or conveyed at moderate temperature to subsequent consumers.

Ammonia flash and purge gases are treated in a scrubbing system and a hydrogen recovery unit (not shown), and the remains are used as fuel.

Commercial plants: Fourteen ammonia plants were commissioned between 1990 and 2000, with capacities ranging from 500 mtpd to 1,800 mtpd.

Licensors: Krupp Uhde GmbH.

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Ammonia

Application: The Linde ammonia concept (LAC) produces ammonia from light hydrocarbons. The process is a simplified route to ammonia, consisting of a modern hydrogen plant, standard nitrogen unit and a high-efficiency ammonia synthesis loop.

Description: Hydrocarbon feed is preheated and desulfurized (1). Process steam, generated from process condensate in the isothermal shift reactor (5) is added to give a steam ratio of about 2.7; reformer feed is further preheated (2). Reformer (3) operates with an exit temperature of 850°C.

Reformed gas is cooled to the shift inlet temperature of 250°C by generating steam (4). The CO shift reaction takes place in a single stage in the tube-cooled isothermal shift reactor (5), where process steam is generated from condensate. No process condensate effluent from the LAC plant is generated, thus eliminating a condensate treatment system.

After further heat recovery, final cooling and condensate separation

(6), the gas is sent to the pressure swing adsorption (PSA) unit (7). Loaded adsorbers are regenerated isothermally using a controlled sequence of depressurization and purging steps.

Nitrogen is produced by the low-temperature air separation in a cold box (10). Air is filtered, compressed and purified before being supplied to the cold box. Pure nitrogen product is further compressed and mixed with the hydrogen to give a pure ammonia synthesis gas. The synthesis gas is compressed to ammonia-synthesis pressure by the syngas compressor (11), which also recycles unconverted gas through the ammonia loop. Pure syngas eliminates the loop purge and associated purge gas treatment system.

The ammonia loop is based on the Ammonia Casale axial-radial three-bed converter with internal heat exchangers (13), giving a high conversion. Heat from the ammonia synthesis reaction is used to generate HP steam (14), preheat feed gas (12) and the gas is then cooled and refrigerated to separate ammonia product (15). Unconverted gas is recycled to the syngas compressor (11) and ammonia product chilled to -33°C (16) for storage. Utility units in the LAC plant are the power-generation system (17), which provides power for the plant from HP superheated steam, BFW purification unit (18) and the refrigeration unit (19).

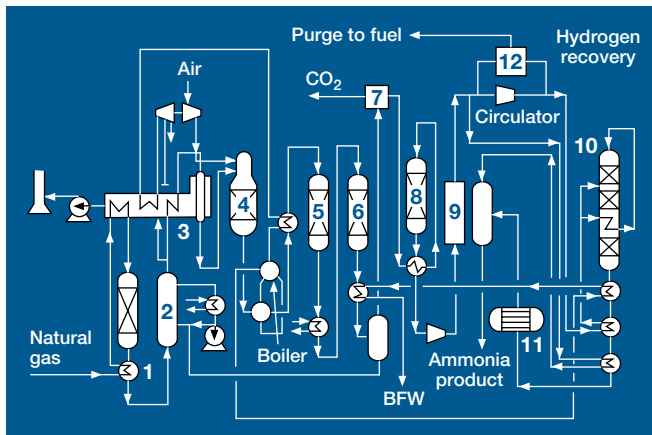
Economics: Simplification over conventional processes gives important savings such as: investment, catalyst-replacement costs, maintenance costs, etc. Total feed requirement (process feed plus fuel) is approximately 7 Gcal/metric ton (mt) ammonia (25.2 MMBtu/short ton) depending on plant design and location.

Commercial Plants: The first complete LAC plant, for 1,350-mtd ammonia, has been built for GSFC in India. Two other LAC plants, for 230- and 600-mtd ammonia, are under construction in Australia. There are extensive reference lists for Linde hydrogen and nitrogen plants and Ammonia Casale synthesis systems.

References: "A Combination of Proven Technologies," *Nitrogen*, March-April 1994.

Licensor: Linde AG.

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Ammonia

Application: The ICI AMV process produces ammonia from hydrocarbon feedstocks. The AMV process concept offers excellent energy efficiency together with simplicity and reduced capital cost for plant capacities between 1,000 tpd and 1,750 tpd. Key features include reduced primary reformer duty, low-pressure synthesis loop and hydrogen recovery at synthesis loop pressure.

Description: Natural gas feed is desulfurized and passed to a feed gas saturator where it is contacted with circulating hot process condensate. Feed gas from the saturator is mixed with a further quantity of steam to give a steam-to-carbon ratio of 3:1, preheated in the

reformer flue gas duct and reformed at 700°C to 800°C and 28 to 35 bar. The gas mixture is then fed to a secondary reformer for further reforming with excess process air. The secondary reformer operates at a temperature of 900°C to 950°C. A typical slip from the secondary reformer is about 1%. Reformed gas is then cooled by generating super heated high-pressure steam and then shifted in high- and low-temperature shift converters. Cooling reformed gas between HT and LT shift converters is effected by preheating the feed gas saturator circulating water. Heat in the gas leaving the LT shift converter preheats high-pressure boiler feedwater.

Cooled gas from the LT shift converter is taken to a low-energy CO₂ removal plant.

Gas leaving the CO₂ removal plant is methanated, cooled, dried and fed to an ammonia synthesis loop operating at 80 to 110 bar.

Circulating gas from the ammonia synthesis loop is mixed with the dried synthesis gas and fed to a circulator. Gas from the circulator is heated and passed over a low-pressure, ammonia synthesis catalyst to produce ammonia.

Hot gas leaving the ammonia converter is cooled by heating high-pressure boiler feedwater and feed gas to the converter. Ammonia is separated from partially cooled gas using mechanical refrigeration.

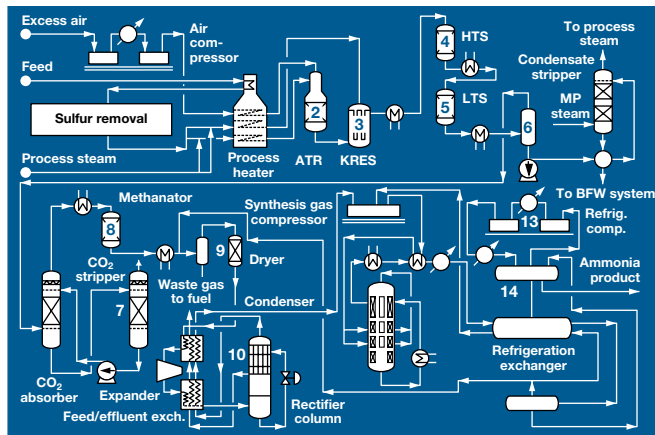
Inerts and excess nitrogen from the ammonia synthesis loop are removed by a purge from the circulator delivery and treated in a hydrogen recovery unit. Recovered hydrogen is recycled to the circulator suction.

Economics: Production costs are dominated by feedstock, fuel and capital charges. Feedstock and fuel requirements are 6.5 to 7.0 Gcal/te (23.4 to 25.2 MMBtu/st).

Commercial plants: Three plants have been built using the AMV process, one in Canada and two in China.

Licensor: Syntetix.

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the remaining hydrocarbon feed. The autothermal reformer effluent, fed on the shell side of the KRES reforming exchanger, supplies heat to the reforming reaction taking place inside the tubes.

Reforming-exchanger effluent is cooled in a waste-heat boiler, where high-pressure steam is generated, and delivered to the CO shift converters containing two catalyst types: One (4) is a high-temperature catalyst and the other (5) is a low-temperature catalyst.

Shift-reactor effluent is cooled, condensed water separated (6) and then routed to the gas-purification section. CO₂ is removed from synthesis gas using a wet-CO₂ scrubbing system, e.g., hot potassium carbonate, MDEA (methyl diethanolamine), etc. (7).

After CO₂ removal, final purification includes methanation (8) gas drying (9) and cryogenic purification (10). The resulting pure synthesis gas is compressed in a single-stage compressor and mixed with a recycle stream (11). The gas mixture is passed to the ammonia converter (12), which is based on the Kellogg Brown & Root Advanced Ammonia Process (KAAP). It uses a precious metal-based, high-activity ammonia synthesis catalyst to allow for high conversion at the relatively low pressure of 90 bar.

Effluent vapors are cooled by ammonia refrigeration (13) and unreacted gases are recycled. Anhydrous liquid ammonia is condensed and separated (14) from the effluent. New energy-efficient and cost-effective designs are in operation with energy consumption of less than 25 MMBtu (LHV)/short-ton, with about 10% capital cost savings over the conventional process.

Commercial plants: Over 200 large-scale single-train ammonia plants of Kellogg Brown & Root design are onstream or have been contracted worldwide. The KAAP plus advanced ammonia technology provides low-cost, low-energy design of ammonia plants, minimizes environmental impact, reduces maintenance and operating requirements and provides enhanced reliability. Two 1,850-mtpd grassroots KAAP plants were completed in Trinidad in 1998 and currently, are in full operation.

Licensors: Kellogg Brown & Root, Inc.

Ammonia, KAAP plus

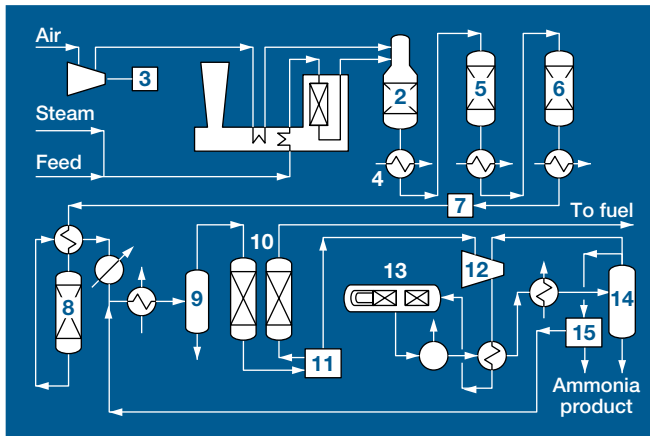
Application: To produce ammonia from hydrocarbon feedstocks using a high-pressure heat exchange-based steam reforming process integrated with a low-pressure advanced ammonia synthesis process.

Description: The catalytic-steam hydrocarbon reforming process produces raw synthesis gas by steam reforming in a heat exchange-based system under pressure based on the Kellogg Brown & Root Reforming Exchange System (KRES).

Following sulfur removal (1), the autothermal reformer (2) and reforming exchanger (3), which operate in parallel, convert the hydrocarbon feed into raw synthesis gas in the presence of steam using a nickel catalyst.

In the autothermal reformer, excess air supplies nitrogen. The heat of combustion of the partially reformed gas supplies energy to reform

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(1) with exit at less than 700°C. Primary reformer effluent is reacted with excess air in the secondary reformer (2) with exit at less than 900°C. The air compressor is normally driven by a gas turbine (3). Turbine exhaust is fed to the primary reformer for use as preheated combustion air.

Secondary reformer exit gas is cooled by generating steam at 100 to 125 bar (4). The shift reaction is carried out in two steps, HTS (5) and LTS (6), and water is separated. Carbon dioxide removal (7) is by licensed processes. Following CO₂ removal, residual carbon oxides are converted to methane in the methanator (8). Methanator effluent is cooled and water is separated (9) before the raw gas is dried (10).

Dried raw gas flows to the cryogenic purifier (11), where it is separated into syngas and waste gas. The syngas is essentially a 75:25 ratio of hydrogen and nitrogen. The waste gas contains unconverted methane from the reforming section and excess nitrogen and argon. This stream is used to regenerate the driers and then is burned as fuel in the primary reformer.

The purified syngas is compressed in the syngas compressor (12), mixed with the loop-recycle stream and fed to the converter (13). Converter effluent is cooled and then chilled by ammonia refrigeration. Ammonia product is separated (14) from unreacted syngas. Unreacted syngas is recycled back to the syngas compressor. A small purge is scrubbed with water (15) and recycled to the driers.

Commercial plants: Over 200 single-train plants of KBR design have been contracted worldwide. Sixteen of these plants use the KBR Purifier process.

Licensor: Kellogg Brown & Root, Inc.

Ammonia, KBR purifier

Application: To produce ammonia from hydrocarbon feedstocks and air.

Description: The key features of the Kellogg Brown & Root (KBR) Purifier process are mild primary reforming, secondary reforming with excess air, cryogenic purification of syngas, and synthesis of ammonia over magnetite catalyst in a horizontal converter.

Desulfurized feed is reacted with steam in the primary reformer

Aromatics recovery— liquid-liquid extraction

Application: Simultaneous recovery of benzene, toluene and xylenes from reformat or pyrolysis gasoline using liquid-liquid extraction.

Description: In the extractor, the solvent—N-Formylmorpholin with 4% to 6% water—is fed from top to bottom as a continuous phase. The feedstock—reformat or pygas—is fed to the column several stages above the base of the extractor. The difference in density causes the feedstock to bubble upwards in countercurrent to the solvent. During this procedure the aromatics pass into the solvent and the nonaromatics stay in the light phase. Internals, structured packing or sieve trays ensure that the phases are well distributed throughout the cross-sectional area of the column. The overhead product from the second column, which mainly comprises relatively low-boiling nonaromatics, is fed to the base of the extractor as a countercurrent solvent. The head and the base of the extractor act as phase separating vessels. The non-aromatics with a slight concentration of NFM in solution are drawn off overhead, and the solvent containing all the aromatics and some non-aromatics is drawn off at the base.

The extractor is operated under atmospheric condition, 30°C to 50°C and 1 to 3 bar pressure. Column 2 is divided in 2 sections. The bottom product from the extractor is fed into the column (from above) between sections 1 and 2, and additional solvent is fed in above section 1. Section 3 is used to strip the aromatics from the solvent. Some of the vapors produced in the bottom are used to heat the ED and some are fed into a small lateral column where the pure aromatic product is separated from the solvent. The overhead vapor of the lateral column are condensed. The reflux washes down the solvent traces in the vapors.

This lateral column does not have a bottom boiling section and consequently the bottom product still contains some aromatics. For this reason the bottom product is returned to the ED which is oper-

ated at reduced pressure as a result of the boiling temperature threshold.

The stripped solvent is practically free from water. The water undergoes overhead azeotropic distillation and is produced as separate subphase in the reflux drum. This water is then fed to the solvent recovery stage of the extraction process.

Typical feedstock composition, %	Hydrotreated pyrolysis	Reformat
	gasoline	
Benzene	40	3
Toluene	20	13
Xylenes	4,5	18
Ethylbenzene	2,5	5
Higher aromatics	3	16
Total aromatics	70	55
Nonaromatics	30	45
	100	100

Economics:

Consumption per feedstock:

Steam (20 bar), t	0.46
Water, cooling (t = 10°), m ³	12
Electric power, kWh	18

Production yield, wt%:

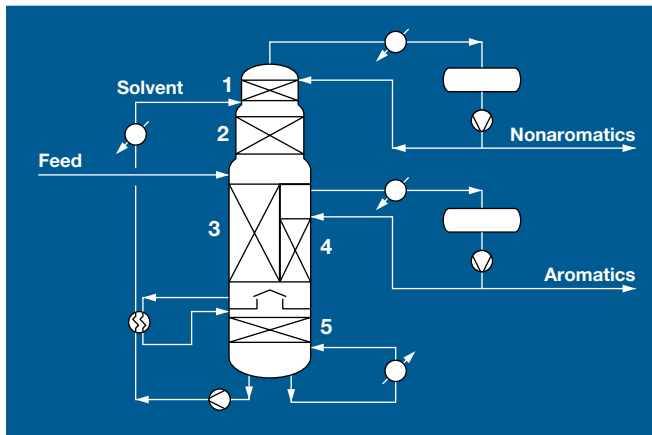
Benzene	~ 100
Toluene	99.7
EB, Xylenes	94.0

Purity, wt%:

Benzene	99.999
Toluene	> 99.99
EB, xylenes	> 99.99

Installation: One Morphylex plant was erected.

Licensors: Krupp Uhde GmbH.



Aromatics—progressive extractive distillation

Application: Recovery of high-purity benzene, toluene and xylenes from reformat, pyrolysis gasoline or coke-oven light oil and the debenzene of motor gasoline using the progressive extractive distillation technology.

Description: The progressive Morphylane extractive distillation is a single-column extractive distillation configuration. The aromatics are removed from the vaporized feed material by the solvent in packing (2) until a residual content of 0.5–1% is reached. However, some of the nonaromatics are also dissolved. These are stripped off by aromatics vapors in packing (3). The solvent traces which go to the column head with the nonaromatics proportionate to the vapor pressure of the solvent are washed back with the nonaromatics reflux.

Solvent traces are removed from the aromatics vapors in packing (4), again by reflux. It is, however, packing (5), where the aromatics are stripped off from the solvent that is of crucial importance. Extractive distillation can only be effective if the aromatics content is drastically reduced to ~0.1%. Intensive aromatics stripping is crucial for the aromatics yield.

The wall forms two separate chambers. The vapors, which enter both sides have the same composition and their nonaromatics content must conform with the product quality for pure aromatics. The purity of the aromatics is regulated in packing (3), the yield is regulated in packings (2 and 5) and the solvent is retained in packings (1 and 4).

Economics:

Typical composition, wt%:

Component	Pyrolysis gasoline	Reformat	Coke oven light oil
Benzene	40	3	65
Toluene	20	13	18
Xylenes	4	18	6
Ethylbenzene	3	5	2
C ₉ -Aromatics	3	16	7
Total Aromatics	70	55	98
Naphthenes	High	Low	High
Olefins	High	High	High
Paraffins	Low	High	Low

Purity, wt%:

Benzene	> 99.99
Toluene	> 99.95

Yield, wt%:

Benzene	99.9–99.95
Toluene	99.5

Solvent losses

0.005 kg/aromatics

Steam consumption (18 bar):

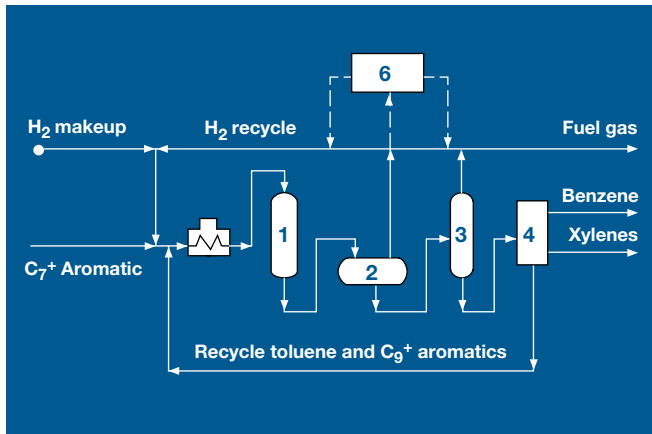
	Catalytic feed	Reformat aromatics	Pyrolysis feed	Gasoline aromatics
kg/t	330	940	410	555

Installation: Intensive pilot plant testing.

Conventional design: 45

Licensors: Krupp Uhde GmbH.

PETROCHEMICAL PROCESSES 2001



Benzene

Application: To produce high-purity benzene and heavier aromatics from toluene and heavier aromatics using the Detol process.

Description: Feed and hydrogen are heated and passed over the catalyst (1). Benzene and unconverted toluene and/or xylene and heavier aromatics are condensed (2) and stabilized (3).

To meet acid wash color specifications, stabilizer bottoms are passed through a fixed-bed clay treater, then distilled (4) to produce the desired specification benzene.

Unconverted toluene and/or xylenes and heavier aromatics are recycled.

Yields: Aromatic yield is 99.0 mol% of fresh toluene or heavier aromatic charge. Typical yields for production of benzene and xylenes are:

Type production	Benzene	Xylene
Feed, wt%		
Nonaromatics	3.2	2.3
Benzene	—	11.3
Toluene	47.3	0.7
C ₈ aromatics	49.5	0.3
C ₉ ⁺ aromatics	—	85.4
Products, wt% of feed		
Benzene*	75.7	36.9
C ₈ aromatics**	—	37.7

*5.45°C minimum freeze point

**1,000 ppm nonaromatics maximum

Economics: Basis of 100 MMgpy:

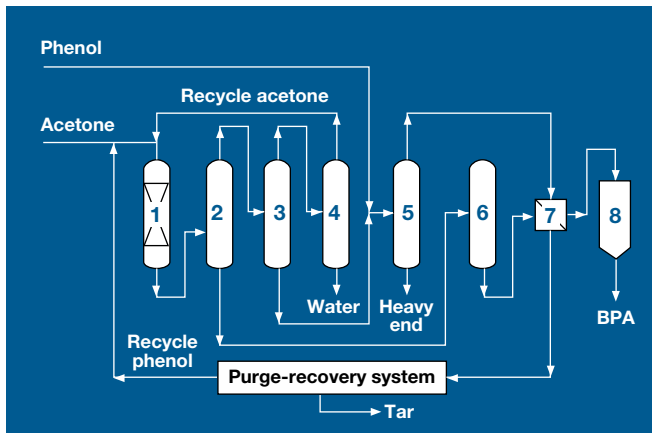
Estimated investment, \$/bpsd	3,100
Typical utility requirements, per bbl feed:	
Electricity, kWh	5.8
Fuel, MMBtu	0.31*
Water, cooling, gal	450
Steam, lb	14.4

* No credit taken for vent gas streams

Commercial plants: Twelve plants with capacities ranging from about 12 million to 100 million gallons per year have been licensed.

Licensor: ABB Lummus Global.

PETROCHEMICAL PROCESSES 2001



Bisphenol-A

Application: The process, CT-BISA, is used to manufacture bisphenol-A (BPA) from phenol and acetone. The process can produce both grades of polycarbonate (including optical grade) and epoxy resins.

Description: Acetone and excess phenol are reacted in a BPA synthesis reactor (1), which is packed with a cation-exchange resin catalyst. Higher acetone conversion and selectivity to BPA and long lifetime are characteristic of the catalyst. These properties reduce byproduct formation and catalyst volume. Unreacted acetone, water and some phenol are separated from the reaction mixture by distillations (2–4). Acetone is recycled to the BPA reactor (1); water is efficiently discharged; phenol is mixed with feed phenol and purified by distillation (5). The crude-product stream containing BPA, phenol and impurities is transferred to the crystallizer (6), where crystalline product is formed and impurities are removed by the mother liquor. Sep-

arated crystals are washed with purified phenol in a solid-liquid separator (7).

Crystals are then melted and sent to the prilling tower (8), where spherical prills are produced as final product. Or, molten BPA is solidified by alternative devices to form other shapes such as flakes and pellets. Solidified BPA can be conveyed to bagging and storage facilities.

The mother liquor containing impurities, phenol and dissolved BPA is recycled back to the BPA reactor. Part of the mother liquor is sent to the purge-recovery system, where impurities are partially decomposed and recombined to form BPA. Effluents are mixed with mother liquor and recycled to the BPA reactor. Undesirable impurities are condensed at the purge-recovery system and discharged as tarry materials, which can be used as fuels. The optimal purge ratio from the mother liquor controls product quality, while minimizing raw material consumption.

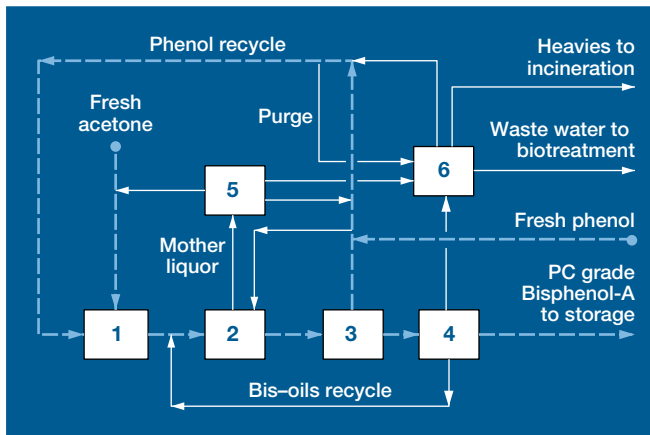
Product quality: Typical values for BPA prills:

Freezing point, °C	156.8
Melt color @175°C	5 APHA
Free phenol, wt ppm	10
2,4 BPA isomer, wt ppm	50 to 100
Iron, wt ppm	<0.1

Commercial plants: The first commercial plant incorporating CT-BISA with a 70,000-tpy capacity was constructed for Shin Nippon Bisphenol Co., Japan, and has been successfully operated since 1991, in collaboration with Nippon Steel Chemical Co., Ltd. This plant has been revamped by Chiyoda to 95,000 tpy in 1999. A second facility, with 25,000-tpy capacity for Taiwan Prosperity Chemical Corp., Taiwan, has been successfully operated since 1995. A third facility, with 70,000-tpy capacity for Mitsubishi Chemical Corp., Japan, started up in 1998 and has been revamped to 100,000 tpy by Chiyoda in 2000. In 2000, two new contracts have been awarded to CT-BISA Process, i.e., a 100,000-tpy BPA plant by Mitsubishi Chemical Corp., Japan and a 25,000-tpy plant by Bluestar, China..

Licensors: Chiyoda Corp.

PETROCHEMICAL PROCESSES 2001



Bisphenol-A

Application: A highly efficient process to produce bisphenol-A (BPA) from phenol and acetone. The BPA product is suitable for high-quality polycarbonate (PC) and epoxy resins applications, including optical-media grade PC.

Description: In the bisphenol reaction section (1), acetone is reacted with excess phenol in multiple fixed-bed reactors, containing a DOWEX resin catalyst, to form BPA and water. The outlet from the reactors is fed to the adduct crystallizers (2) where a crystal adduct

of phenol/bisphenol is produced. After washing and separating, mother liquor is recycled to the reactors via the acetone recovery/drying section (5). Here unreacted acetone and the water of reaction are removed. The acetone is dried and recycled to the reactors, and water is sent to the phenol-recovery (6) section. The separated adduct crystals are melted, and the phenol is stripped off (3) and recycled. Molten bisphenol-A is sent to product crystallization (4) where BPA is recrystallized in water to polycarbonate-grade specifications. The crystals are centrifuged, washed, dried, and then sent to product storage prior to bulk loadout and/or packaging. The finished product is a white crystalline solid.

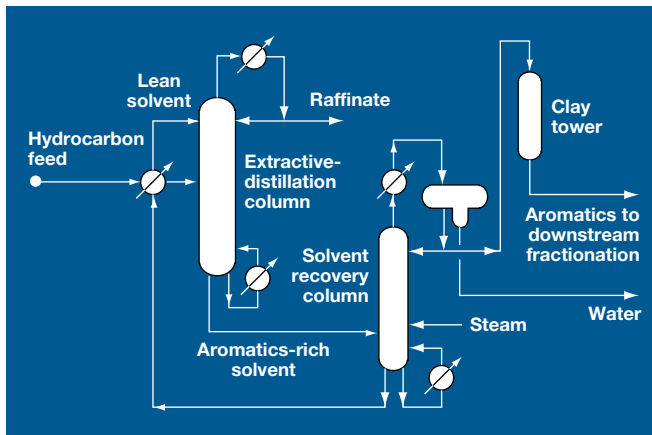
The phenol recovery (6) section separates and recycles the phenol contained in various streams from different plant sections.

Economics: This process uses a proprietary resin catalyst system; it has consistently achieved greater than 98% efficiency of raw-material utilization. The process is simple and requires few processing steps resulting in a low equipment count and capital cost.

Installations: The Dow Chemical Co. (Dow), developed their ion exchange resin based BPA technology in the late 1960's. Dow has continued to improve the technology, especially in the areas of product quality, higher operating efficiency and reduced capital cost. Dow has a total production capacity exceeding 300,000 mty in four plants located in Texas and Stade, Germany.

The process has been licensed to Nan Ya Plastics Corp., for their 90,700 mty grassroots BPA plant at Mailiao, Taiwan, which came on-stream early in 1999.

Licensors: Kellogg Brown & Root, Inc., is the exclusive licensor of the Dow BPA Process.



BTX aromatics

Application: An aromatics process based on extractive distillation, GT-BTX efficiently recovers benzene, toluene and xylenes from refinery or petrochemical aromatics streams, such as catalytic reformat or pyrolysis gasoline.

Description: Hydrocarbon feed is preheated with hot circulating solvent and fed at a midpoint into the extractive distillation column (EDC). Lean solvent is fed at an upper point to selectively extract the aromatics into the column bottoms in a vapor/liquid distillation operation. Nonaromatic hydrocarbons exit the column top and pass through a condenser. A portion of the overhead stream is returned to the column top as reflux to wash out any entrained solvent. The balance of the overhead stream is the raffinate product, requiring no

further treatment.

Rich solvent from the bottom of the EDC is routed to the solvent-recovery column (SRC), where the aromatics are stripped overhead. Stripping steam from a closed-loop water circuit facilitates hydrocarbon stripping. The SRC operates under vacuum to reduce the boiling point at the column base.

Lean solvent from the bottom of the SRC is passed through heat exchange before returning to the EDC. A small portion of the lean circulating solvent is processed in a solvent-regeneration step to remove heavy decomposition products, which are purged daily.

The process advantages over conventional liquid-liquid extraction processes include lower capital and operating costs and simplicity of operation. Advantages over other extractive processes include: superior solvent system, fewer equipment pieces, small equipment and expanded feedstock range. Design flexibility allows use for grassroots aromatics recovery units or debottlenecking conventional systems in many revamp configurations.

Economics:

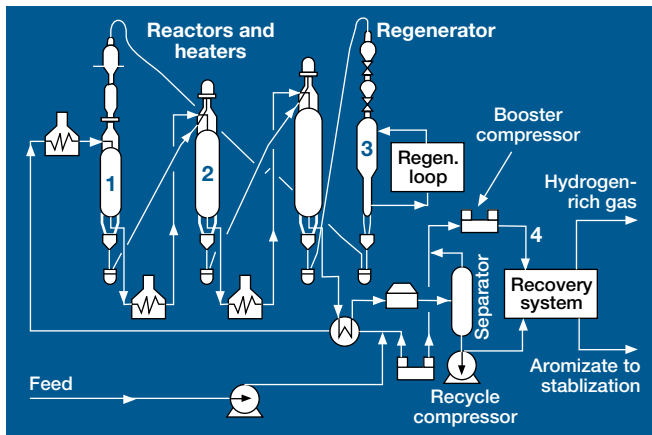
	New unit	Expansion of conventional BTX recovery unit
Feed, bpd	3,500 Lt. reformat	4,000 incremental
Capital cost, \$MM	6.5	3.5
Simple pretax payout, yr	2.2	1.2
ROI, %	44	85

Commercial plants: Three commercial applications.

Reference: "Benzene reduction in motor gasoline—obligation or opportunity", *Hydrocarbon Processing* Process Optimization Conference, April 1997. "Improve BTX processing economics," *Hydrocarbon Processing*, March 1998.

Licensors: GTC Technology Corp.

PETROCHEMICAL PROCESSES 2001



(latest generation AR 501) catalyst moves downward through each reactor. Leaving the reactor, the catalyst is gas-lifted to the next reactor's feed hopper where it is distributed for entry. After the last reactor, an inert gas lift system isolates and transports the catalyst to the recently-introduced RegenC regeneration section (3). Coke is removed; catalyst is returned to its original state and sent to the first reactor; the cycle begins again. A recovery system (4) separates hydrogen for use in downstream units and the Aromate is sent to a stabilization section. The unit is fully automated and operating controls are integrated into a DCS, requiring only a minimum of supervisory and maintenance effort.

Yields: (%)

	Feed	Products
TBP cut, °C	80-150	Hydrogen 4.1
Paraffins	57	C ₅ + 87
Naphthenes	37	Benzene 8.5
Aromatics	6	Toluene 26.3
		Xylenes 26.1
		Total aromatics 74.3

Economics: The ISBL investment for a typical 25,000-bpsd CCR Aromizing unit with a RegenC regenerator, 2000 Gulf Coast location.

Investment including initial catalyst inventory,*

\$U.S. million 50

Typical utility requirements:

Fuel, 10⁶ kcal/h 76

Steam, HP t/h (net export) (17)

Electricity, kWh/h 5,900

Catalyst operating cost, \$/ton feed 0.5

* Exclusive of noble metals

Commercial plants: Seven Aromizing plants are in operation and four are under design.

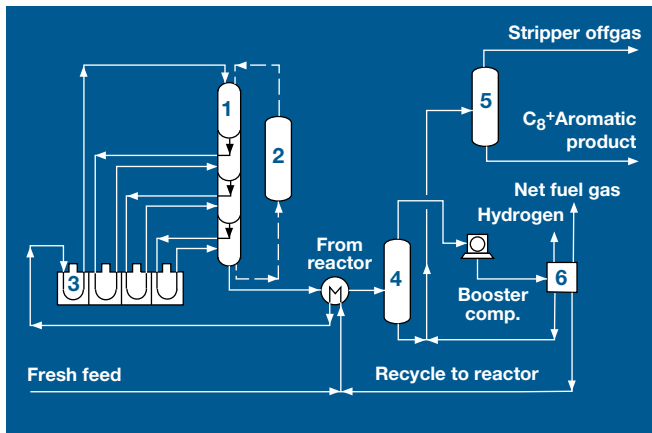
Licensors: IFP, IFPNA.

BTX aromatics

Application: To produce high yields of benzene, toluene, xylenes and hydrogen from naphthas via the CCR Aromizing process coupled with RegenC continuous catalyst regeneration technology. Benzene and toluene cuts are fed directly to an aromatics extraction unit. The xylenes fraction, obtained by fractionation and subsequent treatment by the Arofining process for diolefins and olefins removal, is ideal for paraxylene and orthoxylene production.

Description: This process features moving bed reactors and a continuous catalyst regeneration system coupled with a hard, smooth-flowing catalyst. Feed enters the reactor (1), passes radially through the moving catalyst bed, exits at the reactor bottom and proceeds in the same manner through the 2-3 remaining reactors (2). The robust

PETROCHEMICAL PROCESSES 2001



BTX aromatics

Application: To produce petrochemical-grade benzene, toluene and xylenes via the aromatization of propane and butanes using the BP-UOP Cyclar process.

Description: The process consists of a reactor section, continuous catalyst regeneration (CCR) unit and product-recovery section. Stacked radial-flow reactors (1) are used to facilitate catalyst transfer to and from the CCR catalyst regeneration section (2). A charge heater and interheaters (3) are used to achieve optimum conversion and selectivity for endothermic reaction. Reactor effluent is separated

into liquid and vapor products (4). The liquid product is sent to a stripper column (5) to remove light saturates from the C_6^- aromatic product. Vapor from the separator is compressed and sent to a gas recovery section (6) for separation into a 95% pure hydrogen coproduct, a fuel gas stream of light byproducts and a recycled stream of unconverted LPG.

Yields: Total aromatics yields as a wt% of fresh feed range from 61% for propane to 66% for mixed-butanenes feed. The hydrogen yield is approximately 7 wt% of fresh feed. Typical product distribution is 27% benzene, 43% toluene, 22% C_8 aromatics and 8% C_9^+ aromatics.

Economics: U.S. Gulf Coast inside battery limits are based on processing 15,000 bpsd of C_3 to C_4 feed. Gas turbine driver assumed for product compressor.

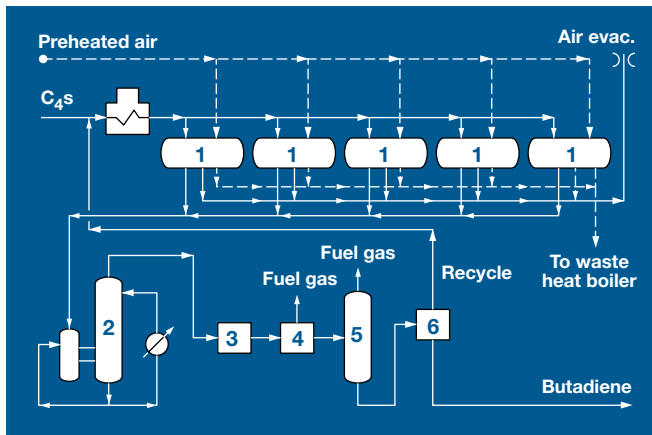
Investment, \$ per bpsd capacity	3,500 to 4,700
Typical utility requirements, unit per bbl feed:	
Electricity, kWh	9
Steam (600 psig), lb (credit)	(94)
Steam (50 psig), lb	26
Fuel, 10^3 Btu	440
Water, cooling, gal	270
Water, boiler feed, gal	9

Commercial plants: One 1,000-bpd plant at the BP oil refinery in Grangemouth, Scotland. A 46,000-bpd unit started operation in late 1999 and is licensed to Sabic, Yanbu, Saudi Arabia.

Reference: Doolan, P. C., and P. R. Pujado, "Make aromatics from LPG," *Hydrocarbon Processing*, September 1989, pp. 72–76. Gosling, C. D., et al., "Process LPG to BTX products," *Hydrocarbon Processing*, December 1991.

Licensors: UOP.

PETROCHEMICAL PROCESSES 2001



Butadiene

Application: To produce butadiene from butane or mixed butane/butylenes; isoprene from isopentane or mixed isopentane/isoamylenes; using the Catadiene process.

Description: A one-step, fixed-bed catalytic process operates on a single-component or mixed feedstock to selectively produce diolefins. Feed is preheated, then contacted with catalyst in parallel fixed-

bed reactors (1). Hot reactor effluent is quenched (2), compressed (3), cooled and cryogenically recovered (4) and stabilized (5). The product goes to extraction (6) for high-purity product recovery. Unconverted paraffins and mono-olefins can be recycled.

A cycle timer controls the reactors being regenerated or onstream. Catalyst is regenerated/reheated by heating and coke burn-off during each cycle with preheated air.

Catadiene catalysts are robust, base metal, cylindrical pellets.

Operating conditions: Normally within the ranges:

Temperature, °F	1,000 –1,200
Pressure, in. HG absolute	4 –10

Yields: Typical ultimate yield is 60 to 65 wt%.

Economics: Basis of 90,000 tpy butadiene from n-butane:

Estimated investment: (Onsite, excluding extraction),	
	\$/tpy 1,710

Typical utility requirements, per hour:

Electricity, kWh	700
Steam, lb	13,100
Fuel, 10 ⁶ Btu	135
Water, cooling (20°F rise), 10 ⁶ gal	1.44
Water, boiler feed, 10 ³ gal	5.9

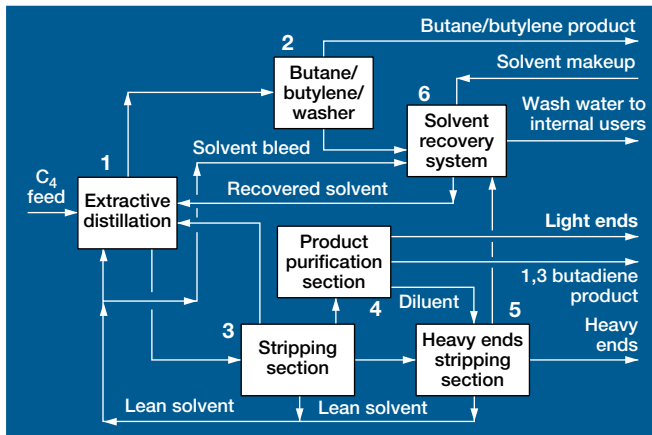
Catalyst and chemicals, \$/ton prod 12.0

Maintenance, per yr as % of investment 2

Commercial plants: Twenty plants have been licensed, with operating experience in excess of 25 years.

Licensor: ABB Lummus Global.

PETROCHEMICAL PROCESSES 2001



Butadiene extraction

Application: To produce a polymer-grade butadiene product from mixed C_4 streams by extractive distillation using acetonitrile (ACN) as the solvent.

Description: This butadiene extraction process developed by Shell has been optimized and updated by Kellogg Brown & Root (KBR) to reduce capital and operating costs. The process scheme consists of contacting mixed C_4 feed with lean solvent in the extractive distil-

lation column (1). The raffinate, butenes and butanes, which are not absorbed, flow overhead to the wash column (2) for solvent recovery. The butadiene-rich solvent flows to the stripper system (3) where the butadiene is separated from the solvent. Raw butadiene is purified to meet specifications in the purification section (4). Additional steps include heavy ends recovery (5) and solvent recovery (6).

Use of acetonitrile is advantageous due to its lower boiling point, which results in lower reboiler temperatures and low fouling rates. Only low-pressure steam is required for reboiling, and the run lengths between reboiler cleaning are very long. ACN has high selectivity to butadiene, which results in low solvent-circulation rates and smaller equipment. ACN is also very stable, noncorrosive and biodegradable.

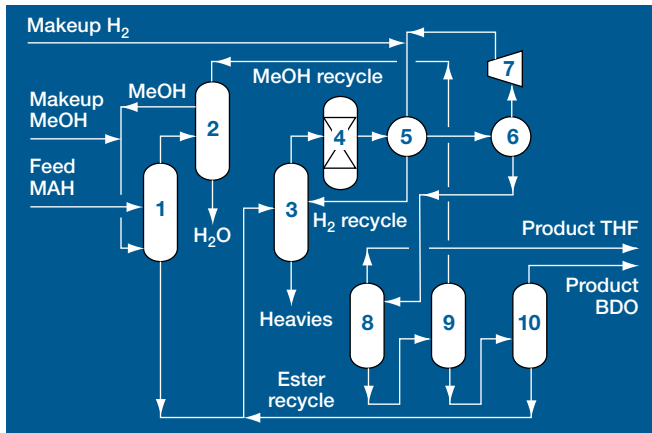
Yields: This process will recover more than 98% of the butadiene contained in the feed as product. This product will meet all butadiene derivative requirements with typical specifications shown below.

Component	Value	Units
1,3-Butadiene	99.5	% wt. Minimum
Total acetylenes	25	Ppmwt maximum
Methyl acetylene	15	Ppmwt maximum
Vinyl acetylenes	10	Ppmwt maximum
Propadiene	10	Ppmwt maximum
1,2-Butadiene	10	Ppmwt maximum
C_5 Hydrocarbons	200	Ppmwt maximum

Installations: Over 35 operating butadiene units use the Shell ACN technology. Unit capacities range from 20 ktpy to over 225 ktpy.

Licensors: Kellogg Brown & Root.

PETROCHEMICAL PROCESSES 2001



Butanediol, 1,4-

Application: To produce 1,4 butanediol (BDO) from butane via maleic anhydride and hydrogen using ester hydrogenation.

Description: Maleic anhydride is first esterified with methanol in a reaction column (1) to form the intermediate dimethyl maleate. The

methanol and water overhead stream is separated in the methanol column (2) and water discharged.

The ester is then fed directly to the low-pressure, vapor-phase hydrogenation system where it is vaporized into an excess of hydrogen in the vaporizer (3) and fed to a fixed-bed reactor (4), containing a copper catalyst. The reaction product is cooled (5) and condensed (6) with the hydrogen being recycled by the centrifugal circulator (7).

The condensed product flows to the lights column (8) where it is distilled to produce a small co-product tetrahydrofuran (THF) stream. The heavies column (9) removes methanol, which is recycled to the methanol column (2). The product column (10) produces high-quality butanediol (BDO). Unreacted ester and gamma butyrolactone (GBL) are recycled to the vaporizer (3) to maximize process efficiency.

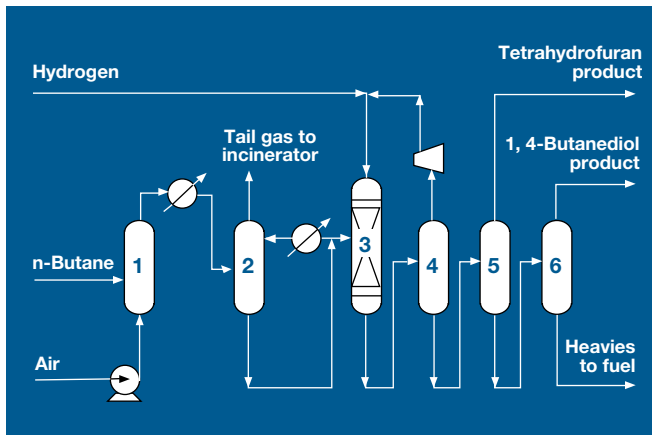
The process can be adapted to produce higher quantities of co-product THF and to extract the GBL as a co-product if required.

Economics: per ton of BDO equivalent

Maleic anhydride	1.125
Hydrogen	0.116
Methanol	0.050
Electric power, Kwh	164
Steam, tons	3.6
Water, cooling, m ³	326

Commercial plants: Since 1989, six plants have been licensed with a total capacity of 300,000 tpy.

Licensors: Kvaerner Process Technology, UK.



Butanediol, 1,4-

Application: To produce 1,4-butanediol (BDO), or mixture of BDO with tetrahydrofuran (THF) and/or gamma-butyrolactone (GBL) from normal butane using a fluid-bed oxidation and fixed-bed hydrogenation reactor combination.

Description: BP Amoco Chemicals, has combined its 40 years of experience in fluid-bed oxidation technology with Lurgi Öl-Gas-Chemie GmbH's 30 years of hydrogenation expertise to jointly develop a direct, dual-reactor process, called the GEMINOX BDO.

Air and n-butane are introduced into a fluid-bed, catalytic reactor (1). The fluid-bed reactor provides a uniform temperature profile for optimum catalyst performance. Reaction gases are cooled and fil-

tered to remove small entrained catalyst particles and then routed to the recovery section. Reactor effluent is contacted in an aqueous scrubber (2), where essentially 100% of the reactor-made maleic anhydride is recovered as maleic acid. The process has the capability of co-producing maleic anhydride (MAH) with the addition of the appropriate purification equipment. Scrubber overhead gases are sent to an incinerator for safe disposal.

The resulting maleic acid from the scrubber is then sent directly to the fixed-bed, catalytic hydrogenation reactor (3). Reactor yields exceed 94% BDO. By adjustments to the hydrogenation reactor and recovery-purification sections, mixtures of BDO with THF and/or GBL can be directly produced at comparable, overall yields and economics.

The hydrogenation reactor effluent is then sent through a series of distillation steps (4, 5 and 6) to produce final market quality product(s). Two, unique process features are:

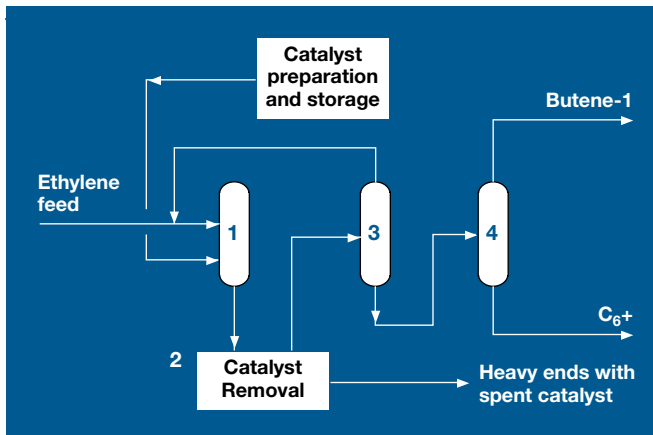
- No continuous liquid waste stream to treat—the water separated in the product purification section is recycled back to the aqueous MAH scrubber (2).
- No pretreatment nor post-treatment of the two catalysts is necessary; no other chemicals are added.

Economics: The GEMINOX BDO technology uses fewer processing steps, as found in competing BDO technologies, leading to significant capital cost savings and lower operating costs. Overall, 25%–40% cost of production savings are possible compared to competing technologies. The unique product flexibility afforded by this process also allows the user to quickly meet changing customer and market needs.

Commercial plants: BP Amoco Chemicals is currently constructing a worldscale GEMINOX BDO plant in Lima, Ohio. This 60,000-tpa facility is scheduled to start up in mid-2000.

Licensors: BP Amoco Chemicals and Lurgi Öl-Gas-Chemie GmbH.

PETROCHEMICAL PROCESSES 2001



Butene-1

Application: To produce high-purity butene-1 that is suitable for copolymers in LLDPE production via the Alkylbutol ethylene dimerization process developed by IFP in cooperation with SABIC.

Description: Polymer-grade ethylene is oligomerized in the liquid-phase reactor (1) with a catalyst system that has high activity and selectivity. Liquid effluent and spent catalyst are then separated (2); the liquid is distilled (3) for recycling of unreacted ethylene to the reactor and fractionated (4) into high-purity butene-1. Spent cata-

lyst is treated to remove volatile hydrocarbons and recovered.

The Alkylbutol process features are: simple processing, high turn-down, ease of operation, low operating pressure and temperature, liquid-phase operation and carbon steel equipment. The technology has advantages over other production or supply sources: uniformly high-quality product, low impurities, reliable feedstock source, low capital costs, high turndown and ease of production.

Yields: LLDPE copolymer grade butene-1 is produced with a purity exceeding 99.5 wt%. Typical product specification is:

Other C ₄ s (butenes+ butanes)	<0.3 wt%
Ethane	<0.15 wt%
Ethylene	<0.05 wt%
C ₆ olefins	<100 ppmw
Ethers (as DME)	<2ppmw
Sulfur, chlorine	<1ppmw
Dienes, acetylenes	<5ppmw each
CO, CO ₂ , O ₂ , H ₂ O, MeOH	<5ppmw each

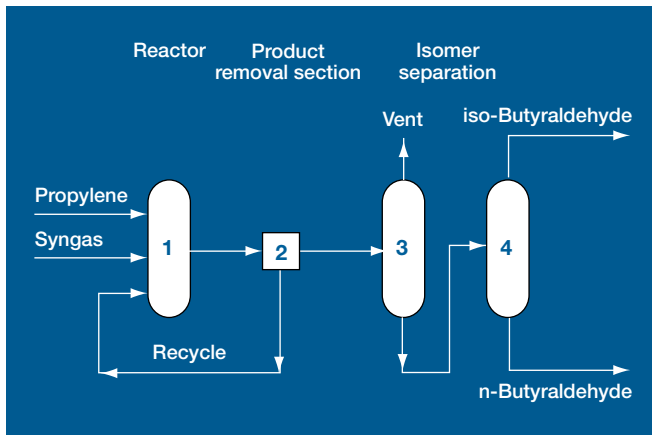
Economics: Case for a 2000 ISBL investment at a Gulf Coast location for producing 20,000-tpa of butene-1 is:

Investment, million U.S.	8
Raw material	
Ethylene, tons per ton of butene-1	1.1
Byproducts, C₆⁺ tons per ton of butene-1	0.08
Typical operating cost, U.S.\$ per ton of butene-1	38

Commercial plants: IFP has licensed 20 units producing 318,000 tpy. Thirteen units are in operation; the others under design or construction.

Licensor: IFP, IFPNA.

PETROCHEMICAL PROCESSES 2001



Butylaldehyde, n and i

Application: To produce normal and iso-butylaldehyde from propylene and synthesis gas ($\text{CO} + \text{H}_2$) using the LP Oxo process, which is a low-pressure, rhodium-catalyzed oxo process.

Description: The process reacts propylene with a 1:1 syngas at low pressure ($<20 \text{ kg/cm}^2\text{g}$) in the presence of a rhodium catalyst complexed with a ligand (1). The oxonation reaction produces normal and iso-butylaldehyde in a n/i ratio, which is typically 10:1, but ratios of

up to 30:1 and down to 1:1 are possible with alternate ligands. The butylaldehyde product is removed from the catalyst solution (2) and purified by distillation (3). N-butylaldehyde is separated from the iso (4).

The process is characterized by its simple flow sheet and low-operating pressure. This results in low capital and maintenance expenses and product cost, and high plant availability. Mild reaction conditions minimize byproduct formation. Low byproduct formation also contributes to higher process efficiencies and product qualities.

Technology for hydrogenation to normal or iso-butanols or aldolization and hydrogenation to 2-ethylhexanol exists and has been widely licensed. A version of the LP Oxo process has been licensed to produce a mixture of C_{10} alcohols (predominantly 2-propylheptanol) from an n-butene feedstock.

Economics: Typical performance data (per ton of mixed butylaldehyde):

Feedstocks

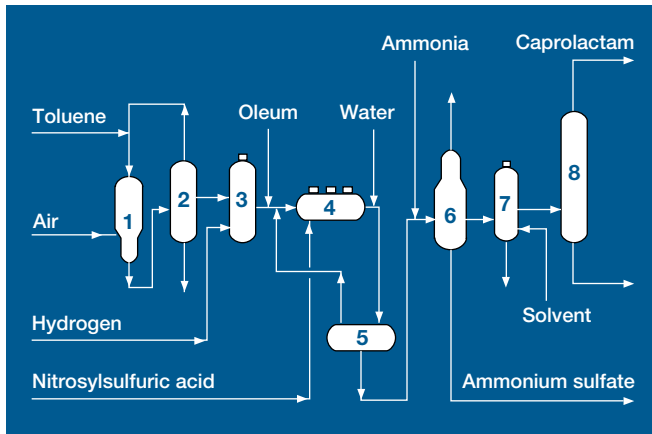
Propylene, kg (contained in chemical grade)	600
Synthesis Gas ($\text{CO} + \text{H}_2$), Nm^3	639

Commercial plants: The LP Oxo process has been licensed for 19 plants worldwide and is now used to produce more than 60% of the world's butylaldehyde capacity. Plants range in size from 30,000 to 350,000 tpy. The rhodium-based catalyst has a long life, and spent catalysts can be reactivated onsite. The technology is also practiced by Union Carbide Corp., at its Texas City and Taft plants.

Licensees: Nineteen worldwide since 1978.

Licensor: Kvaerner Process Technology/Union Carbide Corp., UK and U.S.

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Caprolactam

Application: A process to manufacture caprolactam from nitration-grade toluene. Fiber-grade flaked or molten caprolactam and white ammonium sulfate crystals are produced.

Description: Toluene and air are fed to the reactor (1) in which the oxidation to benzoic acid 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 byproducts. Fractionation (2) separates unconverted toluene for recycle, pure benzoic and a bottom fraction of heavy byproducts.

Benzoic acid is hydrogenated under pressure in presence of palladium catalyst in a series of continuous stirred tank reactors (3) at 170°C and 16 atm.

Conversion is complete in a single pass. Cyclohexane-carboxylic acid is blended with oleum and fed to a multistage reactor (4) 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.

Reactor effluent is diluted with water (5), and unconverted cyclohexane carboxylic acid is recycled to the process, while the lactam solution flows to the crystallization plant (6) where it is neutralized with ammonia. Ammonium sulfate crystallizes at bottom and the top organic layer of caprolactam is recovered and purified through a two-solvent (toluene and water) extraction (7) and a continuous fractionation (8).

Economics: Based on a 90,000-tpy battery limits plant, W. Europe, 1990:

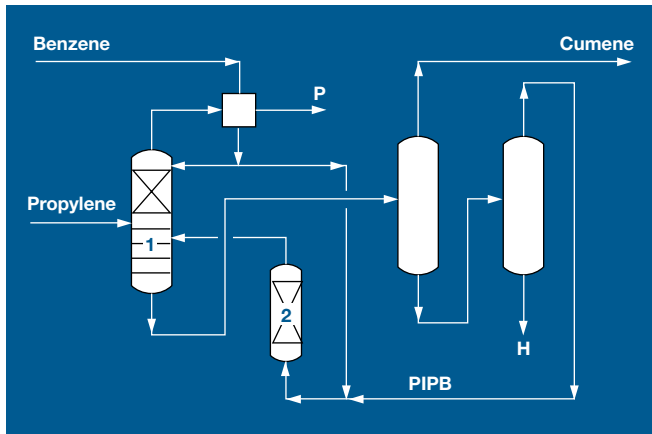
Investment, \$/tpy	2,800
Typical raw material and utility requirements, per kg of caprolactam:	
Toluene, kg	1.08
Ammonia, kg	1.14
Sulfur, kg	0.9
Hydrogen, Nm ³	0.8
Ammonium sulfate, kg, (credit)	(3.5)
Electricity, kWh	0.8
Steam, kg	11
Fuel gas, Nm ³	0.25
Water, cooling, m ³	0.6
Water, chilled, m ³	0.13

Commercial plants: 20,000-tpy SNIA BPD factory in Torviscosa, Italy; 80,000-tpy ANIC factory in Manfredonia, Italy; expansion to 88,000-tpy ELECTROCHIMPROM factory in Chirchik, URSS; 50,000-tpy plant, Shijiazhuang, China.

Reference: Taverna, M., and M. Chiti, *Hydrocarbon Processing*, November 1970, p. 137.

Licensors: SNIA BPD S.p.A., exclusive contractor: SNAICO Engineering S.p.A.

PETROCHEMICAL PROCESSES 2001



Cumene

Application: Advanced technology to produce ultra-high-purity cumene from propylene and benzene using catalytic distillation (CD) technology. The CDCumene process uses a specially formulated zeolite alkylation catalyst packaged in a proprietary CD structure and another specially formulated zeolite transalkylation catalyst in loose form.

Description: The CD column (1) combines reaction and fractionation in a single-unit operation. Alkylation takes place isothermally and at low temperature. CD also promotes the continuous removal of reaction products from reaction zones. These factors limit byproduct impurities and enhance product purity and yield. Low operating temperatures and pressures also decrease capital investment, improve operational safety and minimize fugitive emissions.

In the mixed-phase CD reaction system, propylene concentration in the liquid phase is kept extremely low (<0.1 wt%) due to the higher volatility of propylene to benzene. This minimizes propylene oligomerization, the primary cause of catalyst deactivation and results in catalyst run lengths of 3 to 5 years. The vapor-liquid equilibrium effect provides propylene dilution unachievable in fixed-bed systems, even with expensive reactor pumparound and/or benzene recycle arrangements.

Overhead vapor from the CD column (1) is condensed and returned as reflux after removing propane and lights (P). The CD column bottom section strips benzene from cumene and heavies. The distillation train separates cumene product and recovers polyisopropylbenzenes (PIPB) and some heavy aromatics (H) from the net bottoms. PIPB reacts with benzene in the transalkylator (2) for maximum cumene yield. Operating conditions are mild and noncorrosive; standard carbon steel can be used for all equipment.

Yields: 100,000 tons of cumene are produced from 65,100 tons of benzene and 35,100 tons of propylene giving a product yield of over 99.8%. Cumene product is at least 99.95% pure and has a Bromine Index less than 2, without clay treatment.

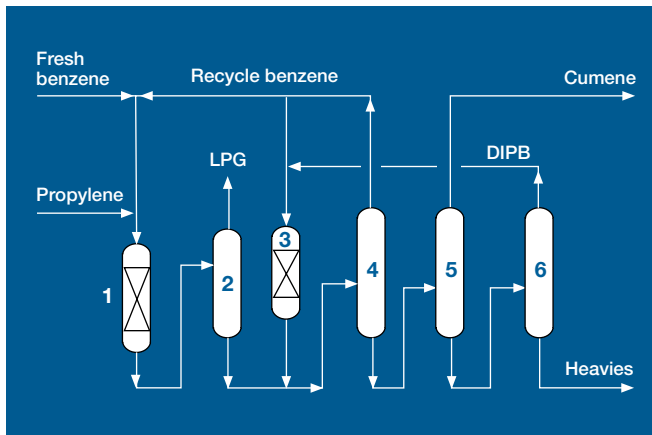
Economics: Based on a 100,000-tpy cumene plant located in the U.S. Gulf Coast, the inside-battery-limits investment is:

Typical operating requirements, per metric ton of cumene:

Catalyst, \$ avg	<3.0
Chemicals, \$	none
Utilities:	
Electricity, kWh	3
Heat (import), 10 ⁶ kcal	0.35
Steam (export), t	(0.893)
Water, cooling, m ³	2.9

Commercial plants: Formosa Chemicals & Fibre Corporation, Taiwan—270,000 mtpy.

Licensors: CDTECH, a partnership between ABB Lummus Global, and Chemical Research & Licensing.



Cumene

Application: The UOP Q-Max process produces high-quality cumene (isopropylbenzene) by alkylating benzene with typically refinery- or chemical-grade propylene. The process uses a proprietary zeolite catalyst that is regenerable and noncorrosive. Higher alkylate is converted to cumene via transalkylation, resulting in essentially stoichiometric cumene yield. Minimal impurities are formed, thus providing unsurpassed cumene product quality.

Description: Liquid propylene is mixed with fresh and recycle benzene and then fed to the fixed-bed alkylation reactor (1), where the propylene is completely consumed by alkylation with benzene. Alkylation reactor effluent flows to the depropanizer column (2), where the propane that accompanied the propylene leaves as LPG overhead product. The depropanizer bottoms flows to the benzene column

(4), where unreacted benzene is distilled to the overheads and recycled. Benzene column bottoms flows to the cumene column (5), where cumene product is recovered as the overhead stream. Cumene column bottoms, containing mostly diisopropylbenzene (DIPB), flow to the DIPB column (6). A small quantity of heavy byproduct is distilled to the DIPB column bottoms and is typically blended into fuel oil. The DIPB is combined with recycle benzene and fed to the transalkylation reactor (3), where the DIPB transalkylates with benzene to produce cumene. The transalkylation reactor effluent then flows to the benzene column (4).

Cumene yield of 99.7 wt% and higher along with cumene product purity of 99.96–99.97 wt% are achieved.

The zeolite catalyst is noncorrosive and operates at mild conditions, allowing carbon-steel construction. Catalyst cycle lengths are two years and longer. The catalyst is regenerable for ultimate catalyst life of six years and longer. Existing plants that use SPA or A1C13 catalyst can be revamped to gain the advantages of Q-Max cumene technology while increasing plant capacity.

Economics: Based on a world-scale plant (500,000-tpa cumene production):

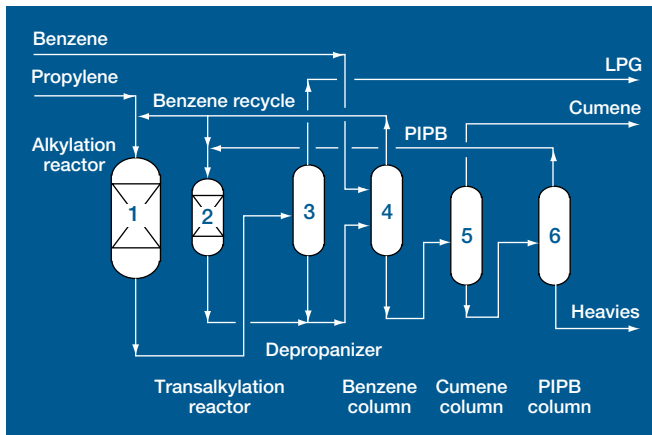
Inside battery limits erected cost, U.S.	
Gulf Coast, \$million	22
Utility requirements, per metric ton of cumene product:	
Power, electric, kWh	11
Heat input, million kcal	0.32
Water, cooling, m ³	5

The Q-Max design is typically tailored to provide optimal utility advantage for the plant site, such as minimizing heat input for stand-alone operation or recovering heat as steam for use in a nearby phenol plant.

Commercial plants: Three commercial units are in operation, one unit is in design/construction.

Licensors: UOP.

PETROCHEMICAL PROCESSES 2001



section. The distillation section consists of as many as four columns in series. The depropanizer (3) recovers propane overhead as LPG. The benzene column (4) recovers excess benzene for recycle to the reactors. The cumene column (5) recovers cumene product overhead. The PIPB column (6) recovers PIPB overhead for recycle to the transalkylation reactor.

Process features: The process allows substantial increase in capacity to existing cumene plants while improving product purity, feedstock consumption and utility consumption. The new catalyst is environmentally inert, does not produce byproduct oligomers or coke and can operate at extremely low benzene to propylene ratios with proven commercial cycle lengths of over three years. Expected catalyst life is well over five years.

Yield and product purity: This process is essentially stoichiometric and product purity above 99.97 wt% has been regularly achieved in commercial operation.

Economics: Estimated ISBL investment for a 300,000 mtpy unit on the U.S. Gulf Coast (2000 construction basis), is \$ U.S. 15 million.

Utility requirements, per ton of cumene product:

Heat, MMkcal (import)	0.32
Steam, ton (export)	(0.60)

The utilities can be optimized for specific site conditions/economics and integrated with an associated phenol plant.

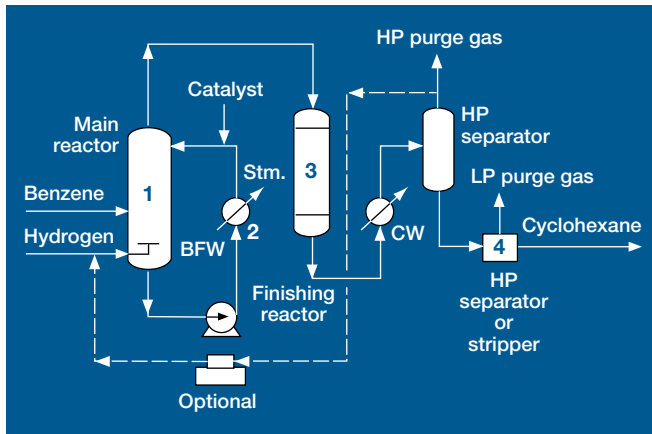
Commercial plants: The first commercial application of this process came onstream in 1996. At present, there are seven operating plants with a combined capacity exceeding 3 million mtpy. In addition, three revamped facilities and one grassroots plant with a combined capacity of over 1.5 million mtpy will be onstream by the year 2001. At that time, more than 50% of the worldwide cumene production will be from plants using the Mobil/Badger process.

Licensors: The Badger Technology Center of Washington Group International, Inc.

Cumene

Application: To produce cumene from benzene and any grade of propylene—including lower-quality refinery propylene-propane mixture—using the Mobil/Badger process and a new generation of zeolite catalysts from ExxonMobil.

Description: The process include: a fixed-bed alkylation reactor, a fixed-bed transalkylation reactor and a distillation section. Liquid propylene and benzene are premixed and fed to the alkylation reactor (1), where propylene is completely reacted. The alkylation reactor effluent is fed to the distillation section. Separately, recycled polyisopropylbenzene (PIPB) is premixed with benzene and fed to the transalkylation reactor (2), where PIPB reacts to form additional cumene. The transalkylation reactor effluent is fed to the distillation



Cyclohexane

Application: Produce high-purity cyclohexane by liquid-phase catalytic hydrogenation of benzene.

Description: The main reactor (1) converts essentially all the feed isothermally in the liquid phase at a thermodynamically-favorable low temperature using a continuously-injected soluble catalyst. The catalyst's high activity allows use of relatively low hydrogen partial pressure, which results in fewer side reactions, e.g., isomerization

or hydrocracking. The heat of reaction vaporizes cyclohexane product and, using pumparound circulation through an exchanger, also generates steam (2). With the heat of reaction being immediately removed by vaporization, accurate temperature control is assured. A vapor-phase fixed-bed finishing reactor (3) completes the catalytic hydrogenation of any residual benzene. This step reduces residual benzene in the cyclohexane product to very low levels. Depending on the purity of the hydrogen make-up gas, the stabilization section includes either an LP separator (4) or a small stabilizer to remove the light ends.

A prime advantage of the liquid-phase process is its substantially lower cost compared to vapor phase processes: investment is particularly low because a single, inexpensive main reactor chamber is used compared to multiple-bed or tubular reactors used in vapor phase processes. Quench gas and unreacted benzene recycles are not necessary and better heat recovery generates both the cyclohexane vapor for the finishing step and a greater amount of steam. These advantages result in lower investment and operating costs. Operational flexibility and reliability are excellent; changes in feedstock quality and flows are easily handled. Should the catalyst be deactivated by feed quality upsets, fresh catalyst can be injected without shutting down.

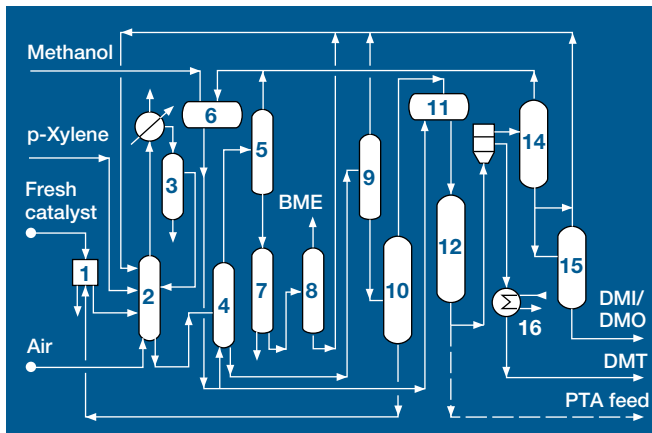
Yield: 1.075 kg of cyclohexane is produced from 1 kg of benzene.

Economics: Basis: 200,000-tpa cyclohexane complex, ISBL 2000 Gulf Coast location with PSA hydrogen is 7.6 million \$U.S. Catalyst cost is \$U.S. 2/metric ton of product.

Installation: Twenty-nine cyclohexane units have been licensed.

Licensor: IFP, IFPNA.

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Dimethyl terephthalate

Application: To produce fiber-grade dimethyl terephthalate (DMT) from p-xylene and methanol.

Description: A mixture of p-xylene and p-methyl toluate is oxidized (2, 3) with air in the presence of heavy metal catalysts to produce p-toluic acid and monomethyl terephthalate. These acids are then converted to p-methyl toluate and DMT. No reaction solvent is necessary during oxidation. The p-xylene and p-methyl toluate are continuously oxidized at 140°C to 170°C and 4 to 8 bar:

The oxidate is esterified (4) at 250°C to 280°C and 20 to 25 bar. Overhead methanol from the esterifier is distilled (5) and recycled (6).

Crude ester from the esterifier bottoms (4) is distilled in a column (9) where overhead p-methyl toluate is recycled to the oxidizer and bottom product is separated in a second column (10) into crude DMT overhead (11) and residue bottom.

Further purification of DMT is done by crystallization from methanol (12). DMT is separated from methanol in centrifuges (13) to fiber-grade DMT (melting point of approximately 141°C). Filtrate is distilled (14) while overhead methanol is recycled to the methanol tank (6). The isomers are purged (15) of recycle material. DMT in molten form (16) can be fed directly into polycondensation or transported in tankcars to the fiber plant.

Economics: Basis is a 200,000-tpy standard plant, West German conditions, December 2000, including compressor station, incinerator for wastewater and offgas, hot-oil heating system and catalyst regeneration.

Investment, German conditions,

Total, DM/tpy 1,100

Raw materials and utilities consumption, per ton of product:

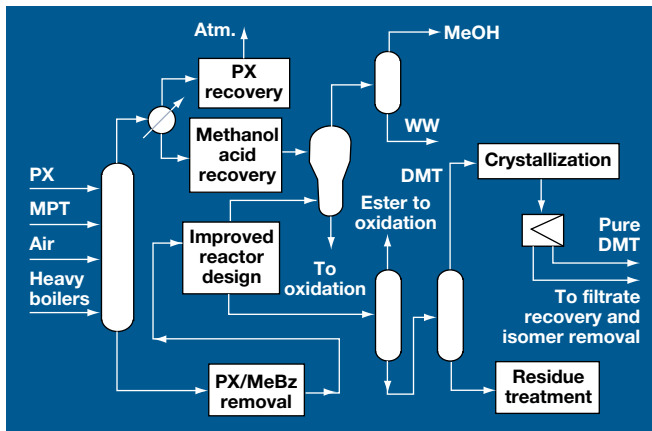
p-Xylene, kg	610
Methanol, kg	360
Fuel, GJ	3.7
Electric power, kWh	400

Joint PTA and DMT production in one plant is possible.

Commercial plants: Degussa AG operates plants at Lüssdorf and Steyerberg with a total capacity of 480,000 tpy. The process has been licensed worldwide for more than 25 plants with a total capacity of about 3 MMtpy.

Reference: *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A26, 1995, pp. 193–204.

Licensors: Degussa AG.



Dimethyl terephthalate

Application: To increase capacity and reduce energy usage of existing or grassroots dimethyl terephthalate (DMT) production facilities using variations of GT-DMT proprietary technology.

Description: The common production method of DMT from paraxylene and methanol is through successive oxidations in four major steps: oxidation, esterification, distillation and crystallization. A mixture of p-xylene and methyl p-toluate (MPT) is oxidized with air using a heavy-metal catalyst. All organics are recovered from the offgas and recycled to the system. The acid mixture from the oxidation is esterified with methanol and produces a mixture of esters. The crude ester mixture is distilled to remove all heavy boilers and residue produced; lighter esters are recycled to the oxidation section. Raw DMT is then sent to the crystallization section

to remove DMT isomers and aromatic aldehydes.

The technology improvements enhance the traditional processing in each section. The adaptations include: changes in process configurations and operating conditions, altering the separation schemes, revising the recovery arrangement, increasing the value of the byproducts and reducing the overall plant recycles.

GTC Technology offers complete implementation of the technology and overall plant reviews for selective improvements to reduce operating and overall production costs. Some separate improvements available are:

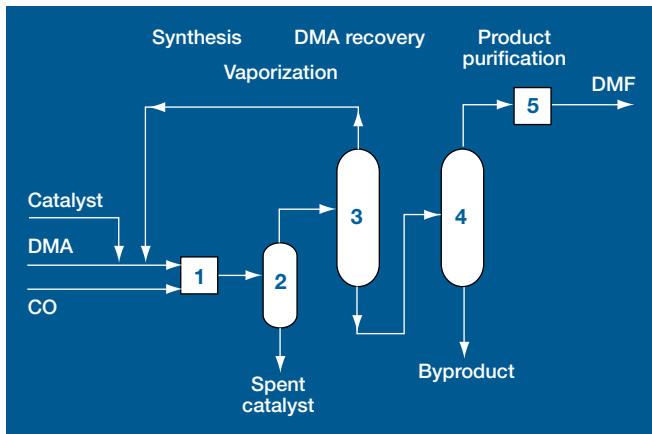
1. Oxidation optimization reduces byproduct formation, thus lowering p-xylene consumption
2. Recoveries of byproducts for sale such as methyl benzoate (MeBz) and acetic and formic acid
3. Improved esterifier reactor design enables higher throughputs and improves methanol usage
4. Enhanced isomer removal minimizes DMT losses
5. Improved crystallization schemes for reduced energy, lowers methanol handling and losses, improves purity and operating flexibility
6. Integration of steam usage in the plant for considerable savings on operating costs
7. Operating reviews to reduce operating downtime and extend online factors
8. Advanced control models for improved operability.

Economics: Based on process modifications, an existing DMT plant can increase production with an investment of \$200 to \$600/ton/yr of additional capacity. A new plant will have an investment reduction of about 20% equipment cost. Raw material consumption per ton of product (with the complete modification) is 605 ton of paraxylene and 360 ton of methanol.

Commercial plants: GT-DMT technology is used by seven DMT producers.

Licensor: GTC Technology Corp.

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Dimethylformamide

Application: To produce dimethylformamide (DMF) from dimethylamine (DMA) and carbon monoxide (CO).

Description: Anhydrous DMA and CO are continuously fed to a specialized reactor (1), operating at moderate conditions and containing a catalyst dissolved in solvent. The reactor products are sent to a separation system where crude product is vaporized (2) to separate the spent catalyst. Excess DMA and catalyst solvent are stripped (3) from the crude product and recycled back to the reaction system. Vacuum distillation (4) followed by further purification (5) produces a high-quality solvent and fiber-grade DMF product. A saleable byproduct stream is also produced.

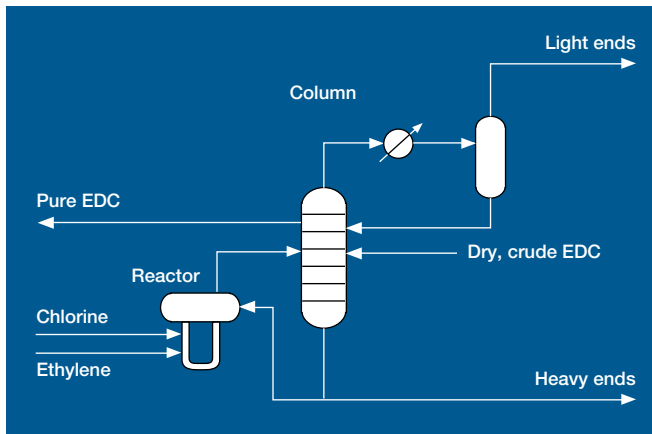
Yields: Greater than 95% on raw materials. CO yield is a function of its quality.

Economics: Typical performance data per ton of product:

Dimethylamine, t	0.63
Carbon monoxide, t	0.41
Steam, t	1.3
Water, cooling, m ³	100
Electricity, kWh	10

Commercial plants: Thirteen plants in eight countries use this process with a production capacity exceeding 100,000 mtpa.

Licensors: Kvaerner Process technology, UK.



EDC by direct chlorination—high temperature

Application: Inovyl's high temperature chlorination (HTC) is an energy-efficient process to produce ethylene dichloride (EDC) from ethylene and chlorine. Energy is conserved by using the exothermic heat of reaction to vaporize the EDC, thus product purification can be done by fractional distillation. Unlike with the LTC process, waterwashing the product to remove dissolved ferric chloride is not necessary. Therefore, no aqueous effluent treatment is required.

Sufficient heat is available to purify other EDC streams in a bal-

anced VCM plant, the EDC from oxychlorination and LTC EDC. Steam consumption is substantially reduced.

Description: The unique reactor design uses a simple vertical U-shaped leg connected to a horizontal gas-liquid separation vessel. Reactant gases are fed to the bottom of the "U" where they dissolve and combine under sufficient static pressure to prevent boiling in the reaction zone. Above this zone, the heat of reaction produces vapor bubbles that flow upwards into the horizontal vessel. A natural circulation of EDC is induced by the density difference in the two legs of the "U."

Since its original development by Stauffer Chemical Co. about 22 years ago, the technology has been widely licensed with 11 operating units. Much expertise has gone into process development. The key to good performance lies in choosing appropriate materials of construction, distribution of feed gases and minimizing tars production.

Advantages: The principle advantages for the HTC process are:

- **Energy savings.** The net import of steam in a balanced plant may be reduced by about 0.8 tons of steam per ton of VCM product.
- **Product purity.** EDC produced from the HTC system can be sent directly to a cracking furnace or sold externally.
- **High safety performance.** Inovyl has developed a robust instrument control and protective system to cater for all known process hazards.
- **High raw material efficiencies.** The HTC reactor converts ethylene and chlorine feed gases to pure EDC at efficiencies of 98.5% and 99.0% respectively.
- **Well-proven, reliable design.** With no moving parts, and well-chosen materials of construction the HTC reactor has a demonstrated long life and low maintenance demands. Many licensees have achieved onstream factors of 98% exclusive of programmed plant turnarounds.
- **Reduced wastewater.** The EDC product needs no washing, thus, lowering wastewater volume to be post treated. Also, caustic soda consumption is very low for the HTC process.

Licensors: Inovyl B.V., the technology business of EVC.

EDC via lean oxychlorination

Application: The modern Vinnolit oxychlorination process produces EDC by an exothermic reaction from feedstocks including ethylene, anhydrous hydrogen chloride and oxygen. Anhydrous hydrogen chloride can be used from the VCM process as well as from other processes like isocyanates (MDI, TDI), chlorinated methanes, chlorinated ethanes, epichlorohydrin, etc.

Description: Oxygen can be used from air separation plant, as well as, from the cost-effective pressure swing adsorption (PSA) process. The Vinnolit oxychlorination process is also able to handle ethylene and/or anhydrous hydrogen chloride containing vent streams from direct chlorination, acetaldehyde, monochloro acetic acid and other processes.

The exothermic reaction is catalyzed by a copper chloride catalyst in a single-step, fluidized-bed reactor at temperatures of 200°C–220°C. The heat of reaction is recovered by producing 10-barg steam or heating other heat-transfer fluids.

Catalyst fines are removed with a newly developed hot-gas catalyst filter or alternatively by wastewater treatment that meets even the strictest regulations for copper, dioxins and furanes. The environmentally friendly process uses recycle gas, which is fed back to the reactor after condensing EDC and water. After EDC removal, the process water meets even the most stringent environmental requirements.

After removal of carbon dioxide (CO₂) and chloral/chloroethanol, the crude EDC is purified in the EDC distillation unit; it can be used as furnace feed or sales EDC. The important process features and advantages are:

- **Reliability:** A stable temperature control combined with an excellent heat transfer and a uniform temperature profile (no hot spots) in the fluidized bed easily achieves an on - stream time > 99 % per year. A specially designed raw-material sparger system allows

operation spans of two years without maintenance. Larger heat-transfer area allows a higher steam temperature and pressure in the cooling coils, which improves the safety margin to the critical surface temperature where hydrochloric acid dewpoint corrosion may occur.

- **Safety:** The oxygen is mixed with anhydrous hydrochloride outside the reactor and is fed independently of the ethylene into the fluidized bed. The oxygen concentration in the recycle stream is approx. 0.5 vol%, which are well outside the explosion range.

- **Flexibility:** A turndown ratio as low as 20 % capacity utilization can be achieved, as well as, quick load changes.

- **Low manufacturing costs:** The unlimited catalyst service is combined with the low losses via the highly efficient cyclone system (less than 20g catalyst per ton of produced EDC). High raw-material yields (98.5 % ethylene, 99 % anhydrous hydrochloride and 94 % oxygen) and the possibility to use low-cost oxygen from PSA units ensure a highly competitive process with low production costs.

- **Environmentally friendly:** Yields of 99 % are the key for a low byproduct formation. A highly efficient, hot-gas filtration system recovers the small quantities of catalyst fines. Besides the EDC removal via steam stripping, no additional wastewater treatment is required. The charter for European Council for Vinyl Manufacturers (ECVM) is easily met (EDC < 5 g/t of EDC purification capacity, copper < 1 g/t of Oxychlorination capacity, dioxin- like components < 1 µg TEQ/t of Oxychlorination capacity).

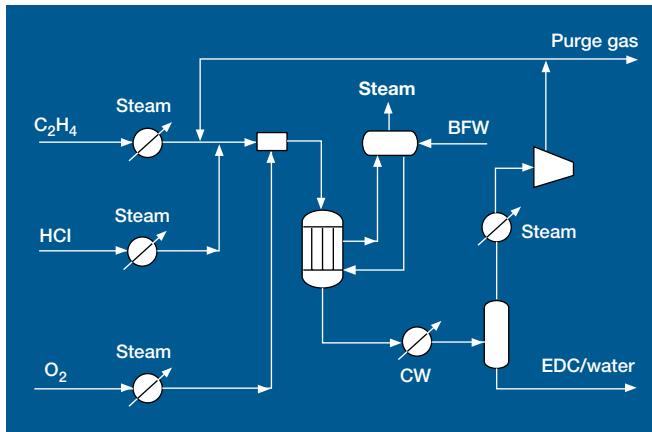
Process data and crude EDC purity:

Operating temperature, °C:	200–225
Operating pressure, barg:	2.5–4
Steam pressure, barg:	10

Commercial plants: The process is used in 13 reactors at 10 sites, alone as HCl-consuming plant or as part of the balanced VCM process. In some cases, it has replaced oxychlorination technologies by modifying existing reactors that do not use the Vinnolit process. Two reactors at two sites will be commissioned soon.

Licensor: Vin Tec; **preferred contractor:** Krupp Uhde GmbH.

PETROCHEMICAL PROCESSES 2001



EDC via oxychlorination-single stage

Application: In the balanced vinyl chloride (VCM) process, pure oxygen and ethylene are used in the oxychlorination (also known as oxy) step to convert hydrogen chloride into ethylene dichloride (EDC) with minimum vent gas, and without any micro-pollutant or heavy metals contamination of wastewater, or costly catalyst sludge accumulation.

Description: A single jacketed fixed-bed reactor removes the heat of the reaction by producing high-pressure steam. The process is carried out with a large ethylene excess. The flexibility of catalyst staging, reactor temperature profiles, and feed flowrates with EVC's single reactor system, produces maximum throughput with minimal byproducts. After condensation and separation of the reaction products (EDC and water), excess ethylene is compressed and recirculated.

A purge gas stream is withdrawn to control inerts buildup. This purge is normally dried and can be sent to direct chlorination for recovery of its ethylene content.

Operation conditions. A specially designed oxygen mixer and the interlock system assure safe operation outside the flammability envelope. Simple design and high quality material specifications result in two to three year intervals between major turnarounds and on stream times as high as 98+% over one year. The heat of reaction is recovered as high-pressure steam (18+ barg), which can be used by other parts of the VCM process (e.g., pyrolysis). Wastewater does not contain suspended catalyst fines; therefore, there is no need to settle them and then dispose as a hazardous waste. Copper levels in fixed-bed effluents are below 0.3 ppm; thus, no treatment is required.

Economics: For a balanced plant producing 300,000 mtpy of VCM, the estimated U. S. Gulf Coast ISBL capital investment is U.S. \$20 million.

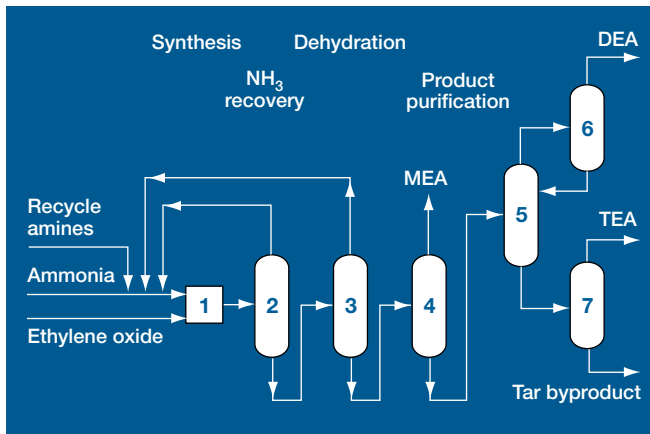
Raw material and utilities: Ethylene and hydrogen chloride selectivities of 98+% are typical with HCl conversion of 99.8+%. Operating in an ethylene-rich environment, the process produces only about half as much CO and CO₂ as typical fluid-bed processes. Typical operating requirements per metric ton of EDC are:

Hydrogen chloride, t	0.748
Ethylene, t	0.288
Oxygen, t	0.170
Water, cooling, m ³	48
Electricity, kWh	50
Refrigeration, kcal	1320
Steam generated at 17.5 bar g, t	0.850

Commercial plants: EVC's fixed-bed oxygen-based oxy process has been in commercial operation since 1979. Since then, 18 plants have been commissioned with capacities ranging from 50,000 to 600,000 mtpy. EVC's single-stage fixed-bed oxy process is operating in Runcorn, UK.

Licensors: Inovyl B.V., the technology business of EVC.

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Description: Ammonia solution, recycled amines and ethylene oxide are fed continuously to a reaction system (1) that operates under mild conditions and simultaneously produces MEA, DEA and TEA. Product ratios can be varied to maximize MEA, DEA or TEA production. The correct selection of the NH₃/EO ratio and recycling of amines produces the desired product mix. The reactor products are sent to a separation system where ammonia (2) and water are separated and recycled to the reaction system. Vacuum distillation (4,5,6,7) is used to produce pure MEA, DEA and TEA. A saleable heavy tar byproduct is also produced. Technical grade TEA (85 wt%) can also be produced if required.

Yields: Greater than 98% on raw materials.

Economics: Typical performance data per ton amines MEA/DEA/TEA product ratio of 1/2 : 1/2 : 1/2

Ethylene oxide, t	0.82
Ammonia, t	0.19
Steam, t	5
Water, cooling, m ³	300
Electricity, kWh	30

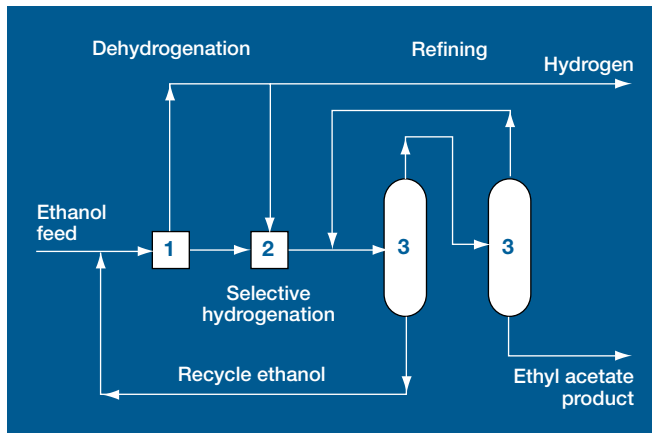
Commercial plants: One 20,000-mtpa original capacity facility.

Licensor: Kvaerner Process Technology, UK.

Ethanolamines

Application: To produce mono-(MEA), di-(DEA) and triethanolamines (TEA) from ethylene oxide and ammonia.

PETROCHEMICAL PROCESSES 2001



Ethyl acetate

Application: To produce ethyl acetate from ethanol without acetic acid or other co-feeds.

Description: Ethanol is heated and passed through a catalytic dehydrogenation reactor (1) where part of the ethanol is dehydrogenated to form ethyl acetate and hydrogen. The product is cooled in an

integrated heat-exchanger system; hydrogen is separated from the crude product. The hydrogen is mainly exported. Crude product is passed through a second catalytic reactor (2) to allow “polishing” and remove minor byproducts such as carbonyls.

The polished product is passed to a distillation train (3) where a novel distillation arrangement allows the ethanol/ethyl acetate water azeotrope to be broken. Products from this distillation scheme are unreacted ethanol, which is recycled, and ethyl acetate product.

The process is characterized by low-operating temperatures and pressures, which allow all equipment to be constructed from either carbon steel or low-grade stainless steels. It allows ethyl acetate to be made without requiring acetic acid as a feed material. The process is appropriate for both synthetic ethanol and fermentation ethanol as the feed. The synthetic ethanol can be impure ethanol without significantly affecting the conversion or selectivity. The product ethyl acetate is greater than 99.95%.

Economics: Typical performance data per ton of ethyl acetate produced:

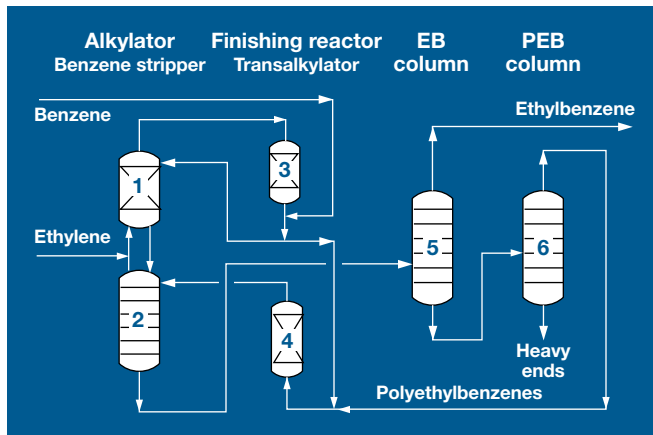
Feedstock	1.12 tons of ethanol
Product	45 kg of hydrogen

Commercial plants: The technology has been developed during the mid to late 1990's. The first commercial plant is a 50,000-tpy plant in South Africa, using synthetic ethanol.

Licensees: One since 1998.

Licensor: Kvaerner Process Technology, UK.

PETROCHEMICAL PROCESSES 2001



Ethylbenzene

Application: To produce ethylbenzene (EB) by alkylating benzene with ethylene using a patented ethylbenzene (EB) fixed-bed, catalytic distillation technology with a zeolite catalyst.

Description: The alkylator (1) and benzene stripper (2) operate together as a distillation column. Alkylation and distillation occur in the alkylator (1) in the presence of a zeolite catalyst packaged in patented structured packing. Unreacted ethylene and benzene vapor from the alkylator top are condensed and fed to the finishing reactor (3) where the remaining ethylene reacts over zeolite catalyst pellets. The benzene stripper bottoms is fractionated (5&6) into EB prod-

uct, higher ethylated benzenes and heavy ends. The higher ethylated benzenes are transalkylated with benzene over zeolite catalyst pellets in the transalkylator (4) to produce additional EB. The ethylene can be polymer grade or, with only minor differences in the process scheme, dilute ethylene containing as little as 10 mol% ethylene. The catalyst is removed and sent to an outside facility for regeneration (ex situ). Reactors are designed for 2 to 4 years of uninterrupted run-length. The process does not produce any hazardous effluent. Low operating temperatures allow using carbon steel for all equipment.

Yields and product quality: Both the alkylation and transalkylation reactions are highly selective, producing few byproducts. The EB product has a high purity (99.9 wt% minimum) and is suitable for styrene-unit feed. Xylene make is less than 50 ppm, thus ensuring that the styrene product is acceptable for polymerization usage. The process has an overall theoretical yield of 99.5%.

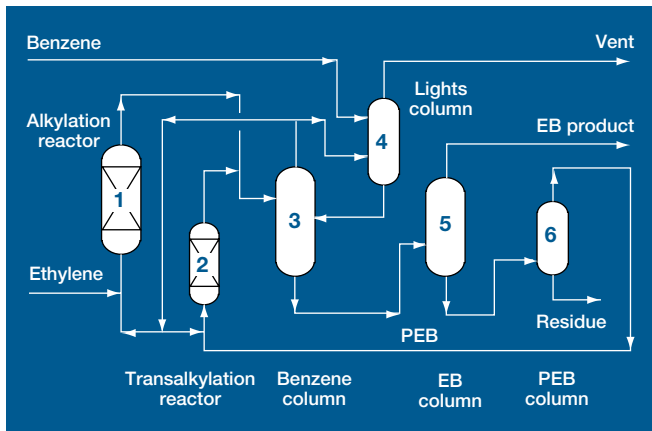
Economics: The EB process features consistent product yields, high-product purity, low-energy consumption, low investment cost and easy, reliable operation.

Raw materials and utilities, based on one metric ton of EB:

Ethylene, kg	266
Benzene, kg	739
Electricity, kWh	27
Water, cooling, m ³	9
Steam, tons (export)	1.5
Hot oil, 10 ⁶ kcal	0.7

Commercial plants: Two commercial plants are in operation in Argentina and Canada with capacities from 140,000 tpy to 477,000 tpy. They process ethylene feedstocks with purities ranging from 75% ethylene to polymer-grade ethylene.

Licensor: ABB Lummus Global.



EB enter the transalkylation reactor. Effluents from the alkylation and transalkylation reactors are fed to the benzene column (3), where unreacted benzene is recovered from crude EB. The fresh benzene feedstock and a fraction of the benzene distillate are fed to the lights column (4) to reject light impurities. The lights column bottoms is returned to the benzene column. The bottoms from the benzene column is fed to the EB column (5) to recover EB product. The bottoms from the EB column is fed to the PEB column (6) where recyclable alkylbenzenes are recovered as a distillate and diphenyl compounds are rejected in a bottoms stream that can be used as fuel.

Catalysts: Cycle lengths in excess of four and three years are expected for the alkylation and transalkylation catalysts respectively. Process equipment is fabricated entirely from carbon steel. Capital investment is reduced as a consequence of the high activity and extraordinary selectivity of the alkylation catalyst and the ability of both the alkylation and transalkylation catalysts to operate with very low quantities of excess benzene.

Product quality: The ethylbenzene product contains less than 100 ppm of C₈ plus C₉ impurities. Product purities of 99.95% to 99.99% are expected.

Economics:

Raw materials and steam, tons per ton of EB product

Ethylene	0.266
Benzene	0.739
Steam, high-pressure used	1.01
Steam, medium-and low-pressured generated	1.42

Utilities can be optimized for specific-site conditions.

Commercial plants: Since the commercialization of the Mobil/Badger EB technology in 1980, 42 licenses have been granted. Total licensed capacity for the EBMax technology exceeds 5.2 million mtpy.

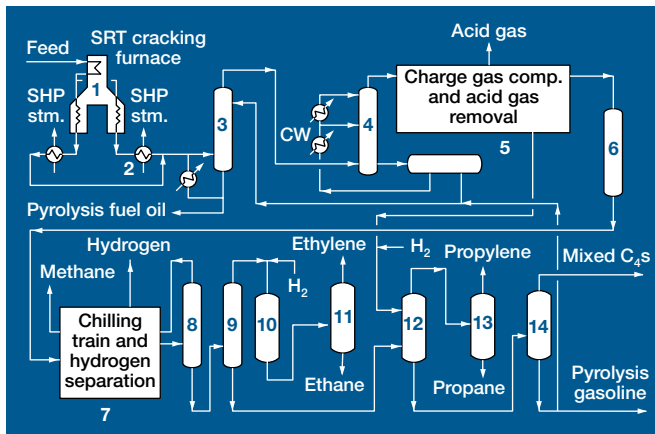
Licensor: The Badger Technology Center of Washington Group International, Inc.

Ethylbenzene

Application: To produce ethylbenzene (EB) from benzene and a polymer-grade ethylene or an ethylene-rich ethylene/ethane feedstock using the Mobil/Badger EBMax process and proprietary ExxonMobil alkylation and transalkylation catalysts. The technology can be applied in the design of grassroots units, upgrading of existing vapor-phase technology plants, or conversion of aluminum chloride technology EB plants to zeolite technology.

Description: Ethylene reacts with benzene in a liquid-filled alkylation reactor (1) containing multiple fixed-beds of ExxonMobil's proprietary catalyst, forming EB and very small quantities of polyethylbenzenes (PEB). In the transalkylation reactor (2), PEB is converted to EB by reaction with benzene over ExxonMobil's transalkylation catalyst. PEB and benzene recovered from the crude

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Ethylene

Application: To produce polymer-grade ethylene (99.95 vol%). Major byproducts are propylene (chemical or polymer-grade), a butadiene-rich C₄ stream, C₆ to C₈ aromatics-rich pyrolysis gasoline and high-purity hydrogen.

Description: Hydrocarbon feedstock is preheated and cracked in the presence of steam in tubular SRT (short residence time) pyrolysis furnaces (1). This approach features extremely high olefin yields, long runlength and mechanical integrity. The products exit the furnace at 1,500°F to 1,600°F and are rapidly quenched in the transfer line exchangers (2) that generate super high-pressure (SHP) steam. The latest generation furnace design is the SRT VI.

Furnace effluent, after quench, flows to the gasoline fractionator (3) where the heavy oil fraction is removed from the gasoline and lighter fraction (liquids cracking only). Further cooling of furnace effluents is

accomplished by a direct water quench in the quench tower (4).

Raw gas from the quench tower is compressed in a multistage centrifugal compressor (5) to greater than 500 psig.

The compressed gas is then dried (6) and chilled. Hydrogen is recovered in the chilling train (7), which feeds the demethanizer (8). The demethanizer operates at about 100 psia, providing increased energy efficiency. The bottoms from the demethanizer go to the deethanizer (9).

Acetylene in the deethanizer overhead is hydrogenated (10) or recovered. The ethylene-ethane stream is fractionated (11) and polymer-grade ethylene is recovered. Ethane leaving the bottom of the ethylene fractionator is recycled and cracked to extinction.

The deethanizer bottoms and condensate stripper bottoms from the charge compression system are depropanized (12). Methylacetylene and propadiene are hydrogenated in the depropanizer using CDHYDRO catalytic distillation hydrogenation technology. The depropanizer bottoms is separated into mixed C₄ and light gasoline streams (14). Polymer-grade propylene is recovered in a propylene fractionator (13).

Yields: Data for various feedstocks to maximize ethylene are:

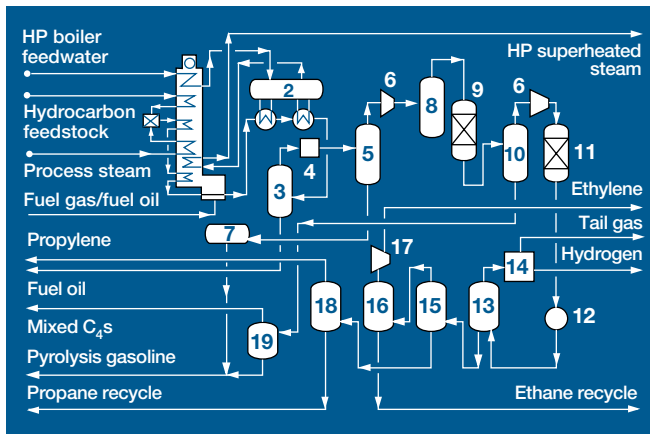
Feedstock	Ethane	Propane	n-Butane	Full range naphtha	Gas oils			
					Atm. Light	Atm. Heavy	Vacuum	Hydrocrackate
Ethylene, wt%	84.0	45.0	44.0	34.4	28.7	25.9	22.0	34.7
Propylene, wt%	1.4	14.0	17.3	14.4	14.8	13.6	12.1	14.2
Butadiene, wt%	1.4	2.0	3.0	4.9	4.8	4.9	5.0	5.2
Aromatics, wt%	0.4	3.5	3.4	14.0	16.6	13.3	8.5	13.0

Energy consumption: Energy consumptions are 3,300 kcal/kg of ethylene produced for ethane cracking and 5,000 kcal/kg of ethylene for naphtha feedstocks. Energy consumption can be as low as 4,000 kcal/kg of ethylene for naphtha feedstocks with gas turbine integration.

Commercial plants: Approximately 40% of the world's ethylene plants use Lummus' ethylene technology. Many existing units have been significantly expanded (above 150% of nameplate) using Lummus' MCET (maximum capacity expansion technology) approach.

Licensors: ABB Lummus Global.

PETROCHEMICAL PROCESSES 2001



Ethylene

Application: High-performance steam cracking and recovery to produce polymer-grade ethylene, polymer-grade propylene, butadiene-rich mixed C₄s, aromatic-rich pyrolysis gasoline, hydrogen and fuel streams. Cracking feedstocks range from ethane to vacuum gas oils.

Description: Kellogg Brown & Root's proprietary SCORE olefins technology is the integration of the technologies of the former M.W. Kellogg and Brown & Root companies combined with olefins technology developed by ExxonMobil Chemical Co., through a long-term, worldwide licensing agreement. In addition to their cracking technology contributions to the SCORE technology, ExxonMobil provides a unique enhancement to bring the benefits of extensive operating experience to further improve operability and reliability, and further reduce production costs.

The SCORE pyrolysis furnace portfolio includes a range of designs to satisfy any operating company requirements in terms of feedstock

flexibility and performance. The straight tube SC-1 design provides low reaction times, in the range of 0.1 seconds, high outlet temperatures, in the range of 870°C and low operating pressures. The designs and operating conditions enhance olefin-forming reactions, and thus produce higher olefin yields.

The pyrolysis furnace effluent is processed for heat and product recovery in an efficient, low-cost recovery section. The recovery section design can be optimized for specific applications and/or selected based on operating company preferences. Flow schemes based on demethanizer first, deethanizer first and depropanizer first configurations are available for particular applications. Shown above is the depropanizer first scheme, which is primarily applicable to liquid crackers.

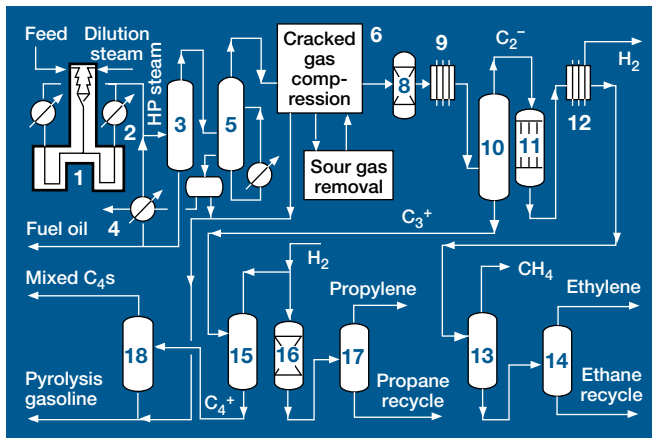
The cracked gases are cooled and fractionated to remove fuel oil and water (2–5) then compressed (6), processed for acid-gas removal (8) and dried (9). The C₃ and lighter material is separated as an overhead product in the depropanizer (10) and acetylene is hydrogenated in the acetylene converter (11). The acetylene converter effluent is processed in the demethanizer system (12–14) to separate the fuel gas and hydrogen products. The demethanizer bottoms is sent to the deethanizer (15) from which the overhead flows to the C₂-splitter (16), which produces the polymer-grade ethylene product and the ethane stream, which is recycled to the furnaces as a feedstock. The deethanizer bottoms flows to the C₃-splitter (18) where the polymer-grade propylene is recovered as the overhead product. The C₃-splitter bottoms product, propane, is typically recycled to the furnaces as a feedstock. The depropanizer bottoms product, C₄s and heavier, flow to the debutanizer (19) for recovery of the mixed-C₄ product and aromatic-rich pyrolysis gasoline.

Yields: Ethylene yields to 84% for ethane, 38% for naphtha and 32% for gas oils may be achieved depending upon feedstock characteristics.

Installations: KBR has been involved in over 140 ethylene projects worldwide with 21 new grassroots ethylene plants since 1990. Facilities using KBR olefins technology have included feedstocks ranging from ethane to vacuum gas oil and single-train ethylene capacities of nearly 1.3 million tpa.

Licensors: Kellogg Brown & Root.

PETROCHEMICAL PROCESSES 2001



Ethylene

Application: To produce polymer-grade ethylene and propylene by thermal cracking hydrocarbon fractions—ethane through naphtha and hydrocracker residue. Byproducts are a butadiene-rich C_4 stream, C_6 – C_8 gasoline stream rich in aromatics and fuel oil.

Description: Fresh feedstock and recycle streams are preheated and pyrolyzed in the presence of dilution steam in highly selective pyrocrack type furnaces (1). Pyrocrack furnaces are optimized with respect to residence time, temperature and pressure profiles for each feedstock, thus achieving the highest olefin yields. Furnace effluent is cooled in transfer line exchangers (TLEs) (2), generating HP steam, and by direct quenching with oil for liquid feedstock processing.

Combined cracked-gas stream is cooled and purified in the primary fractionator (3) and quench-water tower (5). Waste heat is recovered

by a circulating oil cycle, generating dilution steam (4), and a water cycle (5) to provide heat to reboilers and process heaters. Purified gas from the quench tower is compressed (6) in a 4- or 5-stage compressor and dried in gas and liquid adsorbers (8). CO_2 and H_2S are removed in a caustic-wash system located prior to the last compressor stage.

Compressed-cracked gas is further cooled (9) and fed to the recovery process; front-end deethanizer (10), isothermal C_2 front-end hydrogenation reactor (11), cold train (12), demethanizer (13) and the heat-pumped low-pressure ethylene fractionator (14) which is integrated into the ethylene refrigeration cycle. This well proven Linde process is highly optimized, resulting in high flexibility, easy operation, low-energy consumption, low investment costs and long intervals between major turnarounds (typically five years).

C_3^+ material from the deethanizer bottom (10) is depropanized (15), hydrotreated (16) to remove methylacetylene and propadiene and fractionated to recover polymer-grade propylene. C_4 components are separated from heavier components in the debutanizer (18) to recover raw C_4 product and a C_5 stream that forms a gasoline product when combined with hydrocarbon condensates from the hot section.

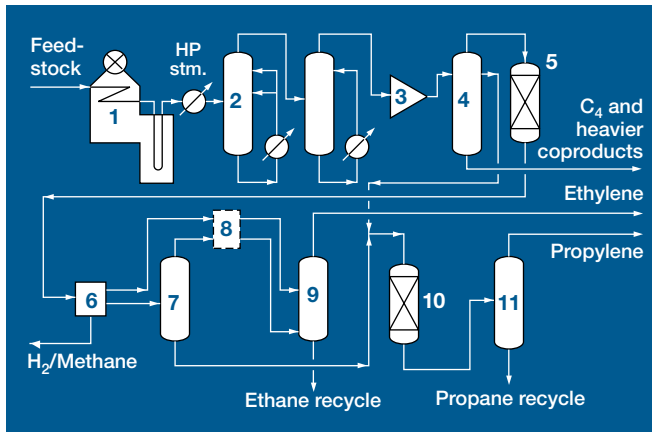
Economics: Ethylene yields vary between 25%, 35%, 45% and 83% for gas oils, naphtha, LPG and ethane, respectively. Related specific energy consumption ranges from 6,000, 5,000, 4,000, 3,000 kcal/kg C_2H_4 . Typical installation costs for a large-scale inside battery limit gas (naphtha) cracker on a Gulf Coast basis are 500 (750) \$U.S./ton of installed ethylene capacity.

Commercial plants: Over 15 million tons of ethylene production in more than 40 plants are in commercial use. Many plants have been expanded in capacity by 50%.

Recent awards for world-scale ethylene plants for Borouge in Abu Dhabi, Optimal in Malaysia, Amir Kabir in Iran and Marun in Iran. The latter plant represents the largest olefin plant with a production of 1.1 million mtpy ethylene and 200,000 mtpy propylene.

Licensors: Linde AG.

PETROCHEMICAL PROCESSES 2001



Ethylene

Application: To produce polymer-grade ethylene and propylene by thermally cracking paraffinic feedstocks (ethane through hydrocracked residue). Two main process technologies are used:

1. USC (ultra selective cracking)—Pyrolysis and quench systems
 2. ARS (advanced recovery system)—Cold fractionation.
- Designs have been incorporated to meet environmental restrictions.

Description: Feeds are sent to USC cracking furnaces (1). Contaminants removal may be installed upstream. A portion of the cracking heat may be supplied by gas turbine exhaust. Pyrolysis occurs within the temperature-time requirements specific to the feedstock and product requirements. Rapid quenching preserves high-olefin yield and the waste heat generates high-pressure steam. Lower temperature waste heat is recovered in the downstream quench oil and quench water towers (2) and used in the recovery process. Pyrolysis fuel oil and gaso-

line distillate are fractionated. Cracked gas (C₄ and lighter) is then compressed (3), scrubbed with caustic to remove acid gases and dried prior to fractionation. C₂ and lighter components are separated from the C₄ and heavier components in the low fouling front-end dual pressure depropanizer (4). Overhead vapor is hydrogenated to remove acetylene (5) and is routed to the ARS (6).

ARS minimizes refrigeration energy by using simultaneous heat and mass transfer in the dephlegmator (exclusive arrangement with Air Products) and distributed distillation. Two C₂ streams of varying composition are produced. Hydrogen and methane are separated overhead.

The heavier C₂ stream is deethanized (7) and C₂ overhead passes to the ethylene-ethane fractionator (9). The wider C₂ stream is routed directly to the ethylene-ethane fractionator (9). Polymer-grade ethylene product is sent overhead from the ethylene-ethane fractionator. Acetylene recovery may optionally be installed upstream of the ethylene-ethane fractionator (8).

C₃s are combined and hydrogenated to remove methyl acetylene and propadiene (10). Polymer or chemical-grade propylene is then produced overhead from the C₃ superfractionator (11).

C₄ and heavier coproducts are further separated in a sequence of distillation steps. Ethane and propane are typically recycle cracked. Refrigeration is supplied by cascade ethylene/propylene systems.

Specific advantages of ARS technology are: 1. reduced chilling train refrigeration requirements in the dephlegmator, 2. simultaneous chilling/prefractionation in the dephlegmator, 3. reduced methane content in feed to demethanizer, 4. partial deethanizer bypassing, 5. dual feed ethylene fractionator (lower reflux ratio) and 6. reduced refrigeration demand (approx. 75%).

Economics: Ethylene yields range from 57% (ethane, high conversion) to 28% (heavy hydrogenated gas oils). Corresponding specific energy consumptions range from 3,000 kcal/kg to 6,000 kcal/kg.

Commercial plants: Over 100 ethylene units have been built by Stone & Webster. Expansion techniques based on ARS technology have achieved up to 70% capacity increase.

Licensors: Stone & Webster Inc., a Shaw Group Co.

Ethylene

Application: To produce polymer-grade ethylene and propylene, a butadiene-rich C_4 cut, an aromatic C_6 – C_8 rich-raw pyrolysis gasoline and high-purity hydrogen by steam pyrolysis of hydrocarbons ranging from ethane to vacuum gas oils.

Description: For either gaseous (ethane/propane) or liquid (C_4 /naphtha/gasoil) feeds, this technology is based on Technip's proprietary pyrolysis furnaces and progressive separation. It produces olefins at low energy consumption and particularly low environmental impact.

Hydrocarbon feedstocks are preheated (also to recover heat) and then cracked with steam in a tubular pyrolysis furnace with outlet temperatures ranging from 1,500°F to 1,600°F. The furnace technology can be either an SMK type (for gas cracking) or GK style (for liquid cracking). The GK design can be oriented to a high olefins yield with very flexible propylene/ethylene ratios (GK5 or the latest generation GK6), or to a high BTX production (GK3 type). This approach allows long run length, excellent mechanical integrity and attractive economics.

The hydrocarbon mixture at the furnace outlet is quenched rapidly in the transfer line exchangers (TLE or SLE), generating high-pressure steam. In liquid crackers, cracked gas flows to a primary fractionator, after direct quench with oil, where fuel oil is separated from gasoline and lighter components, and then to a quench-water tower for water recovery (to be used as dilution steam) and heavy gasoline production (end-point control).

A multistage compressor, driven by a steam turbine, compresses the cooled gas. LP and HP condensate are stripped in two separate strippers where medium gasoline is produced and part of the C_3 + cut is recovered respectively. A caustic scrubber removes acid gases.

Compressed gas at 450 psig is dried and then chilled. A double demethanizing stripping system operating at medium pressure and reboiled by cracked gas minimizes the refrigeration required (heat integration), as well as, the investment for separating methane (top) and C_2 + cut (bottoms). A dual-column concept (absorber concept) is applied between the secondary demethanizer overheads and the chilled

cracked that minimizes the ethylene losses with a low energy requirement. The high-purity hydrogen is produced in a cold box.

The bottoms from the two demethanizers (of different quality) are sent to the deethanizer. The progressive separation allows the deethanizer reflux ratio to be reduced. The deethanizer overhead is selectively hydrogenated for acetylene conversion before the ethylene splitter where ethylene is separated from ethane. The residual ethane is recycled for further cracking.

The HP stripper and deethanizer bottoms (of different quality) are fed to a two-column dual pressure depropanizing system for C_3 -cut separation from the C_4 cut and heavies, thus providing low fouling at minimum energy consumption.

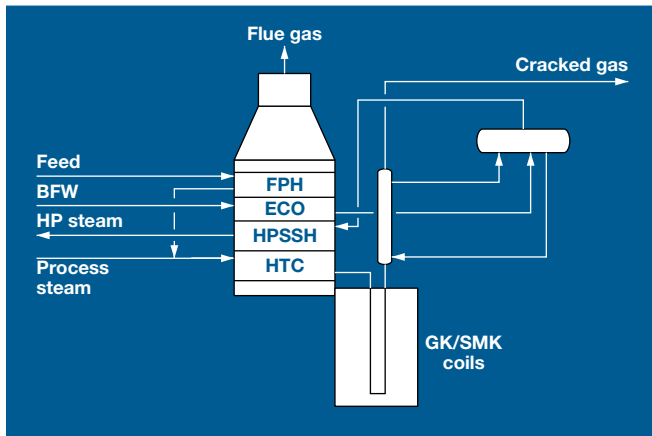
The methyl-acetylene and propadiene in the C_3 cut are hydrogenated to propylene in a liquid-phase reactor. Polymer-grade propylene is separated from propane in a C_3 -splitter. The residual propane is either recycled for further cracking, or exported. C_4 s and light gasoline are separated in a debutanizer. Gas expansion (heat recovery) and external cascade using ethylene and propylene systems supply refrigeration.

Economics: Ultimate range of ethylene yields vary from 83% (ethane) to around 25% (vacuum gas oils), 35% for the intermediate full-range naphtha. These correspond to the respective total olefins yields (ethylene and propylene) from 84% (ethane) to 38% (vacuum gas oils), and 49% for an intermediate full range naphtha. The specific energy consumption range is 3,00 kcal/kg ethylene (ethane) to 5,500 kcal/kg ethylene (gas oil), and 4,700 Kcal/Kg ethylene for an intermediate full-range naphtha.

Commercial plants: Technip has been awarded a 1 MMtpy in late 2000, while over 300 cracking furnaces have been built, and 15 units operate world-wide. Numerous expansions over the nominal capacity based on progressive separation techniques are under way, with up to an 80% increase in capacity.

Licensors: Technip.

PETROCHEMICAL PROCESSES 2001



Ethylene

Application: Thermal cracking of a wide range of feedstocks into light olefins and aromatics using proprietary cracking coils.

Feedstocks: Ethane through to heavy feeds up to 600°C EP.

Products: Cracked gas rich in ethylene, propylene, butadiene and BTX.

Description: Thermal cracking occurs in presence of steam at high temperatures in cracking coils located centrally in the firebox. Coil outlet temperatures vary up to 880°C depending on feed quality and cracking severity. The proprietary cracking coils are the GK5, GK6 and SMK coils. They feature high selectivity to ethylene and propylene, together with low coking rates (long run lengths).

Cracked gases from the furnace pass through a transferline exchanger (TLE) system, where heat is recovered to generate high-pressure steam. The primary TLEs are linear or special S and T type exchangers. The selected exchanger type ensures low to very low fouling rates and, thus extends run lengths. Heat from the flue gases is recovered in the convection section to preheat feed and process steam, and to superheat generated HP Steam. The technology may be applied to retrofit furnaces. Furnace performance is optimized using proprietary SPYRO programs. NO_x abatement technology is incorporated.

Performance data:

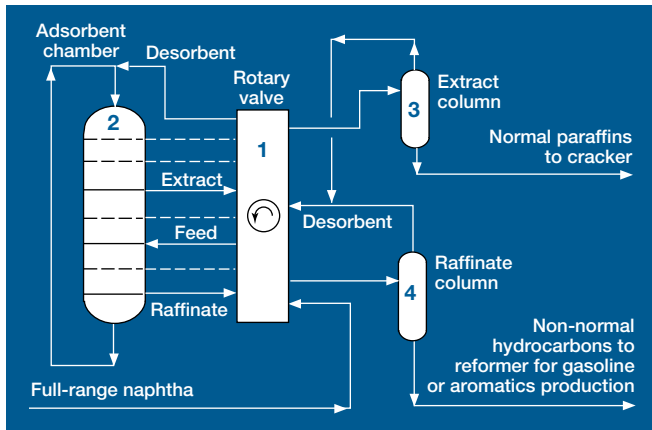
Ethane conversion, %	65–75
Naphtha cracking severity (as P/E)	0.40–0.70
Overall thermal efficiency,	92–95
Coil residence time, sec	—GK5/GK6 coils 0.15–0.25
	—SMK coil 0.35–0.40

Once-through ethylene yields depend on feed characteristics and severity, and range from 58% for ethane to 36% for liquid feeds.

Installations: Over 450 installations since the mid-1960.

Licensor: Technip.

PETROCHEMICAL PROCESSES 2001



Description: The separation takes place in an adsorption chamber (2) that is divided into a number of beds. Each bed contains proprietary shape-selective adsorbent. Also, each bed in the chamber is connected to a rotary valve (1). The rotary valve is used along with the shape-selective adsorbent to simulate a moving bed counter-current adsorptive separation. Four streams are distributed by the rotary valve to and from the adsorbent chamber. The streams are as follows:

- **Feed:** The naphtha feed contains a mixture of hydrocarbons.
- **Extract:** This stream contains n-paraffin and a liquid desorbent. Naphtha, rich in n-paraffin, is recovered by fractionation (3) and is sent to the naphtha cracker.
- **Raffinate:** This stream contains non-normal paraffin and a liquid desorbent. Naphtha, depleted in n-paraffin, is recovered by fractionation (4) and is sent to a refinery or an aromatics complex.
- **Desorbent:** This stream contains a liquid desorbent that is recycled from the fractionation section to the chamber.

The rotary valve is used to periodically switch the position of the liquid feed and withdrawal points in the adsorbent chamber. The process operates in a continuous mode at low temperatures in a liquid phase.

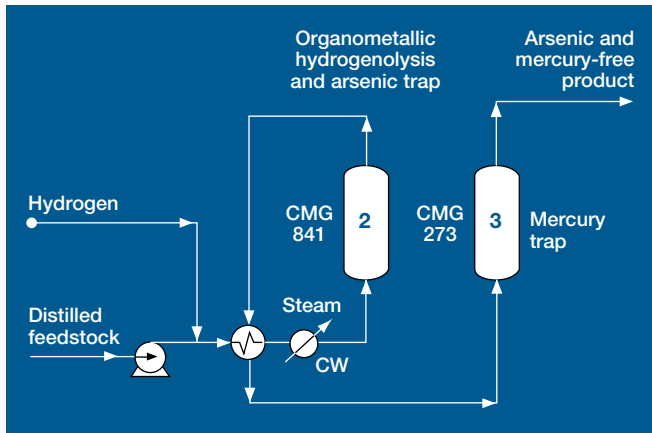
Economics: For increase in naphtha-cracker ethylene production from 247,000 mtpy to 330,000 mtpy, based on U.S. Gulf Coast:

Investment cost, \$ million	80
Increased margin, \$ million/yr	28.6
Simple ROI, %	36

Licensors: UOP.

Ethylene

Application: The MaxEne process increases the ethylene yield from naphtha crackers by raising the concentration of normal paraffins (n-paraffins) in the naphtha-cracker feed. The MaxEne process is the newest application of UOP's Sorbex technology. The process uses adsorptive separation to separate C_5 - C_{11} naphtha into a rich n-paraffins stream and a stream depleted of n-paraffins.



Ethylene feed pretreatment—mercury, arsenic and lead removal

Application: Upgrade natural gas condensate and other contaminated streams to higher-value ethylene plant feedstocks. Mercury, arsenic and lead contamination in potential ethylene plant feedstocks precludes their use, despite attractive yield patterns. The contaminants poison catalysts, cause corrosion in equipment and have undesirable environmental implications. For example, mercury compounds poison hydrotreating catalysts and, if present in the steam-cracker feed, are distributed in the C_2 – C_5^+ cuts. A condensate containing mercury may have negative added-value as a gas field product.

Description: Three RAM processes are available to remove arsenic (RAM I); arsenic, mercury and lead (RAM II); and arsenic, mercury and sulfur from liquid hydrocarbons (RAM III). Described above is the RAM II process. Feed is heated by exchange with reactor effluent and steam (1). It is then hydrolyzed in the first catalytic reactor (2) in which organometallic mercury compounds are converted to elemental mercury, and organic arsenic compounds are converted to arsenic-metal complexes and trapped in the bed. Lead, if any, is also trapped on the bed. The second reactor (3) contains a specific mercury-trapping mass. There is no release of the contaminants to the environment, and spent catalyst and trapping material can be disposed of in an environmentally acceptable manner.

Typical RAM II Performance

Contaminant	Feedstock	Product
Mercury, ppb	2000	< 1*
Arsenic, ppb	100	< 1*

* 3 ppb is the threshold limit of the analytical procedure commonly used. With provisions for eliminating solid matter, water and free oxygen and using a more sensitive method, levels of less than one ppb can be achieved.

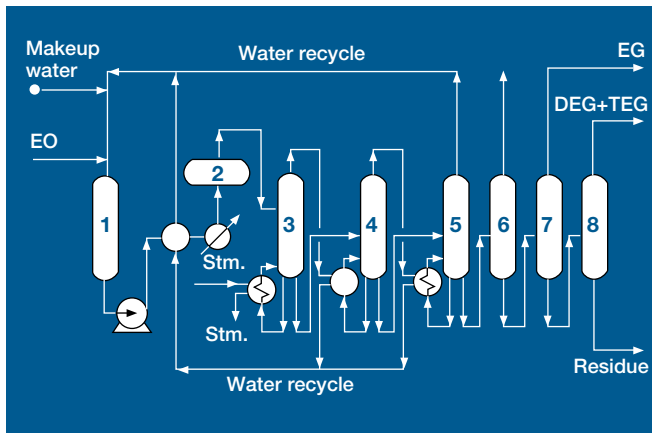
Economics: The ISBL 2000 investment at a Gulf Coast location for two condensates each containing 50-ppb average mercury content (max. 500 ppb), 10 ppb arsenic and 120 ppb lead excluding basic engineering, detailed engineering, offsites, contractor fees:

	Clear, oxygen-free condensate	Aerated condensate with particulate matter
Investment, \$U.S./bpd	125	170
Utilities, \$U.S./bpd	0.08	0.23
Catalyst cost, \$U.S./bpd	0.03	0.03

Commercial plants: Fourteen RAM units have been licensed worldwide.

References: Didillon, B., L. Savary, J. Cosyns, Q. Debuisschert, and P. Travers, "Mercury and Arsenic Removal from Ethylene Plant Feedstocks," Second European Petrochemicals Technology Conference, Prague, 2000.

Licensor: IFP, IFPNA.



Ethylene glycols

Application: To produce ethylene glycols (MEG, DEG, TEG) from ethylene oxide (EO).

Description: The flowsheet shown is only one of several possible schemes. The raw materials to a free-standing glycol plant are refined ethylene oxide and pure water. These are mixed with recycle waters and pumped from a feed tank (1) to the hydration reactor after being preheated with hot recycle water and steam. When the glycol unit is part of a combined oxide/glycol plant, it is economically desirable to feed it bleed streams from the ethylene oxide

unit. Since this stream can affect product quality, additional proprietary treatment is necessary. The SD process is also able to simplify the combined oxide/glycol plants by feeding crude oxide solution (aqueous) from the ethylene oxide reaction unit directly to the glycol reaction and omitting the usual oxide refining step.

In the glycol reactor (2), sufficient residence time is provided to react (noncatalytically) all of the ethylene oxide. Operating pressure of the reaction is controlled at a level that limits or avoids vaporization of ethylene oxide from the aqueous solution.

The water-glycol mixture from the reactor is fed to the first stage (3) of a multiple stage evaporator, which is reboiled using high pressure steam. The remaining stages (4, 5) of the evaporator operate at successively lower pressures, with the final stage (5) normally under vacuum. Evaporated water is recovered as condensate and recycled back to the glycol reaction feed-mixing tank (1)—or to the oxide reaction section in combined oxide/glycol plants.

Concentrated crude glycol solution from the final evaporation stage is stripped of remaining water and light ends in the light-ends column (6). The water-free glycol mixture is then fractionated in a series of vacuum distillation towers (7, 8) to produce purified monoethylene glycol (MEG) of fiber-grade quality and byproduct diethylene glycol (DEG) and triethylene glycol (TEG).

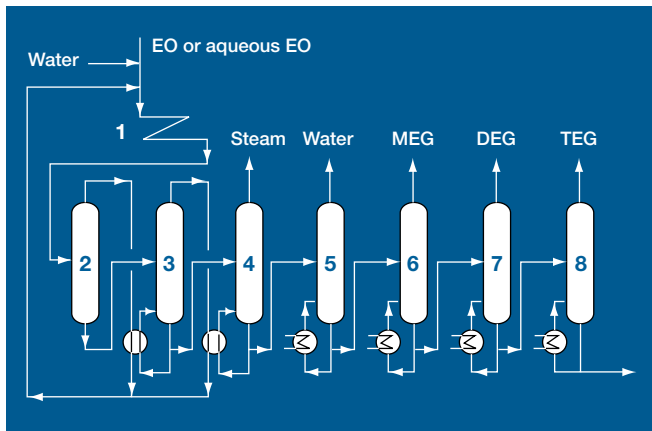
Product quality: The glycol quality produced in these plants has set a new standard in the industry.

Yields: Conversion is essentially complete and quantitative.

Commercial plants: Over 60 ethylene glycol projects have been completed or are in the design stage.

Reference: *Encyclopedia of Chemical Processing and Design*.

Licensors: Scientific Design Co., Inc.



Ethylene glycols

Application: To produce ethylene glycols (MEG, DEG and TEG) from ethylene oxide (EO).

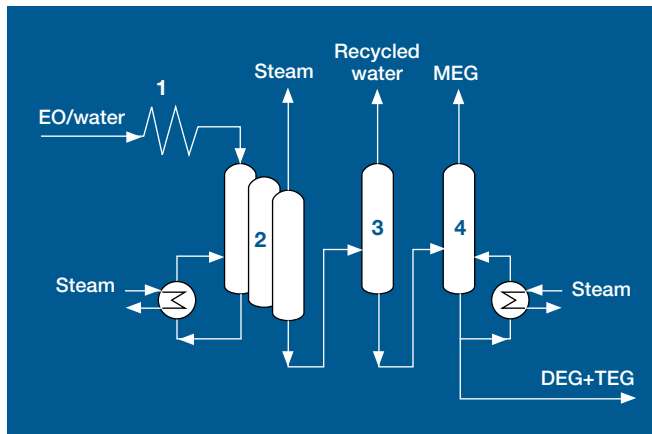
Description: Purified EO or a water/EO mixture is combined with recycle water and heated to reaction conditions. In the tubular reactor (1), essentially all EO is thermally converted into monoethylene glycol (MEG) with diethylene glycol (DEG) and triethylene glycol (TEG) as co-products in minor amounts. Excess water, required to achieve a high MEG selectivity is evaporated in a multi-stage evaporator (2,3). The last evaporator (4) produces low-pressure steam, which is used as a heat medium for other units in the plant. Crude glycol is purified in a series of vacuum columns (5,6,7,8). Selectivity toward MEG can be controlled with the feed composition.

Most MEG plants are integrated with EO plants. In an integrated EO/MEG plant, the steam system can be optimized to fully exploit the benefits from the high selectivity catalyst in the EO plant. However, stand-alone MEG plants have been designed and built.

Glycols manufactured by this process are among the highest quality in the world; these products easily and consistently meet the most stringent specifications used in polyester fiber and PET production.

Commercial plants: Since 1958, 60 MEG plants have been started up or are under construction.

Licensor: Shell International Chemicals B.V.



Ethylene glycol

Application: To produce ethylene glycols (MEG, DEG, TEG) from ethylene Oxide (EO) using the Union Carbide Meteor process.

Description: In the Meteor Process, an EO/water mixture is preheated and fed directly to an adiabatic reactor (1), which can operate with or without a catalyst. An excess of water is provided to achieve high selectivities to monoethylene glycol (MEG). Diethylene (DEG) and triethylene (TEG) glycols are produced as coproducts. In a catalyzed mode, higher selectivities to MEG can be obtained,

thereby reducing DEG production to one-half that produced in the uncatalyzed mode. The reactor is specially designed to fully extract all of the EO and to minimize back-mixing, which promotes enhanced selectivity to MEG.

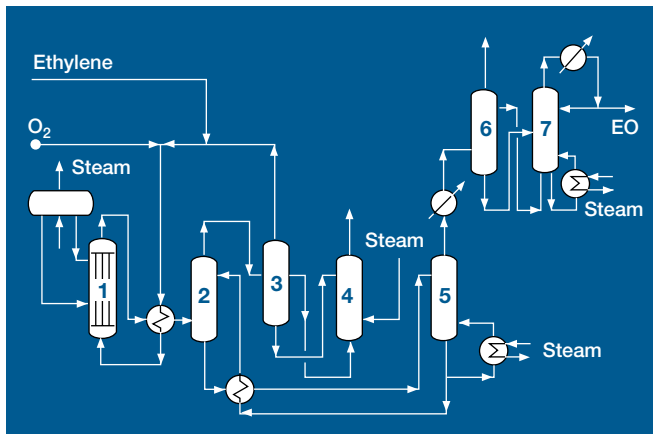
Excess water from the reactor effluent is efficiently removed in a multi-effect evaporation system (2). The last-effect evaporator overhead produces low-pressure steam, which is a good low-level energy source for other chemical units or other parts of the EO/MEG process. The concentrated water/glycols stream from the evaporation system is fed to the water column (3) where the remaining water and light ends are stripped from the crude glycols. The water-free crude glycol stream is fed to the MEG refining column (4) where polyester-grade MEG, suitable for polyester fiber and PET production, is recovered. DEG and TEG exiting the base of the MEG refining column can be recovered as high-purity products by subsequent fractionation.

Economics: The conversion of EO to glycols is essentially complete. The reaction not only generates the desired MEG, but also produces DEG and TEG that can be recovered as coproducts. The production of more DEG and TEG may be desirable if the manufacturer has a specific use for these products or if market conditions provide a good price for DEG and TEG relative to MEG. A catalyzed process will produce less and heavier glycols. The ability to operate in catalyzed or uncatalyzed mode provides flexibility to the manufacturer to meet changing market demands.

Installations: Since 1954, 18 UCC-designed glycol plants have been started up or are under construction.

Licensors: Union Carbide Corp., a subsidiary of The Dow Chemical Co. Univation Technologies is the licensor of the UNIPOL PE process.

PETROCHEMICAL PROCESSES 2001



Ethylene oxide

Application: To produce ethylene oxide (EO) from ethylene using oxygen as the oxidizing agent.

Description: The flowsheet for an oxygen-based unit is one of several possible process schemes. Compressed oxygen, ethylene and recycle gas are mixed and fed to a multitubular catalytic reactor (1). The temperature of oxidation is controlled by boiling water in the shell side of the reactor.

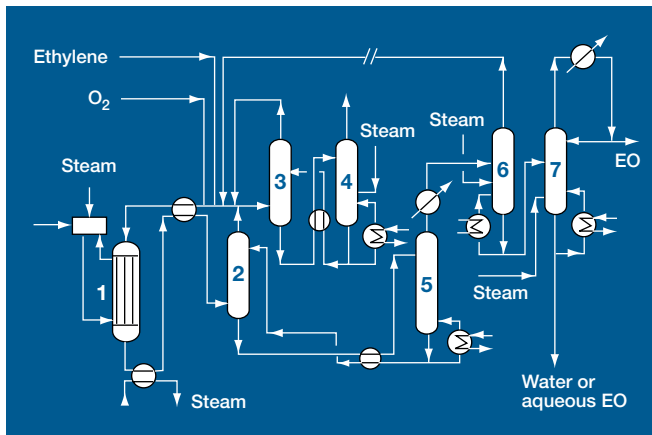
From the reactor, the effluent gases containing ethylene oxide are first cooled by recuperative exchange with recycle gases. The gases then pass to a scrubber (2) where the ethylene oxide is absorbed as a dilute aqueous solution. Most of the unabsorbed gases are compressed and returned to the reactor via the recuperative exchanger, thus completing a closed circuit. A portion of the recycle gas is diverted through a CO₂ removal system (3, 4) before being returned to the reaction system.

Ethylene oxide is steam-stripped (5) from the EO-rich absorber bottoms and recovered as refined or purified product in a fractionation train (6, 7).

Yields: The weight yield of purified EO (kg per kg ethylene feed) is in excess of 120%. In addition, a significant amount of technical-grade glycol may be recovered by processing waste streams.

Commercial plants: Over 100 ethylene oxide projects have been completed or are being designed. This represents a total design capacity of about 5 MMtpy of ethylene oxide.

Licensors: Scientific Design Co., Inc.



Ethylene oxide

Application: To produce ethylene oxide (EO) in a direct oxidation process from ethylene and oxygen.

Description: In the direct oxidation process, ethylene and oxygen are mixed with recycle gas and passed through a multi-tubular catalytic reactor (1) to selectively produce EO. A special silver catalyst (high-selectivity catalyst) is used; it has been improved significantly over the years. Methane is used as ballast gas. Heat generated by

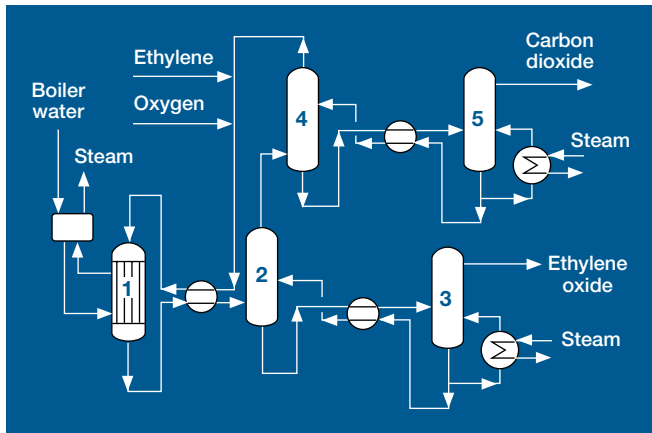
this reaction is absorbed by boiling water at elevated pressure in the reactor's shell side; this recovered energy is then used to produce steam. EO contained in the reactor-product gas is absorbed in water (2). Unabsorbed gases are compressed, mixed with fresh feed and returned to the reactor. Part of the recycle gas is treated in the activated CO_2 removal section, to remove the inevitably co-produced CO_2 (3,4). The EO-containing water stream from the absorber is concentrated in a stripper (5). Light impurities in the crude EO are removed (6) and compressed back into the recycle gas. Crude EO can be further concentrated into high-purity EO (7), or a water/EO mixture can directly be sent to the monoethylene glycol (MEG) plant and converted into ethylene glycols.

Most EO plants are integrated with MEG facilities. When only EO is required, a small amount of technical grade MEG is inevitably co-produced. In a combined EO/MEG plant, all MEG produced is fiber grade. In an integrated EO/MEG facility, the steam system can be optimized to fully exploit benefits of the high selectivity catalyst.

Yields: Recent plants are designed for and operate at a molar selectivity approaching 90% with fresh catalyst, resulting in more than 1.4 tons of EO produced per ton of ethylene. The process is designed to operate for three years at average cycle selectivity of over 86%. However, this technology is flexible, thus a four-year operating run length is possible.

Commercial plants: Since 1958, 60 Shell-designed plants have been started up or are under construction. Almost seven millions tons of EO equivalents per year (approximately 43% of the total world capacity) are produced in Shell-designed plants.

Licensors: Shell International Chemicals B.V.



Ethylene oxide

Application: To produce ethylene oxide (EO) from the direct oxidation of ethylene using the Union Carbide Meteor process.

Description: The Meteor Process, a technology first commercialized by Union Carbide in 1994, is a simpler, safer process for the production of EO, having lower capital investment requirements and lower operating costs. In the Meteor Process, ethylene and oxygen are mixed with methane-ballast recycle gas and passed through a single-train, multitubular catalytic reactor (1) to selectively produce EO. Use of a single reactor is one example of how the Meteor process is a simpler, safer technology. It lowers facility investment costs.

The technology is used in the only operating world-scale EO facilities with a single reactors. The special high-productivity Meteor EO catalyst provides very high efficiencies while operating at high loadings. Heat generated by the reaction is removed and recovered by the direct boiling of water to generate steam on the shell side of the reactor. Heat is recovered from the reactor outlet gas before it enters the EO absorber (2) where EO is scrubbed from the gas by water. The EO-containing water from the EO absorber is concentrated by stripping (3). The cycle gas exiting the absorber is fed to the CO₂ removal section (4,5) where CO₂, which is co-produced in the EO reactor, is removed via activated, hot potassium carbonate treatment. The CO₂ lean cycle gas is recycled by compression back to the EO reactor.

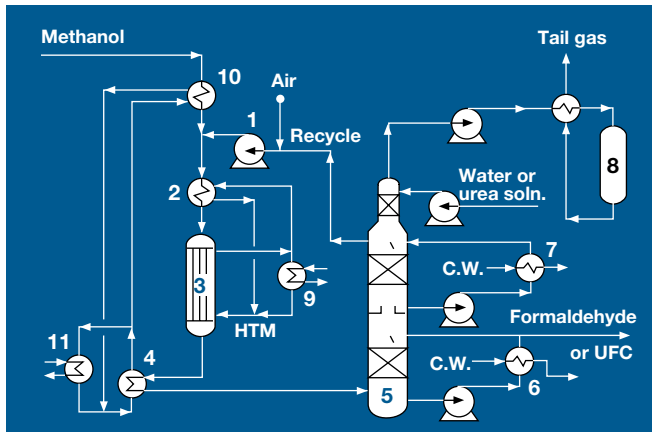
Most EO plants are integrated with glycol production facilities. When producing glycols, the EO stream (3) is suitable for feeding directly to a Meteor glycol process. When EO is the desired final product, the EO stream (3) can be fed to a single purification column to produce high-purity EO. This process is extremely flexible and can produce the full range of product mix between glycols and purified EO.

Economics: The process requires a lower capital investment and has lower fixed costs due to process simplicity and the need for fewer equipment items. Lower operating costs are also achieved through the high-productivity Meteor EO catalyst, which has very high efficiencies at very high loadings.

Installations: Union Carbide was the first to commercialize the direct oxidation process for EO in the 1930's. Since 1954, 18 UCC-designed plants have been started up or are under construction. Three million tons of EO equivalents per year (approximately 20% of total world capacity) are produced in UCC-designed plants.

Licensors: Union Carbide Corp., a subsidiary of The Dow Chemical Co. Univation Technologies is the licensor of the UNIPOL PE process.

PETROCHEMICAL PROCESSES 2001



Formaldehyde

Application: To produce aqueous formaldehyde (AF) or urea formaldehyde precondensate (UFC) from methanol using Haldor Topsøe A/S FK-Series iron/molybdenum-oxide catalysts.

Description: The process is carried out in a recirculation loop at low pressure (0 to 6 psig) (1 to 1.5 bar abs). Vaporized methanol is mixed with air and recycle gas that were boosted by the blower (1). The mixture may be preheated to about 480°F (250°C) in the optional heat exchanger (2) or it may be sent directly to the reactor (3). In the reactor, methanol and oxygen react in the catalyst-filled tubes to make formaldehyde. Reaction heat is removed by an oil heat transfer medium (HTM). The reacted gas exits the reactor at approximately 540°F (290°C) and is cooled in the LP steam boiler (4) to 260°F (130°C) before entering the absorber (5). In the absorber, the formaldehyde is absorbed in water or urea solution. Heat is removed by one or two cooling circuits (6, 7). From the lower circuit (6)

either aqueous formaldehyde or UFC is withdrawn. Gas for recycling is withdrawn from the absorber, whereas the remaining gas is further scrubbed with fresh water or urea solution in the absorber top section before optionally being catalytically incinerated in the reactor (8). Tail gas purity applies to environmental standards of any country. Hot oil vapor from heat transfer system is used in the gas preheat (2) and heat recovery (9),—maximum 600 psig (40 bar)—steam production. Steam produced by reactor effluent exchanger (4) is used in the methanol evaporator (10) and in the boiler feedwater preheater (11).

Yield:

- Capacity increase up to 25% is possible by installation of an Adiabatic Pre or Post Converter (APC) with additional injection of liquid methanol.
- Capacity increase of 50% to 80% can be economically implemented by installation of a cooled series reactor in addition to the original one.

Product specification: Typical wt%:

Product	AF	UFC
Formaldehyde	37–55	≤60
Urea	—	≤25
Methanol	<0.7	<0.3
Formic acid	<0.03	<0.05

Economics: Turnkey cost including tail gas incineration, Gulf Coast basis, 37 wt%, formaldehyde:

27 tpd (skid mounted, modular type)	U.S.\$90,000 per ton
100 tpd (conventional plant layout)	U.S.\$50,000 per ton

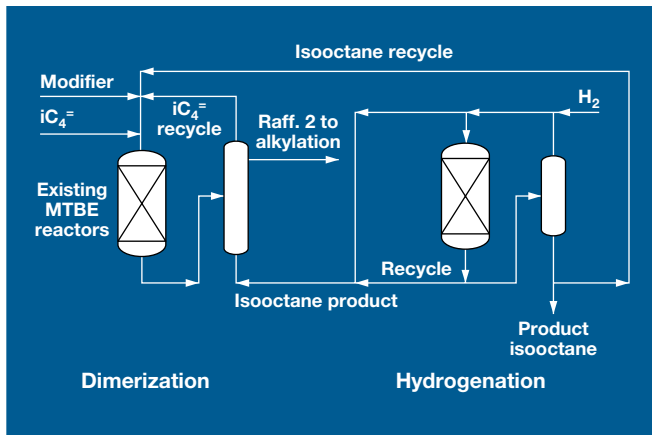
Utility requirements, per 1,000 kg of 37 wt% formaldehyde:

Product	55 wt% AF	85 wt% UFC
Methanol, kg	420–425	420–425
70% urea solution, kg	—	220
Water, demin., kg	572	572
Water, process, kg	250	72
Water, cooling, m ³	42	38
Electricity, kWh	65	76

Commercial plants: Twenty-one commercial units built. Three additional units are under construction.

Licensors: Haldor Topsøe A/S and Nippon Kasei Chemical Co., Ltd.

PETROCHEMICAL PROCESSES 2001



Isooctane

Application: To produce isooctane from isobutylene, based on two-step process involving catalytic dimerization followed by hydro-

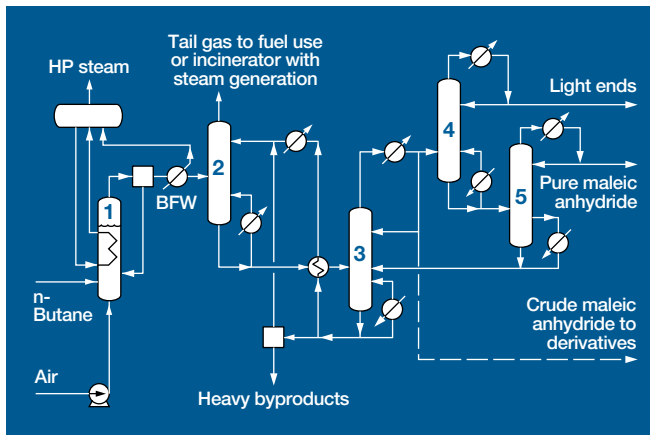
genation; with intermediate and final fractionation as required to meet final product specifications. Ideally, it is a “drop-in” to an existing MTBE reactor with patented use of modifier to improve selectivity and prolong catalyst life.

Description: The process produces an iso-octene intermediate starting with either a mixed C₄ feed or on-purpose isobutylene production. It is based on a highly selective conversion of isobutylene to iso-octene followed by hydrogenation, which will convert over 99.5% of the iso-octene to iso-octane. The product has high-gasoline blending quality with superior octane rating and low Rvp vapor pressure. The design has the added advantage of being inter-convertible between iso-octene/iso-octane and MTBE production.

Economics: The “drop-in” design capability offers an efficient and cost-effective approach to conversion of existing MTBE units. In retro-fit applications, this feature allows for maximum utilization of existing equipment and hardware, thus reducing the capital costs of conversion to an alternate process/production technology. For the production of isooctane, the process uses low-risk conventional hydrogenation with slight design enhancements for conversion of iso-octene.

Commercial plants: Preliminary engineering and licensing is under evaluation at several MTBE producers worldwide.

Licensor: Lyondell Chemical and Kvaerner.



Maleic anhydride

Application: To produce maleic anhydride from n-butane using a fluid-bed reactor system and an organic solvent for continuous anhydrous product recovery.

Description: N-butane and air are fed to a fluid-bed catalytic reactor (1) to produce maleic anhydride. The fluid-bed reactor elimi-

nates hot spots and permits operation at close to the stoichiometric reaction mixture. This results in a greatly reduced air rate relative to fixed-bed processes and translates into savings in investment and compressor power, and large increases in steam generation. The fluid-bed system permits online catalyst addition/removal to adjust catalyst activity and reduces downtime for catalyst change out.

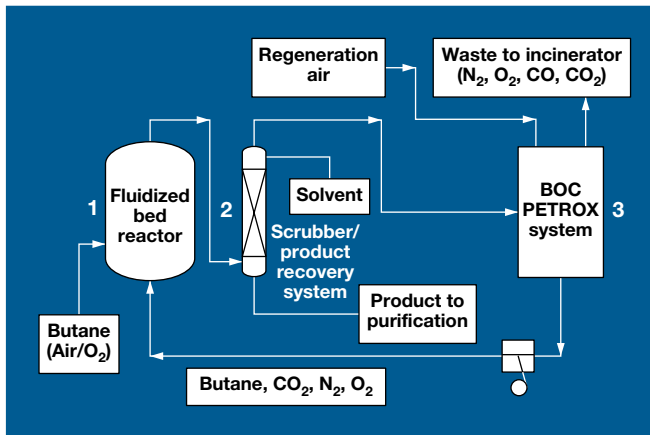
The recovery area uses a patented organic solvent to remove the maleic anhydride from the reactor effluent gas. A conventional absorption (2)/stripping (3) scheme operates on a continuous basis. Crude maleic anhydride is distilled to separate light (4) and heavy (5) impurities. A slipstream of recycle solvent is treated to eliminate any heavy byproducts that may be formed. The continuous non-aqueous product recovery system results in superior product quality and savings in steam consumption. Relative to an aqueous recovery system, it reduces investment, product degradation loss (and byproduct formation) and wastewater.

Economics: The ALMA process produces high-quality product with attractive economics. The fluid-bed process is especially suited for large single-train plants.

Commercial plants: Nine commercial plants have been licensed. The largest commercial installation in Lonza's 50,000-tpa plant in Ravenna, Italy. Second generation process optimizations and catalyst have elevated the plant performances in 1998.

Licensors: ABB Lummus Global/Lonza S.p.A.

PETROCHEMICAL PROCESSES 2001



Maleic anhydride

Application: To produce maleic anhydride from butane using a fluidized-bed reactor. The reactor is operated at lower butane per-pass conversion to maximize selectivity, and recover and recycle unreacted butane to achieve a higher total process yield.

Description: N-butane and air are normally fed to a fluidized-bed reactor in the presence of a catalyst to produce maleic anhydride. In this process option, the reactor (1) is operated at a lower butane conversion by either reducing the reaction temperature or by increas-

ing the space velocity. Unreacted butane along with the reaction products—maleic anhydride, CO and CO₂—are sent through a scrubber (2) to recover product maleic anhydride. The scrubber solvent can be either water or organic solvent. The scrubber offgases are normally sent to an incinerator. In this application, the offgases are sent to an adsorption-based recovery system (3) to selectively separate unreacted butane from N₂, CO and CO₂. A proprietary hydrophobic adsorbent is used. The process is designed to operate at near atmospheric pressure—closer to the operating pressure of the maleic anhydride process. Part of the air required for the butane-to-maleic anhydride reaction is used as the regeneration gas to desorb butane from the adsorbent. Recovered butane is recycled back to the reactor for further processing.

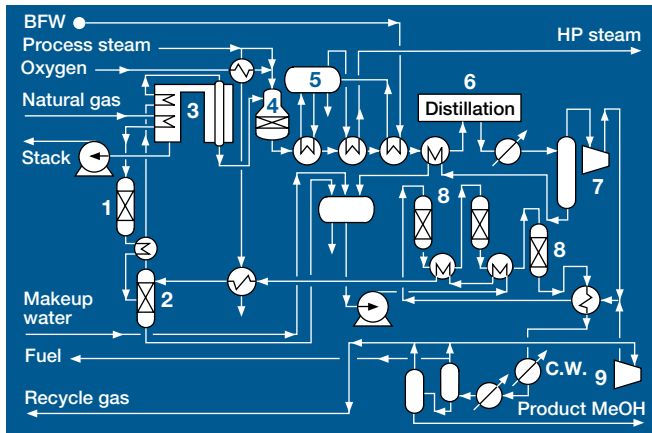
Economics: By operating the reactor at a lower conversion to increase selectivity and subsequent recycle, the total yield can be increased by 20% compared to once through processes. This in combination with oxygen enrichment can raise throughput very substantially. The detailed economics suggest that the capital investment can be decreased by 10% to 20%, while the operating costs by about 10% compared to once-through processes.

One additional benefit of the yield increase is the substantial reduction in CO₂ production in the process (> 50%). This new process can be implemented either for grassroots plants or for retrofitting existing plants.

Technology status: Integrated process technology successfully demonstrated in a large pilot plant at Mitsubishi Chemical Corp., Japan, for butane oxidation to maleic anhydride. Commercial plant designs are in progress

Licensors: BOC Gases.

PETROCHEMICAL PROCESSES 2001



Methanol

Application: To produce methanol from natural or associated gas feedstocks using two-step reforming followed by low-pressure synthesis. This technology is well-suited for worldscale plants. Topsøe also offers technology for smaller as well as very large methanol facilities up to 10,000 tpd; and technology to modify ammonia capacity into methanol production.

Description: The gas feedstock is compressed (if required), desulfurized (1) and sent to a saturator (2) where process steam is generated. All process condensate is reused in the saturator resulting in a lower water requirement. The mixture of natural gas and steam

is preheated and sent to the primary reformer (3). Exit gas from the primary reformer goes directly to an oxygen-blown secondary reformer (4). The oxygen amount and the balance between primary and secondary reformer are adjusted so that an almost stoichiometric synthesis gas with a low inert content is obtained. The primary reformer is relatively small and the reforming section operates at about 35 kg/cm²g.

The flue gas's heat content preheats reformer feed. Likewise, the heat content of the process gas is used to produce superheated high-pressure steam (5), boiler feedwater preheating, preheating process condensate going to the saturator and reboiling in the distillation section (6).

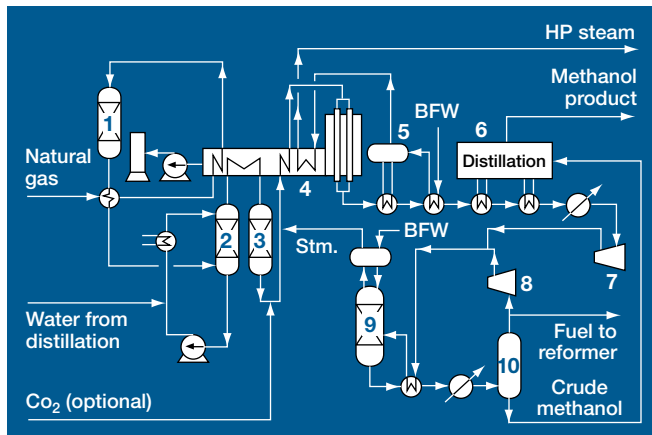
After final cooling by air or cooling water, the synthesis gas is compressed in a one-stage compressor (7) and sent to the synthesis loop (8), comprised of three adiabatic reactors with heat exchangers between the reactors. Reaction heat from the loop is used to heat saturator water. Steam provides additional heat for the saturator system. Effluent from the last reactor is cooled by preheating feed to the first reactor, by preheating demineralized water and by air or water cooling. Raw methanol is separated and sent directly to the distillation (6), featuring a very efficient three-column layout. Recycle gas is sent to the recirculator compressor (9) after a small purge to remove inert compound buildup.

Topsøe supplies a complete range of catalysts that can be used in the methanol plant. Total energy consumption for this process scheme is about 7.0 Gcal/ton including energy for oxygen production.

Economics: Total investments, including an oxygen plant, are approximately 10% lower for large plants than for a conventional plant based on straight steam reforming.

Commercial plants: The most recent large-scale plant is a 3,030-tpd facility in Iran scheduled to come onstream in 2002.

Licensors: Haldor Topsøe A/S.



Methanol

Application: Improved low-pressure methanol process to produce methanol from natural or associated gas using two-stage steam reforming followed by compression, synthesis and distillation. Capacities, ranging from 5,000 to 7,000 mtpd, are practical in a single stream. Carbon dioxide (CO₂) can be used as a supplementary feedstock to adjust the stoichiometric ratio of the synthesis gas.

Description: Gas feedstock is compressed (if required), desulfurized (1) and sent to the optional saturator (2) where some process steam is generated. The saturator is used where maximum water recovery is important. Further process steam is added, and the mixture is preheated and sent to the pre-reformer (3), using the Catalytic-Rich-Gas process. Steam raised in the methanol converter is added, along with available CO₂, and the partially reformed mixture is preheated

and sent to the reformer (4). High-grade heat in the reformed gas is recovered as high-pressure steam (5), boiler feedwater preheat, and for reboil heat in distillation system (6). The high-pressure steam is used to drive the main compressors in the plant.

After final cooling, the synthesis gas is compressed (7) and sent to the synthesis loop. The loop can operate at pressures between 70 to 100 bar. The converter design does impact the loop pressure, with radial-flow designs enabling low loop pressure even at the largest plant size. Low loop pressure reduces the total energy requirements for the process.

The synthesis loop comprises a circulator (8), the converter operates around 200°C to 270°C, depending on the converter type. Reaction heat from the loop is recovered as steam, and is used directly as process steam for the reformer.

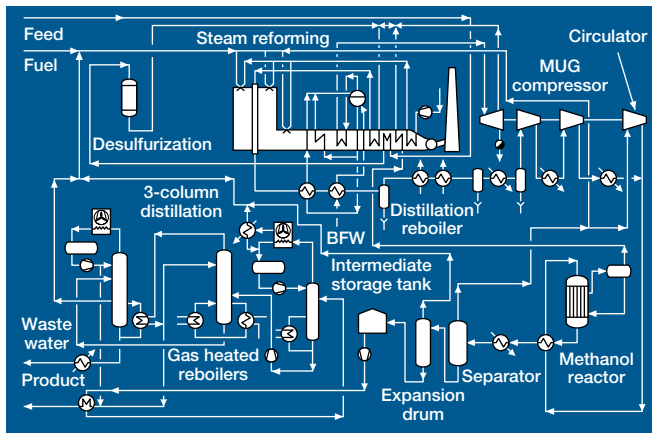
A purge is taken from the synthesis loop to remove inerts (nitrogen, methane), as well as, surplus hydrogen associated with non-stoichiometric operation. The purge is used as fuel for the reformer. Crude methanol from the separator contains water, as well as, traces of ethanol and other compounds. These impurities are removed in a two-column distillation system (6). The first column removes the light ends such as ethers, esters, acetone and dissolved noncondensable gases. The second column removes water, higher alcohols and similar organic heavy ends.

Economics: Recent trends have been to build methanol plants in regions offering low-cost gas (such as Chile, Trinidad and the Arabian Gulf). In these regions, total economics favor low investment rather than low-energy consumption. Recent plants have an energy efficiency of 7.2 to 7.8 Gcal/ton. A guideline figure to construct a 5,000-mtpd plant is U.S. \$370–400 million.

Commercial plants: Thirteen plants with capacities ranging from 2,000 to 3,000 mtpd, as well as, 50 smaller plants have been built using the ICI low-pressure methanol technology. Presently, one 5,000-mtpd plant is under construction.

Licensor: Kvaerner Process Technology/Synetix, UK.

PETROCHEMICAL PROCESSES 2001



Methanol

Application: To economically produce high-purity methanol from hydrocarbon feedstocks such as natural gas and LPG up to heavy naphtha using on steam reforming technology.

Description: The methanol plant concept consists of these process steps: feed purification, steam reforming, syngas compression, synthesis and crude methanol distillation.

The feed is desulfurized and mixed with process steam before entering the steam reformer. This steam reformer is a top-fired box type furnace with a cold outlet header system developed by Krupp Uhde. The reforming reaction occurs over a nickel catalyst. Outlet reformed gas is a mixture of H_2 , CO , CO_2 and residual methane. It

is cooled from approximately $880^\circ C$ to ambient temperature. Most of the heat from the synthesis gas is recovered by steam generation, BFW preheating, heating of crude methanol distillation and demineralized water preheating.

Also, heat from the flue gas is recovered by feed/feed-steam preheating, steam generation and superheating as well as combustion air preheating. After final cooling, the synthesis gas is compressed to the synthesis pressure, which ranges from 30–100 bara (depending on plant capacity) before entering the synthesis loop.

The synthesis loop consists of: a recycle compressor, feed/effluent exchanger, methanol reactor, final cooler and crude methanol separator. Krupp Uhde's methanol reactor is an isothermal tubular reactor with a copper catalyst contained in vertical tubes and boiling water on the shell side. The heat of methanol reaction is removed by partial evaporation of the boiler feedwater, thus generating 1–1.4 tons of MP steam per ton of methanol. Advantages of this reactor type are: low byproduct formation due to almost isothermal reaction conditions, high heat of reaction recovery, and easy temperature control by regulating steam pressure. To avoid inert buildup in the loop, a purge is withdrawn from the recycle gas and is used as fuel for the reformer.

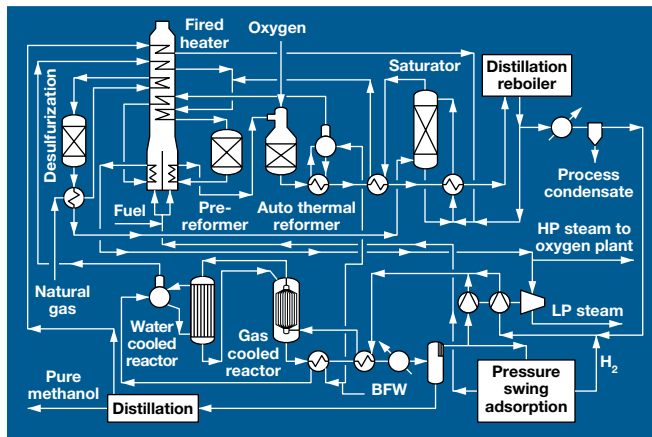
Crude methanol that is condensed downstream of the methanol reactor is separated from unreacted gas in the separator and routed via an expansion drum to the crude methanol distillation. Water and small amount of byproducts formed in the synthesis and contained in the crude methanol are removed by an energy-saving three-column distillation system.

Economics: Typical consumption figures (feed+fuel) range from 7 to 8 Gcal per metric ton of methanol and will vary on individual plant concept.

Commercial plants: Eleven plants have been built and revamped worldwide using Krupp Uhde's methanol technology.

Licensors: Krupp Uhde GmbH.

PETROCHEMICAL PROCESSES 2001



Methanol

Application: To produce methanol in a single-train plant from natural gas or oil-associated gas with capacities up to 10,000 mtpd. It is also well suited to increase capacities of existing steam-reforming-based methanol plants.

Description: Natural gas is preheated and desulfurized. After desulfurization, the gas is saturated with a mixture of preheated process water from the distillation section and process condensate in the saturator. The gas is further preheated and mixed with steam as required for the pre-reforming process. In the pre-reformer, the gas is converted to H₂, CO₂ and CH₄. Final preheating of the gas is achieved in the fired heater. In the autothermal reformer, the gas is reformed with steam and O₂. The product gas contains H₂, CO, CO₂ and a small amount of unconverted CH₄ and inerts together with undercomposed steam. The reformed gas leaving the autothermal reformer represents a considerable amount of

heat, which is recovered as HP steam for preheating energy and energy for providing heat for the reboilers in the distillation section.

The reformed gas is mixed with hydrogen from the pressure swing adsorption (PSA) unit to adjust the synthesis gas composition. Synthesis gas is pressurized to 5–10 MPa by a single-casing synthesis gas compressor and is mixed with recycle gas from the synthesis loop. This gas mixture is preheated in the trim heater in the gas-cooled methanol reactor. In the Lurgi water-cooled methanol reactor, the catalyst is fixed in vertical tubes surrounded by boiling water. The reaction occurs under almost isothermal condition, which ensures a high conversion and eliminates the danger of catalyst damage from excessive temperature. Exact reaction temperature control is done by pressure control of the steam drum generating HP steam.

The “preconverted” gas is routed to the shell side of the gas-cooled methanol reactor, which is filled with catalyst. The final conversion to methanol is achieved at reduced temperatures along the optimum reaction route. The reactor outlet gas is cooled to about 40°C to separate methanol and water from the gases by preheating BFW and recycle gas. Condensed raw methanol is separated from the unreacted gas and routed to the distillation unit. The major portion of the gas is recycled back to the synthesis reactors to achieve a high overall conversion. The excellent performance of the Lurgi combined converter (LCC) methanol synthesis reduces the recycle ratio to about 2. A small portion of the recycle gas is withdrawn as purge gas to lessen inerts accumulation in the loop.

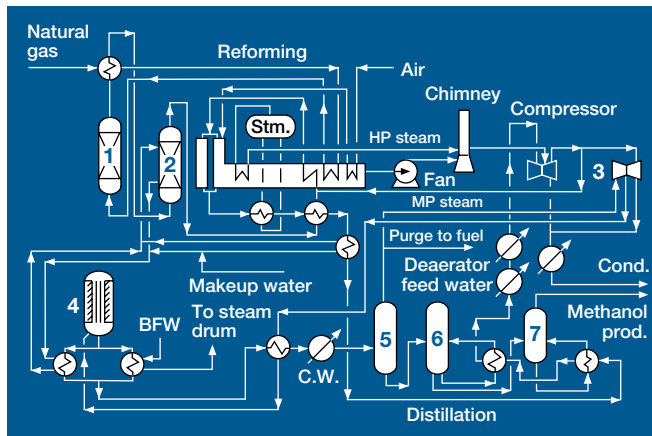
In the energy-saving-three-column distillation section, low-boiling and high-boiling byproducts are removed. Pure methanol is routed to the tank farm, and the process water is preheated in the fired heater and used as make-up water for the saturator.

Economics: Energy consumption for a stand-alone plant, including utilities and oxygen plant, is about 30 GJ/metric ton of methanol. Total installed cost for a 5,000-mtpd plant including utilities and oxygen plant is about U.S. \$ 300 million, depending on location.

Commercial plants: Thirty-five methanol plants have been built using Lurgi's low-pressure methanol technology. Two contracts for 5,000-mtpd plants using Lurgi's mega methanol technology have been awarded.

Licensors: Lurgi Öl-Gas-Chemie GmbH.

PETROCHEMICAL PROCESSES 2001



Methanol, LPM

Application: The low-pressure methanol (LPM) process produces a refined, high-purity methanol from a variety of hydrocarbon feedstocks, principally natural gas but including naphtha, coal and miscellaneous petrochemical offgas streams.

Description: The LPM process can be divided into three main sections, (I) syngas production, (II) methanol synthesis and (III) methanol distillation. (I) Syngas is normally produced by steam reforming natural gas. It produces a stream containing predominantly hydrogen and carbon oxides. The process catalyst is nickel-based; thus, the feed gas must be free of poisons. Consequently, desulfurization is the first processing stage (1). Reaction steam is provided by contact with hot water in a saturator (2) and by adding steam generated within the methanol plant. The saturator offers further beneficial use. Waste streams from within the process, containing organic components, can be fed into the saturator cir-

cuit and organic compounds will be recycled back into process; thus, minimizing liquid effluent streams. The syngas leaving the methane-steam reformer is typically at 880°C and up to 20 bar; it is cooled to ambient temperature before being compressed up to synthesis pressure.

(II) A typical synthesis loop will consist of a circulator (3), the methanol converter (4), heat recovery and coolers and a methanol separator (5). The methanol synthesis catalyst is copper-based and works at pressures between 50 to 100 bar and temperatures between 200°C and 290°C. Larger plants have an operating pressure range of 80 to 100 bar.

The reaction is limited by equilibrium, and the methanol level at the exit of the converter may only be up to 7%. Unreacted gases are recycled back through the methanol converter after cooling them to condense out the product methanol. Because the syngas contains some inert gases—nitrogen or unreacted methane—and excess of hydrogen, a purge stream is taken from the recycle gas and can be burned as fuel in the methane-steam reformer.

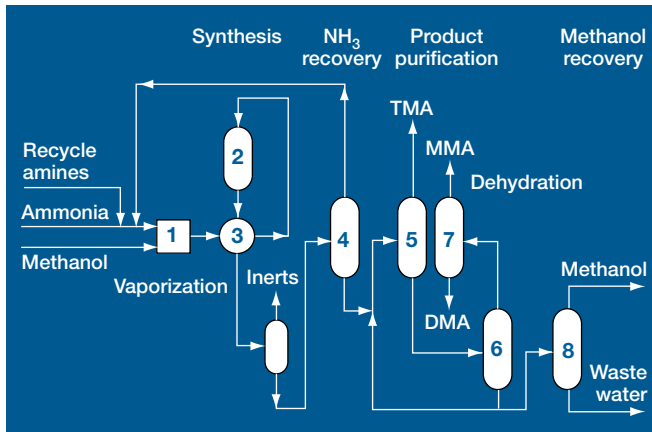
(III) Crude methanol manufactured in the synthesis stage contains water and small quantities of unwanted byproducts. These are removed in a two-column distillation system. The topping column (6) removes all light ends, such as, dissolved gases, light hydrocarbons, ethers, esters and acetone. The refining column (7) separates methanol from water with the higher hydrocarbons and alcohols removed by a side-draw.

Economics: Variable production cost is dominated by feedstock pricing, especially for natural gas. The installed plant cost is the other main contributor to the total product cost. Total energy usage for a self-contained plant is typically around 7.8 Gcal/ton of methanol (31 MMBtu/ton) on an LHV basis. Capital investment varies tremendously with size and location; however, a guideline installed cost for a 3,000-tpd plant is approximately U.S.\$ 250-300 million. Syntex's LCM process offers improved economics over conventional processes. It is ideal for large capacities (over 3,000 tpd) where conventional plants cannot be used, such as, offshore production.

Commercial plants: Currently 58 plants have been built using the ICI LPM process with two under design.

Licensors: Syntex.

PETROCHEMICAL PROCESSES 2001



DMA and TMA. Product ratios can be varied to maximize MMA, DMA, or TMA production. The correct selection of the N/C ratio and recycling of amines produces the desired product mix. Most of the exothermic reaction heat is recovered in feed preheating (3). The reactor products are sent to a separation system where firstly ammonia (4) is separated and recycled to the reaction system. Water from the dehydration column (6) is used in extractive distillation (5) to break the TMA azeotropes and produce pure anhydrous TMA. The product column (7) separates the water-free amines into pure anhydrous MMA and DMA. Methanol recovery (8) improves efficiency and extends catalyst life by allowing greater methanol slip exit from the converter. Addition of a methanol-recovery column to existing plants can help to increase production rates.

Anhydrous MMA, DMA and TMA, can be used directly in downstream processes such as MDEA, DMF, DMAC, choline chloride and/or diluted to any commercial specification.

Yields: Greater than 98% on raw materials.

Economics: Typical performance data per ton of product amines having MMA/DMA/TMA product ratio of 1/3 : 1/3 : 1/3

Methanol, t	1.38
Ammonia, t	0.40
Steam, t	8.8
Water, cooling, m ³	500
Electricity, kWh	20

Commercial plants: Twenty-six companies in 18 countries use this process with a production capacity exceeding 300,000 mtpa.

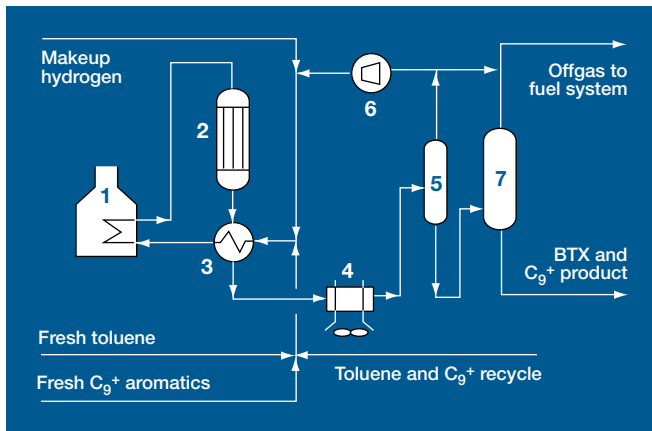
Licensors: Kvaerner Process Technology, UK.

Methylamines

Application: To produce mono- (MMA), di- (DMA) and trimethylamines (TMA) from methanol and ammonia.

Description: Anhydrous liquid ammonia, recycled amines and methanol are continuously vaporized (1), superheated (3) and fed to a catalyst-packed converter (2). The converter utilizing a high activity, low byproduct amination catalyst simultaneously produces MMA,

PETROCHEMICAL PROCESSES 2001



Mixed xylenes

Application: To convert C₉⁺ heavy aromatics, alone or in conjunction with toluene or benzene co-feed, primarily to mixed xylenes using Mobil's TransPlus process.

Description: Fresh feed, ranging from 100% C₉⁺ aromatics to mixtures of C₉⁺ aromatics with either toluene or benzene, are con-

verted primarily to xylenes in the TransPlus process. Co-boiling C₁₁ aromatics components, up to 435°F NBP, can be included in the C₉⁺ feed. In this process, liquid feed along with hydrogen-rich recycle gas, are sent to the reactor (2) after being heated to reaction temperature through feed/effluent heat exchangers (3) and the charge heater (1). Primary reactions occurring are the dealkylation of alkylaromatics, transalkylation and disproportionation, producing benzene/toluene and C₈ aromatics containing over 95% xylenes. The thermodynamic equilibrium of the resulting product aromatics is mainly dependent on the ratio of methyl groups to aromatic rings in the reactor feed. Hydrogen-rich gas from the high-pressure separator (5) is recycled back to the reactor with make-up hydrogen (6). Unconverted toluene and C₉⁺ aromatics are recycled to extinction.

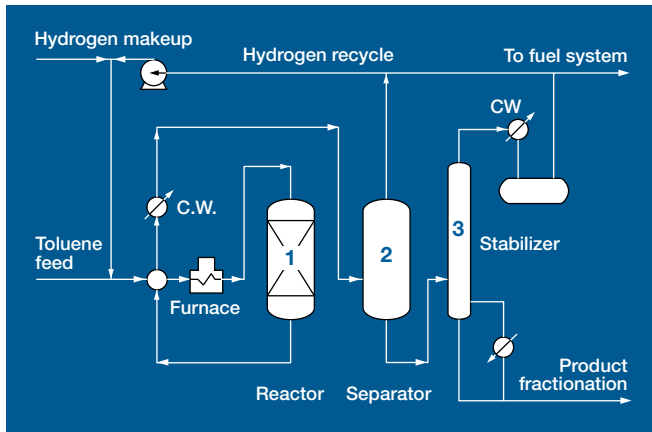
The ability of TransPlus to process feeds rich in C₉⁺ aromatics enhances the product slate towards xylenes. Owing to its unique catalyst, long cycle lengths are possible.

Economics: Favorable operating conditions, relative to other alternative technologies, will result in lower capital and operating costs for grassroots units and higher throughput potential in retro-fit applications.

Commercial plants: The first commercial unit was started up in Taiwan in 1997. Performance of this unit has been excellent.

Licensors: ExxonMobil Chemical, (retro-fit applications); IFP (grassroots applications).

PETROCHEMICAL PROCESSES 2001



Mixed xylenes

Application: To selectively convert toluene to mixed xylene and high-purity benzene using Mobil's Toluene DisProportionation 3rd Generation (MTDP-3) process.

Description: Dry toluene feed and up to 25 wt% C₉ aromatics along with hydrogen-rich recycle gas are pumped through feed effluent heat exchangers and the charge heater into the MTDP-3 reactor (1). Toluene disproportionation occurs in the vapor phase to produce the mixed xylene and benzene product. Hydrogen-rich gas from the high-pressure separator (2) is recycled back to the reactor together with makeup hydrogen. Unconverted toluene is recycled to extinction.

Reactor yields, wt%:

	Feed	Product
C ₅ and lighter		1.3
Benzene		19.8
Toluene	100.0	52.0
Ethylbenzene		0.6
p-Xylene		6.3
m-Xylene		12.8
o-Xylene		5.4
C ₉ ⁺ aromatics		1.8
	<u>100.0</u>	<u>100.0</u>
Toluene conversion, wt%		48

Operating conditions: MTDP-3 operates at high space velocity and low H₂/hydrocarbon mole ratio. These conditions could potentially result in increased throughput without reactor and/or compressor replacement in retrofit applications. The third generation catalyst offers long operating cycles and is regenerable.

Economics: Estimated onsite battery limit investment for 1997 open shop construction at U.S. Gulf Coast location is \$1,860 per bpsd capacity.

Typical utility requirements, per bbl feed converted:

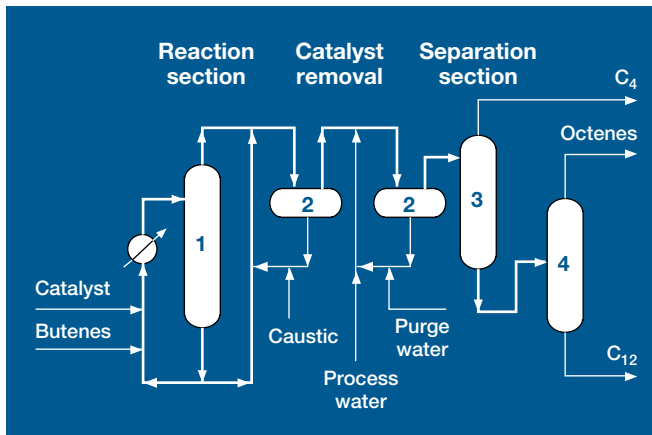
Electricity, kWh	3.0
Fuel, 10 ³ kcal/hr	87.8
Water, cooling (10°C rise), cm/hr	0.3
Catalyst fill, lb/lb feed converted	1.5 3 10²⁵
Maintenance, per year as % of investment	2.0

Commercial plants: Three MTDP-3 licensees since 1995.

Reference: *Oil & Gas Journal*, Oct. 12, 1992, pp. 60–67.

Licensors: ExxonMobil Chemical, (retrofit applications); IFP (grass-roots applications).

PETROCHEMICAL PROCESSES 2001



Octenes

Application: The Dimersol-X process transforms butenes to octenes, which are ultimately used in the manufacture of plasticizers via isononanol (isononyl alcohol) and diisononyl phthalate units.

Description: Butenes enter the Dimersol-X process, which comprises three sections. In the reactor section, dimerization takes place in multiple liquid-phase reactors (1) using homogeneous catalysis and an efficient recycle mixing system. The catalyst is generated in situ by

the reaction of components injected in the recycle loop. The catalyst in the reactor effluent is deactivated in the neutralization section and separated (2). The stabilization section (3) separates unreacted olefinic monomer and saturates from product dimers while the second column (4) separates the octenes. A third column can be added to separate dodecenes.

Yields: Nearly 80% conversion of n-butenes can be attained and selectivities towards octenes are about 85%. The typical C₈ product is a mixture having a minimum of 98.5% octene isomers with the following distribution:

n-Octenes	7%
Methyl-heptenes	58%
Dimethyl-hexenes	35%

Dimersol-X octenes exhibit a low degree of branching resulting in higher downstream oxidation reaction yields and rates, and better plasticizer quality.

Economics: Basis: ISBL 2000 for a Gulf Coast location using 50,000 tpa of a raffinate-2 C₄ cut containing 75% n-butenes.

Investment, \$U.S. million 5.3

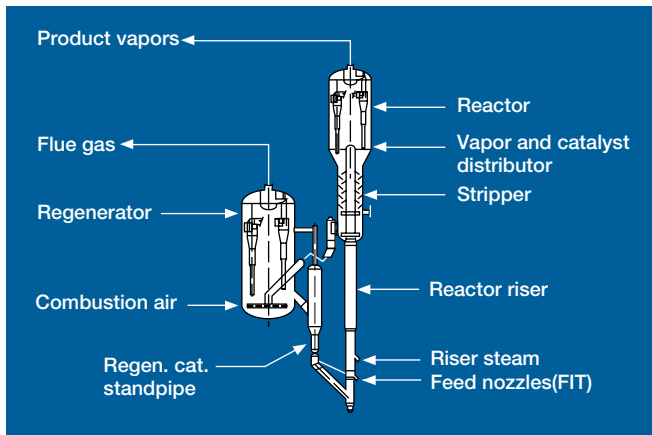
Typical operating cost, \$U.S. 60 per metric ton of octenes

Commercial plants: Thirty-five Dimersol units treating various olefinic C₃ and C₄ cuts have been licensed. Typical octenes production capacities range from 20,000 tpa up to 90,000 tpa.

Reference: Convers, A., D. Commereuc, and B. Torck, "Homogeneous Catalysis," IFP Conference.

Licensor: IFP, IFPNA.

PETROCHEMICAL PROCESSES 2001



Olefins

Application: To selectively convert vacuum gas oils and the resulting blends of each into C₂-C₅ olefins, aromatic-rich, high-octane gasoline and distillate using deep catalytic cracking (DCC) methods.

Description: DCC is a fluidized process to selectively crack a wide variety of feedstocks into light olefins. Propylene yields over 24 wt% are achievable with paraffinic feeds. A traditional reactor/regenerator unit design uses a catalyst with physical properties similar to tra-

ditional FCC catalyst. The DCC unit may be operated in two operational modes: maximum propylene (Type I) or maximum iso-olefins (Type II). Each operational mode utilizes unique catalyst as well as reaction conditions. DCC maximum propylene uses both riser and bed cracking at severe reactor conditions, while Type II utilizes only riser cracking like a modern FCC unit at milder conditions.

The overall flow scheme of DCC is very similar to a conventional FCC. However, innovations in catalyst development, process variable selection and severity enables the DCC to produce significantly more olefins than FCC in a maximum olefins mode of operation.

Products,

wt% FF	DCC Type I	DCC Type II	FCC
Ethylene	6.1	2.3	0.9
Propylene	20.5	14.3	6.8
Butylene	14.3	14.6	11.0
in which IC ₄ =	5.4	6.1	3.3
Amylene	—	9.8	8.5
in which IC ₅ =	—	6.5	4.3

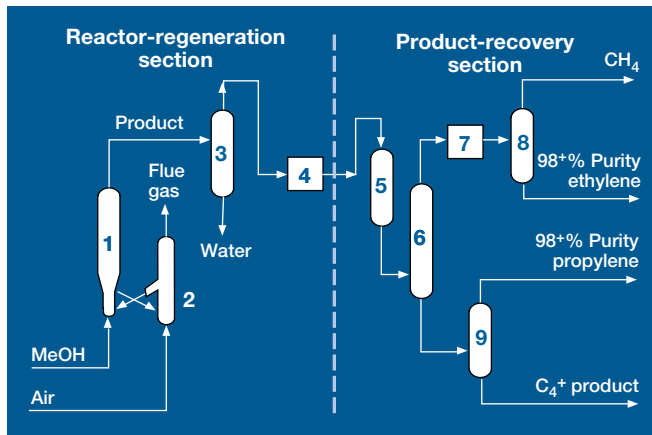
This technology is suitable for revamps as well as grassroot applications.

Commercial plants: Currently seven units are in operation, six in China and one in Thailand.

Reference: Chapin, Letzsch and Swaty, "Petrochemical options from deep catalytic cracking and the FCCU," 1998 NPRA, AM-98-44.

Licensors: Stone & Webster Inc., a Shaw Group Co./Research Institute of Petroleum Processing.

PETROCHEMICAL PROCESSES 2001



methanol with very high selectivity to ethylene and propylene. The recovery section design depends on product use, but will contain a product water recovery and recycle system (3), a CO₂ removal system (4), a dryer (5), a deethanizer (6), an acetylene saturation unit (7), a demethanizer (8), and a depropanizer (9). The process can produce 99+% (polymer-grade) ethylene and propylene by adding simple product splitters to the recovery section.

Yields: The process gives very high total olefins yields. A typical product yield structure is shown based on 5,204 mt/d raw methanol feed-rate to an MTO plant:

	Metric tons/day
Ethylene	882
Propylene	882
Total light olefins	1,762
Butenes	272
C ₅ ⁺	100
Fuel gas	88
Other (water, coke, CO _x)	2,980

Olefins

Application: To produce ethylene, propylene and butenes from natural gas or equivalent, via raw methanol, using the UOP/HYDRO MTO (methanol to olefins) process.

Description: This new process consists of a reactor section, a continuous catalyst regeneration section and product recovery section. One or more fluidized-bed reactors (1) are used with continuous catalyst transfer to and from the continuous catalyst regenerator (2). The robust regenerable MTO-100 catalyst is based on a nonzeolitic molecular sieve. Raw (nondewatered) methanol is fed to the low-pressure reactor (1), which offers very high (99%⁺) conversion of the

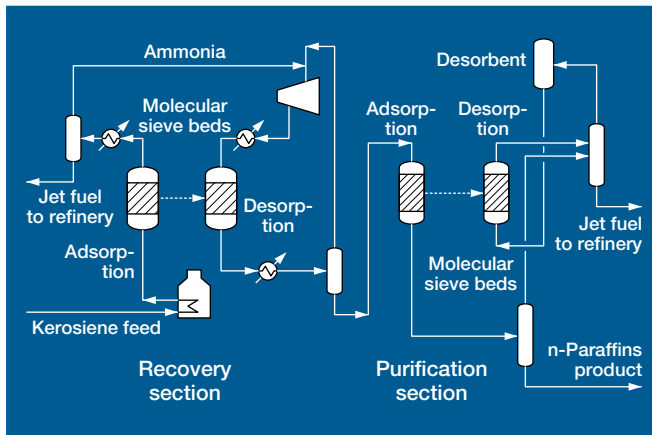
The process is flexible. Ethylene to propylene product weight ratio can be modified between the range of 0.75 to 1.5 by altering reactor operating severity. The total yield of olefins varies slightly throughout this range.

Economics: The MTO process competes favorably with conventional liquid crackers due to lower capital investment. It is also an ideal vehicle to debottleneck existing ethylene plants and, unlike conventional steam crackers, the MTO process is a continuous reactor system with no fired heaters.

Commercial plants: NA.

Licensors: UOP/HYDRO.

PETROCHEMICAL PROCESSES 2001



Paraffins, normal

Application: A low-cost process for the production of high purity normal paraffins from kerosene.

Description: Hydrofined kerosene feedstock is fed to the recovery section, where n-paraffins are recovered and the rest of the hydrocarbons are rejected and returned to the refinery kerosene pool.

ExxonMobil's technology is unique. Since the process is very sulfur tolerant, the kerosene feedstocks only require mild, low-pressure hydrofining.

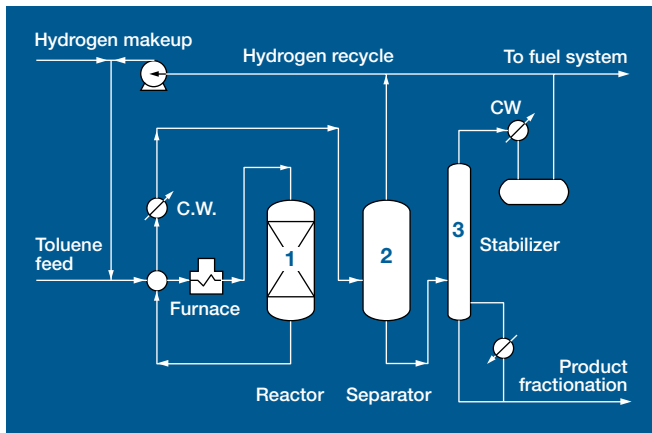
The recovery process is a vapor phase fixed-bed adsorption technology featuring desorption with ammonia. This process has paraffins' recovery and product purity in the high 90%'s. Ammonia is a very efficient desorbent. Since it is easily separated from the n-paraffins product, fractionation capital and energy requirements are substantially reduced. Furthermore, ammonia has the added advantage of protecting the adsorbents from coking.

In this process, adsorbents have been able to demonstrate long life (20+ years). The n-paraffins product from the recovery section is then processed by the purification section, where residual aromatics and other impurities are removed. The purification process is a liquid-phase fixed-bed adsorption method using a hydrocarbon desorbent. The high purity n-paraffins product can then be fractionated into the desired carbon number distribution fractions. The n-paraffins product produced using ExxonMobil's technology has among the highest purity on the market. The unique advantages of this technology result in lower capital and operating costs to a producer.

Commercial Plants: ExxonMobil Chemical has 40 years of experience in the production of n-paraffins and is the second largest producer in the world. ExxonMobil's n-paraffins plant at Baytown, TX has a current capacity of 250 kTA.

Licensor: Kellogg Brown & Root, Inc.

PETROCHEMICAL PROCESSES 2001



Paraxylene

Application: To selectively convert toluene to high-purity (90%+) paraxylene-rich (PX) xylenes and benzene using ExxonMobil's technologies licensed under the name PxxMax.

Description: Dry toluene feed and hydrogen-rich recycle gas are pumped through feed/effluent exchangers and charge heater and into the PxxMax reactor (1). Selective toluene disproportionation (STDP) occurs in the vapor phase to produce the paraxylene-rich xylene and benzene co-product. Byproduct yields are small. Reactor efflu-

ent is cooled by heat exchange and liquid products are separated from the recycle gas. Hydrogen-rich gas from the separator (2) is recycled back to the reactor together with makeup hydrogen. Liquid product is stripped of remaining light gas in the stabilizer (3) and sent to product fractionation. Unconverted toluene is recycled to extinction.

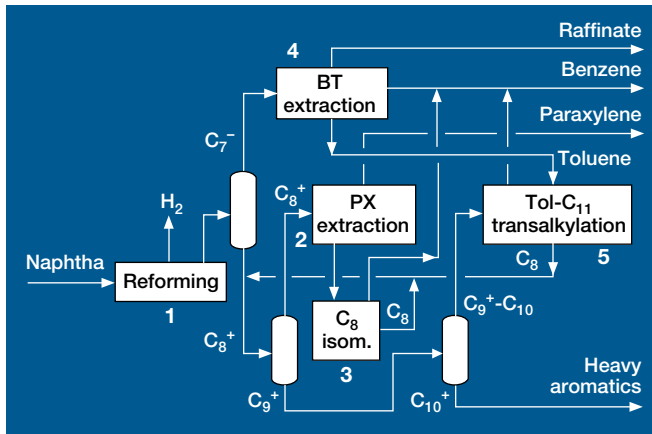
Two technology versions are licensed under the name PxxMax. One version involves catalyst (EM-2200), which is coke selectivated in-situ and the other version uses catalyst (MTPX) in which the selectivity is provided by pretreatment during catalyst manufacture. Both technologies provide significantly higher selectivity and longer operating cycles than other STDP technologies. Operating costs associated with downstream recovery are also reduced by the high paraxylene purity from PxxMax.

Operating conditions: PxxMax operates at lower start-of-cycle temperatures and lower hydrogen to hydrocarbon recycle ratios than other STDP technologies, resulting in longer cycles and lower utilities. By eliminating the in-situ selectivation step, the MTPX version of this technology results in simplified operation and lower capital costs. The PxxMax catalysts both offer long operating cycles and are regenerable.

Commercial plants: There are eight MSTDP units (predecessor technology to PxxMaxsm) and three commercial units using the PxxMax technology. The first two PxxMax units utilized the MTPX catalyst and started up in 1996 and 1997 at Chalmette Refining's Louisiana Refinery and Mobil Chemical's Beaumont plant, respectively. The third unit, using EM-2200 technology, started up in 1998 at ExxonMobil's Baytown Chemical Plant.

Licensor: ExxonMobil Chemical (retrofit applications); IFP (grass-roots applications).

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Paraxylene

Application: Suite of advanced aromatics technologies combined in the most effective manner to meet customers' investment and production objectives for paraxylene and benzene and are licensed under the name ParamaX.

Description: Aromatics are produced from naphtha in the Aromizing section (1), and separated by conventional distillation. The xylene fraction is sent to the Eluxyl unit (2), which produces 99.9% paraxylene via simulated countercurrent adsorption. The PX-depleted raffinate is isomerized back to equilibrium in the isomerization section (3) with either EB dealkylation-type (XyMax) processes or EB isomerization-type (Oparis) catalysts. High-purity benzene and toluene are separated from non-aromatic compounds with extractive distillation (Morphylane**) processes (4). Toluene and C₉ to C₁₁ aromat-

ics are converted to more valued benzene and mixed xylenes in the TransPlus* process (5), leading to incremental paraxylene production.

Eluxyl technology has the industrially-proven ability to meet ultimate single train PX purity and capacities as high as 750,000 mtpy. Proprietary hybrid Eluxyl configurations integrate an intermediate purity adsorption section with a single-stage crystallization, ideal for retrofits. IFP is the licensor of all the technologies involved in the ParamaX suite.

* Mobil and ** Krupp-Uhde technologies licensed by IFP for grassroots applications

Production: Typical paraxylene single train complex from naphtha to paraxylene, featuring Aromizing, Eluxyl, XyMax and TransPlus units.

	Thousand tpa
Feed—60–175 Arab light naphtha	1,378
Paraxylene	600
Benzene	168
Net producer of hydrogen	

Economics: The ISBL 2000 Gulf Coast location erected cost, including first load of catalysts and chemicals, with 30% allowance for off-sites.

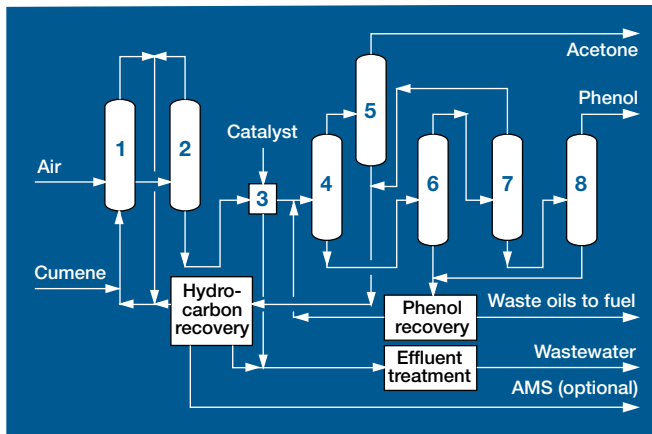
Investment, million \$U.S.	410
Annual utilities, catalyst and chemical operating cost (million U.S.\$/yr)	41

Installation: As of first quarter 2001, eight Eluxyl units have been licensed, accounting for 3 million tpy of paraxylene and three units are in operation. Nineteen Octafining units and twenty-one Mobil isomerization units have been put into operation. One TransPlus unit is currently in operation.

Reference: Rault, J., P. Renard, and F. Alario, "Maximizing Paraxylene Production with ParamaX," IFP March 2000. Dupraz, C., F. Alario, J. Magne-Drisch, E. Merlen, and J. Rault, "Aromatics Isomerization," WRA 2000, Amsterdam, March 2000.

Licensor: IFP, IFPNA.

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Phenol

Application: A high-yield process to produce high-purity phenol and acetone from cumene with optional byproduct recovery of alpha methylstyrene (AMS) and acetophenone (AP).

Description: Cumene is oxidized (1) with air at high efficiency (+95%) to produce cumene hydroperoxide (CHP), which is con-

centrated (2) and cleaved (3) under high-yield conditions (+99%) to phenol and acetone in the presence of an acid catalyst. The catalyst is removed and the cleavage mixture is fractionated to produce high-purity products (4–8), suitable for all applications. AMS is hydrogenated to cumene and recycled to oxidation or optionally recovered as a pure byproduct. Phenol and acetone are purified. A small aqueous effluent is pretreated to allow efficient biotreatment of plant wastewater. With AMS hydrogenation, 1.31 tons of cumene will produce 1 ton of phenol and 0.615 tons of acetone. This high-yield process produces very little heavy ends.

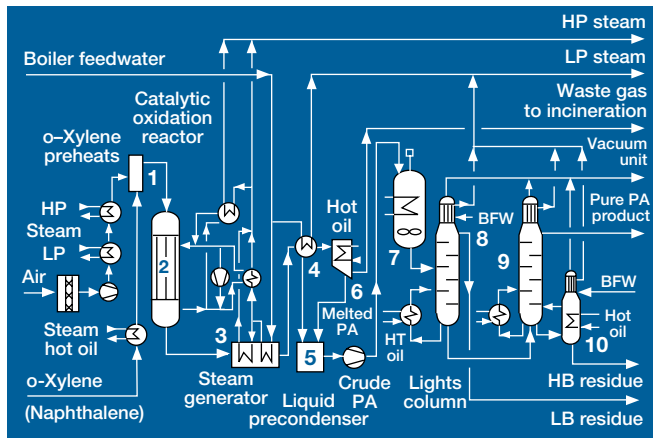
With over 40 years of continuous technological development, the Kellogg Brown & Root (KBR) phenol process features low cumene and energy consumptions, coupled with unsurpassed safety and environmental systems.

Commercial plants: Thirty plants worldwide have been built or are now under construction with a total phenol capacity over 2.8 MMtpy. Three grassroots phenol plants, using KBR's phenol technology started up in 1999/2000: 100,000-tpy for Aristech Chemical, Ohio; 225,000-tpy for Shell Chemical, Texas; and 37,500-tpy for Shanghai Gaogiao Petrochemicals, Shanghai, China. An additional three plants are in design. More than 50% of the world's phenol is produced via this process.

Reference: *Hydrocarbon Engineering*, December/January 1999.

Licensors: Kellogg Brown & Root, Inc.

PETROCHEMICAL PROCESSES 2001



part of the PA vapor is condensed to a liquid in the preconductor (4) and is continuously discharged to the crude PA tank (5). The remainder of about 65 g PA/m³ in the reaction gas is condensed as solid sublimate in switch condensers (6) on specially designed finned tubes. The switch condensers are periodically cooled and heated in a discontinuous operation of an automated switching cycle using heat transfer oil circuits. During the heating phase, solid PA is melted through the condenser tubes and discharged as a liquid to crude PA tank. Effluent gas is vented to the atmosphere after water scrubbing and/or incineration.

The crude PA is thermally pretreated (7) and then fed to the vacuum distillation system. Low boiling (LB) impurities are removed in the lights column (8) as LB residues. The high-boiling (HB) residue from the pure PA column (9) is sent to the residue boil-out vessel for PA recovery. Pure PA obtained as a distillate can be stored either in the molten state or flaked and bagged.

Catalyst: Special high-performance catalysts oxidize o-xylene as well as oxidizing naphthalene, o-xylene and mixtures of both feedstocks in any proportions. All catalysts are ring-shaped.

Yield: 110–112 kg PA from 100 kg of pure o-xylene; 97–99 kg PA from 100 kg of pure naphthalene.

Economics: Excellent energy utilization and minimized offgas volume are due to high hydrocarbon/air ratio. Plants can be designed to operate independently of external power supply and export electric energy or HP steam.

Commercial plants: More than 110 plants with typical production capacities of 20,000–75,000 tpy, with a maximum capacity of 140,000 tpy, have been designed and built by Lurgi.

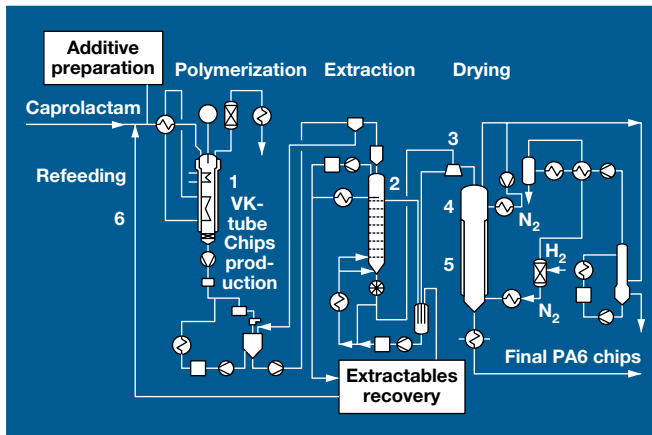
Licensors: Wacker Chemie GmbH; **exclusive contractor:** Lurgi Öl Gas Chemie GmbH.

Phthalic anhydride

Application: To produce phthalic anhydride (PA) from o-xylene, naphthalene or mixtures of both feedstocks using a fixed-bed vapor phase process, originally known as the von Heyden Process.

Description: Air is heated and loaded with evaporated (1) o-xylene and/or naphthalene. The hydrocarbon/air mixture enters a multi-tubular reactor (2) containing catalyst. An agitated salt melt removes the heat of reaction and maintains constant temperature conditions. Reaction heat generates high-pressure steam.

Modern plants operate with o-xylene feedstock loadings of 90–100 g/Nm³ air. Reactor effluent gas is pre-cooled in a gas cooler (3) before



Polycaproamide

Application: INVENTA-FISCHER's VK-tube process polymerizes ϵ -caprolactam (LC) monomer to produce polycaproamide (nylon-6) chips.

Description: Liquid LC is continuously polymerized in a VK-tube (1) in the presence of water, stabilizer and modifying additives at ele-

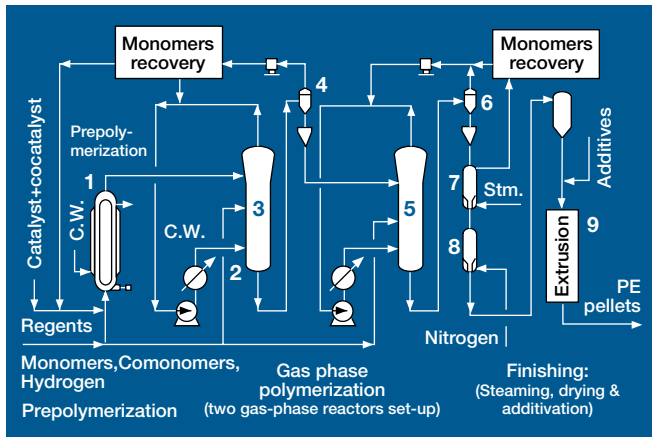
vated temperatures. The polymerization process has proven to be very reliable, easy to operate and economical. Prepolymerization is available to reduce reactor volume for large capacity units. The polycaproamide chips are formed from the melt using strand cutters and are conveyed to the extraction column (2).

The chips—containing about 9 % of monomer and cyclic oligomers—are treated with hot water in the extraction column. The extractables are, therefore, removed to a very large extent, to achieve a good polymer quality and high performance when processing further. Wet chips are sent to the centrifuge (3) and dried by hot, dry nitrogen in a two-zone dryer (4, 5). The nitrogen gas is regenerated in separate cycles. In the bottom zone of the dryer, the chips are cooled by means of a heat exchanger. The drying unit can be extended to a solid state postcondensation, i.e., drying and solid-state postcondensation take place in one process stage. Thus, high-viscosity chips for industrial yarns, films and foils can be produced.

Low utility and energy consumption are achieved by using closed circuits of water and nitrogen as well as by recovering heat. The recovery process for the recycling of the extractables reduces raw material cost. The extract water is concentrated and directly re-fed (6) to the polymerization. Alternatively, the concentrated extract is fed to a separate, specially designed, continuous re-polymerization unit.

Batch and continuous process units are available to meet all potential requirements regarding polymer grades as well as regarding flexibility in output rates and capacities. Special attention is devoted during plant design to attain minimal operating expenses for raw material, utilities and personnel.

Licensor: INVENTA-FISCHER.



Polyethylene

Application: To produce linear polyethylene from very low density polyethylene (VLDPE) to linear low density polyethylene (LLDPE) to high density polyethylene (HDPE) and other specialty types using the Spherilene gas-phase technology and a single Ziegler-Natta titanium-based catalysts family.

Description: Catalyst components are mixed and fed directly to prepolymerization (1) with a light inert hydrocarbon, where a first bulk polymerization occurs under mild controlled conditions. This step exploits the catalyst system potential in terms of morphology, mileage and complete reliability in the following gas-phase reaction sections.

The slurry flows continuously into the first gas-phase reactor (GPR) (3). Reactor gas is circulated at high speed by a centrifugal compressor through a distribution grid. A cooler on the circulation gas

loop (2) removes reaction heat. Polymer quality and rate are controlled by gas composition, monomers feedrate and residence time. Product is discharged continuously from the first GPR, via a proprietary device, to a second GPR (5) with similar configuration. Resultant discharged gas is recovered and no gas enters the second stage, due to a low-pressure receiver and a proprietary “lock hopper” system (4). Thus, an independent gas composition can be built up and kept in each GPR, allowing growth to a different, if required, polymer within the first stage polymeric matrix. Pressure and temperature GPRs’ conditions are also independently selected and no additional catalytic components are required.

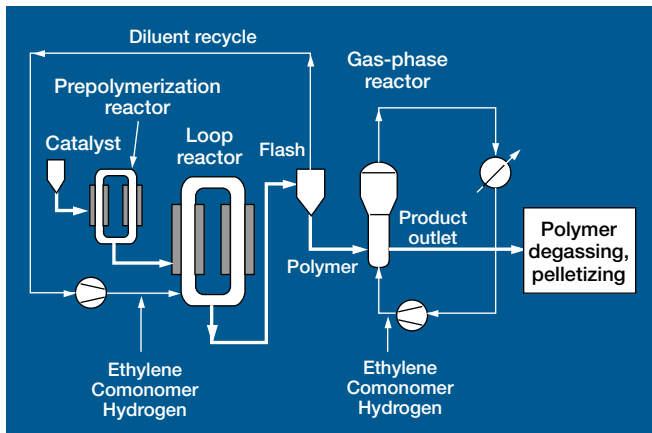
The polymer is then discharged in a receiver recovering the resultant gas (6) and to a proprietary unit for monomer stripping and catalyst deactivation in the polymer spheres (7). Residual hydrocarbons are stripped out and recycled to reaction, while the polymer is dried by a close-loop nitrogen system (8) and, free from volatile substances, sent to liquid and/or solid additives’ incorporation step (9).

Products: Product density is controlled from ultra low density polyethylene (ULDPE) (<900 g/ml) to HDPE (>960 g/ml). Melt index (MI) “E” capability ranges from 0.01 to 100 gr/10’.

Because of the two GPRs set-up, the Spherilene technology enables production of bimodal reactor grades (MIE, density) and specialty polymers based on new molecular models. For example, “High performance” (HP) terpolymer grades guarantee superior properties to those of conventional butene LLDPE/VLDPE, and enhanced hexene HP “Quattropolymer” grades are optimal economical choices to replace hexene/octene-based LLDPE. LDPE replacement grades for clarity and shrink applications have also been developed.

Commercial plants: Licensed from 1992, total Spherilene licensed capacity is 1.8 MMtpy. Six plants are in operation (1 in the U.S., 2 in Korea, 2 in Brazil and 1 in India) two other plants (1 in India and 1 in Iran) are under implementation. Single-line ranges from 100,000 to 300,000 tpy.

Licensors: Basell Technology Co. BV. Basell is a joint venture between Royal Dutch/Shell Group and BASF.



Polyethylene

Application: The Borstar polyethylene (PE) process is used when producing bimodal and unimodal linear low density (LLDPE), medium density (MDPE) and high density (HDPE) polyethylene using loop and gas-phase low pressure reactors in series. All products can be produced in one cycle.

Description: Polyethylene with densities of 918–970 kg/m³ and melt flowrate of 0.1–100 can be produced with the Borstar PE process. Currently, Ziegler Natta catalysts are used, but there is a potential to use single-site catalysts latter.

The catalyst is mixed with propane diluent and fed into the compact prepolymerization reactor. Cocatalyst, ethylene, comonomer and hydrogen are also fed into this reactor. The pre-polymerized slurry is then fed into a second larger slurry loop reactor, which is designed for supercritical conditions and is typically operated at 75°C–100°C

and 55–65 bar. Typically, lower molecular weight and higher density components of the bimodal product are produced in the loop reactor.

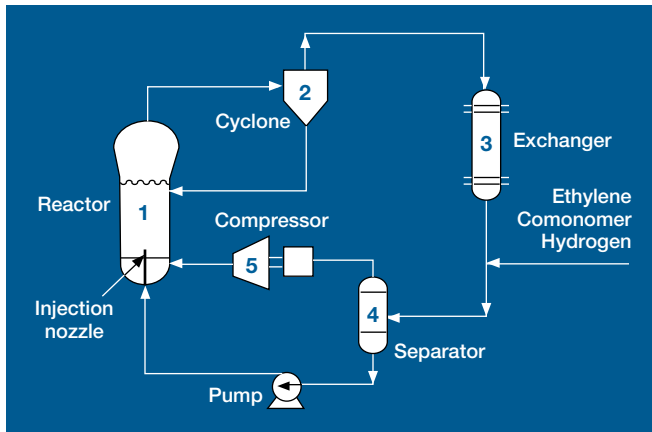
Diluent and unreacted components are separated from the polymer, produced in the loop reactor, in a flash tank, thus the loop reactor and the gas-phase reactor are fully independent from each other. This enables easy control of reactor conditions and a wide product range.

Polymer coming from the flash tank polymerizes further in a fluidized bed gas-phase reactor. No additional new catalyst is needed. The polymer continues to grow on the same catalyst particles, resulting in a homogeneous polymer. The gas-phase reactor is operated at 75°C–100°C and 20 bar. Fresh ethylene, comonomer and hydrogen are fed into the reactor. Typically, high molecular weight components are produced in this step, thus broadening the molecular weight distribution of the final polymer and giving strength to the product. The production rate ratio between the reactors can be adjusted to meet the targeted product properties. After removing hydrocarbon residuals, the polymer powder is transferred into powder silos. Later, the powder is sent to the extruder where additivition and pelletization is done.

Products: A wide range of bimodal and unimodal products, with a full control of comonomer distribution, can be produced, with densities ranging from 918 to 970 kg/m³ and melt flowrate from less than 0.1 to over 100. The molecular weight distribution can be controlled from narrow to broad. Advanced properties are tailor-made applications such as pipe strength, film bubble stability as well as high ESCR and stiffness in blow molding. Other special applications include extrusion coating and wire & cable.

Commercial plants: The first commercial scale plant has been operating in Finland since 1995. Two lines being built in Abu Dhabi will be completed in late 2001 and will produce 450,000 tpy. The newly retrofitted HDPE Borstar plant at Stenungsund, Sweden has started up and has added 225,000 tpy capacity. A fifth new 250,000-tpy plant is under construction in China at Shanghai Petrochemicals and will be China's largest PE plant. Maximum design size for one line is 300,000 tpa.

Licensor: Borealis A/S.



Polyethylene

Application: To produce linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) using the gas phase Innovene process with either Ziegler-Natta, chromium and metallocene catalysts.

Description: Catalyst or metallocene is injected directly into the reactor as received in the case of Ziegler-Natta or after activation for chromium catalyst. Chromium catalysts give broad molecular-weight products and supported Ziegler-Natta catalysts produce narrow molecular-weight distribution products. The BP metallocene catalysts offer exceptional strength and clarity normally associated with metallocenes but combined with easy processing.

Density and melt index are the most important product proper-

ties. Accurate control is achieved by continuous and automatic adjustment of the process gas composition and operating conditions.

The reactor (1) is designed to ensure good mixing and a uniform temperature. Operating conditions within the bed are mild; the pressure is about 20 bar g and the temperature is between 75°C and 110°C. Polymer particles grow in a fluidized-bed reactor where the fluidization gas is a mixture of ethylene, comonomer, hydrogen and nitrogen. Fine particles leaving the reactor with the exit gas are collected by cyclones (2) and recycled to the reactor. This feature ensures that these particles do not circulate in the reaction loop, where they could foul the compressor, exchanger and reactor grid. It also prevents product contamination. Unreacted gas is cooled (3) and separated from liquid (4), compressed (5) and returned to the reactor, maintaining the growing polymer particles at the desired temperature. Catalysts are incorporated into the final product without any catalyst removal step.

The reactor and almost all other equipment is made from carbon steel. Polymer powder is withdrawn from the reactor by a proprietary lateral discharge system and separated from associated process gas in a simple degassing stage using hot recirculating nitrogen. The powder is then pneumatically conveyed to the finishing section where additives are incorporated before pelletization and storage.

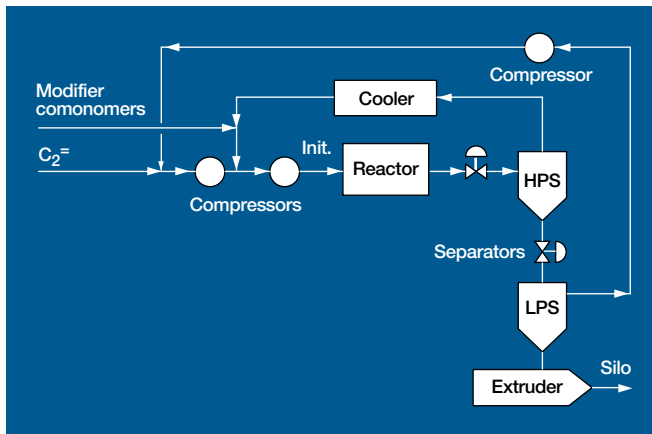
Products: A wide range of LLDPE and HDPE products can be produced. LLDPE is used in film, injection molding, rotational molding and extrusion applications and can be made using either butene or hexene as the comonomer.

Narrow molecular-weight HDPE provides superior injection molding grades. Broad molecular-weight HDPE is used for blow molding, pipe, film and other extrusion applications.

Commercial plants: Thirty reactor lines are operating, in design or under construction worldwide with capacities ranging from 50,000 tpy to 350,000 tpy.

Licensors: BP.

PETROCHEMICAL PROCESSES 2001



Polyethylene

Application: To produce low density polyethylene (LDPE) homopolymers and EVA copolymers using the high pressure free radical process. Large scale tubular reactors with a capacity in the range of 130 to 350 Mtpy, as well as stirred autoclave reactors with capacity around 100 Mtpy can be used.

Description: A variety of polymers are produced on these large reactors for various applications. The melt index, polymer density and molecular weight distribution are controlled with temperature profile, pressure, initiator and comonomer concentration. Autoclave reactors can give narrow or broad molecular weight distribution depending on the selected reactor conditions, whereas tubular reac-

tors typically give narrow molecular weight distribution polymers.

Gaseous ethylene is supplied to the battery limits and boosted to 300 bar by the primary compressor. This makeup gas, together with the recycle gas stream, is compressed to reactor pressure in the secondary compressor. The tubular reactors operate at pressures up to 3,000 bar, whereas autoclaves normally operate below 2,000 bar. The polymer is separated in a high- and low-pressure separator; nonreacted gas is recycled from both separators. Molten polymer from the low-pressure separator is fed into the extruder; polymer pellets are then transferred to storage silos.

The main advantages for the high pressure process compared to linear PE processes are short residence time and the ability to switch from homopolymers to copolymers incorporating polar comonomers in the same reactor. Also, the high pressure process allows fast and efficient transition for a broad range of polymers.

Products: Polymer density in the range 0.912 up to 0.935 for homopolymers; the melt index may be varied from 0.2 to greater than 150. Vinylacetate content up to 30 wt%.

Economics:

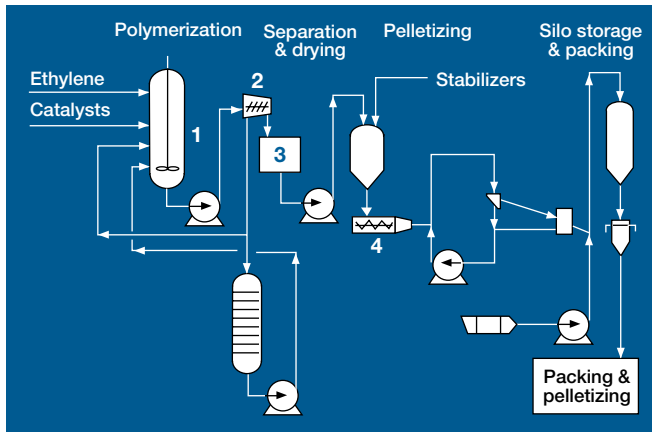
Raw materials and utilities, per metric ton of pelletized polymer:

Ethylene, ton/ton	1.008
Electricity, kWh	800
Steam, ton/ton	0.35
Nitrogen, Nm ³ /t	5

Commercial plants: ExxonMobil Chemical Co. and its affiliates operate 23 high-pressure reactors on a worldwide basis with a capacity of approximately 1.7 MMtpy. Homopolymers and a variety of copolymers are produced. Since 1996, ExxonMobil Chemical Co. has sold licenses with a total installed capacity (either in operation or under construction) of approximately 800 Mtpy.

Licensors: ExxonMobil Chemical Co.

PETROCHEMICAL PROCESSES 2001



Polyethylene

Application: To produce high density polyethylene (HDPE) and medium density polyethylene (MDPE) under low-pressure slurry process—"CX process."

Description: The CX process offers products having bimodal molecular-weight distribution, where width is freely and easily controlled by adjusting the reactor arrangement without changing the catalyst system. This process produces a wide melt index range. Innovative catalyst chemistry is combined with a sophisticated polymerization process. The control system allows the plant to operate very stably,

easily and without daily variation. Simple catalyst system and simple polymerization operation provide easy product switch-over that results in short transition time and negligible amount of off-spec product from switch-over. Ethylene, hydrogen, comonomer and superhigh activity catalyst are fed into the reactors (1), and polymerization reaction takes place under slurry state. The automatic polymer property control system plays a very effective role in product-quality control. Superhigh activity catalyst requires no catalyst removal from the products. Slurry from the reactors is pumped to the separation system (2), and the wetcake is dried into powder in the dryer system (3). As much as 90% of the solvent separated from the slurry is directly recycled to the reactors without any treatment. The dry powder is pelletized in the pelletizing system (4) along with required additives.

Product: Broad range of homopolymer and copolymer can be produced.

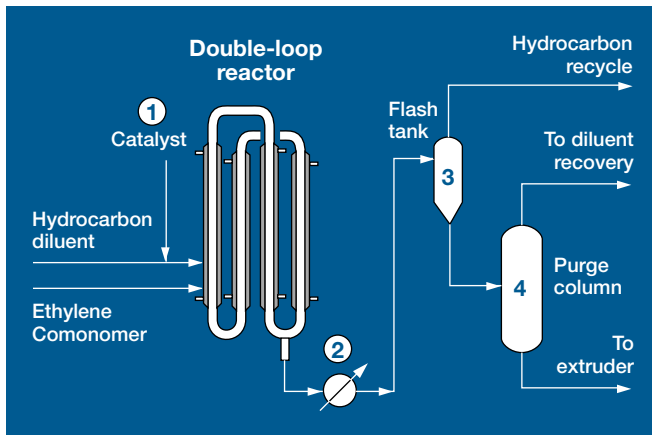
Melt index	0.01 to >50
Molecular-weight distribution	Freely controlled from narrow to very wide
Density	0.93 to 0.97

Economics: Consumption per metric ton of natural pellets of typical product type:

Ethylene and comonomer, kg	1,010
Electricity, kWh	305
Steam, kg	340
Water, cooling, t	190
Nitrogen, Nm ³	30

Commercial plants: Thirty-five reaction lines of CX process are in operation or construction worldwide with a total production capacity of over 3.6 MMtpy.

Licensors: Mitsui Chemicals, Inc.



1, pentene and octene-1. High-activity catalysts eliminate the need for catalyst removal. No waxes or other byproducts are formed during polymerization, thereby minimizing environmental emissions.

Ethylene, isobutane, comonomer and catalyst are continuously fed to the loop reactor where polymerization occurs at temperatures lower than 100°C and pressures of approximately 40 kg/cm² and residence times of approximately one hour. Ethylene conversion exceeds 97% per pass. Reactor effluent is flashed to separate the solid resin from the gaseous stream (3). Polyethylene powder is purged (4) with nitrogen to remove traces of hydrocarbons and pneumatically conveyed to the extrusion area for stabilization and pelletizing. The gaseous stream is compressed, purified and recycled back to the reactor.

Products: Homopolymers and copolymers are produced for applications in film, blow molding, injection molding, roto molding, pipe, sheet and thermoforming, and wire and cable.

Economics: Representative of conditions for both homopolymer and copolymer production:

Typical raw material and utility requirements, per metric ton of pelleted resin:

Ethylene, mt	1.007
Catalyst and chemicals, U.S.\$*	2.00–10.00
Steam, mt	0.25
Electricity, kWh	350
Water, cooling (circulating), mt	185
Nitrogen, Nm ³	30

* Depends on product slate

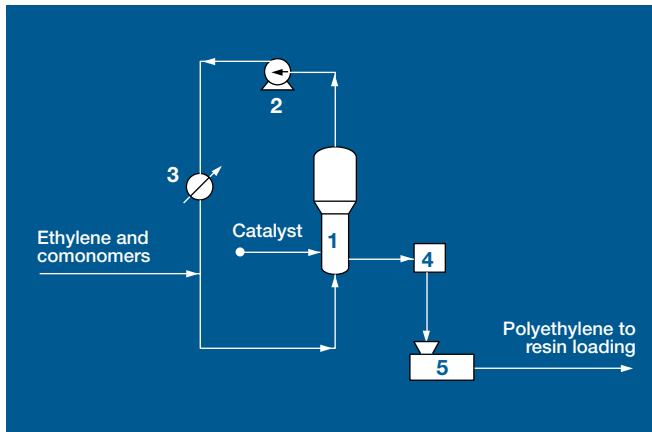
Commercial plants: Eighty-two reactor lines are either in operation or construction worldwide and account for 34% of worldwide capacity.

Licensors: Chevron Phillips Chemical Co., LP.

Polyethylene

Application: Produce linear polyethylene (LPE) using the Phillips Petroleum Co., LPE process.

Description: Polyethylene resins ranging in melt indices from less than 2 HLMI to greater than 200 MI, densities from slightly less than 0.920 to 0.970 gr/cc, and molecular weight distribution from very narrow to very broad are produced by the Phillips LPE process. Polymerization occurs in an isobutane slurry using very high activity proprietary catalysts (1) in a loop reactor (2). Melt index and molecular weight distribution are controlled by catalyst, operating conditions and hydrogen. Density is controlled by comonomer incorporation. Comonomers that can be used include butene-1, hexene-1, 4-methyl-



Polyethylene

Application: To produce linear low-density polyethylene (LLDPE) to high-density polyethylene (HDPE) using the low-pressure, gas phase UNIPOL PE process.

Description: A wide range of polyethylenes is made in a gas-phase, fluidized-bed reactor using proprietary solid and slurry catalysts. The product is in a dry, free-flowing granular form substantially free of fines as it leaves the reactor and is converted to pellet form for sale. Melt index and molecular weight distribution are controlled by

selecting the proper catalyst type and adjusting operating conditions. Polymer density is controlled by adjusting comonomer content of the product. High productivity of conventional and metallocene catalysts eliminates the need for catalyst removal.

The simple and direct nature of this process results in low investment and operating costs, low levels of environmental pollution, minimal potential fire and explosion hazards, and easy operation and maintenance.

Gaseous ethylene, comonomer and catalyst are fed to a reactor (1) containing a fluidized bed of growing polymer particles and operating near 25 kg/cm^2 and approximately 100°C . A conventional, single-stage, centrifugal compressor (2) circulates reaction gas, which fluidizes the reaction bed, provides raw material for the polymerization reaction, and removes the heat of reaction from the bed. Circulating gas is cooled in a conventional heat exchanger (3).

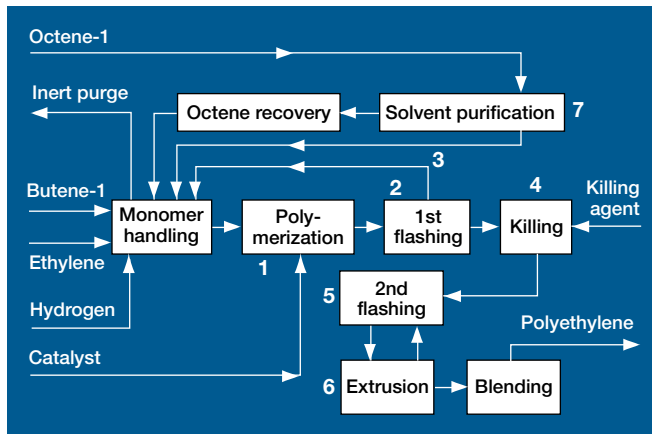
The granular product flows intermittently into product discharge tanks (4) where unreacted gas is separated from the product and returned to the reactor. Hydrocarbons remaining with the product are removed by purging with nitrogen. The granular product is subsequently pelletized in a low-energy system (5) with the appropriate additives for each application.

Products: Polymer density is easily controlled from 0.915 to 0.970 g/cm. Depending on catalyst type, molecular weight distribution is either narrow or broad. Melt index may be varied from less than 0.1 to greater than 200. Grades suitable for film, blow-molding, pipe, rotomolding and extrusion applications are produced.

Commercial plants: Eighty-nine reaction lines are in operation, under construction or in the design phase worldwide with single-line capacities ranging from 40,000 tpy to more than 450,000 tpy.

Licensor: Univation Technologies.

PETROCHEMICAL PROCESSES 2001



Polyethylene (COMPACT solution process)

Application: To produce polyethylene with a very wide density range from .900 to .970 using the COMPACT solution process with a single proprietary, advanced Ziegler Natta-type catalyst. As comonomers, either propylene (for high-density range), butene or octene or combinations are used.

Description: Liquid or gaseous ethylene is fed, together with a solvent and required comonomer(s) into a stirred, liquid-filled, vessel-type reactor (1). The reactor is operated adiabatically; thus, the feed is pre-cooled. All heat of reaction is used to raise polymerization temperature up to approximately 200°C. Hydrogen is used to control polymer molecular weight. A high-activity, proprietary catalyst is prepared onsite from commercially available components. Ethylene

conversions exceed 95% per pass are obtainable.

The latent heat of the polymer solution leaving the reactor is used to flash off the solvent, unconverted ethylene and light comonomers in flash vessel (2). Vapors from this vessel are condensed in an overhead-system (3) and recycled back to the reactor feed without purification.

A killing agent (4) is added to the concentrated polymer solution which is pumped to the second flashing through a solution heater. No catalyst removal step is necessary.

In the second flash vessel (5), further concentrating to over 95% polymer is done and the product is fed into a degassing extruder (6) to remove the last traces of solvent and octene (when used as comonomer). Vapors from the second flash vessel and degassing extruder are purified in the purification section (7) and then recycled to the reactor section. In the degassing extruder, specified additives are added, and the polymer is pelletized. After drying, the pelletized resins are transported to the silos.

The COMPACT solution process is characterized by its low residence time (few minutes in the reactor and less than 30 minutes in total), thus enabling fast grade changes and wide flexibility for usage with various comonomers. Especially, the octene copolymers are the ultimate in LLDPE grades.

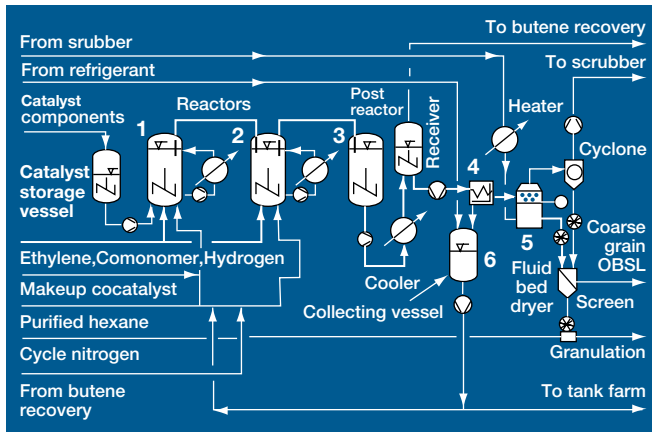
Products: Almost any density PE can be cost-effectively produced with comonomers—propylene, butene, octene or combinations. Densities range from .900 to .970 with MFI's ranging from 0.8 to 100. Major applications are film, injection molding, rotational molding, sheet, pipe and crosslinking, where extreme mechanical properties are required.

Economics: Typical raw materials and utilities consumption per metric ton (mt) of pelletized product:

Ethylene and comonomer, mt	1.016
Electricity, kWh	500
Steam, kg	400
Water, cooling, m ³	230
Steam, LP, kg, credit	330

Commercial plants: Presently, a total capacity of 650 mtpy is licensed with five plants in commercial operation.

Licensors: Stamicarbon bv.



Polyethylene, HDPE

Application: To produce high-density polyethylene (HDPE) using the stirred tank, heavy diluent Hostalen process (former HOECHST AG).

Description: The Hostalen process is a slurry polymerization with two reactors parallel or in series. Switching from a single reaction to a reaction cascade enables producing top quality unimodal and bimodal polyethylene (PE) from narrow to broad molecular weight distribution with the same catalyst.

The catalyst is only fed to the first reactor. Polymerization occurs in a dispersing medium like n-hexane using a Ziegler catalyst with very high activity. No deactivation and catalyst removal is necessary because a very low level of catalyst residue remains in the polymer. For unimodal-grade production, the catalyst, dispersing medium, monomer and hydrogen are fed to the first reactor (1) where the first polymerization takes place. The slurry is then sent to the post reactor (2). In the case of bimodal grade production, the second polymerization occurs under different reaction conditions with respect to the first reactor. Also, ethylene, butene and further dispersing medium are fed to the second reactor. Reaction conditions are controlled with a state observer and fuzzy logic, thus very high quality PE is manufactured.

Finally, the HDPE-slurry from the second reactor is sent to the post reactor (3) to reduce dissolved monomer. The process' total conversion is up to 99.5%. In the decanter (4), the polymer is separated from dispersing medium. The polymer containing the remaining hexane is dried in the fluid bed dryer (5) and then pelleted in the granulation section. The separated and collected dispersing medium of the fluid separation step (6) with the dissolved cocatalyst and comonomer is recycled to the polymerization reactors. A small part of the dispersing medium is distilled to maintain the composition of the diluent.

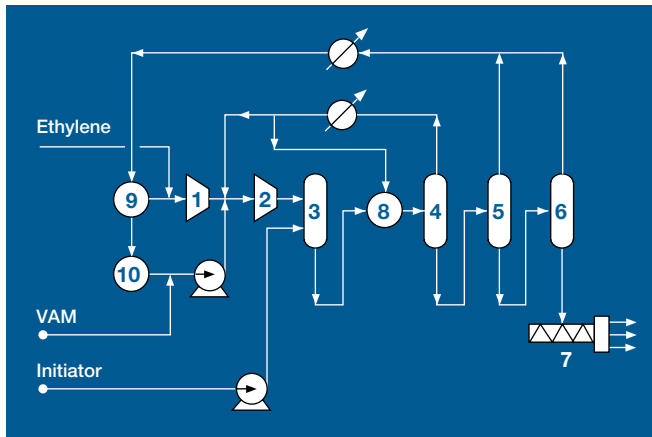
Products: The cascade technology enables manufacturing tailor-made products with a definite molecular weight distribution (MWD)—between narrow to broad MWDs. The melt flow index may vary from less 0.01 (bimodal product) to greater than 50 (unimodal product). Homopolymers and copolymers are used in various applications such as blow molding (large containers, small bottles), extrusion molding (film, pipes, tapes and monofilaments, functional packaging) and injection molding (crates, refuse bins, transport containers, fibers).

Economics: Raw material and utility requirements per metric ton (mt) of HDPE pellets

Ethylene and comonomer, kg/mt PE	1,015
Steam, mt/mt PE	400
Electricity, MWh/mt PE	0.350
Water, cooling ($\Delta T=10^{\circ}\text{K}$), mt/mt PE	165

Commercial plants: Twenty-three reaction lines with different capacities, adjusted to the market conditions, are in operation or under construction. Nearly 2.9 million tpa of HDPE are produced with the Hostalen technology.

Licensors: Basell Polyolefins; **preferred contractor:** Krupp Uhde GmbH.



vides a great flexibility and permits tailor-made resins by adjusting molecular-weight distribution.

To avoid secondary reactions, the flow is cooled by cold ethylene injected by a proprietary device (8). Such quenching controls acetic acid at negligible values and corrosions are undetectable.

Unreacted gas is stripped from molten resin in high (4), medium- (5) and low-pressure separators (6). The medium-pressure separator has been added for energy savings.

The resin flows into the extruder (7). Pelletized resin is dried and transferred to the silos. Gaseous streams are recycled to P (1) and S (2) compressors.

VAM condensed (9), after medium-pressure recycle, is purified (10) and then, with makeup, is sent to the compressor suction (2) by piston pumps.

Products: Homopolymers and EVA copolymers are used in film, injection molding, profiles, sheets, cable sheetings, crosslinking and foaming.

Economics:

Raw materials and utilities, per 1,000 kg of pelleted resin:

	LDPE	EVA 18/3
Ethylene, kg/t	1,010	835
Comonomer, kg/t		195
Electricity, kWh/t	825	1,000
Nitrogen, Nm ³ /t	1	1
Steam, kg/t	150	150
LP steam, kg/t, credit	(>300)	(>300)
Water, cooling, m ³ /t	200	200
Catalyst and chemicals, \$/t	23	25

Commercial plants: Twenty-four reactor lines are either in operation or in construction worldwide up to 200,000 tpa single line tubular and autoclave systems.

Licensor: EniChem through Snamprogetti.

Polyethylene, LDPE-EVA

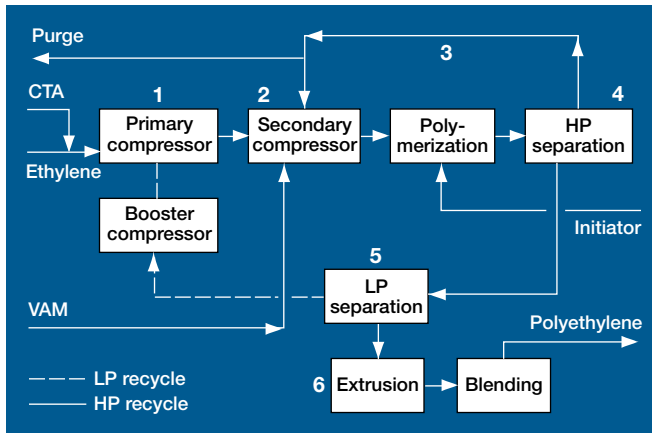
Application: To produce low density polyethylene (LDPE) and ethylene vinyl acetate (EVA) by the high-pressure, autoclave or tubular EniChem process.

Description: The EniChem swing process produces LDPE with MFI ranging from 0.1 to 400 and densities from 0.918 to 0.935, as well as EVA with vinyl acetate monomer (VAM) content from 3% to 40%.

After primary compression (1), ethylene, with recycled gas and VAM, enters the secondary compressor (2) to reach the required polymerization pressure. The gas is split into several streams, and injected in selected zones of the multizone reactor (3) where the polymerization occurs.

The combined control of pressure, temperature profile and comonomer content as well as choice of reactor injection points pro-

PETROCHEMICAL PROCESSES 2001



Polyethylene LDPE-EVA

Application: To produce low-density polyethylene (LDPE) and EVA copolymers by an unique high-pressure clean tubular reactor (CTR) process. Single-line capacities up to 400 mtpy are available.

Description: The clean tubular reactor (CTR) process is characterized by a nonfouling reactor for all grades. This is realized without "pressure pulsing"; hence, constant pressure and temperature profiles produce a more consistent and better quality product. Also, the absence of mechanical fatigue and decompositions are important features.

Gaseous ethylene is fed to a primary compressor (1) with recycled ethylene from an LP system and chain-transfer agent to control density and molecular weight. The mixture leaves the primary compressor at 250 bar and is subsequently compressed by the secondary compressor (2), together with the unconverted ethylene from the HP recycle (3) and VAM to produce EVA copolymers, to a polymerization

pressure of up to 3,000 bar.

Only peroxides are used as initiators and are added to the tubular reactor at several points. In combination with the unique CTR design, this process offers ethylene conversions up to 40%, at constant reactor pressure. A cleaning system nor a sequence system, for regularly fluctuating the reactor pressure during production, are not required.

After leaving the reactor, the polymer is separated from unconverted ethylene in the HP separator (4) and LP separator (5). The latter is installed at the inlet of the extruder (6) where the necessary additives are added and the product is pelletized. After drying, the pelletized resin is transferred to the silos.

The CTR technology enables lowest cost production of polyethylene that favorably compares with LLDPE processes by the absence of (expensive) comonomers and catalysts. Due to short residence times, faster grade-changes, without wide-spec product generation, are feasible as compared to most linear PE processes.

Products: LDPE grades produced with MFI's ranging from 0.2–70 and densities from .918–.930 while EVA's with VA percentages of up to 10% can be produced economically. Applications include injection molding, sheets, flexible pipes, cable sheathing, blow molding, crosslinking, foam, etc. Due to its extreme good processability, LDPE is also often added as a processing aid in LLDPE's.

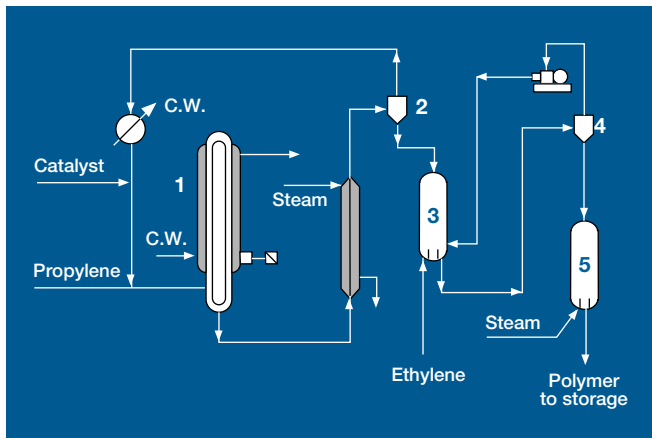
Economics: Typical raw materials and utilities consumption per metric ton of pelletized product:

Ethylene, mt	1.005
Electricity, kWh	800
Steam, HP, kg	230
Water, cooling, m ³	120
Steam, LP, kg, credit	650

Commercial plants: DSM operates three tubular lines with single-line capacities up to 220,000 mtpy. Since 1996, various licensed plants are in operation or under construction with single-line capacities ranging from 150,000 to 300,000 mtpy and have a total licensed capacity exceeding 1.8 Mtpy.

Licensors: Stamicarbon bv.

PETROCHEMICAL PROCESSES 2001



consumption. Dissolved monomer is removed from the polymer by a steam sparge (5).

The process can use lower-assay chemical-grade propylene (94%) or the usual polymerization grade (99.5%).

Yields: Polymer yields of more than 40,000 kg/kg of supported catalyst are obtained. The polymer has a controlled particle-size distribution and an isotactic index of 90% to 99%.

Economics: The Spheripol process offers the broadest range of products, with excellent quality and low capital and operating costs.

Raw materials and utilities, per 1,000 kg PP:

Propylene (plus ethylene for copolymers), kg	1,002–1,005
Catalyst, kg	0.025
Electricity, kWh	80*
Steam, kg	280
Water, cooling, m ³	90

*In case of copolymer production, an additional 20 kWh is required.

Product specifications: The process can produce a broad range of propylene-based polymers, including homopolymer polypropylene, random copolymers and terpolymers, heterophasic impact and specialty impact (up to 25% bonded ethylene) copolymers as well as high stiffness, high-clarity copolymers.

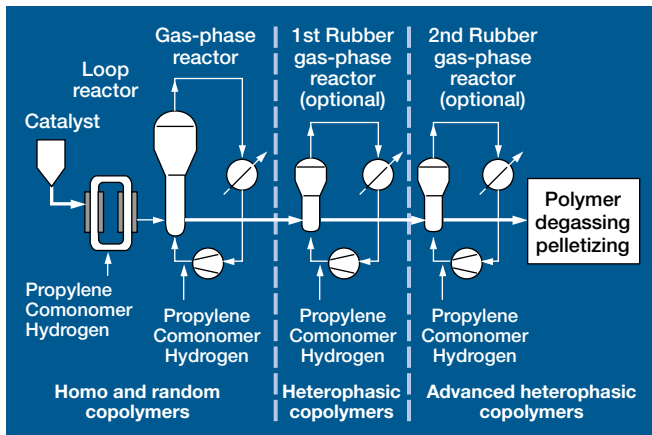
Commercial plants: Sixty-three Spheripol process plants with a total capacity of more than 11 million tpy are in operation worldwide. An additional 13 plants are under engineering design or construction. Total licensed capacity exceeds 13.5 MMtpy. Single-line ranges from 40,000 to 400,000 tpy.

Licensors: Basell Technology Co. BV. Basell is a joint venture between Royal Dutch/Shell Group and BASF.

Polypropylene

Application: To produce propylene-based polymers including homopolymer polypropylene, random and heterophasic impact and specialty impact copolymers using Spheripol process technology.

Description: In the Spheripol process, homopolymer and random copolymer polymerization takes place in liquid propylene within a loop tubular reactor (1). Heterophasic impact copolymerization is done by adding a gas-phase reactor (3) operated in series. Removal of catalyst residue and amorphous polymer is not required. Unreacted monomer is flashed in a two-stage pressure system (2, 4) and recycled back to the reactors. This improves yield and minimizes energy



Polypropylene

Application: The Borstar polypropylene (PP) process is a versatile technology. Through the choice of reactor combinations, homopolymers, random copolymers, heterophasic copolymers, and very high-rubber content heterophasic copolymers can be produced.

Description: Polypropylene with a melt flowrate ranging from 0.1 to 1,200 can be produced with the Borstar PP process. Currently, Ziegler Natta catalysts are used, but there is a potential to use single-site catalysts later. When producing homopolymers and random copolymers, the process consists of a loop reactor and a gas-phase reactor in series. One or two gas-phase reactors are combined with this arrangement when heterophasic copolymers are produced.

Propylene, catalyst, cocatalyst, donor, hydrogen, and comonomer

are fed into the loop reactor, where propylene is used as polymerization medium (bulk polymerization). The loop reactor, which is designed for supercritical conditions, is typically operated at 80°C–100°C and 50–60 bar. The propylene and polymer mixture coming from the loop reactor goes to a fluidized bed gas-phase reactor, where propylene is consumed in polymerization. The reactor is typically operated at 80°C–90°C and 25–35 bar. Fresh propylene, hydrogen and comonomer are fed into the reactor.

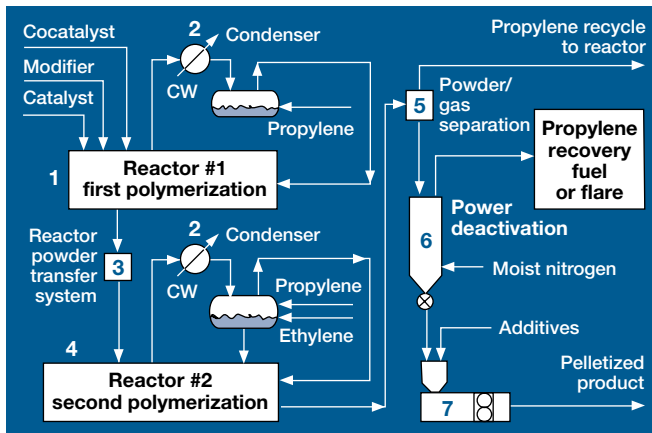
For homopolymers or random copolymers, hydrocarbon residuals are removed from the polymer powder, and it is then transferred into powder silos. Later, the power is sent to an extruder, where additiviation and pelletizing is made.

In the case of heterophasic copolymers, the polymer from the gas-phase reactor is transferred into another, smaller gas-phase reactor where the rubbery copolymer is made. After this step, hydrocarbon residuals are removed, and the powder is transferred to the extrusion section. Polymerization conditions in each reactor can be independently controlled, enabling production of both standard unimodal and broad molecular weight multimodal grades. The production rate ratios between the reactors can be adjusted to meet the targeted product properties.

Products: A wide range of polypropylenes with melt flowrates from 0.1 to 1,200, and from very stiff to very soft polymers are produced and can be tailored to customer needs. The products have reactor-made basic properties thus minimizing the need for additional compounding or other post-reactor treatment. Grades suitable for molding, film, and fiber and pipe as well as for engineering applications are produced.

Commercial Plants: The first Borstar PP plant was started up in May 2000 at Schwechat, Austria—ahead of schedule and below budget. The plant has a capacity of 200,000 tpy.

Licensor: Borealis A/S.



Polypropylene

Application: To produce polypropylene (PP) homopolymer, random copolymer and impact copolymer using the BP Amoco gas phase process with proprietary 4th generation supported catalyst.

Description: Catalyst in mineral-oil-slurry is metered into the reactor together with co-catalyst and modifier. The proprietary supported catalyst developed by BP Amoco has control morphology, super-high activity and very high stereospecificity. The resulting PP product is characterized by narrow particle size distribution, good powder flowability, minimum catalyst residues, noncorrosiveness, excellent color and low odor.

The horizontal stirred-bed reactor (1) is unique in the industry in that it approaches plug-flow type of performance, which contributes

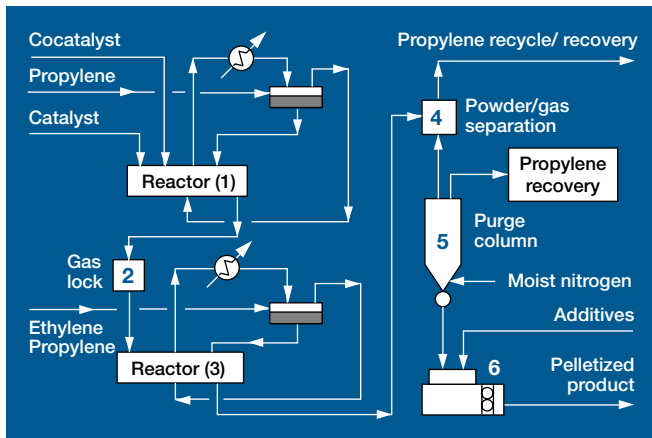
to two major advantages. First, it minimizes catalyst bypassing, which enables the process to produce very high-performance impact copolymer. Second, it makes product transitions very quick and sharp, which minimizes off spec transition materials. The reactor is not a fluidized bed, and powder mixing is accomplished by very mild agitation provided by a proprietary-designed horizontal agitator. Monomer leaving the reactor is partially condensed (2) and recycled. The condensed liquid together with fresh makeup monomer is sprayed onto the stirred reactor powder bed to provide evaporative cooling (remove the heat of polymerization) and control the bed temperature. Uncondensed gas is returned to the reactor.

For impact copolymer production, a second reactor (4) in series is required. A reliable and effective gas-lock system (3) transfers powder from the first (homopolymer) reactor to the second (copolymer) reactor, and prevents cross contamination of reactants between reactors. This is critically important when producing the highest quality impact copolymer. In most respects, the operation of the second reactor system is similar to that of the first, except that ethylene in addition to propylene is fed to the second reactor. Powder from the reactor is transferred and depressurized in a gas/powder separation system (5) and into a purge column (6) for catalyst deactivation. The deactivated powder is then pelletized (7) with additives into the final products.

Products: A wide range of polypropylene products (homopolymer, random copolymer and impact copolymer) can be produced to serve many application, including injection molding, blow molding, thermoforming, film, extrusion, sheet and fiber. Impact copolymer produced using this process exhibit a superior balance of stiffness and impact resistance over a broad temperature range.

Commercial plants: Twelve plants are either in operation or in design/construction worldwide with capacities ranging from 65,000 to 350,000 mty.

Licensors: BP.



and very high selectivity. The process provides low energy consumption, superior ethylene-propylene impact co-polymer properties; minimum transition products, high polymer throughput and a high operating factor. Each process step has been simplified; consequently, the technology offers a low initial capital investment and reduced manufacturing costs while providing product uniformity, excellent quality control and versatile product capability.

Particles of polypropylene are continuously formed at low pressure in the reactor (1) in the presence of catalyst. Evaporated monomer is partially condensed and recycled. The liquid monomer with fresh propylene is sprayed onto the stirred powder bed to provide evaporative cooling. The powder is passed through a gas-lock system (2) to a second reactor (3). This acts in a similar manner to the first, except that ethylene as well as propylene is fed to the system for impact co-polymer production. The horizontal reactor makes the powder residence time distribution approach that of plug-flow. The stirred bed is well suited to handling some high ethylene co-polymers that may not flow or fluidize well.

The powder is released periodically to a gas-powder separation system (4). It is depressurized to a purge column (5) where moist nitrogen deactivates the catalyst and removes any remaining monomer. The monomer is concentrated and recovered. The powder is converted into a variety of pelletized resins (6) tailored for specific market applications.

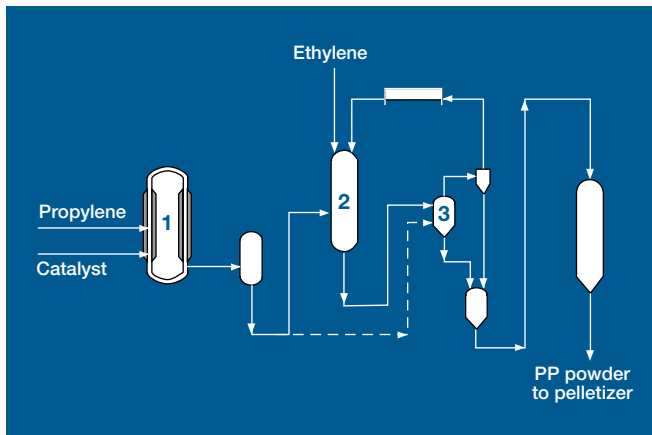
Commercial plants: Eight polypropylene plants are in operation, or under construction, with capacities ranging from 65,000 tpy to 300,000 tpy. Total operational capacity is 1.5 million tpy.

Licensor: Chisso Corp.

Polypropylene

Application: A process to produce homopolymer polypropylene and ethylene-propylene random and impact co-polymers using gas-phase polymerization in a special horizontal plug-flow reactor.

Description: The process features a horizontal agitated reactor and a high-performance catalyst specifically developed by the licensor. The catalyst has a controlled morphology, very high activity



Polypropylene

Application: To produce polypropylene including homopolymer, random copolymer and impact copolymer.

Description: The process, with a combination of the most advanced high-yield and high-stereospecificity catalyst, is a nonsolvent, non-deashing process, eliminating atactic polymers and catalyst residue removal. The process can produce various grades of polypropylene

with outstanding product quality. Polymer yields of 20,000 to 100,000 kg/kg of supported catalyst are obtained and the total isotactic index of polymer can reach 98% to 99.9%. The reactor polymer has a narrow and controlled particle size distribution that not only serves to stabilize plant operation but also permits easy shipment as powder.

In the process, homopolymer and random copolymer polymerization takes place in the loop-type reactor or vessel-type reactor system (1). For impact copolymer production, copolymerization is performed in a gas-phase reactor (2) after homopolymerization. The polymer is discharged from a gas-phase reactor and transferred to the separator (3). Unreacted gas accompanying the polymer is removed in the separator and recycled to the reactor system.

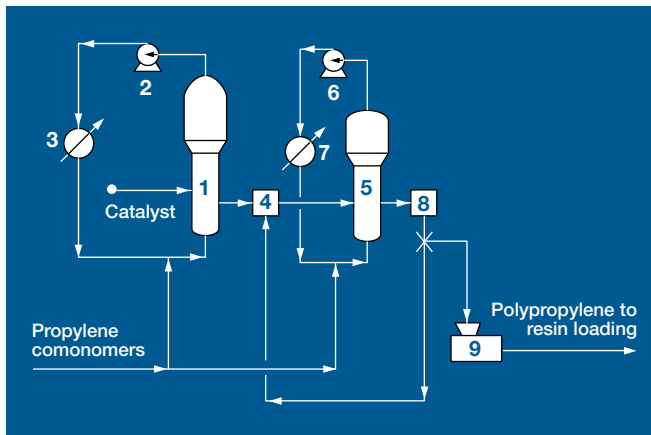
Products: The process can produce a broad range of polypropylene polymers, including homopolymer, random copolymer and impact copolymer, which become high-quality grades that can cover varied applications.

Economics: Consumption per metric ton of polypropylene powder:

Propylene (and ethylene for copolymers), kg	1,005
Electricity, kWh	130
Steam, kg	300
Water, cooling, t	70

Commercial plants: Twenty-five reaction lines of the process plants are in operation, engineering design or construction worldwide with a total production capacity of 2.2 MMtpy.

Licensors: Mitsui Chemicals, Inc.



Polypropylene

Application: To produce homopolymer, random copolymer and impact copolymer polypropylene using the Union Carbide gas-phase UNIPOL PP process.

Description: A wide range of polypropylene is made in a gas-phase, fluidized-bed reactor using proprietary catalysts. Melt index, isotactic level and molecular weight distribution are controlled by utilizing the proper catalyst, adjusting operating conditions and adding molecular-weight control agents. Random copolymers are produced by adding ethylene or butene to the reactor. Ethylene addition to a second reactor in series is used to produce the rubber phase of impact copolymers.

The UNIPOL PP process' simple, direct nature results in low investment and operating costs, low pollution levels, minimal potential fire and explosion hazards, and easy operation and maintenance. To produce homopolymers and random copolymers, gaseous

propylene, comonomer and catalyst are fed to a reactor (1) containing a fluidized-bed of growing polymer particles and operating near 35 kg/cm² and approximately 70°C. A conventional, single-stage, centrifugal compressor (2) circulates the reaction gas, which fluidizes the reaction bed, provides raw materials for the polymerization reaction and removes the heat of the reaction from the bed. Circulating gas is cooled in a conventional heat exchanger (3). Granular product flows intermittently into product discharge tanks (4), and unreacted gas is separated from the product and returned to the reactor.

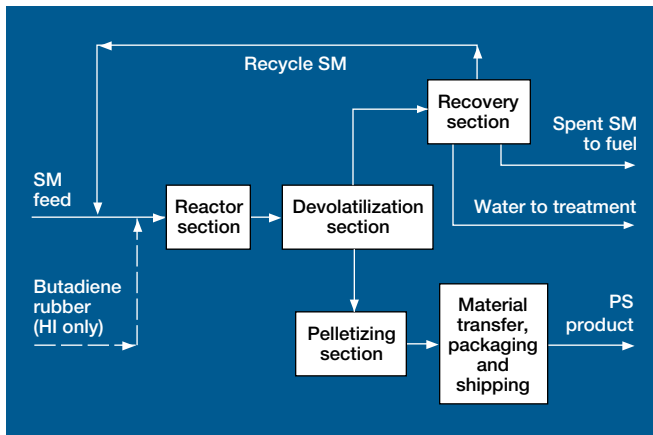
The polypropylene resin formed in the first reactor (1) is transferred into the impact reactor (5). Gaseous propylene and ethylene, with no additional catalyst, are fed into the impact reactor to produce the polymeric rubber phase within the existing polypropylene particles. The impact reactor operates in the same manner as the initial reactor, but at approximately half the pressure, with a centrifugal compressor (6) circulating gas through a heat exchanger (7) and back to the fluid-bed reactor. Impact copolymer is removed by product discharge tanks (8) and unreacted gas is returned to the reactor. Hydrocarbons remaining in the product are removed by purging with nitrogen. Granular products are pelletized in a proprietary low-energy system (9). Controlled rheology, high melt-flow grades are produced in the pelleting system through the addition of selected peroxides.

Products: Homopolymers can be produced with melt flows from less than 0.1 to 3,000 and isotactic content up to 99%. Random copolymers can be produced with up to 12 wt% ethylene or up to 21 wt% butene over a wide melt flow range (<0.1 to >100). A full range of impact copolymers can be polymerized with a good stiffness to impact balance. Products from narrow to broad molecular-weight distribution can be manufactured in grades suitable for film injection, molding, blow molding, extrusion and textile applications.

Commercial plants: Thirty-six reaction lines are in operation, under construction or in design with capacities ranging from 80,000 tpy to 260,000 tpy.

Licensors: Union Carbide Corp., a subsidiary of The Dow Chemical Co. Univation Technologies is the licensor of the UNIPOL PE process.

PETROCHEMICAL PROCESSES 2001



Polystyrene

Application: The NSCC/UOP polystyrene process produces a wide range of polystyrene (PS) grades. General-purpose or “crystal” polystyrene (GPPS) is a clear, amorphous polymer used widely in packaging of food, compact disks, etc. When more impact resistance is required for items like computer and television housings, polybutadiene rubber is incorporated into the polystyrene matrix to produce high-impact or “rubber-modified” polystyrene (HIPS). The technology is also capable of producing a family of premium high-strength, high-gloss HIPS resins that can be substituted for more expensive acrylonitrile-butadiene-styrene resins (ABS) in many applications.

Description: The process involves continuous, bulk-phase polymerization of styrene using a combination of thermal and chemical initiation. A typical unit design consists of separate reaction trains for GPPS and HIPS grades, which have been optimized for each resin

type. The GPPS reactor train is capable of producing numerous grades of GPPS that range from low-molecular-weight, high-flow grades to high-molecular-weight, heat-resistant grades. The HIPS reactor train includes a proprietary reactor design that gives unprecedented control over the distribution of rubber through the polystyrene matrix. The efficient distribution of rubber means that this process can produce a given polymer strength with less rubber than is required by other technologies. This process can also precisely control the size of rubber particles, down to less than one micron in diameter. Small rubber particles result in high-strength HIPS resins with smooth, glossy finishes that rival the mechanical properties and surface finish of ABS.

The GPPS and HIPS reactor sections each contain several polymerization reactors in series, two-stage devolatilization and a pelletizing line. The devolatilization equipment is designed to deliver polystyrene product with a concentration of residual volatile material (TVM) of less than 100 wt-ppm. Common equipment includes sections for feed preparation, SM recovery, water removal and bulk-resin handling.

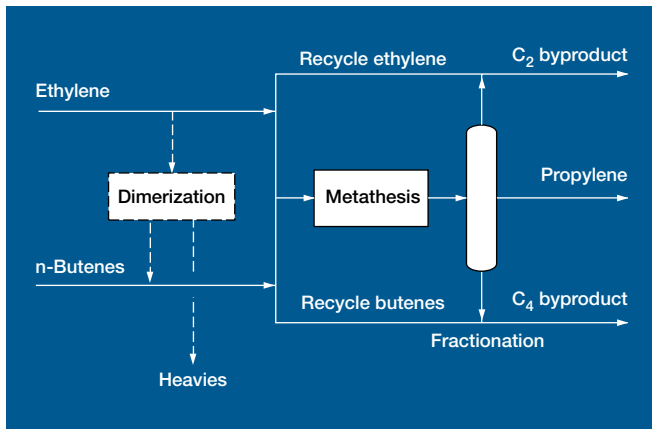
Economics: basis: 50,000 tpy GPPS + 50,000 tpy HIPS, U.S. Gulf Coast)

Investment, U.S. \$/tpy	300
Raw material consumption, per metric ton of GPPS	
Styrene	0.999–1.007
Raw material consumption, per metric ton of HIPS	
Styrene	0.926–0.948
Rubber	0.052–0.064
Utilities, U.S. \$/ton PS	3.6

Commercial plants: Nippon Steel Chemical Co. (NSCC), currently operates two units in Kimitsu, Japan, with a total polystyrene capacity of 200,000 tpy. NSCC produces more than 50 different grades of GPPS and HIPS, including a family of premium, high-performance HIPS resins that have successfully displaced ABS in certain applications.

Licensor: UOP.

PETROCHEMICAL PROCESSES 2001



Propylene

Application: To produce propylene from ethylene and butenes using Lummus' olefin conversion technology (OCT). Other OCT process configurations involve interconversion of light olefins and production of C₂-C₅ mono-olefins.

Description: Ethylene feedstream (plus recycle ethylene) and butenes feedstream (plus recycle butenes) are introduced into the fixed-bed, metathesis reactor. The catalyst promotes reaction of ethylene and 2-butene to form propylene and simultaneously iso-

merizes 1-butene to 2-butene. Effluent from the metathesis reactor is fractionated to yield high-purity, polymerization-grade propylene, as well as ethylene and butenes for recycle and small byproduct streams. Due to the unique nature of the catalyst system, the mixed C₄ feed stream can contain a significant amount of isobutylene without impacting performance of the OCT process.

Yields: Process selectivity to propylene is typically greater than 98%. Overall conversion of n-butenes is 85%–92%. Ethylene and butenes feedstreams can come from steam crackers or many refinery sources and in varying concentrations. Alternatively, butenes can come from ethylene dimerization, which is also licensed by Lummus.

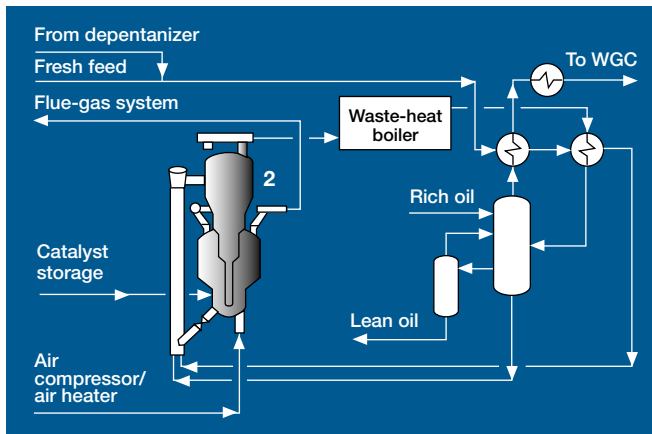
Economics: Based on a 300,000-tpy propylene plant, U.S. Gulf Coast, mid-2000 (assuming 86% n-butenes in feedstream).

Investment, total direct field cost, U.S.\$	20.5 million
Utilities required per pound of product:	
Fuel gas (fired), Btu	340
Electricity, kWh	36
Steam, 50 psig saturated, Btu	704
Cooling duty, Btu	1,033
Nitrogen, scf	2.1
Catalyst, cost (est.) per yr, U.S.\$	325,000
Maintenance, per yr as % of investment	1.5

Commercial plants: Lyondell Petrochemical Co., Channelview, Texas, uses both the OCT technology and ethylene dimerization technology. Two other plants have used related technology, including a Phillips 66 Co. plant at Pasadena, Texas. A 690-million lb/yr unit is under construction for BASF Fina Petrochemicals in Port Arthur, Texas.

Licensors: ABB Lummus Global.

PETROCHEMICAL PROCESSES 2001



Propylene

Application: To produce propylene and ethylene from low-value, light hydrocarbon streams in the carbon number range of C_4 to C_8 , such as C_4 and C_5 olefins produced from ethylene plants or light refinery streams such as cat cracker or coker gasolines.

Description: The SUPERFLEX process is a proprietary technology patented by ARCO Chemical Technology, Inc. (now Lyondell Chemical Co.), and is exclusively offered for license by Kellogg Brown & Root. It uses a fluidized catalytic reactor system with a proprietary catalyst to convert low-value feedstocks to desirable propylene and ethylene products. The catalyst is very robust; thus, no feed pre-treatment is required for typical contaminants such as sulfur, water, oxygenates or nitrogen. Attractive feedstocks include C_4 and C_5

olefin-rich streams from ethylene plants, FCC naphthas or C_4 s, thermally cracked naphthas from visbreakers or cokers, BTX or MTBE raffinate and C_5 olefins removed from motor gasolines.

The fluidized reactor system is similar to that of a refinery FCC unit and consists of riser reactor, regenerator vessel, air compression, catalyst handling, flue-gas handling and feed and effluent heat recovery. Using this reactor system with continuous catalyst regeneration allows higher operating temperatures than with fixed-bed reactors so that paraffins, as well as olefins, are converted. The conversion of paraffins allows substantial quantities of paraffins in the feedstream and recycle of unconverted feed without need to separate olefins and paraffins.

The cooled reactor effluent can be processed in a nearby, existing ethylene plant recovery section to minimize capital investment. Alternatively, the effluent can be processed in a partial recovery unit to recover recycle streams and concentrate olefin-rich streams for further processing in a nearby ethylene plant. If desired, KBR can provide an efficient design for a dedicated unit to process the whole stream for recovery of a full range of products, including polymer-grade propylene and ethylene.

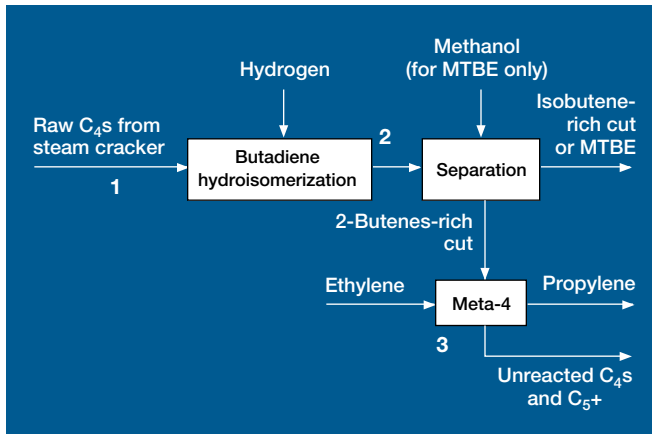
Yields: The technology produces up to 70 wt% propylene plus ethylene, with a propylene yield about twice that of ethylene, from typical C_4 and C_5 raffinate streams. Some typical yields are:

Feedstock	FCC LCN	Coker LN	Pyrolysis	Pyrolysis
			C_4 s	C_5 s
Ultimate yield, wt%*				
Fuel gas	13.6	11.6	7.2	12.0
Ethylene	20.0	19.8	22.5	22.1
Propylene	40.1	38.7	48.2	43.8
Propane	6.6	7.0	5.3	6.5
C_6+ gasoline	29.7	22.9	16.8	15.6

* Ultimate yield with C_4 s and C_5 s recycled.

Licensor: Kellogg Brown & Root.

PETROCHEMICAL PROCESSES 2001



Propylene

Application: To produce polymer-grade propylene plus either an isobutylene-rich stream or MTBE by upgrading low-value pyrolysis C₄ cuts or butene-rich streams via selective hydrogen and Meta-4 processes. This process is particularly profitable when butadiene markets are weak and propylene demand is strong.

Description: Crude C₄ streams are converted into propylene and an isobutylene-rich stream in three IFP process steps: (1) butadiene and C₄ acetylenes selective hydrogenation and butenes hydroisomeriza-

tion, (2) isobutylene removal via distillation or MTBE production and (3) metathesis (Meta-4).

The hydroisomerization step features: complete C₄ acetylenes and butadiene conversion to butenes, maximum 2-butenes production, flexibility to process different feeds, polymer-free product and no residual hydrogen. The second step separates isobutylene either by conventional distillation, or by reacting the isobutylene with methanol to produce MTBE.

The CCR Meta-4 process features are: a hard, highly active and robust catalyst, low catalyst inventory, low operating temperature and pressure, outstanding yields, liquid-phase operation, and continuous operation and catalyst regeneration.

Yields: Process selectivity to propylene is typically greater than 98%. Overall conversion of 2-butenes can reach 90%.

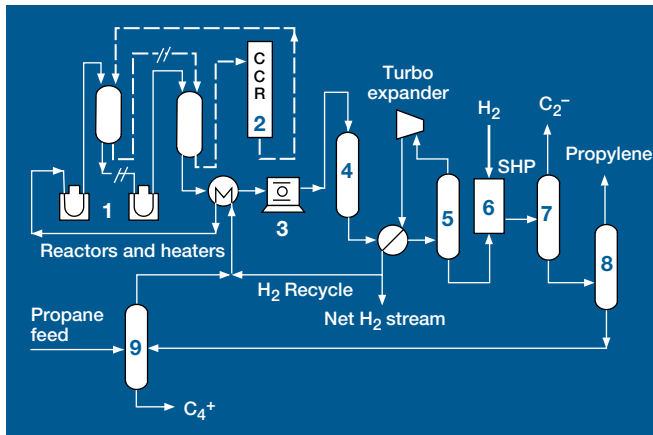
Economics: ISBL 2000 investment for a Gulf Coast location of a Meta-4 process producing 180,000 tpa propylene is \$U.S.19 million. Typical operating cost is \$18 per metric ton of propylene.

Installation: Over 100 C₄ hydrogenation units have been built using IFP technology. The CCR Meta-4 technology has been developed jointly with the Chinese Petroleum Corp., and demonstrated on real feedstock at Kaohsiung, Taiwan, industrial complex. The same type of moving-bed, continuous catalyst regeneration technology is industrially proven in 50 IFP catalytic reformers.

Reference: Chodorge, J. A., J. Cosyns, D. Commereuc, Q. Debuisschert, and P. Travers, "Maximizing propylene and the Meta-4 process," Oil Gas 2000.

Licensors: IFP, IFPNA.

PETROCHEMICAL PROCESSES 2001



Propylene

Application: To produce polymer-grade propylene from propane using the UOP Oleflex process in a propylene production complex.

Description: The complex consists of a reactor section, continuous catalyst regeneration (CCR) section, product separation section and fractionation section. Four radial-flow reactors (1) are used to achieve optimum conversion and selectivity for the endothermic reaction. Catalyst activity is maintained by continuously regenerating catalyst (2). Reactor effluent is compressed (3), dried (4) and sent to a cryogenic

separation system (5). A net hydrogen stream is recovered at approximately 90 mol% hydrogen purity. The olefin product is sent to a selective hydrogenation process (6) where dienes and acetylenes are removed. The propylene stream goes to a deethanizer (7) where light-ends are removed prior to the propane-propylene splitter (8). Unconverted feedstock is recycled back to the depropanizer (9) where it combines with fresh feed before being sent back to the reactor section.

Yields: Propylene yield from propane is approximately 85 wt% of fresh feed. Hydrogen yield is about 3.6 wt% of fresh feed.

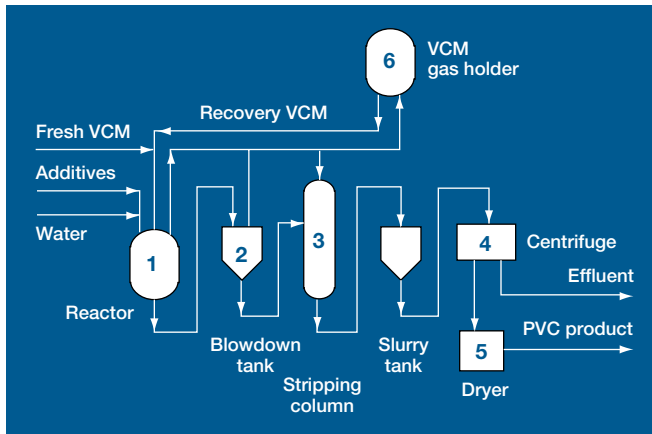
Economics: U.S. Gulf Coast inside battery limits are based on an Oleflex complex unit for production of 350,000 mtpy of polymer-grade propylene. The utility summary is net utilities assuming all light ends are used as fuel.

Inside battery limits investment, \$ million	145
Total project investment, \$ million	210
Typical net utility requirements, per ton of propylene product	
Electricity, kWh	200
Water, cooling, m ³	50
Net fuel gas, MMkcal (export credit)	1.2
Catalyst and chemical cost, \$/metric ton product	14

Commercial plants: Nine Oleflex units are in operation to produce propylene and isobutylene. Four of these units produce propylene. Two additional Oleflex units are under construction or in detailed design. These units will produce propylene. Over 1.3 million mta of propylene will be produced using Oleflex technology by 2001.

Licensors: UOP.

PETROCHEMICAL PROCESSES 2001



PVC (suspension)

Application: A process to produce polyvinyl chloride (PVC) from vinyl chloride monomer (VCM) using suspension polymerization. Many types of PVC grades are produced including: commodity, high K-value, low K-value, matted type and co-polymer PVC. The PVC possesses excellent product qualities such as easy processability and good heat stability.

Description: PVC is produced by batch polymerization of VCM dispersed in water. Standard reactor sizes are 60, 80, 100 or 130 m³.

The stirred reactor (1) is charged with water, additives and VCM. During polymerization reaction, the temperature is controlled at a defined temperature depending on the grade by cooling water or chilled water. At the end of the reaction, the contents are discharged into a blowdown tank (2) where most of the unreacted VCM is flashed off. The reactor is rinsed and sprayed with an anti-fouling agent, and is ready for the following batch.

The PVC slurry containing VCM is continuously fed to the stripping column (3). The column has a proprietary design and effectively recovers VCM from the PVC slurry without any deterioration of PVC quality. After stripping, the slurry is de-watered (4), and dried effectively by the proprietary dryer (5). It is then passed to storage silos for tanker loading or bagging.

Recovered VCM is held in a gas holder (6), then compressed, cooled and condensed to be reused for the following polymerization batch.

Economics:

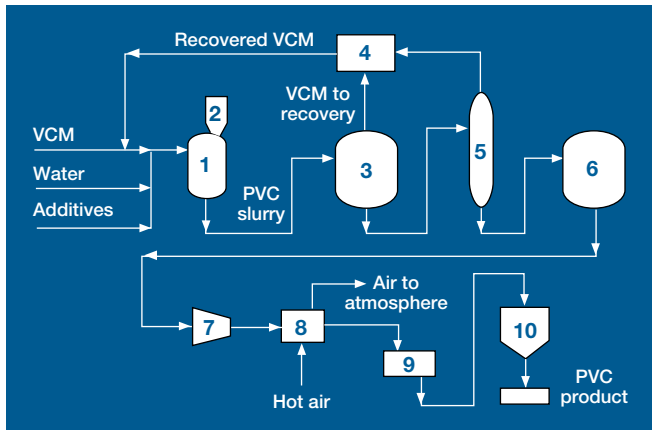
Raw materials and utilities, per ton of PVC:

VCM, t	1.003
Electricity, kWh	160
Steam, t	0.7
Additives, for pipe grade, \$U.S.	12

Commercial plants: The process has been successfully licensed 12 times worldwide. Total capacity of the Chisso process in the world is more than 1 million tpy. In addition, Chisso VCM removal technology has been licensed to many PVC producers worldwide.

Licensor: Chisso Corp.

PETROCHEMICAL PROCESSES 2001



PVC (suspension)

Application: A process producing polyvinyl chloride (PVC) from vinyl chloride monomer (VCM) using suspension polymerization.

Description: PVC is produced by batch polymerization of VCM dispersed in water, using reactors of up to 140 m³. The stirred reactor is charged with water (1), additives (2) and VCM (3) and heated to reaction temperature. The reaction is controlled at a conversion up to 94% to produce the properties for a particular grade. The heat of reaction is removed by cooling water through the reactor jacket and reflux condenser. Chilled water is not needed for reactor cooling, thus capital and operating costs are reduced. At reaction completion, the PVC and water suspension (4) are run down to a blowdown vessel where a proportion of unreacted VCM is flashed off (5) and recovered.

Remaining VCM is removed in a continuous steam-stripping column. The column is specifically designed to minimize product degra-

dation and eliminates periodic cleaning. The stripping column reduces residual VCM in the resin to less than 1 ppm. After stripping, the slurry (6) is centrifuged, dried (7) and stored. Recovered VCM from the blowdown vessel (5) and stripping column (8) is reused in subsequent batches. Vent gas from the recovery plant, containing inerts and VCM, is either sent to an incinerator OSBL or to a vent gas absorption system to recover VCM. All water contaminated with VCM is steam stripped to VCM levels of <1ppm before discharge. No further effluent treatment is required.

Resin deposits in the reactor are prevented by using a proprietary build-up suppressant, EVICAS 90. The closed-reactor process and effective build-up suppressant allow a reactor opening frequency up to once every 700 batches. For the complete PVC plant, total environmental emissions amount to less than 20gm of VCM per ton of PVC.

Economics: ISBL installed cost on the U.S. Gulf Coast, for a 150,000 mtpy suspension PVC plant is U.S. \$45 million.

Raw materials and utilities used per ton of PVC:

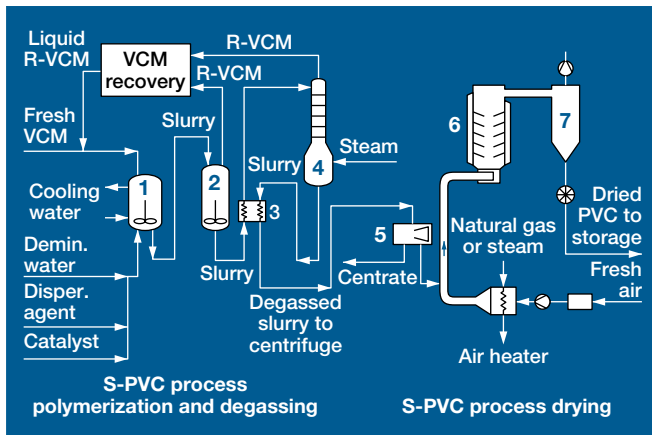
VCM, t/t	1.004
Steam, t/t	0.9
Water, cooling, kcal	480,000 kcal
Electricity, kWh/t	150
Water, demineralized, t/t	2.2
Productivity, t/m ³ /y	up to 600
Additive costs, U.S.\$/t for pipe-grade	11

An existing stripping system can be revamped by installing an EVC slurry stripping column. Cost of such a facility for a 150,000 tpy PVC plant would be U.S. \$ 2.5 million. At the moment, eleven stripping columns are operating worldwide.

Commercial plants: EVC operates six SPVC plants with an installed capacity of more than 1.1 million tpy. These process technologies have successfully been licensed worldwide. Inovyl's build-up suppressant, EVICAS 90, is used in 80% of the worldwide PVC production.

Licensor: Inovyl B.V., the technology business of EVC.

PETROCHEMICAL PROCESSES 2001



PVC (suspension)

Application: Production of suspension polyvinyl chloride (PVC) resins from vinyl chloride monomer (VCM) using the Vinnolit process.

Description: The Vinnolit PVC process uses a new high-performance reactor (1), which is available in sizes up to 150m³. A closed and clean reactor technology is applied; thus, opening of the reactors is not necessary, except for occasional inspections. Equally important, high-pressure water cleaning is not necessary. All process operations of this unit are controlled by a distributed process control system (DCS).

The batch-wise polymerization occurs in the following operation sequence:

- Prepare the reactor, which includes applying a highly effective antifouling agent
- Charge reaction solutions including dispersing agents, additives, chemicals, VCM and water into the reactor
- Exothermic conversion from VCM to PVC
- Discharge of the PVC slurry into the blowdown tank
- Flush the reactor internals.

The PVC slurry and unreacted VCM from the polymerization reactors are fed to the blowdown tank—the intermediate buffer between the discontinuous polymerization and the continuous degassing and drying unit.

In the blowdown tank (2), unreacted VCM is flushed out of the PVC slurry. From the blowdown tank, the slurry is fed through heat recuperator (3) to the sieve-tray type Vinnolit degassing column (4). VCM is stripped out with steam. The VCM concentration of the slurry leaving the degassing column is less than 1 ppm. The unreacted VCM is liquefied in the VCM recovery unit and charged back to polymerization. After dewatering the suspension in the centrifuge (5), the wet PVC cake is fed in the Vinnolit cyclone drying system (6). The solid particles and air are separated in the cyclone separator (7).

Economics: Chilled water for polymerization is not required. High productivity is achieved by using an inner-cooler reactor.

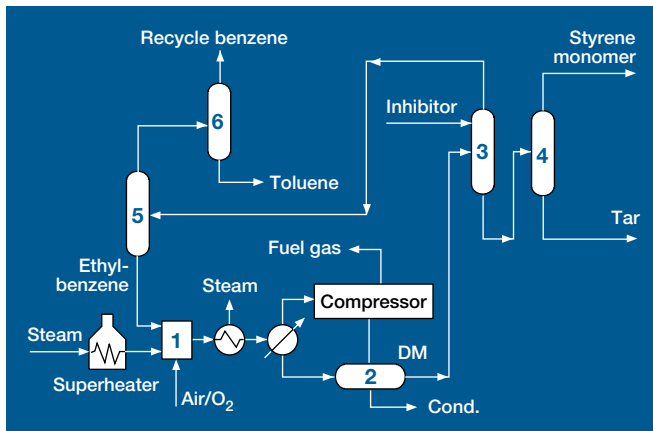
Raw materials and utilities, per ton of PVC:

VCM, t	1.001
Steam, t	0.8
Electricity, kWh	170
Additive costs, for pipe grade U.S. \$	14
Productivity, t/m ³ /y	up to 600

Commercial plants: Vinnolit is producing more than 580,000 t PVC/yr. Total capacity of the Vinnolit process in the world is about one million tpy. Vinnolit cyclone dryer has been licensed to many PVC producers worldwide.

Licensors: VinTec GmbH; **Contractor:** Krupp Uhde GmbH.

PETROCHEMICAL PROCESSES 2001



Styrene

Application: To produce polymer-grade styrene monomer (SM) by dehydrogenating ethylbenzene (EB) to form styrene using the Lummus/UOP “Classic” styrene process for new plants and the Lummus/UOP “SMART” process for revamps.

Description: In the Classic process, EB is catalytically dehydrogenated to styrene in the presence of steam. The reaction is carried out at high temperature under vacuum. The EB (fresh and recycle) and primary steam are combined with superheated steam, and the mixture is dehydrogenated in a multistage reactor system (1). An interheater reheats the process gas between stages. Reactor efflu-

ents are cooled to recover waste heat and condense the hydrocarbons and steam. Uncondensed offgas is compressed and is used as fuel. Condensed hydrocarbons (2) are sent to the distillation section. Process condensate (2) is stripped to remove dissolved aromatics.

A fractionation train (3,4) separates high-purity styrene, unconverted EB, which is recycled, and the relatively minor reaction byproduct tar. Toluene is produced (5,6) as a minor byproduct, and benzene (6) is recycled to the alkylator.

Typical SM-product purity ranges from 99.8% to 99.95%. The process provides high-product yield due to a unique combination of catalyst and operating conditions used in the reactors.

The SMART process is the same except between the dehydrogenation stages, oxygen is introduced to partially oxidize the hydrogen produced over a proprietary catalyst, to reheat the process gas and to remove the equilibrium constraint for the dehydrogenation reaction. The process achieves up to or greater than 80% EB conversion per pass.

Economics: (Classic)

Investment, U.S. \$/tpy

(U.S. Gulf Coast basis, 200,000 tpy) 225

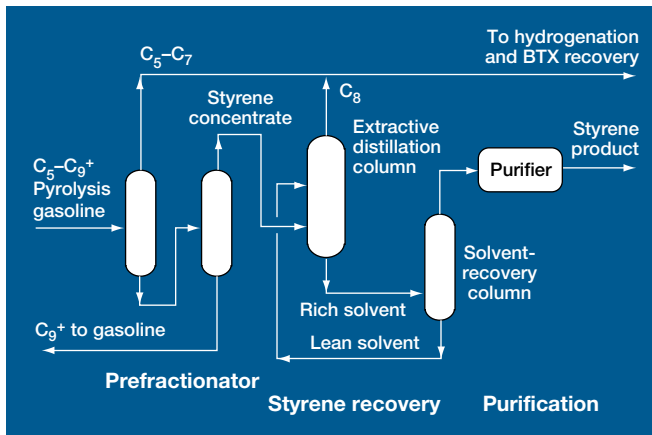
Raw materials consumption, per metric ton of SM:

Ethylbenzene	Classic
Utilities, U.S. \$/ton SM	1.054
	31

Commercial plants: Presently, 36 operating plants incorporate the Lummus/UOP styrene Classic technology. Three operating facilities are using the SMART process technology. Many future units using the SMART process are expected to be retrofits of conventional units, since the technology is well suited for revamps.

Licensor: ABB Lummus Global and UOP.

PETROCHEMICAL PROCESSES 2001



Styrene

Application: To directly recover styrene from raw pyrolysis gasoline derived from steam cracking of naphtha, gas oils and NGLs using the GT-Styrene process.

Description: Raw pyrolysis gasoline is prefractionated into a heart-cut C_8 stream. The resulting styrene concentrate is fed to an extractive-distillation column and mixed with a selective solvent, which extracts styrene to the tower bottoms. The rich solvent mixture is routed to a solvent-recovery column, which recycles lean solvent to the extractive-distillation column and recovers the styrene overhead. A final purification step produces a 99.9% styrene product con-

taining less than 50 ppm phenyl acetylene.

The extractive-distillation column overhead can be further processed to recover a high-quality mixed xylene stream. A typical world-scale cracker could produce approximately 25,000 ton/yr (tpy) styrene and 75,000 tpy mixed xylenes from pyrolysis gasoline.

The styrene is a high-purity product, suitable for polymerization, at a very attractive cost compared with conventional styrene production routes. If desired, the mixed xylenes can also be extracted from the pygas, upgrading their value as chemical feedstock. The process is economically attractive for typical pygas and supplemental feeds, which contain 15,000 tpy or more styrene.

Traditional pygas processing schemes destroy the styrene in the first-stage hydrogenation unit. Hydrotreated pygas is then fractionated to extract benzene and toluene. With the GT-Styrene process, this fractionation is made upstream of the hydrotreaters, which avoids some hydrogen consumption and catalyst fouling by styrene polymers. In many cases, most of the existing fractionation equipment can be re-used in the styrene-recovery mode of operation.

Economics: Styrene recovery (considering styrene upgrade only)

Basis: 25,000 tpy styrene capacity

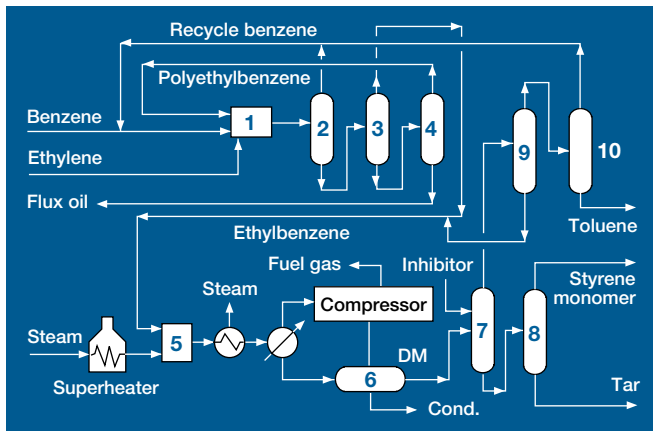
Typical U.S. GC capital cost, \$MM:	20
Styrene value in pygas, \$/t	120
Styrene product sales value, \$/t	450
Processing cost, \$/t	40
Gross margin, \$MM/yr	7.25
Pretax ROI, %	36

Commercial plants: One license has been placed.

Reference: "Generate more revenues from pygas processing," *Hydrocarbon Processing*, June 1997.

Licensors: GTC Technology Corp.

PETROCHEMICAL PROCESSES 2001



Styrene

Application: Production of polymer-grade styrene monomer (SM) from benzene and ethylene. The Lummus/UOP EBOne process is used to alkylate benzene with ethylene to form ethylbenzene (EB). The EB is then dehydrogenated to SM using the Lummus/UOP Classic SM process.

Description: Benzene is alkylated to EB over a zeolite catalyst in a fixed-bed, liquid-phase reactor. Fresh benzene is combined with recycled benzene and fed to the alkylation reactor (1). The benzene feed flows in series through the beds, while fresh ethylene feed is distributed equally between the beds. The reaction is highly exothermic, and heat is removed between reaction stages by generating steam.

In the fractionation section, unreacted benzene is recovered from the overhead of the benzene column (2), and EB product is taken as overhead from the EB column (3). A small amount of poly-benzene (PEB) is recovered in the overhead of the PEB column and recycled

to the reactor section (1), where it is transalkylated with benzene over a second zeolite catalyst to produce additional EB product.

The EB product is sent to the Classic SM unit, where it is hydrogenated over an iron-oxide catalyst in a series of fixed-bed, vapor phase reactors. The reaction is carried out at high temperature, under vacuum, and in the presence of steam. Fresh EB is combined with superheated steam and recycled EB and then fed to the reactor section (5). The dehydrogenation reaction is highly endothermic, and heat is added by exchange with steam. The reactor effluent is cooled and condensed in a multistage exchanger, which generates steam and recovers waste heat. Uncondensed offgas is compressed and used as fuel. The dehydrogenated mixture is separated from process condensate in the oil/water separator (6).

In the fractionation section the SM unit, unconverted EB is separated from SM product in the EB/SM splitter (7). SM product is recovered as overhead from the SM column (8). Typical SM product purity is in the range of 99.9 to 99.95 wt-%. Recycle EB is taken from the bottom of the EB recovery column (9). A benzene-toluene splitter (10) is often used to recycle benzene to the EBOne unit and export toluene as a minor co-product.

Small amounts of heavy byproducts—"flux oil" from the EB unit and "tar" from the SM unit—are usually burned as fuel in the steam superheater of the SM unit.

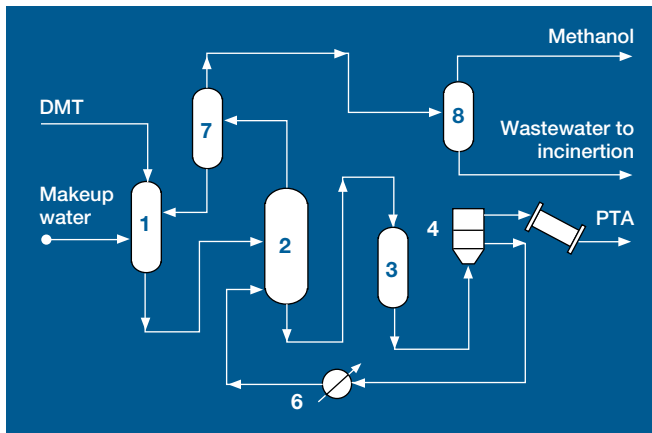
Economics: basis: 500,000 tpy, U.S. Gulf Coast

Investment, U.S. \$/tpy	192
Raw material consumption, per metric ton of SM	
Ethylene	0.281
Benzene	0.781
Utilities, U.S. \$/ton SM	26.0

Commercial plants: Fourteen EBOne units are in operation with a total EB capacity of 3.7 million tpy, and two additional units are under construction. Thirty-six Classic SM units are in operation, with a total SM capacity of 6.7 million tpy. The SMART process is also available for increasing the capacity of existing SM units.

Licensors: UOP and ABB Lummus Global.

PETROCHEMICAL PROCESSES 2001



Terephthalic acid

Application: To produce fiber-grade terephthalic acid (PTA) from dimethyl terephthalate (DMT).

Description: Production of terephthalate from p-xylene and methanol are found under the dimethyl terephthalate description). DMT and the amount of methanol-free water from column (7) needed for the hydrolysis is mixed in a mixing vessel (1) and transferred to hydrolysis reaction column (2) where DMT is hydrolyzed to terephthalic acid.

The formed methanol is stripped off with steam from the evaporator (6). The reaction mixture from the hydrolysis is cooled down by flash distillation in crystallizers (3). After centrifuging (4), the PTA is dried (5) and passed on to storage. The filtrate is recycled back to evaporator (6). Stripping vapor of the hydrolysis reactor (2) is distilled in a column (7) where methanol-free water obtained as bottom product is recycled back to mixing vessel (1). Top product is separated in a second column (8) into the methanol overhead that is recycled to the DMT plant and wastewater bottom is sent to incineration.

Economics: Basis is a 350,000-tpy PTA plant, West German conditions, December 2000, including compressor station, incinerator for wastewater and offgas, hot-oil heating system and catalyst regeneration:

Investment: German conditions,
including DMT production, DM/tpy 1,300

Raw materials and utilities consumption, per ton of product:

p-Xylene, kg	715
Methanol, makeup, kg	60
Water, demineralized, kg	500
Fuel, GJ	5.4
Electric power, kWh	0

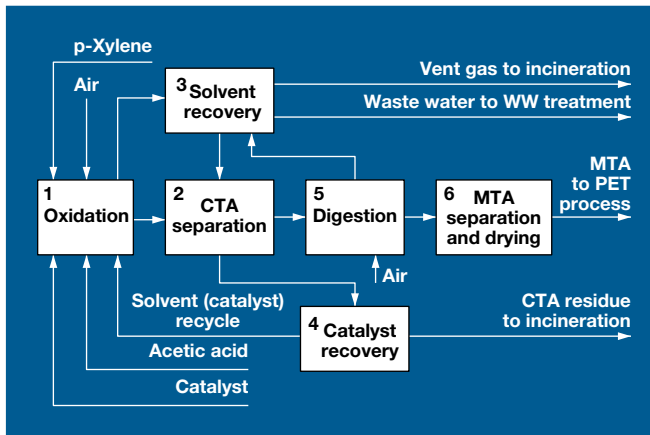
Joint PTA and DMT production in one plant is possible.

Commercial plants: The process is licensed in Taiwan with a 200,000-tpy plant.

Reference: *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A26, 1985, pp. 193–204.

Licensors: Degussa AG.

PETROCHEMICAL PROCESSES 2001



Terephthalic acid (MTA)

Application: Production of polymer-grade terephthalic acid (MTA). MTA is an excellent raw material to produce polyethylene terephthalate resin (PET), which is used for engineering plastics, packaging materials—like bottles and other food containers—as well as films. Also, integrated polyester producers use MTA to make various types of fibers.

Description: The general flow diagram for the production of MTA using Eastman Chemical's proprietary process, can be broken down into three different main sections—crude terephthalic acid (CTA), polymer-grade terephthalic acid (MTA) and catalyst recovery.

- **Crude terephthalic acid (1,2,3):** CTA is produced by catalytic oxidation of p-xylene with air in the liquid phase using acetic

acid as a solvent (1). The feed mix of p-xylene, solvent and catalyst together with compressed air is continuously fed to the reactor, which is a bubble-column oxidizer, operating at a moderate temperature resulting in an extremely high yield. The oxidizer product is known as crude terephthalic acid (CTA) because of the high level of impurities it contains. Many impurities are fairly soluble in the solvent. Hence, in the CTA separation step (2), impurities can be effectively removed from the product by exchanging the reaction liquor with lean solvent received from the solvent-recovery system. The reactor overhead vapor, mainly reaction water, acetic acid, and nitrogen is sent to the solvent-recovery system (3), where water is separated from the solvent by distillation. After recovering its energy, the off-gas is sent to a catalytic oxidation unit for further cleaning.

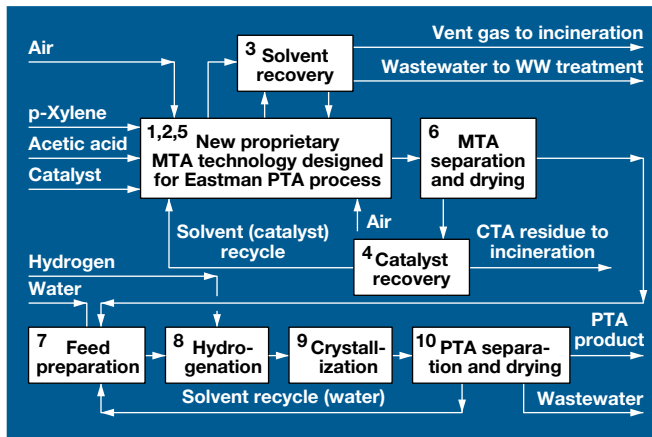
- **Polymer-grade terephthalic acid (5,6):** The crude acid is purified to obtain MTA in a second digestive-oxidation step, at elevated temperature conditions. The digesters serve as reactors for increasing the conversion of partially oxidized compounds to terephthalic acid. This leads to a lower level of 4-carboxy benzaldehyde (4-CBA) and a significantly lower level of p-toluic acid (p-TA)—the main impurities in terephthalic acid. In a final step (6), MTA is separated from the solvent and dried for further processing in the polyester production facilities.

- **Catalyst recovery (4):** After exchanging the liquor in the CTA separation, the impurities are separated and the dissolved catalyst is recycled. The removed impurities as CTA residue can be burned in a fluidized-bed incinerator or, if desirable, used as land fill.

Economics: The advanced Eastman MTA technology uses fewer process steps and in combination with the outstanding mild-oxidation technology, leads to considerable capital cost savings and lower production cost than in most competing processes.

Commercial plants: Commercial plants are operating in the U.S., Europe and Asia Pacific. The latest plant was constructed in Europe during 1998. Total worldwide installed capacity is 1.5 million mtpy.

Licensor: Lurgi Öl-Gas-Chemie GmbH.



Terephthalic acid (PTA)

Application: Production of fiber-grade terephthalic acid (PTA). PTA is the market standard raw material to produce all types of polyester fibers used in the textile industry.

Description: The general flow diagram for the production of PTA using Eastman Chemical's new proprietary process can be broken down into the two main production lines—the production of polymer-grade terephthalic acid (MTA), followed by a hydrogenation process to produce fiber-grade terephthalic acid (PTA).

- **Polymer-grade terephthalic acid (1,2,3,4,5,6):** To produce PTA, basically the same process steps are applied to process polymer-

grade terephthalic acid (MTA). However, some modifications have been made, which significantly reduce capital cost, as well as, optimize the properties of MTA when it is to serve as feed material for the hydrogenation process.

- **Fiber-grade terephthalic acid (7,8,9,10):** To produce a fiber-grade quality, MTA has to undergo a further purification step. In the feed preparation system (7), MTA is dissolved in water at elevated temperatures and sent to the hydrogenation reactor (8) in which it is catalytically treated to remove the impurities. The hydrogenation catalyst is palladium based. The purified terephthalic acid is crystallized by stepwise depressurizing in a unique crystallizer train (9).

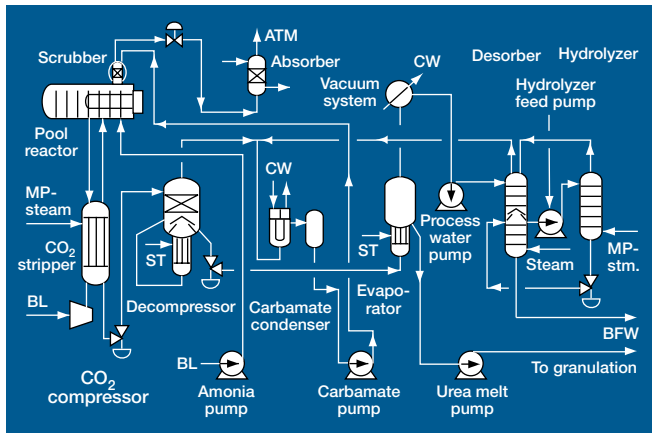
A heat-integration system is attached. The combination of the MTA quality and the unique crystallization system generates less waste. In a following step, the PTA crystals are separated from the mother liquor and finally dried for further processing in the polyester production system.

Economics: Although the PTA purification of terephthalic acid by means of hydrogenation is well known from other competing processes, the integrated advanced Eastman MTA technology requires fewer process steps—including the purification section. Such design offers considerable capital-cost savings and lowers production expenses than in most competing processes.

Commercial plants: Commercial MTA plants are operated in the U.S., Europe and Asia Pacific, with a worldwide installed capacity of 1.5 million mtpy. In its hydrogenation section, the new PTA process using the advanced MTA technology—operated in Europe at a capacity of 300,000 mtpy—has been developed from Eastman's operating isophthalic acid process, which is regarded as one of the best worldwide.

Licensor: Lurgi Öl-Gas-Chemie GmbH.

PETROCHEMICAL PROCESSES 2001



Urea

Application: To produce urea from ammonia and carbon dioxide using the CO₂-stripping process.

Description: Ammonia and carbon dioxide react, at synthesis pressure of 140 bar, to produce urea and carbamate. The conversion of ammonia, as well as, carbon dioxide in the synthesis section is 80% and creates an extremely low recycle flow of carbamate. Due to the high ammonia efficiency, no pure ammonia is recycled. The synthesis temperature of 185°C is low and, consequently, corrosion within

the plant is negligible.

Because of the elevation difference within the synthesis section, internal synthesis recycle is based on gravity flow. Consequently, electrical energy requirement is very low. Synthesis gas condensation in the pool reactor generates steam, which is used downstream by other plant sections. Thus, steam consumption is low.

Process inerts are vented to atmosphere after washing. Consequently, plant ammonia emissions are virtually zero.

Due to high conversions in the synthesis, the recycle section is very small. An evaporation stage with vacuum condensation system produces urea melt with the required concentration either for granulation or for prilling.

Produced process water is treated in a desorption/hydrolyzer section. The treated effluent is suitable for boiler feedwater applications.

Economics: Depending on heat-exchange options included within the design, the raw material and utility consumptions per metric ton (mt) of urea are:

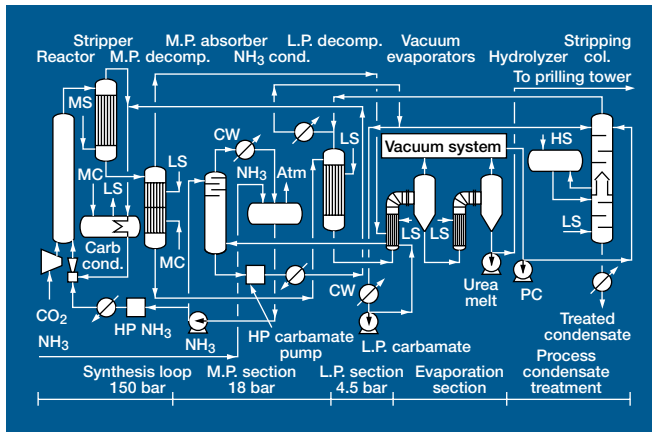
Aromatics, kg	566
Carbon dioxide, kg	733
Steam, 110 bar 510°C, kg	690 ¹
Electric power, kWh	14
Water, cooling, m ³	50

¹ Includes steam for CO₂ compressor drive and steam for desorption/hydrolyzer section.

Commercial plants: More than 100 plants based on Stamicarbon's CO₂-stripping technology are in operation. The largest single-reactor unit produces three thousand mtpd. The proven annual output of this plant exceeds one million mt.

Licensor: Stamicarbon bv.

PETROCHEMICAL PROCESSES 2001



Urea

Application: To produce urea from ammonia and carbon dioxide using ammonia-stripping process.

Description: Ammonia and carbon dioxide react at 150 bar to yield urea and ammonia carbamate. The conversion in the reactor is very high due to favorable NH_3/CO_2 ratio of 3.5:1 and operating temperature of 185°C to 190°C. These conditions prevent corrosion problems. Carbamate is decomposed in three stages at different pressures: in the stripper at the same pressure as the reactor, in the medium-pressure decomposer at 18 bar and in the low-pressure decomposer at 4.5 bar.

Reactants not transformed into urea are recycled to the reactor by an ejector. Main equipment is installed at ground level; this layout

is essential for large plants. Heat recoveries are particularly developed to have low-energy usage.

Any finishing can be coupled with the synthesis: prilling and granulation, both direct or via crystallization. Different product quality (biuret, moisture, hardness and size) are obtained according to client requests.

Snamprogetti granulation technology has been applied in a 1,650-tpd plant operating since 1990. The plant is completely free from pollution problems. All vents are efficiently treated so that they are discharged to atmosphere practically free of ammonia and urea. Process wastewater is hydrolyzed within the plant to achieve boiler feedwater specification and recover ammonia and carbon dioxide.

Economics: Raw materials and utilities per 1,000 kg of urea are (prilling case):

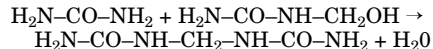
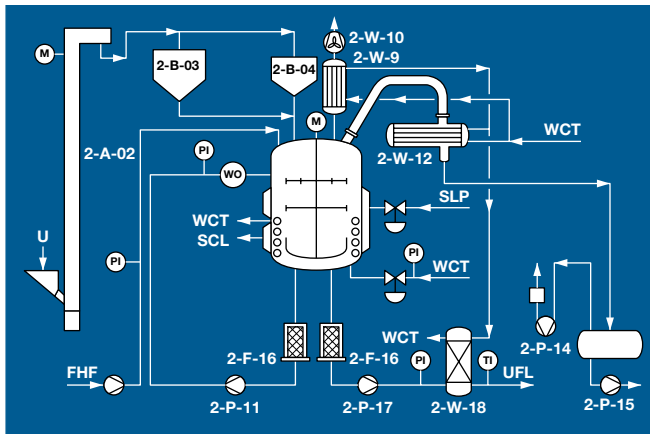
Ammonia, kg	566
Carbon dioxide, kg	735
Steam, 110 bar, 510°C, kg	730 ¹
Electric power, kWh	21
Water, cooling, m ³	80
Condensate, kg	1,045

¹ Includes steam to the CO_2 compressor turbine as well as all utilities for effluent treatment.

Commercial plants: Ninety-nine plants are either in operation or under construction, with capacity up to more than 3,250 tpd on a single line.

Reference: Granelli, F., "Ways to revamp urea units," *Hydrocarbon Processing*, June 1988, Granelli, F., "The granular urea in the world and the experience of the granulation unit at the Ferrara factory (Italy) based on Snamprogetti S.p.A. technology," IFA-Fadinap Regional Conference for Asia and the Pacific, Perth, Australia, Nov. 25–Dec. 1, 1995.

Licensors: Snamprogetti S.p.A.



which is also responsible for the viscosity increase during the storage. The formation of methylene bridges will be accelerated by raising storage temperatures. The technology is based on batchwise production of the aqueous solution, short intermediate storage and continuously operating spray drying in a connected stage.

The formaldehyde is charged into the reactor and the pH value has to be adjusted. Urea is then added and the mixture will be heated up to the reaction temperature. The reactor consists of a stirred kettle based on load cells and is equipped with heating jacket and internal cooling coils. Heating is carried out with low pressure steam. An efficient anchor agitator ensures good heat transmission and uniform reaction conditions. The reaction proceeds in several steps at 70°–100°C.

To control the reaction rate, the pH value is measured continuously, which is re-adjusted by adding formic acid. When the end-point of the reaction is reached, determined by a solubility test with water, the reaction mixture is brought to pH 7 with caustic soda lye. The condensation is complete and the resin is evaporated under reduced pressure. The vapor is condensed in a tubular condenser and collected in a receiver.

After cooling the resin in the reactor, the resin is pumped to the buffer tank of the connected spray dryer plant. Usually, the complete batch processing takes 4–5 h. The urea-formaldehyde resin solution can be dried in a spray dryer based on the co-current flow principle.

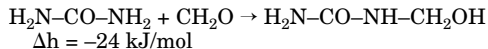
This process cost-effectively produces high-quality glues at large quantities. The product is a low formaldehyde resin adhesive, suitable for veneering, plywood and particle board production by hot pressing process. The quality of the bonding complies with the requirements of *DIN 68705, Part 2* respectively to *DIN 68763*. For particle board, the formaldehyde class E1 will be maintained.

Licensors: INVENTA-FISCHER.

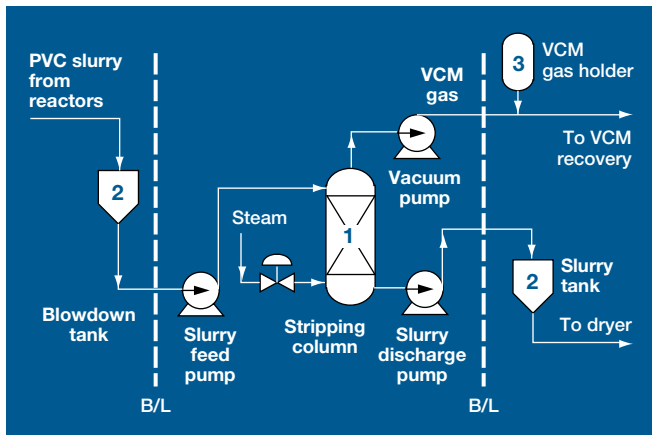
Urea-formaldehyde

Application: Urea-formaldehyde resins are used as adhesives in the wood working industry and are typically used in the production of plywood and particle board. They are available as concentrated solutions or in powder form as a result of the spray-drying process.

Description: The reaction mechanisms of the major components formaldehyde and urea are by polyaddition:



whereby the hydroxymethyl compounds undergoes further slow reaction by polycondensation



process effectively removes the remaining VCM so that the monomer is recovered and reused. Recycling of raw materials drastically reduces VCM emissions from the following dryer. There is no significant change in PVC quality after stripping. Residual VCM level in the PVC product can be lowered below 1 ppm, and in some cases below 0.1 ppm.

The PVC slurry, containing VCM, is continuously fed to the stripping column (1). The slurry passes counter-currently to steam, which is fed into the base of the column. The proprietary internals of the column are specially designed to ensure intimate contact between the steam and the PVC slurry and to ensure that no PVC particles remain inside the column. All process operations, including grade change, are automatically done in a completely closed system.

While steam stripping is widely used, this proprietary technology, which involves sophisticated design and know-how of the column, offers attractive benefits to existing PVC plant sites.

The process design is compact with a small area requirement and low investment cost. The size of the column is 2.5 to 30 t/h.

Economics:

Steam 130 kg / t of PVC

Commercial plants: Chisso has licensed the technology to many PVC producers worldwide. More than 70 columns of the Chisso process are under operation or construction, and total capacity exceeds 4 million tpy of PVC.

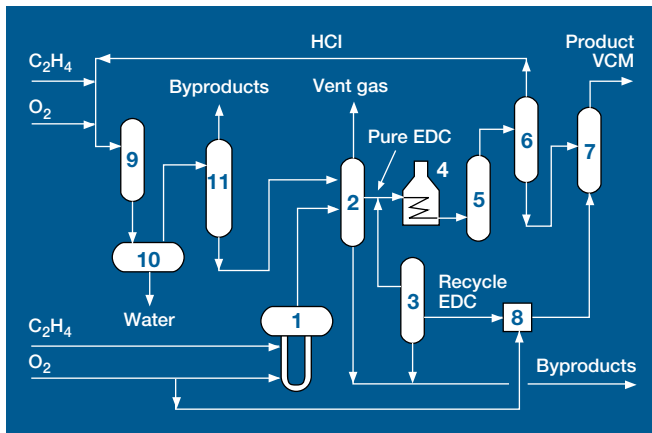
Licensor: Chisso Corp.

VCM removal

Application: Adding a stripping column to existing polyvinyl chloride (PVC) plants to remove vinyl chloride monomer (VCM) from PVC slurry. The recovered VCM can be reused in the PVC process, without any deterioration of PVC polymer quality.

Description: PVC slurry discharged from reactors contains significant amounts of VCM (> 30,000 ppm) even after initial flashing. This

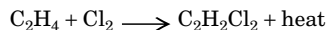
PETROCHEMICAL PROCESSES 2001



Vinyl chloride monomer (VCM)

Application: A process to produce vinyl chloride monomer (VCM) and ethylene dichloride (EDC) from ethylene, chlorine and oxygen using a high efficiency fixed-bed oxychlorination process.

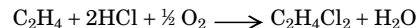
Description : EDC is produced in both the addition chlorination (1) and oxychlorination (9) sections of the process. In addition chlorination, ethylene and chlorine are reacted in the liquid phase to produce EDC:



The heat of reaction is used to distill the EDC produced in direct chlorination and oxychlorination sections of the plant (2). This saves

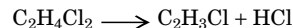
as much as 0.6 tons of steam per ton of VCM over conventional processes. The process won the Kirkpatrick Chemical Engineering Achievement Award in 1983.

In the oxychlorination section, ethylene, oxygen and HCl are reacted to produce EDC:



This is a fixed-bed catalytic vapor phase reaction with the reaction heat used to generate high-pressure steam (18+ barg). Using oxygen rather than air reduces vent gas quantity by 95%, and it also reduces energy and capital cost requirements. The oxy EDC is washed (10) and dried (11) before purification in the direct chlorination unit.

VCM is produced by cracking purified recycle EDC and EDC from direct chlorination in a pyrolysis furnace (4):

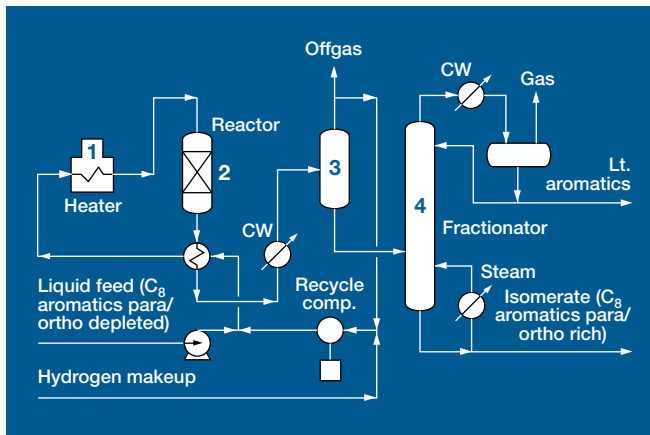


After quenching (5) and energy recovery in a specialized system, products are separated (6) into HCl, which is recycled to oxychlorination, high-purity VCM (7) and unreacted EDC, which is recycled for chlorination (8) and purification (3). Light and heavy ends from the process are converted to HCl and incinerator. The aqueous effluent from the VCM plant is steam stripped and can be treated offsite to reduce BOD.

The VCM process can be “balanced”, so that only VCM is produced, or the plant can be designed to accommodate imported or exported EDC or HCl streams. The process is automated for stable, safe operation with wide turndown capability. Also, the process is designed for easy startup and shutdown. Manpower, capital, operating and maintenance costs are low. Ethylene and chlorine efficiencies exceed 98+%.

Commercial plants : Fifty-two plants are in operation or under construction with a combined capacity of 4.7 million tpy of VCM and 11.2 million tpa of EDC. Plant capacities range from 10,000 mtpy to 650,000 mtpy of VCM.

Licensors: Inovyl B.V., the technology business of EVC.



the fixed, dual-bed catalyst system. Dealkylation of EB and cracking of non-aromatics preferentially occurs in the top bed. The bottom bed promotes isomerization of xylenes, while minimizing loss of xylenes from side reactions. The reactor effluent is cooled by heat exchange and the resulting liquid and vapor phases are separated in the product separator (3). The liquid is then sent to a fractionator (4) for recovery of benzene and toluene from the isomerate.

Two enhanced isomerization catalyst technologies have been developed by ExxonMobil. The first, referred to as Advanced Mobil High Activity Isomerization (AMHAI), provides higher selectivity and lower operating costs compared to isomerization processes used in the past. The AMHAI technology offers increased operating flexibility in terms of a greater range of EB conversion and a lower temperature requirement. The second technology further increases yield performance and debottleneck potential. This technology, using catalyst referred to as EM-4500, can operate at even higher EB conversion, with higher selectivity and significantly lower xylene loss.

Operating conditions: XyMax units operate with a high-space velocity and a low hydrogen-to-hydrocarbon ratio, which results in increased debottleneck potential and decreased utilities costs. By converting a high portion of EB in the feed, XyMax technology can lead to significant savings in associated paraxylene recovery facilities. XyMax technologies result in long operating cycles.

Commercial plants: The AMHAI process was first commercialized in 1999. Five AMHAI units are currently in operation. The first commercial unit using EM-4500 was brought onstream in 2000. Including other ExxonMobil xylene isomerization technologies, there are a total of 21 units in operation.

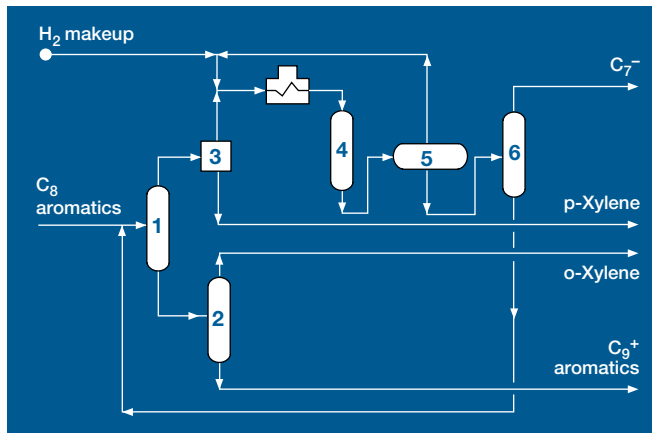
Licensors: ExxonMobil Chemical (retrofit applications); IFP (grass-roots applications).

Xylene isomerization

Application: To selectively isomerize a paraxylene depleted- C_8 aromatics mixture to greater than equilibrium paraxylene concentration using the XyMax process. Simultaneously, ethylbenzene (EB) and nonaromatics in the feed are converted to benzene and light paraffins, respectively. Conversion of EB is typically 60% to 80%.

Description: The para-depleted liquid C_8 aromatics raffinate stream from the paraxylene separation unit, along with hydrogen-rich recycle gas are pumped through feed/effluent exchangers and the charge heater (1) and into the reactor (2). Vapor then flows down through

PETROCHEMICAL PROCESSES 2001



feed and sent to the xylene splitter (1).

The feedstock consists of a mixture of C_8 aromatics typically derived from catalytically reformed naphtha, hydrotreated pyrolysis gasoline or an LPG aromatization unit. The feed may contain up to 40% ethylbenzene, which is converted either to xylenes or benzene by the Isomar reactor at a high conversion rate per pass. Feedstocks may be pure solvent extracts or fractional heartcuts containing up to 25% nonaromatics. Hydrogen may be supplied from a catalytic reforming unit or any other suitable source. Chemical hydrogen consumption is minimal.

o -Xylene product purity of up to 99% is possible, depending on the composition of the feed and fractionation efficiency. The Parex unit is guaranteed to produce 99.9% pure p -xylene with per pass recovery greater than 97%.

Operating conditions: Moderate temperature and pressure requirements permit the use of carbon and low-alloy steel and conventional process equipment.

Yields: Typical mass balance for the Parex-Isomer complex:

Composition	Fresh feed, wt. units	Product, wt. units
Ethylbenzene	25.5	—
p -Xylene	14.0	71.1
m -Xylene	41.0	—
o -Xylene	19.5	19.6

Economics: Estimated inside battery limits (ISBL) erected and utility costs are given for a Parex-Isomar complex, including the xylene splitter column and the o -xylene column, for production of 400,000 tpy of p -xylene, U.S. Gulf Coast, 4th quarter 1996.

EEC (ISBL), \$MM	105
Utilities, \$/mt	35

Commercial plants: Since 1971, UOP has licensed 69 Parex units and 54 Isomar units.

Licensors: UOP.

Xylene isomers

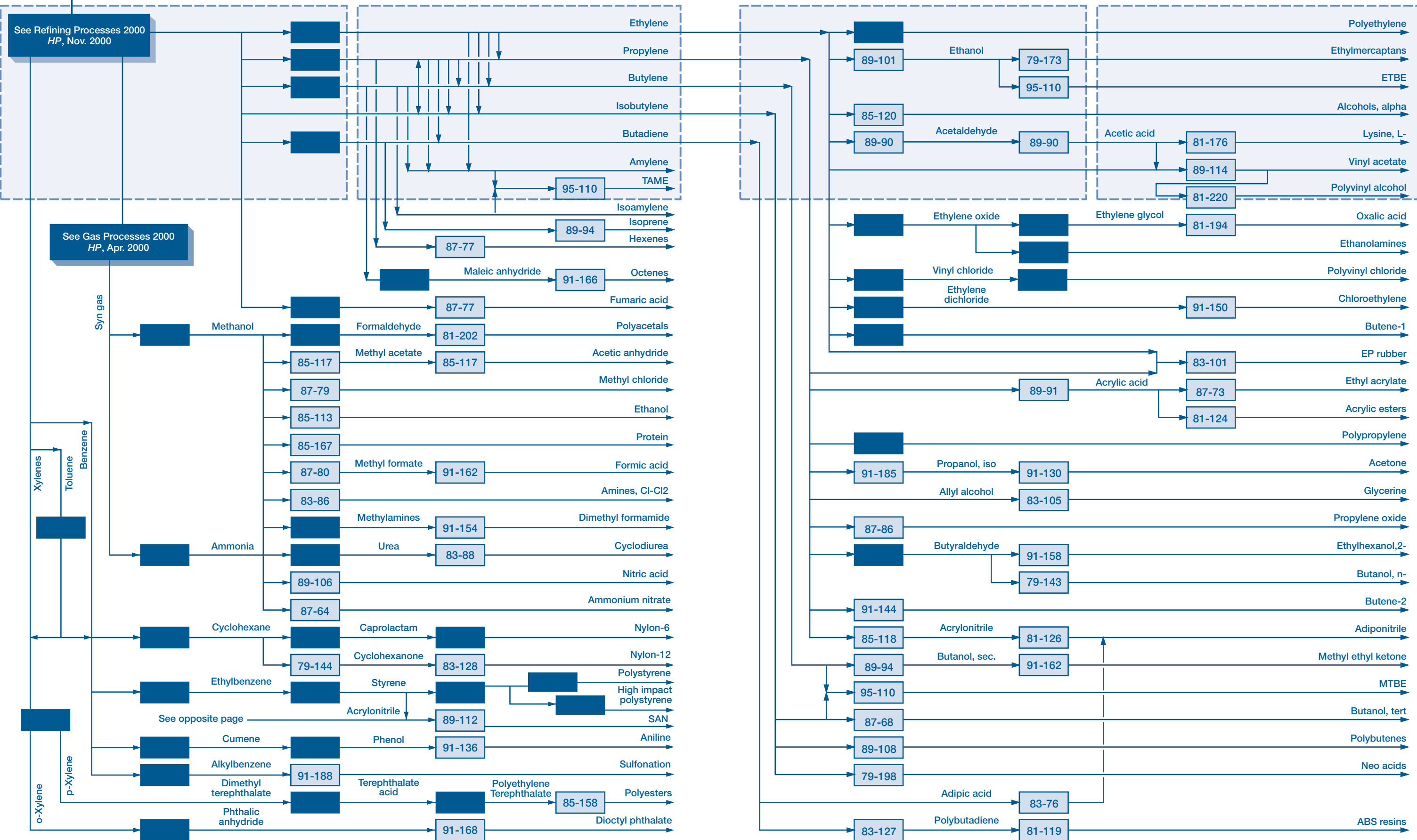
Application: To produce a desired xylene isomer (or isomers) from a mixture of C_8 aromatics using the UOP Isomar and Parex processes.

Description: Fresh feed containing an equilibrium mixture of C_8 aromatic isomers is fed to a xylene splitter (1). Bottoms from the splitter are then separated (2) into an overhead product of o -xylene and a byproduct of C_9^+ aromatics. Overhead from the splitter is sent to a UOP Parex process unit (3) for recovery of ultra-high-purity p -xylene. If desired, high-purity m -xylene may also be recovered using the MX Sorbex process. Remaining components are recycled to the UOP Isomar process unit reactor (4), where they are catalytically converted back toward an equilibrium mixture of C_8 aromatic isomers. Hydrogen-rich recycle gas is separated (5) from the reactor effluent before fractionation (6) to remove light cracked byproducts overhead. The remaining C_8 aromatics are then combined with the fresh



A guide to chemicals from hydrocarbons—some examples

COLOR BLOCKS: Processes in this issue. NUMBERS: Year and page for processes in previous Petrochemical Handbooks.



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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Olefins					
Degussa AG/Linde AG	Acetylene	Hydrocarbons (C ₁ - C ₅)	Electric arc pyrolysis, hydrogen coproduction	1	1988
ABB Lummus Global	Acetylene extraction	C ₂ S	Selective adsorption of acetylene with dimethyl form amine (DMF)	4	1991
Stone & Webster Eng., Corp.	Acetylene extraction	C ₂ S and C ₃ S	Proven extraction design uses DMF solvent. Full acetylene removal	5	1998
ABB Lummus Global	Butadiene	Butane-n or mixed C ₄ S	Dehydrogenation in cyclic-fixed bed reactor yields 61% to 65% wt product using the CATADIENE process	18	1986
CDTECH	Butadiene	C ₄ + from naphtha cracking	Selective hydrogenation of C ₄ acetylenes in a distillation column to produce low acetylene feed for butadiene extraction	2	1998
UOP	Butadiene	Steam cracker C ₄ S	Selective hydrogenation produces acetylene-free butadiene.	8	1997
ABB Lummus Global	Butadiene extraction	Butanes/butenes/ butadienes/acetylenes	Uses extraction distillation with NMP solvent and conventional distillation	26	2000
JSR Corp.	Butadiene monomer BD	C ₄ fraction from naphtha cracker	Extractive distillation at lower temperature, no compressor, popcorn-free and low energy consumption	3	1997
Lurgi Öl Gas Chemie GmbH	Butadiene, 1,3	C ₄ cut from naphtha cracking	Extractive distillation using N-methylpyrrolidone as solvent has high yield, low utilities	24	2001
Degussa AG	Butadiene-free C ₄ hydrocarbons	C ₄ hydrocarbons with butadiene	Selective hydrogenation of C ₄ streams without butene-1 isomerization	5	1992
BASF/ABB Lummus Global	Butadiene-free C ₄ hydrocarbons, mixed	Mixed C ₄ hydrocarbons	Selective hydrogenation of butadiene from mixed C ₄ s stream; product—butadiene-free C ₄ stream	6	2001
UOP	Butene	Butane	Oleflex process converts iso- and n-butane into butenes by catalytic dehydrogenation	7	1997
IFP	Butene-1	Ethylene	Alphabutol uses low investment, low operating cost liquid-phase homogenous catalysts to make high-purity butene-1	20	1999
Sulzer/ABB Lummus Global	Butene-1	Mixed C ₄ hydrocarbons	Super fractionation to produce high purity (99+%) butene-1	5	1998
Degussa AG	Butene-1 recovery	Raffinate-2 containing butene-1	Feed pretreatment and superfractionation	4	1988
Snamprogetti S.p.A.	Butene-1, recovery	Selectively prehydrogenated Raffinate-2 from MTBE	Recovery via superfractionation	2	1991

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Sumitomo Chemical Co., Ltd.	Butene-1/MTBE	Raffinate-I or FCC C4	Low temperature and pressure operating conditions reduce equipment costs	3	1994
Krupp Koppers GmbH	Butenes, n and iso	C ₄ cuts from steam and FCC cracker	Extractive distillation of n- and isobutenes using morpholines as solvents	1	1994
UOP	Butylenes	Butanes	Dehydrogenation of butanes	19	1992
ABB Lummus Global	C ₄ /C ₅ hydrogenation	C ₄ and C ₅ olefins and diolefins	Olefins and diolefins are saturated by concurrent/countercurrent flow	14	2000
UOP	C ₆ -C ₁₂ olefins	FCC and steam-cracker C ₃ /C ₄	Oligmerization of light olefins	100	1993
ABB Lummus Global	Ethylene	Ethane/propane/butane/naphtha/gas oils	Low capital cost, high efficiency/reliable/safe operation, SRT heaters	110	2000
Kellog Brown & Root	Ethylene	Ethane/propane/butane/naphtha/gas oils	Low capital cost, front-end deethanizer or depropanizer, front-end reactor	27	1997
Kellog Brown & Root	Ethylene	Ethane/propane/butane/naphtha/gas oils	ALCET process combines low-capital separation and absorption methods, thus no refrigeration required	1	NA
Kellogg Brown & Root	Ethylene	Ethane/propane/butane/naphtha/gas oils	Millisecond pyrolysis technology produces ethylene and propylene	63	1996
Linde AG	Ethylene	LPG, Naphtha, gas oils and hydrocracker residue	Highly selective furnaces thermally crack hydrocarbons and efficiently recover products	30	1996
Technip	Ethylene	Ethane to HVGO	Ethylene and propylene production using Technip's High Selective Furnaces and progressive separation at low energy and feedstock consumption	18	2000
Stone & Webster Eng., Corp.	Ethylene/propylene	Ethane, propane, butane & naphtha	Uses Ultra-Selective Conversion, USC, for furnace and Advanced Recovery System, ARS	120	2001
ABB Lummus Global	Isobutylene	Isobutane	Dehydrogenation in cyclic-fixed bed reactor yields 57% to 61% per pass	14	1992
CDTECH	Isobutylene	Raffinate 1	Selective hydrogenation of butadiene and hydroisomerization of butene-1 to butene-2 via catalytic distillation to recover isobutylene	1	1994
CDTECH	Isobutylene	Raffinate I	Selective hydrogenation of butadiene and hydroisomerization of butene-1 to butene-2 to produce isobutylene	1	1994
CDTECH/Snamprogetti SpA	Isobutylene	MTBE	Back-cracking process yields high-purity isobutylene (99.9%)		

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
			and methanol	8	1997
CDTECH/Snamprogetti SpA	Isobutylene	Mixed C ₄ hydrocarbons	Integrated MTBE and MTBE backcracking processes to selectively recover high-purity (99.9%) isobutylene	7	1991
Huels AG	Isobutylene	Methyl tertiary butyl ether (MTBE)	Catalytic decomposition, high selectivity, high purity	1	1988
Sumitomo Chemical Co., Ltd.	Isobutylene	MTBE	High-purity isobutylene (99.9%) is produced from MTBE with a high conversion and selectivity catalyst	4	1996
CDTECH	Isobutylene/isoamylene	n-Butenes and n-pentenes	Skeletal isomerization of n-olefins to iso-olefins	3	2000
Snamprogetti S.p.A./Yarsintez	Isobutylene/propylene	Isobutane/ propane or mixtures	Fluid-bed reactor is pollution free, highly flexible, high reliability at low investment	3	1994
CDTECH/Snamprogetti SpA	Isooctene/isooctane	Mixed C ₄ hydrocarbons	Isobutylene diemrization to produce isooctene. Additional process can hydrogenate isooctene to produce isooctane	2	1999
CDTECH	n-Butenes	Mixed C ₄ hydrocarbons	Selective hydrogenation of butadiene to n-butenes in catalytic distillation column	4	1997
IFP	Octene	Butenes	Dimersol-X uses low investment, low-operating cost liquid-phase homogenous catalysis to make octenes with low braching	5	1997
Degussa AG	Octenes	Butenes	Dimerization of butenes	2	1986
Krupp Uhde	Olefins	C ₄ feedstock, raffinate II	BUTENEX extractive distillation process uses selective solvents to separate C ₄ -olefins from feed streams	NA	NA
Neste Oy, Engineering	Olefins	FCCU light gasoline, EC pyrolysis gasoline	Selective hydrogenation of C ₅ , C ₆ and C ₇ diolefins to olefins	1	1995
Phillips Petroleum Co.	Olefins	Light Hydrocarbons to light naphtha	Dehydrogenation of light paraffins uses proprietary catalysts for high selectivities	2	1992
UOP/HYDRO	Olefins	Methanol	Methanol to olefins (MTO) process uses fluidized-bed reactor and efficient product recovery system	NA	NA
UOP/HYDRO	Olefins	Butenes from natural gas, methanol	Methanol to olefins (MTO) process uses fluidized-bed reactor and efficient product recovery system	NA	NA
Stone & Webster Eng., Corp.	Olefins, light	Naphtha, VGO, resid	Deep catalytic cracking (DCC) process to make light olefins, C ₂ -C ₅	7	2000
IFP	Olefins, linear alpha	Ethylene	AlphaSelect process offers flexible product slate, low investment,		

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
			low operating costs, liquid-phase homogenous catalysis to make high-purity C ₄ -C ₁ linear alpha olefins	NA	NA
UOP	Olefins, linear alpha	Ethylene	Linear-1 process uses oligimerization of ethylene to produce a range of C ₄ to C ₂₀₊ alpha olefins	NA	NA
UOP	Olefins, mixed	Kerosine	Produces C ₁₀ -C ₁₈ olefins for alcohols and alkylbenzene	6	1988
UOP	Olefins, mixed	Light paraffins	Light paraffin dehydrogenation to corresponding olefin	34	1998
ABB Lummus Global	Propylene	Ethylene and butenes	Highly selective catalyst simultaneously isomerizes feed to butene-1,2	4	2000
ABB Lummus Global	Propylene	Propane	Dehydrogenation in cyclic-fixed bed reactor yields 45% to 50% per pass conversion	14	1998
BRICI/ABB Lummus	Propylene	C ₃ S	Selective hydrogenation of methyl acetylene and propadiene to propylene	12	1998
CDTECH	Propylene	C ₃ + steam cracker	Selective hydrogenation of methyl acetylene and propadiene to propylene	3	1999
IFP/Chinese Petroleum Corp.	Propylene	FCC and steam-cracker C ₄ cuts	Meta-4 upgrades pyrolysis C ₄ cuts to propylene; has attractive ROI when combined with IFP selective hydroisomerization unit	1	NA
UOP	Propylene	Propane	Converts propane into propylene by catalytic dehydrogenation	5	1999
KTI	Propylene/isobutylene	Butanes (field)	Thermal steam cracking yields 79 mol% of products for MTBE units	NA	NA
Aromatics					
UOP	Alkylbenzene, linear (LAB)	Kerosine	LAB is produced by alkylating benzene with olefins using several processes	41	1998
GTC	Aromatics	C ₆ -C ₈ hydrocarbon mixture	Extractive distillation with selective solvents separates BTX from nonaromatic hydrocarbons	1	1995
Krupp Uhde	Aromatics	Pyrolysis gasoline, reformat or light oils	Extractive distillation process uses selective solvents to separate aromatics from feed streams	30	NA
ABB Lummus Global	Benzene	Toluene rich stream/pyrolysis gasoline	Hydrodealkylation produces high-purity product, single-step process, no hydrotreating	29	1998
IFP	Benzene	Toluene	No catalyst is needed with hydrodealkylation process; onstream time exceeds 95%	6	1998

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Mitsubishi Petrochemical Co.	Benzene	Alkyl-containing hydrocarbons	Easy and stable operation without catalyst. Hydrodealkylation of feeds	7	1992
UOP	Benzene	Toluene	Thermal dealkylation process produces high-purity benzene from toluene	41	1992
UOP	Benzene	Toluene, C ₉ and C ₁₀ aromatics	Disproportionation process upgrades feed into benzene and xylenes	42	1998
Lurgi Öl Gas Chemie GmbH	Benzene/toluene	Pyrolysis gasoline, reformate, coke oven benzole	Extractive distillation using N-methylpyrrolidone as solvent has high yield, low utilities	22	2000
ExxonMobil Chemical Co.	Benzene/xylene	Toluene and up to 25% aromatics	Disproportionation converts toluene and C ₉ aromatics into high-purity benzene and mixed xylenes	3	1998
Kellogg Brown & Root/ Dow Chemical	Bisphenol-A	Phenol, acetone	High quality product with low capital and operating costs	1	1996
SINOPEC/ABB Lummus Global	Bisphenol-A	Phenol and acetone	Catalytic stripping process maximizes phenol/acetone conversion with high selectivity and lower capital costs	1	19930
UOP/Chiyoda Corp.	Bisphenol-A	Phenol and acetone	Process has: highest product purity, high selectivity/conversion using proprietary cation-ion resin catalyst, low operating/capital investment costs	3	1998
Chiyoda Corp.	BTX	Light naphtha, LPG and raffinate	Zeolite catalyst and fixed-bed reactor produce petrochemical grade BTX	1	NA
GTC Technology Corp.	BTX	Kerosine, light diesel	Extractive distillation with selective solvents removes C ₈ -C ₁₂ aromatics from nonaromatics	1	1995
Krupp Koppers GmbH	BTX	Coke oven light oil, reformate, pyrolysis	Extractive distillation for benzene, toluene and xylenes using N-formylmorpholin	22	1994
UOP/BP	BTX aromatics	LPG	New technology yields petrochemical grade BTX in one-step process.	1	1995
IFP	BTX, production	Naphtha	Aromizing maximizes BTX production with high yields of high-quality aromatics	9	1998
IFP	BTX, purification	Reformate	Arofining hydrogenates diolefins reducing or eliminating activated clay consumption	3	1998
UOP	BTX, purification	Reformate	Carom process; extraction of aromatics from non-aromatics at high purity and recovery using a proprietary solvent	5	1996
UOP/Shell	BTX, purification	Reformate, pyrolysis gasoline	Shell Sulfolane process; liquid extraction and/or extractive distillation with sulfolane solvent	123	1998

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
IFP/Lyondell	BTX, separation	Pyrolysis, reformat, light oils	Highly efficient sulfolane solvent separates BTX from feedstocks	19	1996
CDTECH	Cumene	Crude cumene	Selective hydrogenation of alpha methyl styrene in a distillation column to produce purified cumene distillate	NA	NA
CDTECH	Cumene	Propylene and benzene	Catalytic distillation technology with zeolite catalyst, high yield/quality produce ultra-high purity	1	1995
CDTECH, Inc.	Cumene	Propylene and benzene	Catalytic distillation technology with zeolite catalyst, high yield/quality produce ultra-high purity	1	1995
Mitsui Chemicals, Inc.	Cumene	Benzene and propylene	Process has high raw material and utilities consumption efficiency	5	1990
Mobil/Badger	Cumene	Benzene, propylene (dilute/polymer-grade)	Environmentally clean. Achieves stoichiometric yield with high purity	12	2001
UOP	Cumene	Benzene and propylene	Catalytic condensation process produces high-quality cumene (99.9%+) using solid phosphoric acid (SPA) catalyst	16	1996
UOP	Cumene	Benzene and propylene	Process characteristics: high yield and high quality cumene (99.95%+) using rugged, regenerable zeolitic catalyst	7	2001
ABB Lummus Global	Ethylbenzene	Ethylene and benzene	Catalytic distillation technology with zeolite catalyst, high yield/quality	5	2000
ABB Lummus Global	Ethylbenzene	Ethylene and benzene	Liquid-phase alkylation uses soluble aluminum chloride catalyst complex	21	1990
ABB Lummus Global/UOP	Ethylbenzene	Ethylene & benzene	Newest generation liquid-phase alkylation with zeolite catalyst, high yield/quality, long catalyst life	22	2001
CDTECH	Ethylbenzene	Benzene, ethylene	Patented fix-bed, catalytic distillation technology uses zeolite catalyst to alkylate benzene with ethylene	NA	NA
Mobil/Badger	Ethylbenzene	Benzene, ethylene (dilute/polymer-grade)	Highly active, selective zeolite catalyst produces high yields and purity	35	1997
Mobil/Badger	Ethylbenzene	Benzene, polymer-grade ethylene	EBMax process uses proprietary Mobil MCM-22 zeolite catalyst; low capital cost	10	2000
Stamicarbon bv	Ethylbenzene	Butadiene	Butadiene is converted to EB using liquid-phase catalytic dimerization and vapor-phase catalytic dehydrogenation	NA	NA
UOP	Ethylbenzene	Ethylene and benzene	Liquid-phase alkylation of benzene to ethylbenzene. Durable, regenerative zeolite catalyst, 99.85% purity, 99.7% yield	22	2001

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Technip	Ethylene/cracking furnaces	Ethane to HVGO	Thermal cracking of hydrocarbons in the presence of steam by highly selective GK and SMK cracking furnaces	500	2001
Technip	Isobutylene/butacracking	Butanes (field)	Co-production of propylene and iso-butylene by thermal steam cracking of butane at elevated temperatures	NA	NA
JSR Corp.	Isoprene monomer (IP)	C ₅ fraction from naphtha cracker	Low investment cost, energy efficient and low production costs	1	1986
ExxonMobil Chemical Co.	Para di-isopropyl benzene (PDIB)	Cumene, propylene	Zeolite catalyst-based fixed-bed process yields para-DIB selectively at liquid-phase conditions	1	1990
ExxonMobil Chemical Co.	Paraxylene	Toluene	Selectively converts toluene to paraxylene-rich xylenes and high-purity benzene	10	1995
Washington Group International	Para-xylene crystallization	Hydrocarbons with over 65% p-xylene	This suspension crystallization process is ideal for high-purity (99.9+%) p-xylene; can be applied fro crystallization revamps using mixed xylenes	6	2000
IFP	p-Xylene	Mixed xylenes	Octafining isomerizes C ₈ aromatics to paraxylene	22	1997
Fina/Badger	Styrene	Ethylbenzene	Two-stage adiabatic dehydrogenation yields high-purity product	50	2000
Krupp Uhde	Styrene	Pyrolysis gasoline	MORPHYLANE process uses extractive distillation to separate styrene form xylenes and ethylbenzene	NA	NA
Fina/Badger	Styrene catalyst/stabilizer technology	N/A—additive to feeds for styrene dehydrogenation	CST adds potassium to styrene dehydrogenation catalyst; increases productivity and extends catalyst service life	2	2000
ABB Lummus Global/UOP	Styrene monomer	Ethylbenzene	Innovative oxidative reheat technology, 30%–50% expansion of existing SM units with minimal investment for new equipment	5	2001
ABB Lummus Global/UOP	Styrene monomer	Ethylbenzene	Vapor-phase dehydrogenation of EB to styrene monomer, high-temperature, deep-vacuum design, 99.9% purity, 97% selectivity	51	1997
UOP	Styrene monomer	Styrene monomer	Purification of styrene monomer by selective hydrogenation. Less than 10 ppm of PA in SM product	3	1996
Fina/Badger	Styrene/phenylacetylene	Crude styrene reduction	Process reduces phenylacetylene (PA) levels in styrene to less than 20 ppm, Polystyrene makers require low PA levels	6	2000
ExxonMobil Chemical Co.	Xylene isomerization	Paraxylene depleted C ₈ aromatics	High EB dealkylation to benzene; over 100% paraxylene approach equilibrium; long operating cycles	20	2000
UOP	Xylene, meta	Mixed xylenes	Produces 99.5% pure m-xylene at 95% recovery per pass	5	1998

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Washington Group International	Xylene, meta	Hydrocarbons with over 40% meta-xylene	Process separates high-purity m-xylene from hydrocarbon streams using suspension crystallizers with Niro wash columns	NA	NA
ExxonMobil Chemical Co.	Xylene, mixed	Toluene, benzene, C ₉ + aromatics	Transalkylation/disproportionation-based process using benzene, toluene and C ₉ + to produce high yield mixed xylenes	1	1997
UOP	Xylene, mixed	Mixed xylenes	Xylene isomerization of mixture depleted in one or more isomers back to equilibrium	50	1998
UOP/Toray	Xylene, mixed	C ₉ and C ₁₀ aromatics	Toray TAC9 process produces equilibrium mixed xylenes from heavier aromatics	2	1997
UOP	Xylene, mixed isomers	Mixed xylenes	Used with fractionation and other licenses to maximize xylene production	36	1993
UOP	Xylene, mixed isomers	Toluene, C ₉ and C ₁₀ aromatics	Disproportionation process upgrades feed into xylene	42	1998
UOP	Xylene, ortho	Mixed xylenes	Recovered by fractionation in complexes designed for para-xylene	28	1994
IFP	Xylene, para	Mixed xylenes	Eluxyl separates purified p-xylene from C ₈ aromatic streams	8	2000
UOP	Xylene, para	Mixed xylenes	Continuous adsorptive separation technology yields 99.9% p-xylene	71	1998
<u>Polymers</u>					
JSR Corp.	ABS resins	Butadiene, styrene, acrylonitrile	High productivity of various grades of ABS for wide applications	14	2001
BP Chemicals, Inc.	Acrylonitrile	Propylene, ammonia	Fluid-bed reactor design and proprietary catalysts significantly reduces product costs	NA	NA
JSR Corp.	Acrylonitrile butadiene rubber (NBR)	Acrylonitrile and butadiene	Emulsion process. NBR has high oil resistance, processed at low temperature	3	1994
JSR Corp.	AES resins	Styrene/acrylonitrile/ethylene-propylene rubber	Solution polymerization for AES resins	13	1995
Sumitomo Chemical Co., Ltd.	EPDM rubber	Ethylene, propylene, diene	Solution process produces a wide range of high quality grades at low operating costs	1	1989
JSR Corp.	Ethylene propylene rubber (EPR/EPDM)	Ethylene, propylene, termonomer	Solution process. Many grades of EPM/EPDM with excellent characteristics	3	1995

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Mitsui Chemicals, Inc.	Ethylene-propylene rubber	Ethylene, propylene, termonomer	EPM/EPDM process uses solution polymerization with Ziegler catalyst	1	1994
Degussa AG	Oligomers	n-Butene containing hydrocarbons	Depending on the catalyst the oligomers are highly-branched or more linear	1	1986
JSR Corp.	Polybutadiene 1,2	Butadiene	Syndiotactic polybutadiene 1-2 and curable thermoplastic elastomer	NA	NA
JSR Corp.	Polybutadiene, cis	Butadiene	High productivity of cis-butadiene with excellent processability	6	1996
JSR Corp.	Polybutadiene-cis low (LCBR)	Butadiene	High productivity LCBR as impact modifier for plastics such as PS	1	1987
INVENTA-FISCHER	Polybutylene terephthalate (PBT)	Terephthalic acid, 1,4-butanediol	2-reactor continuous process to produce PBT chips ready for conversion of filaments, films and engineered plastics	3	2000
INVENTA-FISCHER	Polycapromamide	Caprolactam and water	Two-stage continuous and batch polymerization process to produce PA-6 chips for textiles, film, engineering plastics	55	1999
Borealis A/S	Polyethylene	Ethylene, butene	Slurry-loop process uses supercritical propane and a series gas-phase reactor produce tailor-made MW, enhanced LLDPEs, MDPEs, HDPEs	4	2000
BP Chemicals, Ltd.	Polyethylene	Ethylene, comonomers	Low Capex and Opex for homo, random and impact co-polymers. "Plug" flow reactor gives quick grade changes and excellent impact co-polymers	24	2000
Hostalen/Krupp Udhe	Polyethylene	Ethylene	Hostalen slurry polymerization process uses 2 reactors in parallel or series to produce a broad range of PEs	NA	NA
Mitsui Chemicals, Inc.	Polyethylene	Ethylene/comonomers	CX process yields bimodal-molecular weight polymers	40	2001
INVENTA-FISCHER	Polyethylene terephthalate (PET)	Terephthalic acid, ethylene glycol	4-reactors continuous process produces amorphous PET chips or fibers and filaments; capacities up to 600 tpd available	300	2000
Equistar Chemicals L. D.	Polyethylene, Bimodal HDPE	Ethylene	Equistar-Maruzen low-pressure slurry process produces bimodal HDPE resins for film, blow molding, pipe and injection molding	3	1985
Mitsubishi Petrochemical Co.	Polyethylene, EVA	Ethylene	Full automatic control (startup, grade change and shutdown)	4	1992
Equistar Chemicals L. D.	Polyethylene, high pressure autoclave LDPE and EVA resins	Ethylene, vinyl acetate	Proven reliable resin production for film, injection molding and wire and cable grades. VA content up to 30% film, adhesives, etc.	10	1988
ExxonMobil Chemical Co.	Polyethylene, high pressure LDPE	Ethylene and EVA	State-of-the-art reactor provides broadest scope for LDPE products; including high-clarity films to medium density polymers	4	1999

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Equistar Chemicals L. D.	Polyethylene, high pressure tubular LDPE and EVA resins	Ethylene, vinyl acetate	Resin production for films, injection molding, adhesives and extrusion coating. VA content up to 40%, capacity 150,000 tpy	5	1992
Stamicarbon bv	Polyethylene, LDPE	Ethylene	Advanced Clean Tubular Reactor LDPE; reliable, flexible and low-cost for any PE product: lines sizes up to 200,000 tpy	9	2000
EniChem	Polyethylene, LDPE-EVA	Ethylene and vinyl acetate monomer	Autoclave or tubular process designs with EVA content of VA up to 40%	15	1995
Stamicarbon bv	Polyethylene, LDPE-EVA	Ethylene and vinyl acetate	Advanced Clean Tubular reactor LDPE/low EVA; reliable, flexible and low cost ; line size up to 400,000 tpy	9	2000
Sumitomo Chemical Co.,Ltd.	Polyethylene, LDPE-EVA	Ethylene and vinyl acetate	Tubular and autoclave processes with EVA up to 41%	8	1994
EniChem	Polyethylene, LDPE-VLDPE	Ethylene and C4-C6 olefins	Unique product flexibility and polymer with densities as low as 0.880	3	1987
Univation Technologies	Polyethylene, LLD-HD	Ethylene	Gas-phase fluidized reactor with proprietary solid catalysts	50	1998
Stamicarbon bv	Polyethylene, LLDPE/HDPE	Ethylene/comonomers	Compact Solution Process; low residence time; fast grade changes for high quality LLDPE/HDPE; line sizes up to 150,000 tpy	8	1998
Phillips Petroleum Co.	Polyethylene, LLDPE-HDPE	Ethylene	Energy efficient loop-reactor technology polymerizes slurry with catalyst	20	1998
Equistar Chemicals L. D.	Polyethylene, Petro high density	Ethylene, isobutane, comonomer, catalyst	Slurry loop HDPE technology for blow molding, injection molding and others	3	1985
Borealis A/S	Polypropylene	Propylene, ethylene	Slurry-loop and a series gas-phase reactor produce tailor-made MW and enhanced PPs, homopolymers, high-comonomers, heterophasic copolymers	1	1999
BP Chemical	Polypropylene	Propylene	Gas-phase horizontal stirred bed	8	2000
Chisso	Polypropylene	Propylene and ethylene	Simplified gas-phase process with horizontal reactor and high-performance catalyst	5	1996
Basell	Polypropylene	Propylene and ethylene	Spheripol process produces a range of homopolymers, random/impact copolymers	45	1994
Mitsui Chemicals, Inc.	Polypropylene	Propylene and ethylene	High yield and high stereo specific catalyst in a simple process scheme	23	2000
Basell	Polypropylene	Propylene or ethylene	Widely used technology since 1983	55	1996
Sumitomo Chemical Co.,Ltd.	Polypropylene	Propylene	Gas phase processes with proprietary high-performance catalyst	9	1994

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Targor GmbH	Polypropylene	Propylene	Novelen process uses 1 or 2 gas-phase reactors connected in series to produce PP homopolymer, copolymer and impact copolymer	NA	NA
Union Carbide Corp.	Polypropylene	Propylene	Gas-phase fluidized reactor with proprietary catalyst/ environmentally safe	29	1998
ABB Lummus Global/ BP Amoco	Polystyrene	Styrene	Wide range production of GPPS and HIPS using bulk continuous process	NA	NA
NSCC/UOP	Polystyrene	Styrene	Sophisticated reactor design for production of high-performance general purpose and high-impact PS resins	2	NA
ABB Lummus Global/BP Amoco	Polystyrene, expandable	Styrene	One-step batch suspension process with high reactor productivity	1	1997
Degussa AG	Polystyrene, expandable beads	Styrene	Expanding agent is fed into the reactor during batch-polymerization	2	1990
Degussa AG	Polystyrene, high impact	Styrene	Continuous bulk-process production of all grades of GPPS and HIPS	2	1990
Mitsui Chemicals, Inc.	Polystyrene, SAN, ABS	Styrene monomer, synthetic rubber, acrylonitrile	High-product quality with good performance. Simply and closed process, continuous bulk process	38	2000
Mitsui Chemicals, Inc.	Polyvinyl chloride	Vinyl chloride monomer	Clean, large reactor technology, high productivity and high-quality product	19	1997
Vin Tec GmbH/Degussa A197AG	Polyvinyl chloride	Vinyl chloride monomer	Up to 200 m ³ reactor technology yields suspension, high-impact and emulsion PVC	10	1992
Inovyl	Polyvinyl chloride (emulsion)	Vinyl chloride monomer	High productivity, high quality grades, low residual VCM, effective condenser usage	2	1991
Vin Tec GmbH/Krupp Uhde	Polyvinyl chloride (emulsion)	Vinyl chloride monomer	Batch process uses 2 or more reactors; special coating/buildup suppressant allows many batch operations before cleaning	NA	NA
ABB Lummus Global/Solvay SA	Polyvinyl chloride (suspension)	Vinyl chloride monomer	On-site initiator synthesis and high reactor productivity minimize operating costs; wide range of high quality products	NA	NA
Chisso	Polyvinyl chloride (suspension)	Vinyl chloride monomer	Batch process manufactures many PVC grades including commodity, high/low K values, matted type and copolymer PVC	12	2000
Vin Tec GmbH/Krupp Uhde	Polyvinyl chloride (suspension)	Vinyl chloride monomer	Batch process uses 2 or more reactors; special coating/buildup suppressant allows many batch operations before cleaning	32	NA

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Inovyl	Polyvinyl chloride (suspension)	Vinyl chloride monomer	High productivity, low residual VCM (< 1ppm), flexible operation, no build up	6	1996
Oxy Vinyls LP	Polyvinyl chloride (suspension)	Vinyl chloride monomer	Efficient, low-cost, high productive technology includes environment, health and safety controls, High level DCS, low RVCM condensers	16	1998
JSR Corp.	Styrene acrylonitrile (SAN)	Styrene and acrylonitrile	Bulk polymerization with high productivity and yield for many SAN grades	5	1995
JSR Corp.	Styrene butadiene latex SBL	Styrene, butadiene and other monomers	High productivity of many grades SBL used for paper coatings, carpets	4	1981
JSR Corp.	Styrene-butadiene rubber, emulsion	Styrene and butadiene	Low cost production of SBR with non-oil and oil extended products	7	1996
JSR Corp.	Styrene-butadiene rubber, solution	Styrene and butadiene	Efficient and advanced technology yields S-SBR with excellent properties	1	1991
Chisso	VCM Removal	PVC slurry with unreacted VCM	Stripping process for PVC plants to recover VCM from PVC slurry; VCM can be reused without deteriorating polymer quality	36	2000
Degussa AG	Vinyl pyridine latex	Vinyl pyridine, styrene, butadiene	After homogenization in a stirred reactor, the batch is heated and degassed when complete	1	1974
Oxygenates					
Kvaerner Process Technology/ Union Carbide Corp.	2-Ethylhexanol	Propylene	Rhodium-catalyzed, low pressure oxo process; high efficiency with minimal coproducts	14	1997
Kvaerner Process Technology/ Union Carbide Corp.	2-Propylheptanol	Raffinate 2	Rhodium-catalyzed, low pressure oxo process uses improved aldol condensation step	1	1994
BP Chemical, Inc./ Lurgi Öl Gas Chemie GmbH	Butanediol, 1-4	n-Butane	Fluid-bed oxidation and fixed-bed hydrogenation reactor combination lowers capital costs	NA	NA
Kvaerner Process Technology	Butanediol, 1-4	Maleic anhydride	Low-pressure, low-temperature ester hydrogenation. High-purity product BDO/THF/GBL options	6	2000
Celanese Chemicals Europe GmbH	Butanol, n	Propylene and syngas	Water-soluble Rh catalyst is easily separated and reused. Very economical	NA	1982
Krupp Udhe	Butanol, n	n-Butyraldehyde and hydrogen	Process uses nickel catalyst to react n-Butyraldehyde with H ₂ to forms-butanol	NA	NA

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Tessag Edeleanu GmbH	Butanol, secondary	Normal butenes rich C ₄ cut and water	Catalytic direct hydration. Catalyst is cation exchange resin	3	1995
Degussa AG	Butanol, tert	C ₄ stream containing isobutylene, water	Liquid-phase catalytic synthesis, high selectivity, two product grades	2	1988
Kvaerner Process Technology/ Union Carbide Corp.	Butanols	Propylene	Rhodium-catalyzed, low-pressure oxo process; high efficiency with wide range of propylene purities	12	1999
Degussa AG	Butyl alcohol, n/iso	Butyraldehyde n/iso and hydrogen	Catalytic hydrogenation	2	NA
Degussa AG	Butyl glycols	Butanol, ethylene oxide	Continuous synthesis with dissolved catalyst followed by distillation	NA	NA
Degussa AG	Butyl phenol, p-	Phenol, isobutylene	Continuous alkylation of phenol with heterogeneous catalyst	NA	NA
Edeleanu	Dimethyl ether	Methanol	Catalytic condensation reaction with 99.9% purity	2	NA
CDTECH/Mobil	DIPE	Refinery C ₃ stream	Ether production from propylene and water using Zeolite catalyst	NA	NA
Lyondell Chemical Co.	Direct olefin hydration	Olefins (ethylene or propylene, butene)	Direct hydration of olefins to corresponding alcohol in vapor phase; ether is prime side reaction	NA	NA
CDTECH/Snamprogetti SpA	ETBE	Mixed C ₄ hydrocarbons	High-conversion catalytic distillation process for ETBE using C ₄ s and ethanol	5	2000
Degussa AG	Ethanol	Ethylene, water	Heterogeneous catalysis, high yield and selectivity and low energy costs	8	1984
CDTECH, Inc.	Ether	Refinery C ₄ and C ₅ streams	Produces high iso-olefin/ether products by hydrogenation and isomerization	5	1992
Neste Oy, Engineering	Ether	Refinery C ₅ , C ₆ and C ₇ tertiary olefins	NEXTAME process produces TAME, C ₆ and C ₇ ethers with high yield and low investment	1	1995
UOP	Ether	FCC raffinate and steam-cracking butadiene	Ethermax process produces MTBE, ETBE or TAME	39	1997
IFP	Ethers	Refinery C ₄ and C ₅ streams	CATACOL technology combines catalysis and distillation separation	26	1996
Neste Oy, Engineering	Ethers	Refinery C ₇ , C ₈ , C ₆ and C ₇ olefinic streams	Nexethers process maximizes profitability by producing MTBE and other ethers in single unit	NA	NA
Kvaerner Process Technology	Ethyl acetate	Ethanol	Ethanol only process—no acetic acid required; byproduct hydrogen can be used as feedstock or fuel	1	1998

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Degussa AG	Ethyl hexanol,2-	Butyraldehyde, hydrogen	Catalytic hydrogenation after aldolisation. Long catalyst lifetime	1	NA
ARCO Chemical Co.	Ethyl tertiary butyl ether (ETBE)	Mixed C ₅ streams and ethanol	Reliable, flexible design with high conversion and long-life catalyst	7	1995
Degussa AG	Ethyl tertiary butyl ether (ETBE)	Isobutylene stream, ethanol	Liquid-phase catalytic synthesis, high selectivity, energy efficient	NA	NA
IFP	Ethyl tertiary butyl ether (ETBE)	FCC and steam-cracker C ₄ cuts and ethanol	CATACOL technology ensures high ETBE yields by combining catalysis and distillation separation	3	1996
Scientific Design . Company, Inc	Ethylene glycol	Ethylene and oxygen or ethylene oxide	Process features variable feed capabilities with high-quality product	55	1998
Shell International Chemicals B.V.	Ethylene glycol	Ethylene, oxygen or ethylene oxide	Highly integrated with EO plant fully benefiting from high selectivity catalyst; yielding superior quality glycols	60	2001
Scientific Design Company, Inc.	Ethylene oxide	Ethylene or ethanol and oxygen	Improved catalyst and computer-aided operations yield high-quality product	95	1998
Shell International Chemicals B.V.	Ethylene oxide	Ethylene and oxygen	Direct oxidation process using high-selectivity catalyst with high product yields	60	2001
Degussa AG	Isopropanol	Propylene, water	Vapor-phase hydration, high yield and selectivity, energy efficient	5	1988
Tessag Edeleanu GmbH	Isopropanol	Refinery-grade propylene and water	Catalytic direct hydration. Catalyst is cation exchange resin	2	1989
BP Chemicals, Inc.	Maleic anhydride	n-Butane	Fluid-bed catalytic oxidation process with an aqueous-based recovery and purification	3	1994
Acid-Amine Technologies, Inc.	Methanol	Carbon monoxide and hydrogen	Two-step carbonylation and hydrogenation for small plants	NA	NA
Haldor Topsoe	Methanol	Natural gas, naphtha, fuel oil	Features one or two step reforming with low energy synthesis/distillation	16	2000
Kellogg Brown & Root	Methanol	Hydrocarbons/natural gas & naphtha	Low energy consumption; high purity; cost-effective	5	1988
Krupp Udhe	Methanol	Natural gas, LPG and heavy naphtha	Steam reforming process cost-effectively manufactures methanol from varying feedstocks	11	NA
Kvaerner Process	Methanol	Synthesis gas	Efficient, modern, reliable process operates at low pressure/		

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Technology/ICI			temperatures—lowest total manufacturing cost	33	2001
Lurgi Öl Gas Chemie GmbH	Methanol	Natural gas, naphtha, vacuum residue, natural gas	Oxygen-operated syngas generation, two-step isothermal synthesis with maximum yield and very large single-train capacity	40	2000
Synetix	Methanol (LCM)	Natural gas, refinery offgas	Heat-exchange reforming and low-pressure loop technology give high efficiencies	1	1996
Synetix	Methanol (LPM)	Natural gas, refinery offgas, naphtha oil	Proven low-pressure methanol synthesis technology and catalysts	58	1999
ARCO Chemical Co.	Methyl tertiary butyl ether (MTBE)	Mixed C ₄ s streams and methanol	Reliable, flexible process optimized by 15 years of commercial operations	31	1995
Degussa AG	Methyl tertiary butyl ether (MTBE)	Methanol, isobutylene-containing stream	Liquid-phase catalytic synthesis, high selectivity, energy efficient	20	1992
IFP	Methyl tertiary butyl ether (MTBE)	FCC and steam-cracker C ₄ cuts and methanol	CATACOL technology ensures high MTBE yields by combining catalysis and distillation separation	21	1996
Phillips Petroleum Co.	Methyl tertiary butyl ether (MTBE)	Isobutene and methanol	Ion exchange resin reactors under mild conditions yield 99 wt% MTBE	7	1991
Snamprogetti Spa/ Ecofuel S.p.A.	Methyl tertiary butyl ether (MTBE)	C ₄ streams containing isobutylene, methanol	High efficiency and reliability, compact and low-investment plants	25	1994
Tessag Edeleanu GmbH	Methyl tertiary butyl ether (MTBE)	C ₄ raffinate and methanol	Catalytic additive reaction for isobutene and methanol	5	1993
CDTECH/Snamprogetti SpA	Mixed ethers	Mixed C ₄ –C ₇ hydrocarbons	MTBE, TAME and heavier ether production from hydrocarbon feeds containing C ₄ , C ₅ , C ₆ and C ₇ iso-olefins	3	2000
CDTECH/Snamprogetti SpA	MTBE	Mixed C ₄ hydrocarbons	High-conversion catalytic distillation process for MTBE using C ₄ s and methanol	107	2000
Sumitomo Chemical Co., Ltd.	MTBE/ butene-1	Raffinate-1 or FCC C ₄	Low temperature and pressure operating conditions reduce equipment costs	3	1994
ARCO Chemical Co.	MTBE/TAME	Mixed C ₄ and C ₅ streams	Produces a mixed MTBE/TAME product using methanol from C ₄ and C ₅ streams	4	1994
Krupp Uhde	Nitric acid	Ammonia	Process oxidizes ammonia into nitric oxide; then oxidizes nitric oxide to nitric acid; has environmental control requirements	22	NA

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Degussa AG	Nonyl phenol	Phenol, tripropylene	Continuous alkylation with heterogeneous catalyst. Environmentally safe	2	1991
ABB Lummus Global	Phenol	Cumene	Cumene oxidation process with advanced cleavage technology for improved yield	2	1995
Kellogg Brown & Root/ Hercules/BP	Phenol	Cumene	Low energy requirements, capital costs, emissions and effluents; high quality products	39	1997
Mitsui Chemicals, Inc.	Phenol	Cumene	A unique purification system produces high-purity product	5	1999
UOP/Sunoco	Phenol	Cumene	Process characteristics: low-pressure oxidation for 1.31 tons of cumene/ton of phenol; high-purity phenol (polycarbonate BPA grade)	11	1996
ARCO Chemical Co.	Polyether polyols	Propylene oxide and ethylene oxide	Produces polyether polyols under mild conditions for multiple grade products	6	1994
CDTECH/Snamprogetti SpA	TAEЕ	Mixed C ₅ hydrocarbons	High-conversion catalytic distillation process for TAEЕ production using C ₅ S and ethanol	1	1991
CDTECH/Snamprogetti SpA	TAME	Mixed C ₅ hydrocarbons	High-conversion catalytic distillation process for TAME production using C ₅ S and methanol	29	2000
Snamprogetti S.p.A.	Tame/high ethers	Light cracked naphtha, methanol	More than 20% reactive isoamylenes, 40–60% reactive isohexene, 20–30% reactive isoheptenes etherified into TAME and higher ethers	NA	NA
Snamprogetti S.p.A.	Tame/high ethers	Light cracked naphtha, methanol	More than 90% pentenes and 40–60% reactive isohexenes/20–30% reactive isoheptenes etherified into TAME and higher ethers	NA	NA
Snamprogetti Spa/EniChem	Tertiary Amy methyl ether (TAME)	C ₅ streams containing isoamylenes, methanol	High efficiency and reliability, compact and low-investment plants	1	1988
Degussa AG	Tertiary amyl ethyl ether (TAEЕ)	Amylene containing hydrocarbons, ethanol	Liquid-phase catalytic synthesis, high selectivity, energy efficient	NA	NA
ARCO Chemical Co.	Tertiary amyl methyl ether (TAME)	Mixed C ₅ S streams and methanol	Flexible design, high conversion, long-life catalyst, low operating costs	4	1994
Degussa AG	Tertiary amyl methyl ether (TAME)	Amylene containing hydrocarbons/methanol	Liquid-phase catalytic synthesis, high selectivity, energy efficient	NA	NA
IFP	Tertiary amyl methyl ether (TAME)	FCC and steam-cracker C ₄ cuts and methanol	Olefinic C ₅ cuts are upgraded to high octane blending value, low RVP TAME	6	1996

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
<u>Aldehydes/ketones</u>					
Degussa AG	Acetaldehyde	Ethanol	High purity, long lifetime catalyst, economical heat recovery	3	1993
IFP	Acetone	Isopropyl alcohol	Process uses a high-activity catalyst in an isothermal reactor	4	1982
Kellogg Brown & Root/ Hercules/BP	Acetone	Cumene	Low energy requirements, capital costs, emissions and effluents; high quality products	39	1997
Mitsui Chemicals, Inc.	Acetone	Cumene	A unique purification system produces high-purity product	5	1999
Tessag Edeleanu GmbH	Acetone	Isopropanol	Dehydrogenation reaction with copper-containing catalyst	3	1983
UOP/Sunoco	Acetone	Cumene	High-quality acetone is produced as a byproduct from this process.	12	1991
Kvaerner Process Technology	Alcohol dehydrogenation	Single or mixed alcohols	Generic process can produce wide range of esters without requiring acid feedstock	1	1998
Cleanese Chemicals Europe GmbH	Butyraldehyde, n	Propylene and syngas	Water-soluble Rh catalyst is easily separated and reused. Very economical	NA	1982
Krupp Udhe/Celanese GmbH/ Rhone-Poulenc	Butyraldehyde, n	Propylene and synthesis gas	Low-pressure rhodium oxo process reacts propylene with synthesis	NA	NA
Kvaerner Process Technology/Union Carbide Corp.	Butyraldehyde, n and iso	Propylene	Features are low environmental impact and mild operating conditions	27	1999
ABB Lummus Global	Formaldehyde	Methanol	High energy efficiency, low catalyst bed pressure drop	12	1990
Haldor Topsøe	Formaldehyde	Methanol	Yields of urea-formaldehyde (UF-85) 60 wt% or aqueous formaldehyde 55 wt%	24	2000
INVENTA-FISCHER	Formaldehyde	Methanol	Silver or metal oxide process, urea-formaldehyde (UF-85)	60	1989
Mitsui Chemicals, Inc.	IPA	Acetone	Flexible proportion of acetone/phenol production; high conversion, high selectivity	1	1995
ABB Lummus/Petroquaisa/ Okiteno	Methyl ethyl ketone (MEK)	Butylenes	Advanced catalytic dehydrogenation has high yield, high conversion	1	1989
Tessag Edeleanu GmbH	Methyl ethyl ketone (MEK)	Secondary butanol	Dehydrogenation reaction with copper-containing catalyst	7	1995
Tessag Edeleanu GmbH	Methyl isobutyl ketone	Acetone and hydrogen	Condensation reaction with noble metal catalyst	3	1994

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Huels AG	Methyl isobutyl ketone (MIBK)	Acetone	One-step condensation/hydrogenation process	2	1985
Acids/salts					
BP Chemicals, Inc./Lurgi Öl Gas Chemie GmbH	1, 4-Butanediol	n-Butane	Fluid-bed oxidation and fixed-bed hydrogenation reactor combination lowers capital costs	NA	NA
Degussa AG	Acetic acid	Acetaldehyde	Pharmaceutical purity, catalyst recovery, oxidation with air or oxygen	2	1993
Mitsubishi Petrochemical Co.	Acrylic acid	Propylene	High yield and long-life catalyst in a simple process scheme	7	1991
Lurgi Öl Gas Chemie GmbH for BP Chemicals/Nippon Kayaku	Acrylic acid--glacial & acrylates	Propylene	Advanced oxidation process, cost-effective fixed-bed tubular reactor, largest single-train	NA	NA
Degussa AG	Butylacetate, n/iso	Butanol n/iso and acetic acid	Catalytic esterification	NA	NA
Degussa AG	Di 2 ethyl hexyl phthalate (DOP)	2-Ethylhexanol, phthalic anhydride	Catalytic esterification, low alpha number	NA	NA
Degussa AG	Dimethyl terephthalate (DMT)	p-Xylene, oxygen, methanol	Liquid oxidation with homogeneous catalysis, mild-noncorrosive conditions	30	NA
GTC Technology Corporation	Dimethyl terephthalate, DMT	p-Xylene	Unique oxidation/esterification process uses and modern distillation/crystallization	7	1997
Celanese GmbH/Krupp Uhde	Ethylhexanol 2	n-Butyraldehyde	Aldolization of n-butyraldehyde with aqueous caustic soda yields 2-ethylhexanol	NA	NA
Hochst AG	Ethylhexanol 2	n-Butyraldehyde and hydrogen	Catalytic hydrogenation of aldo product. Very economic and reliable	NA	1980
Scientific Design Company, Inc.	Fumaric acid	Maleic acid	License available in conjunction with maleic anhydride process	5	1986
Lonza S.p.A.	Fumaric acid	Maleic anhydride	Liquid-phase isomerization, two-step crystallization process	6	1991
Huntsman Petrochemical Corp.	Maleic anhydride	n-Butane	Fixed-bed technology using high-yield/ productivity catalyst and solvent-product recovery	6	1999
Lonza S.p.A.	Maleic anhydride	Benzene and n-butane	Fixed bed technology, aqueous or organic solvent product recovery	3	1988
Lonza S.p.A.	Maleic anhydride	Phthalic anhydride offgas	Maleic anhydride recovery, dehydration and azeotropic distillation	2	1987
Lonza/ABB Lummus Global	Maleic anhydride	Butane	Fluidized bed technology, organic solvent product recovery	9	1993

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Scientific Design Company, Inc.	Maleic anhydride	n-Butanes	Fixed-bed technology; efficient product recovery systems; high product quality	9	1994
Acid-Amine Technology, Inc.	Methyl formate	Methanol and carbon monoxide	AAT Trimode reactor with catalyst yields 95% to 99.5% pure product	7	1992
Sumitomo Chemical Co.,Ltd.	Nitric acid	Ammonia and air (O ₂)	Without pure O ₂ , sulfuric acid or magnesium nitrate, process yields HNO ₃	1	1981
Lonza S.p.A.	Phthalic anhydride	O-xylene, naphthalene	Fixed-bed technology, low energy process, continuous distillation	5	1990
Lurgi Öl Gas Chemie GmbH	Phthalic anhydride	O-xylene, naphthalene	Multi-tubular reactor oxidizes o-xylene at high yield with maximum heat recovery for export HP steam	110	1998
Washington Group International/Interquisa	Purified terephthalic acid	Paraxylene	Commercially proven, economic process for producing highest quality PTA product	1	2000
Mitsui Chemicals, Inc.	Purified terephthalic acid (PTA)	Paraxylene	High quality product with simple and mild oxidation and low product cost	10	1997
Degussa AG	Terephthalic acid	p-Xylene, oxygen, methanol, water	Hydrolysis of DMT, no organic solvent used, no corrosion problems	1	1984
Lurgi Öl Gas Chemie GmbH	Terephthalic acid-polymer grade (MTA)	p-Xylene	Liquid-phase oxidation with unique mild conditions. Advanced purification section. Effective with respect to operation and investment costs	NA	NA
Lurgi Öl Gas Chemie GmbH	Terephthalic acid-polymer grade (PTA)	p-Xylene	Highly advanced MTA technology for oxidation section, newly developed purification by hydrogenation, unique crystallization	NA	NA
<u>Nitrogen compounds</u>					
Kvaerner Process Technology	Amines, C ₁ to C ₁₂ , multiproduct	Alcohol/aldehyde/ketone/ ammonia/hydrogen	Synthesis of mon, di or tri alkylamines by vapor-phase amination	9	1998
Kvaerner Process Technology	Amines, Isopropyl	Acetone/isopropanol and ammonia	Synthesis of monoisopropylamine at high-purity	6	1992
Kvaerner Process Technology	Amines, methyl	Anhydrous ammonia and methanol	Yields tri-, mono- or dimethylamine at 99.6% purity	27	1998
Haldor Topsøe	Ammonia	Natural gas, naphtha, fuel oil	Proven energy-efficient technology using proprietary design	200	1999
Kellogg Brown & Root	Ammonia	Natural gas, LPG, naphtha	Synthesis in B&RB adiabatic converters/mild reforming with gas turbine, cryogenic purifier	26	1997

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Kellogg Brown & Root	Ammonia	Hydrocarbons/natural gas & naphtha	Extremely low energy consumption; cost-effective	175	1996
Krupp Udhe	Ammonia	Natural gas, LPG, LPG, naphtha	Process uses conventional steam reforming synthesis gas generation and a medium pressure ammonia synthesis loop	15	NA
Linde AG	Ammonia	Light hydrocarbons	LCA process simplifies conversion of hydrocarbons to ammonia, highly efficient synthesis loop	1	1993
Synetix	Ammonia (AMV)	All hydrocarbons-natural gas to naphtha	Energy efficient, reliable, low-capital cost process uses low-pressure synthesis loop	3	1996
Synetix	Ammonia (LCA)	Natural gas	Simple to operate, energy efficient and low environmental impact	3	1996
Kellogg Brown & Root	Ammonia, advanced	Hydrocarbons/natural gas & naphtha	Catalytic-steam reforming process uses pressure-based Kellogg Reforming Exchange System (KRES)	NA	NA
Scientific Design Company, Inc.	Aniline	Phenol and ammonia	Low capital costs. Suited for units already producing phenol	2	1981
SNAICO Engineering SpA	Caprolactam	Toluene	Process yields high-purity product via hydrogenation and nitrosation	4	1994
Kvaerner Process Technology	Dimethylformamide	Carbon monoxide and dimethylamine	Single-step synthesis with a catalyst produces 99.9% pure product	11	1998
Haldor Topsøe	DME	Natural gas, naphtha, fuel oil	Low cost/high efficiency conversion of hydrocarbons directly to DME without isolation of purified methanol as intermediate	NA	NA
Kvaerner Process Technology	Ethanolamines	Ethylene oxide and ammonia	Yields mono-, di- and triethanolamines at 97% conversion of raw materials	2	1992
Scientific Design Company, Inc.	Ethanolamines	Ethylene oxide and ammonia	Process offers high-quality product with wide product distribution	4	1979
Kvaerner Process Technology	N-methyl pyrrolidone	Mono methylamine, gamma butyrolactone	Uses a proprietary reactive distillation process to reduce capital costs and improve product quality	NA	NA
Snamprogetti Spa	Urea	Ammonia and carbon dioxide	Process is pollution-free, and energy efficient	98	2000
Stamicarbon bv	Urea	Ammonia and carbon dioxide	CO ₂ stripping technology using proven, innovative Urea 2000 Plus synthesis process for prilled or granulated urea	115	2001
Chlorides					
Inovyn	Direct chlorination, high temperature chlorination	Ethylene, chlorine	Energy efficient process, product purity of 99.95%, low maintenance, no EDC washing	14	1995

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PETROCHEMICAL LICENSOR INDEX

Company	Product	Feedstock	Process description	Number of licenses	Date of last license
Inovy	Direct chlorination, low temperature chlorination	Ethylene, chlorine	Well established system and extensively licensed converts lower purity C ₂ in gaseous stream	24	1993
Vestolit GmbH/Huels AG	Ethyl chloride	Ethylene and hydrogen chloride	Continuous fluid-phase conversion to ethyl chloride with catalyst	NA	NA
ABB Lummus Global/Solvay SA	Ethylene dichloride (EDC)	Ethylene and chlorine	High-yield direct chlorination; no purification prior to cracking; energy efficient	NA	NA
ABB Lummus Global/Solvay SA	Ethylene dichloride (EDC)	Ethylene, hydrogen chlorine and oxygen	Oxychlorination with small fluid-bed reactor design; high per-pass conversion; energy efficient	NA	NA
Oxy Vinyls LP	Ethylene dichloride (EDC)	Ethylene and chlorine	High temperature direct chlorination with catalyst, energy efficient.	8	2000
Oxy Vinyls LP	Ethylene dichloride (EDC)	Ethylene, hydrogen chlorine and oxygen	Oxyhydrochlorination in fluid bed reactor with high efficiency catalyst	46	2000
Vin Tec	Ethylene dichloride (EDC) via lean oxychlorination	Ethylene, chlorine	Oxychlorination process produces EDC cost-effectively with an exothermic, cooper catalyst-based process	NA	NA
Inovy	Ethylene dichloride (EDC), high temperature	Ethylene, chlorine	Energy efficient process, product purity of 99.95%, low maintenance, no EDC washing	14	1999
Inovy	Ethylene dichloride (EDC), low temperature	Ethylene, chlorine	Well established system and extensively licensed converts lower purity C ₂ in gaseous stream	24	1993
Oxy Vinyls LP	Ethylene dichloride (EDC), low temperature	Ethylene and chlorine	Low temperature process for direct chlorination offers high selectivity	21	1997
Inovy	Fixed-bed oxygen-based oxychlorination	Ethylene, oxygen, hydrogen chloride	Environmentally attractive process; simple design offers high selectivity, and capacity; energy efficient	17	1996
Oxy Vinyls LP	Hydrogen chloride	Liquid chlorinated organics	Catalytic oxidation of liquids recovers chlorine and energy value of feedstocks	8	1999
Degussa AG	Methylchloride (MAC)	Isobutylene, chlorine	Substitution reaction of isobutylene and chlorine, high yield	NA	NA
Vestolit GmbH/Degussa AG	Methyl chloride	Methanol, hydrogen, chloride	Continuous gas-phase conversion with solid catalyst	NA	NA
Inovy	Vinyl chloride monomer	Ethylene, chlorine and air/oxygen	Fixed-bed oxygen-based oxychlorination, low temperature, direct chlorination	25	1992
Mitsui Chemicals, Inc.	Vinyl chloride monomer	Chlorine, ethylene, oxygen	Oxygen-based balanced oxychlorination process, high temp. direct chlorination process	23	1998

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Company	Product	Feedstock	Process description	Number of licenses	Date of last license
ABB Lummus Global/Solvay SA	Vinyl chloride monomer (VCM)	EDC and/or ethylene, chlorine	Advanced pyrolysis design with high EDC conversion and long furnace run lengths; energy efficient	NA	NA
Oxy Vinyls LP	Vinyl chloride monomer (VCM)	Ethylene, chlorine and/or EDC	Pyrolysis of EDC yields VCM. Oxyhydrochlorination recycles by-product HCl	60	2000
<u>Sulfur compounds</u>					
Degussa AG	Paraffin sulfonates	n-Paraffins (C ₁₃ - C ₁₇), sulfur dioxide	Reaction of straight-chain paraffins with SO ₂ and O ₂ with UV-radiation	NA	NA
Degussa AG	Sodium methallylsulfonate (MAS)	Methallylchloride (MAC) and sodium sulfite	Reaction of MAS and sodium sulfite with fractionated crystallization	NA	NA
<u>Cyclo-compounds</u>					
IFP	Cyclohexane	Benzene	Liquid-phase homogenous catalysis hydrogenation offers low investment and operating costs than vapor-phase processes	29	2000
UOP	Cyclohexane	Benzene	Fixed-bed catalytic process yields high-quality cyclohexane	15	1993
Kvaerner Process Technology	Cyclohexanone/cyclohexanol	Phenol/hydrogen	Synthesis of KA oil with high selectivity to cyclohexanone	2	1998

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