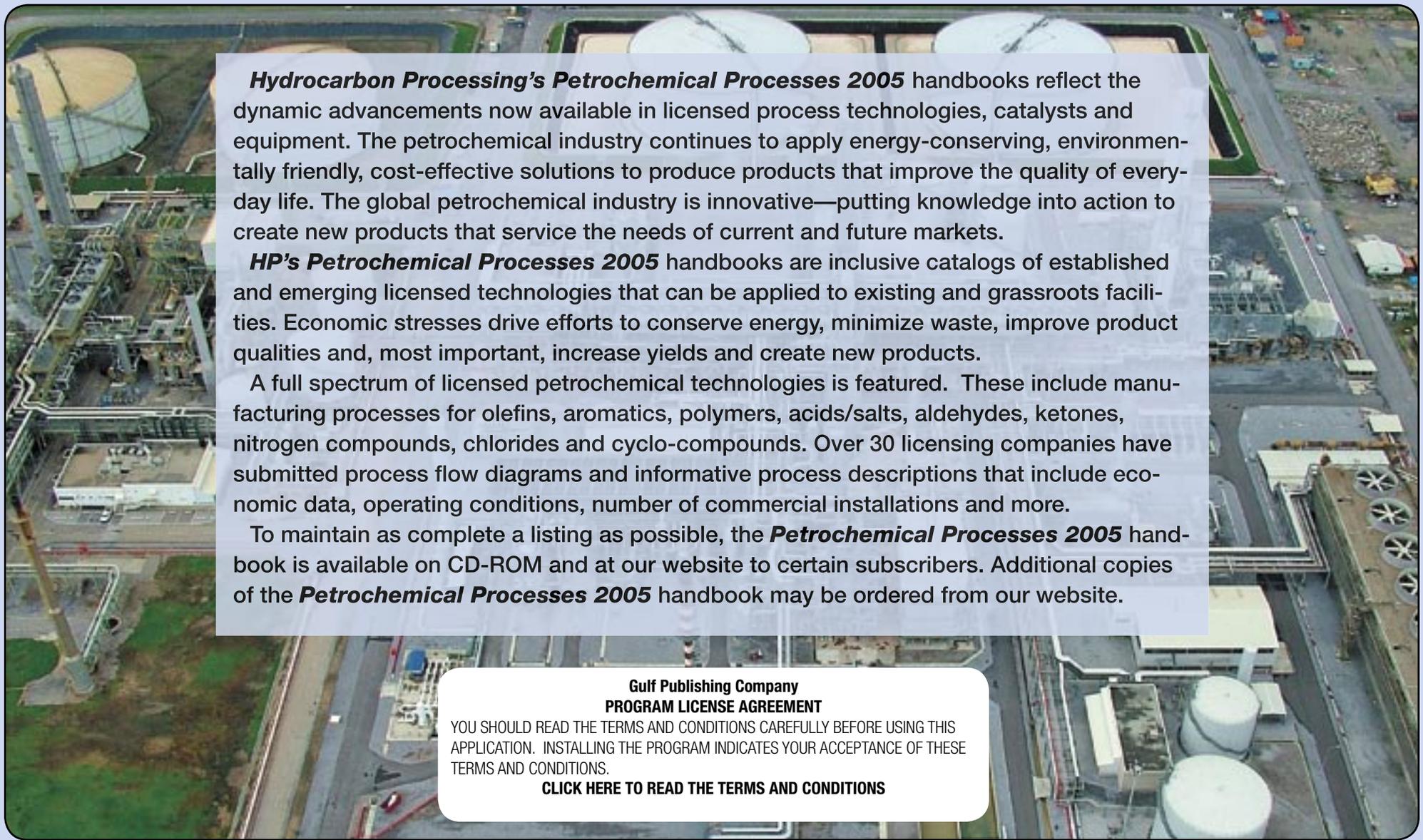


Petrochemical Processes 2005



Hydrocarbon Processing's Petrochemical Processes 2005 handbooks reflect the dynamic advancements now available in licensed process technologies, catalysts and equipment. The petrochemical industry continues to apply energy-conserving, environmentally friendly, cost-effective solutions to produce products that improve the quality of everyday life. The global petrochemical industry is innovative—putting knowledge into action to create new products that service the needs of current and future markets.

HP's Petrochemical Processes 2005 handbooks are inclusive catalogs of established and emerging licensed technologies that can be applied to existing and grassroots facilities. Economic stresses drive efforts to conserve energy, minimize waste, improve product qualities and, most important, increase yields and create new products.

A full spectrum of licensed petrochemical technologies is featured. These include manufacturing processes for olefins, aromatics, polymers, acids/salts, aldehydes, ketones, nitrogen compounds, chlorides and cyclo-compounds. Over 30 licensing companies have submitted process flow diagrams and informative process descriptions that include economic data, operating conditions, number of commercial installations and more.

To maintain as complete a listing as possible, the **Petrochemical Processes 2005** handbook is available on CD-ROM and at our website to certain subscribers. Additional copies of the **Petrochemical Processes 2005** handbook may be ordered from our website.

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Stone & Webster Inc.

Sud-Chemie Inc.

Sunoco

Technip

The Dow Chemical Co.

Toyo Engineering Corp.

Uhde GmbH

Uhde Inventa-Fischer

Union Carbide Corp.

Univation Technologies

UOP LLC

Vinnolit



Axens Axens is a refining, petrochemical and natural gas market focused supplier of process technology, catalysts, adsorbents and services, backed by nearly 50 years of commercial success. Axens is a world leader in several areas, such as:

- Petroleum hydrotreating & hydroconversion
- FCC gasoline desulfurization
- Catalytic Reforming
- BTX (benzene, toluene, xylenes) production & purification
- Selective Hydrogenation of olefin cuts
- Sulfur recovery catalysts.

Axens is a fully-owned subsidiary of IFP.

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Acetic acid

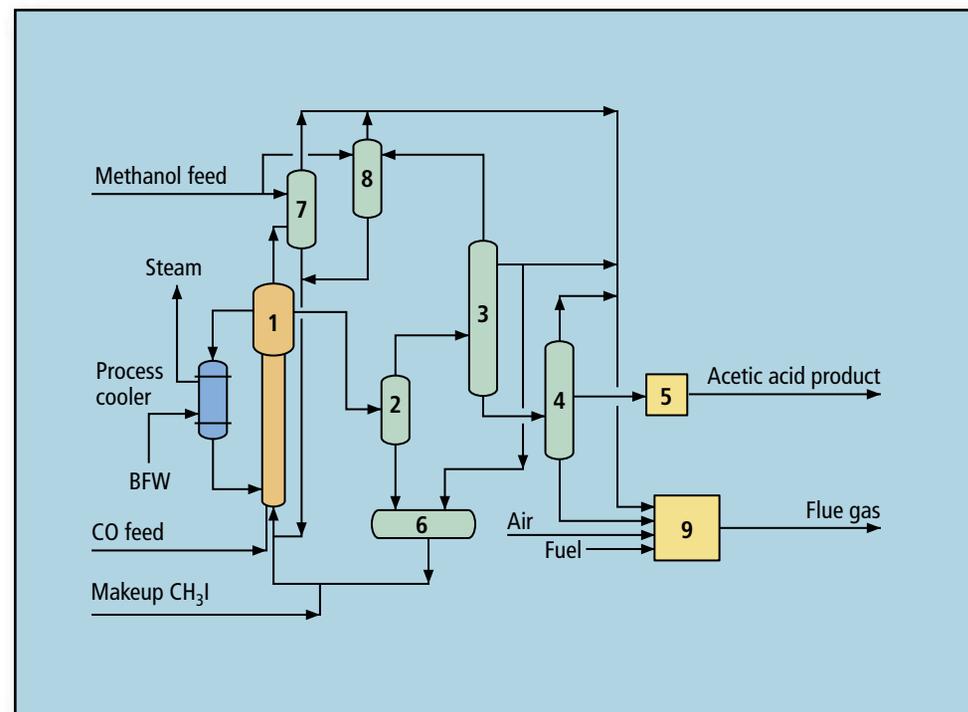
Application: To produce acetic acid using the process, ACETICA. Methanol and carbon monoxide (CO) are reacted with the carbonylation reaction using a heterogeneous Rh catalyst.

Description: Fresh methanol is split into two streams and is contacted with reactor offgas in the high-pressure absorber (7) and light gases in the low-pressure absorber (8). The methanol, exiting the absorbers, are recombined and mixed with the recycle liquid from the recycle-surge drum (6). This stream is charged to a unique bubble-column reactor (1).

Carbon monoxide is compressed and sparged into the reactor riser. The reactor has no mechanical moving parts, and is free from leakage/maintenance problems. The ACETICA Catalyst is an immobilized Rh-complex catalyst on solid support, which offers higher activity and operates under less water conditions in the system due to heterogeneous system, and therefore, the system has much less corrosivity.

Reactor effluent liquid is withdrawn and flash-vaporized in the Flasher (2). The vaporized crude acetic acid is sent to the dehydration column (3) to remove water and any light gases. Dried acetic acid is routed to the finishing column (4), where heavy byproducts are removed in the bottom draw off. The finished acetic-acid product is treated to remove trace iodide components at the iodide removal unit (5).

Vapor streams from the dehydration column overhead contacted with methanol in the low-pressure absorber (8). Unconverted CO, methane, other light byproducts exiting in the vapor outlets of the high- and low-pressure absorbers and heavy byproducts from the finishing column are sent to the incinerator with scrubber (9).



Commercial plant: One unit is under construction for a Chinese client.

Reference: "Acetic Acid Process Catalyzed by Ionically Immobilized Rhodium Complex to Solid Resin Support," *Journal of Chemical Engineering of Japan*, Vol. 37, 4, pp. 536–545 (2004)

"The Chiyoda/UOP ACETICA process for the production of acetic acid," 8th Annual Saudi-Japanese Symposium on Catalysts in Petroleum Refining and Petrochemicals, KFUPM-RI, Dhahran, Saudi Arabia, Nov. 29–30, 1998.

Licensors: Chiyoda Corp.

Feed and utility consumption:

Methanol, mt/mt	0.539
CO, mt/mt	0.517
Power (@CO Supply 0 K/G), kWh/mt	129
Water, cooling, m ³ /mt	137
Steam @100 psig, mt/mt	1.7

Acrylonitrile

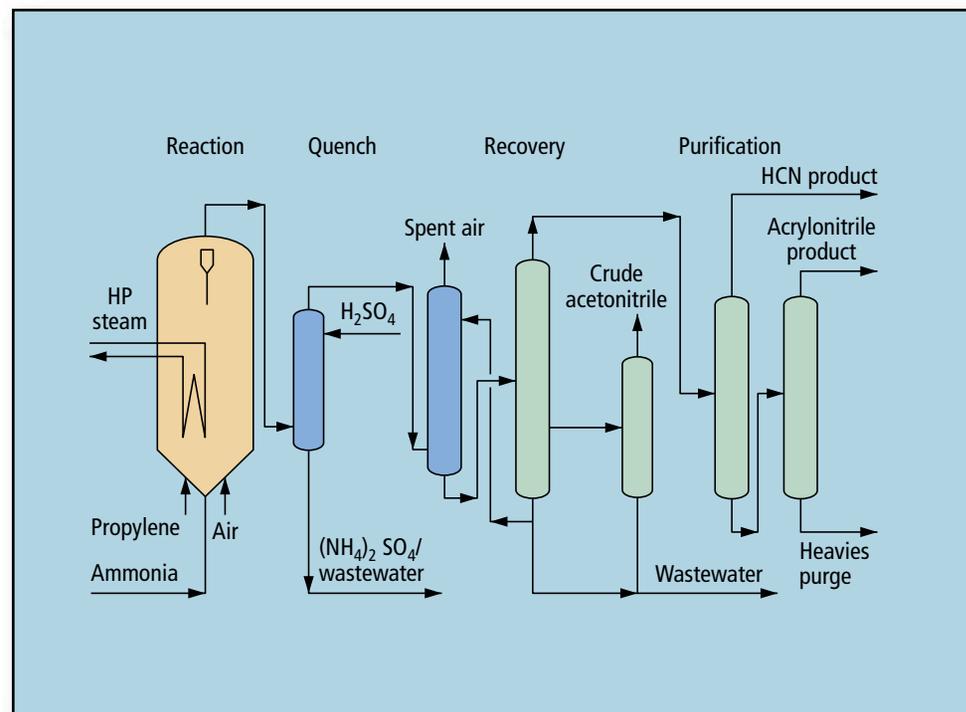
Application: A process to produce high-purity acrylonitrile and high-purity hydrogen cyanide from propylene, ammonia and air. Recovery of byproduct acetonitrile is optional.

Description: Propylene, ammonia, and air are fed to a fluidized bed reactor to produce acrylonitrile (ACRN) using DuPont's proprietary catalyst system. Other useful products from the reaction are hydrogen cyanide (HCN) and acetonitrile (ACE). The reaction is highly exothermic and heat is recovered from the reactor by producing high-pressure steam. The reactor effluent is quenched and neutralized with a sulfuric solution to remove the excess ammonia.

The product gas from the quench is absorbed with water to recover the ACRN, HCN, and ACE. The aqueous solution of ACRN, HCN, and ACE is then fractionated and purified into high-quality products. The products' recovery and purification is a highly efficient and low-energy consumption process. This ACRN technology minimizes the amount of aqueous effluent, a major consideration for all acrylonitrile producers.

This ACRN technology is based on a high-activity, high-throughput catalyst. The propylene conversion is 99% with a selectivity of 85% to useful products of ACRN, HCN, and ACE. The DuPont catalyst is a mechanically superior catalyst, resulting in a low catalyst loss. DuPont has developed a Catalyst Bed Management Program (CBMP) to maintain the properties of the catalyst bed inside the reactor at optimal performance throughout the operation. The catalyst properties, the CBMP and proprietary reactor internals provide an optimal performance of the ACRN reactor, resulting in high yields.

With over 30 years of operating experience, DuPont has developed know-how to increase the onstream factor of the plant. This know-how includes the effective use of inhibitors to reduce the formation of cyanide and nitrile polymers and effective application of an antifoulant system to increase onstream time for equipment.



Commercial plants: DuPont Chemical Solution Enterprise, Beaumont, Texas (200,000 mtpy).

Licensors: Kellogg Brown & Root, Inc.

Alkylbenzene, linear

Application: The Detal process uses a solid, heterogeneous catalyst to produce linear alkylbenzene (LAB) by alkylating benzene with linear olefins made by the Pacol process.

Description: Linear paraffins are fed to a Pacol reactor (1) to dehydrogenate the feed into corresponding linear olefins. Reactor effluent is separated into gas and liquid phases in a separator (2). Diolefins in the separator liquid are selectively converted to mono-olefins in a DeFine reactor (3). Light ends are removed in a stripper (4) and the resulting olefin-paraffin mixture is sent to a Detal reactor (5) where the olefins are alkylated with benzene. The reactor effluent is sent to a fractionation section (6, 7) for separation and recycle of unreacted benzene to the Detal reactor, and separation and recycle of unreacted paraffins to the Pacol reactor. A rerun column (8) separates the LAB product from the heavy alkylate bottoms stream.

Feedstock is typically C_{10} to C_{13} normal paraffins of 98+% purity. LAB product has a typical Bromine Index of less than 10.

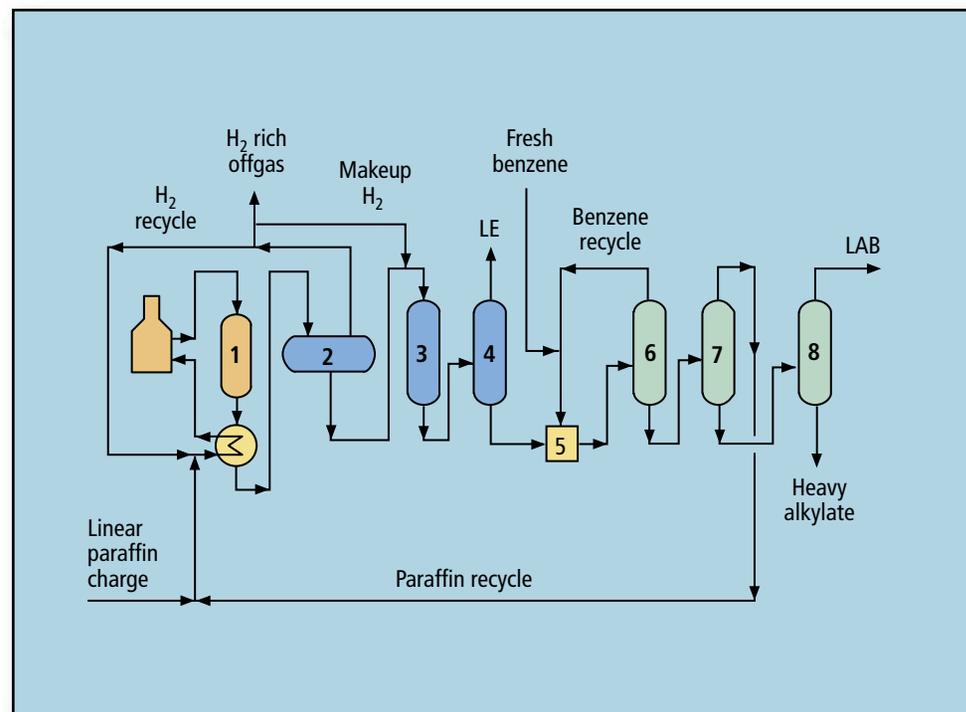
Yields: Based on 100 weight parts of LAB, 81 parts of linear paraffins and 34 parts of benzene are charged to a UOP LAB plant.

Economics: Investment, US Gulf Coast inside battery limits for the production of 80,000 tpy of LAB: \$1,000/tpy.

Commercial plants: Twenty-nine UOP LAB complexes based on the Pacol process have been built. Four of these plants use the Detal process.

Reference: Greer, D., et al., "Advances in the Manufacture of Linear Alkylbenzene," 6th World Surfactants Conference (CESIO), Berlin, Germany, June 2004.

Licensors: UOP LLC.



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 Alpha-Select process:

n-Butene-1	>99
n-Hexene-1	>98
n-Octene-1	>96
n-Decene-1	>92

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.

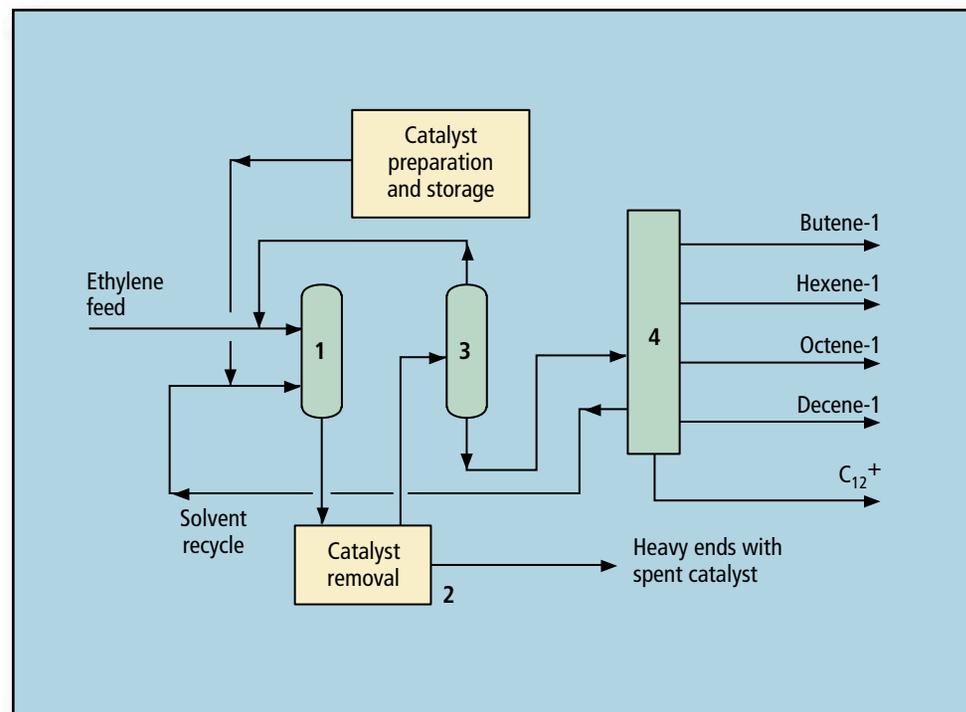
Yields: Yields are adjustable to meet market requirements and very little high boiling polymer is produced as illustrated:

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 2004 ISBL investment at a Gulf Coast location producing 65,000 tpy of C_4-C_{10} alpha-olefins is:

Investment , million US\$	37
Raw material	
Ethylene, tons per ton of product	1.15
Byproducts , ton/ton of main products	
C_{12}^+ olefins	0.1



Fuel gas	0.03
Heavy ends	0.02
Utilities cost , US\$/ton product	51
Catalyst + chemicals , US\$/ton product	32

Commercial plants: The AlphaSelect process is strongly backed by extensive Axens industrial experience in homogeneous catalysis, in particular, the Alphabutol process for producing butene-1 for which there are 19 units producing 312,000 tpy.

Licensor: Axens, Axens NA.

Alpha olefins

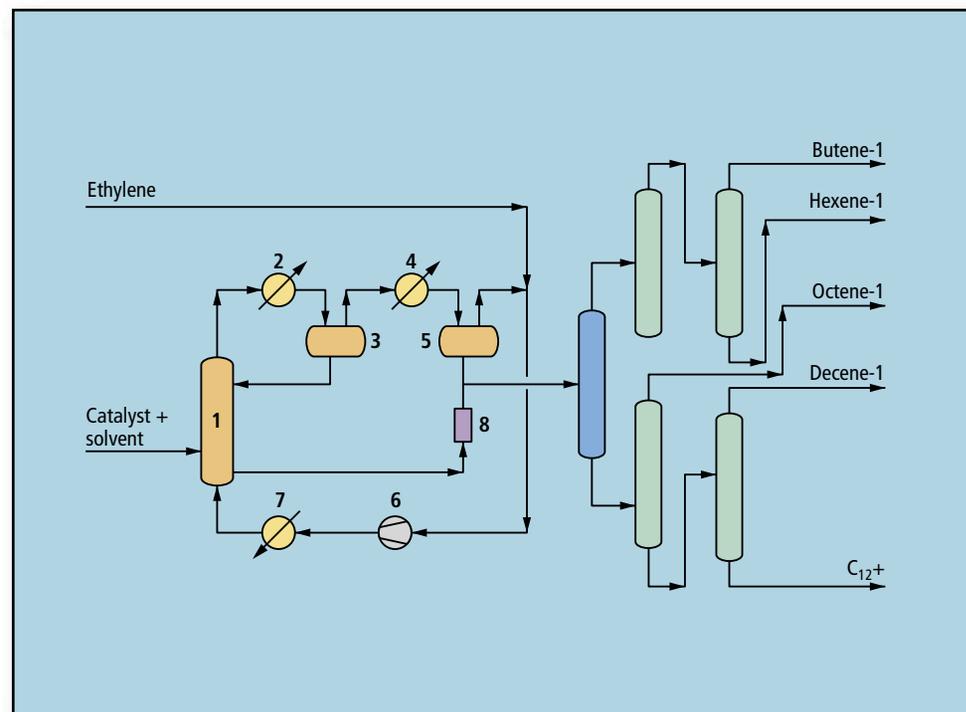
Application: The α -Sablin process produces α -olefins such as butene-1, hexene-1, octene-1, decene-1, etc. from ethylene in a homogenous catalytic reaction. The process is based on a highly active bifunctional catalyst system operating at mild reaction conditions with highest selectivities to α -olefins.

Description: Ethylene is compressed (6) and introduced to a bubble-column type reactor (1) in which a homogenous catalyst system is introduced together with a solvent. The gaseous products leaving the reactor overhead are cooled in a cooler (2) and cooled in a gas-liquid separator for reflux (3) and further cooled (4) and separated in a second gas-liquid separator (5).

Unreacted ethylene from the separator (5) is recycled via a compressor (6) and a heat exchanger (7) together with ethylene makeup to the reactor. A liquid stream is withdrawn from the reactor (1) containing liquid α -olefins and catalyst, which is removed by the catalyst removal unit (8). The liquid stream from the catalyst removal unit (8) is combined with the liquid stream from the primary separation (5). These combined liquid streams are routed to a separation section in which, via a series of columns (9), the α -olefins are separated into the individual components.

By varying the catalyst components ratio, the product mixture can be adjusted from light products (butene-1, hexene-1, octene-1, decene-1) to heavier products (C_{12} to C_{20} α -olefins). Typical yield for light olefins is over 85 wt% with high purities that allow typical product applications. The light products show excellent properties as comonomers in ethylene polymerization.

Economics: Due to the mild reaction conditions (pressure and temperature), the process is lower in investment than competitive processes. Typical utility requirements for a 160,000-metric tpy plant are 3,700 tph cooling water, 39 MW fuel gas and 6800 kW electric power.



Commercial plants: One plant of 150,000 metric tpy capacity is currently under construction for Jubail United in Al-Jubail, Saudi Arabia.

Licensors: The technology is jointly licensed by Linde AG and SABIC.

Ammonia

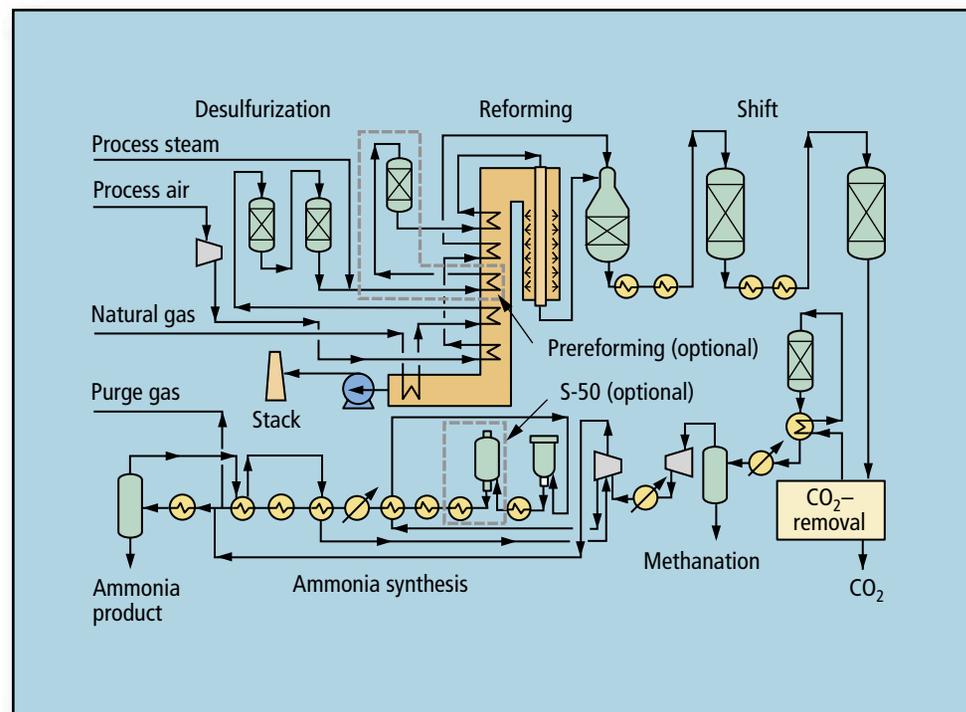
Application: To produce ammonia from a variety of hydrocarbon feedstocks ranging from natural gas to heavy naphtha using Topsøe's low-energy ammonia technology.

Description: Natural gas or another hydrocarbon feedstock is compressed (if required), desulfurized, mixed with steam and then converted into synthesis gas. 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 amount of air is adjusted to obtain an H_2/N_2 ratio of 3.0 as required by the ammonia synthesis reaction. 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 an 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. This process layout is flexible, and each ammonia plant will be optimized for the local conditions by adjustment of various process parameters. Topsøe supplies all catalysts used in the catalytic process steps for ammonia production.

Features, such as the inclusion of a prereformer, installation of a ring-type burner with nozzles for the secondary reformer and upgrading to an S-300 ammonia converter, are all features that can be applied for existing ammonia plants. These features will ease maintenance and improve plant efficiency.

Commercial plants: More than 60 plants use the Topsøe process concept. Since 1990, 50% of the new ammonia production capacity has been based on the Topsøe technology. Capacities of the plants con-



structed within the last decade range from 650 mtpd up to 2,050 mtpd being the world's largest ammonia plant. Design of new plants with even higher capacities are available.

Licensor: Haldor Topsøe A/S.

Ammonia, KAAPplus

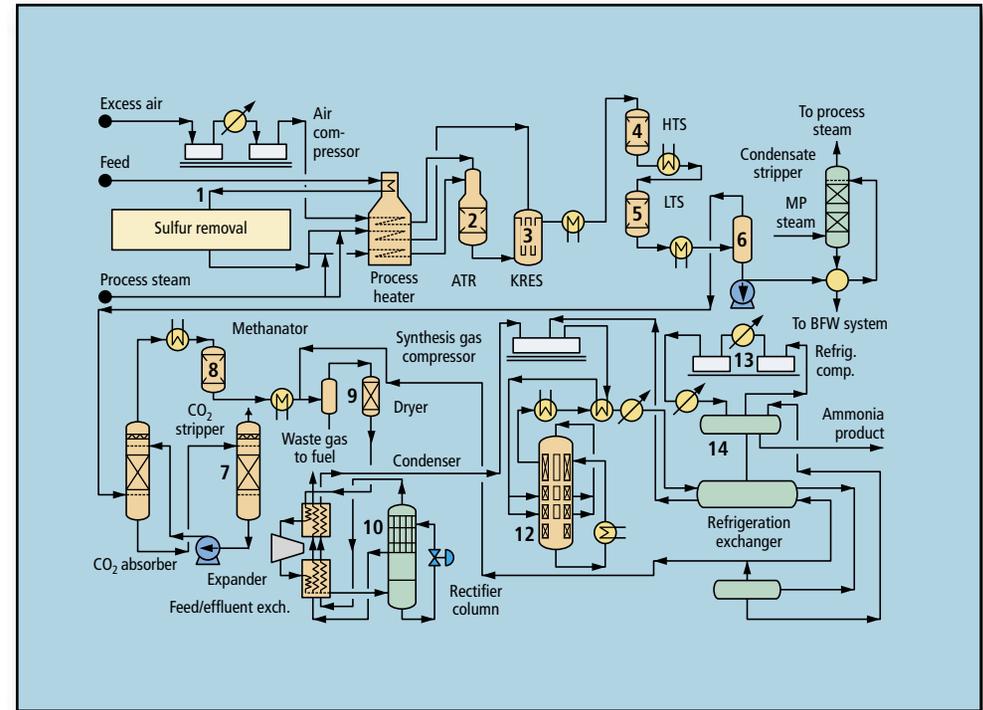
Application: To produce ammonia from hydrocarbon feedstocks using a high-pressure heat exchange-based steam reforming process integrated with a low-pressure advanced ammonia synthesis process.

Description: The key steps in the KAAPplus process are reforming using the KBR reforming exchanger system (KRES), cryogenic purification of the synthesis gas and low-pressure ammonia synthesis using KAAP catalyst.

Following sulfur removal (1), the feed is mixed with steam, heated and split into two streams. One stream flows to the autothermal reformer (ATR) (2) and the other to the tube side of the reforming exchanger (3), which operates in parallel with the ATR. Both convert the hydrocarbon feed into raw synthesis gas using conventional nickel catalyst. In the ATR, feed is partially combusted with excess air to supply the heat needed to reform the remaining hydrocarbon feed. The hot autothermal reformer effluent is fed to the shell side of the KRES reforming exchanger, where it combines with the reformed gas exiting the catalyst-packed tubes. The combined stream flows across the shell side of the reforming exchanger where it supplies heat to the reforming reaction inside the tubes.

Shell-side effluent from the reforming exchanger is cooled in a waste heat boiler, where high-pressure steam is generated, and then flows 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 such as hot potassium carbonate or MDEA (methyldiethanolamine) (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 fed to the KAAP ammonia converter (12), which uses a ruthenium-based, high-activity ammonia synthesis catalyst. It provides high conversion at the relatively low pressure of 90



bar with a small catalyst volume. Effluent vapors are cooled by ammonia refrigeration (13) and unreacted gases are recycled. Anhydrous liquid ammonia is condensed and separated (14) from the effluent.

Energy consumption of KBR's KAAPplus process is less than 25 MM Btu (LHV)/short-ton. Elimination of the primary reformer combined with low-pressure synthesis provides a capital cost savings of about 10% over conventional processes.

Commercial plants: Over 200 large-scale, single-train ammonia plants of KBR design are onstream or have been contracted worldwide. The KAAPplus advanced ammonia technology provides a low-cost, low-en-

Ammonia, KAAP*plus*, *continued*

ergy design for ammonia plants, minimizes environmental impact, reduces maintenance and operating requirements and provides enhanced reliability. Two plants use KRES technology and 17 plants use Purifier technology. Four 1,850-mtpd grassroots KAAP plants in Trinidad are in full operation.

Licensors: Kellogg Brown & Root, Inc.

Ammonia, KBR Purifier

Application: To produce ammonia from hydrocarbon feedstocks and air.

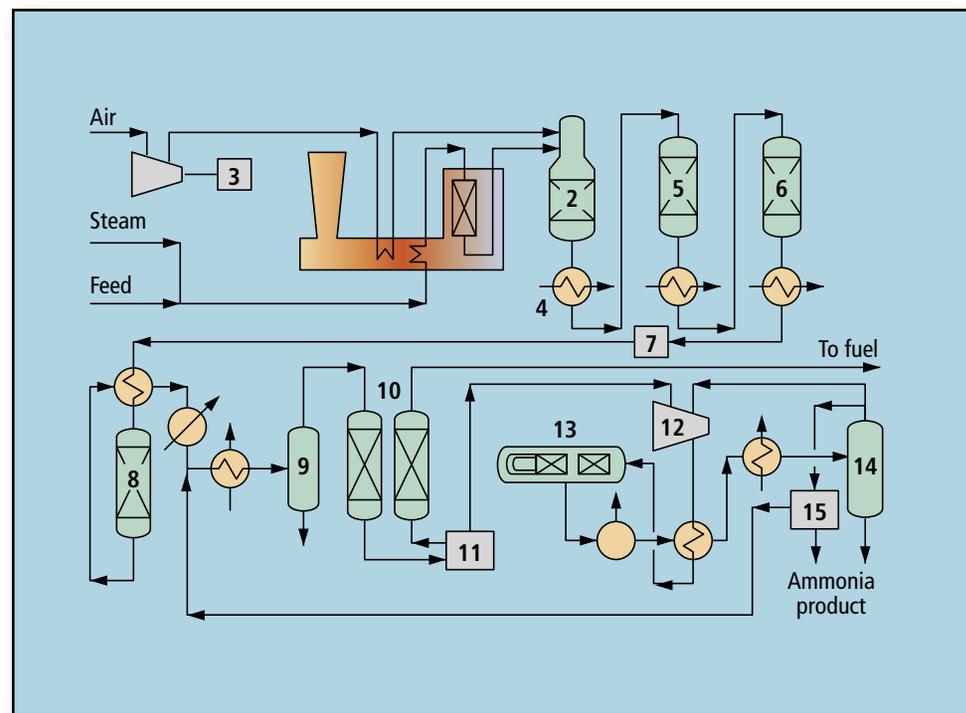
Description: The key features of the KBR Purifier Process are mild primary reforming, secondary reforming with excess air, cryogenic purification of syngas, and synthesis of ammonia over magnetite catalyst in a horizontal converter.

Desulfurized feed is reacted with steam in the primary reformer (1) with exit temperature at about 700°C. Primary reformer effluent is reacted with excess air in the secondary reformer (2) with exit at about 900°C. The air compressor is normally a gas-driven turbine (3). Turbine exhaust is fed to the primary reformer and used as preheated combustion air. An alternative to the above described conventional reforming is to use KBR's reforming exchanger system (KRES), as described in KBR's KAAPplus.

Secondary reformer exit gas is cooled by generating high-pressure steam (4). The shift reaction is carried out in two catalytic steps—high-temperature (5) and low-temperature shift (6). Carbon dioxide removal (7) uses 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 synthesis gas flows to the cryogenic purifier (11), where it is cooled by feed/effluent heat exchange and fed to a rectifier. The syngas is purified in the rectifier column, producing a column overhead that is essentially a 75:25 ratio of hydrogen and nitrogen. The column bottoms is a waste gas that contains unconverted methane from the reforming section, excess nitrogen and argon. Both overhead and bottoms are reheated in the feed/effluent exchanger. The waste gas stream is used to regenerate the dryers and then is burned as fuel in the primary reformer. A small, low-speed expander provides the net refrigeration.

The purified syngas is compressed in the syngas compressor (12), mixed with the loop-cycle 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 dryers.

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

Licensor: Kellogg Brown & Root, Inc.

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.

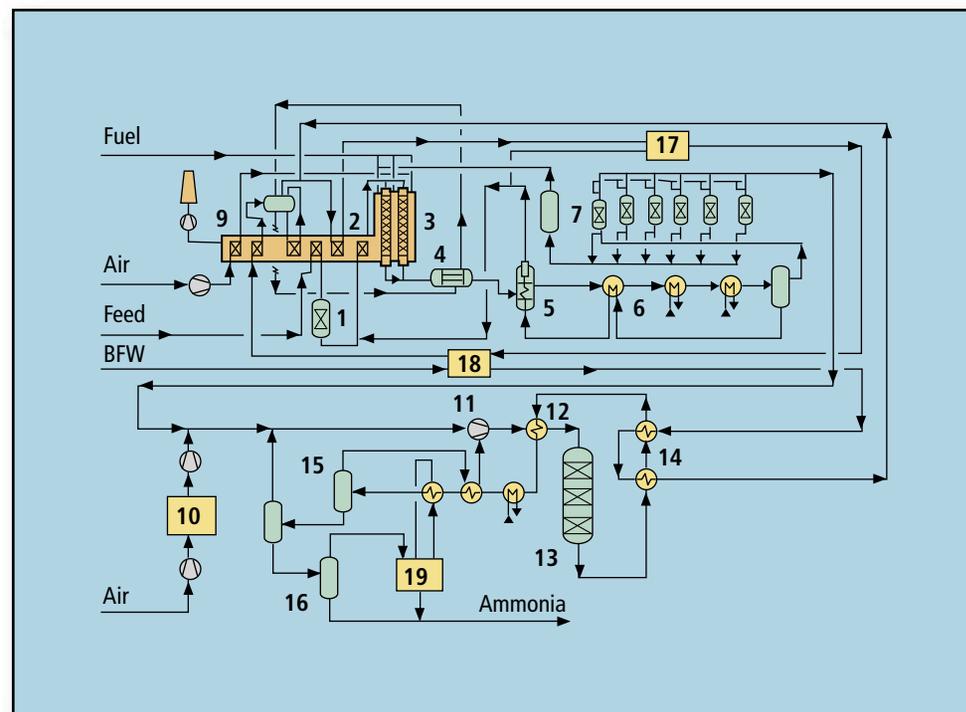
Description: Hydrocarbon feed is preheated and desulfurized (1). Process steam, generated from process condensate in the isothermal shift reactor (5) is added to give a steam ratio of about 2.7; reformer feed is further preheated (2). Reformer (3) operates with an exit temperature of 850°C.

Reformed gas is cooled to the shift inlet temperature of 250°C by generating steam (4). The CO shift reaction is carried out in a single stage in the isothermal shift reactor (5), internally cooled by a spiral wound tube bundle. To generate MP steam in the reactor, de-aerated and reheated process condensate is recycled.

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.

Ammonia, *continued*

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, were commissioned in Australia. The latest LAC contract is under erection in China and produces hydrogen, ammonia and CO₂ under import of nitrogen from already existing facilities. 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.

Licensors: Linde AG.

Ammonia

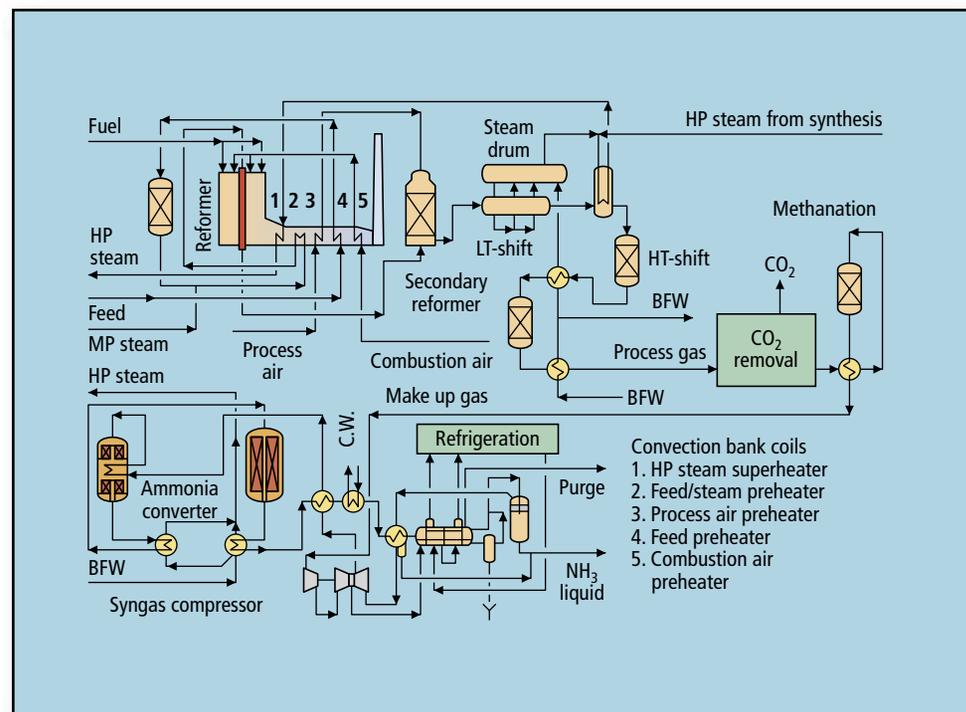
Application: To produce ammonia from natural gas, LNG, LPG or naphtha. Other hydrocarbons—coal, oil, residues or methanol purge gas—are possible feedstocks with an adapted front-end. The process uses conventional steam reforming synthesis gas generation (front-end) and a medium-pressure (MP) ammonia synthesis loop. It is optimized with respect to low energy consumption and maximum reliability. The largest single-train plant built by Uhde with a conventional synthesis has a nameplate capacity of 2,000 metric tons per day (mtpd). For higher capacities refer to Uhde Dual Pressure Process.

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 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 arranged at the circumference of the secondary reformer head that provides a perfect mixture of air and gas. Subsequent high-pressure (HP) 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 catalyst 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 tubesheet 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: Seventeen ammonia plants have been commissioned between 1990 and 2004, with capacities ranging from 600 mtpd up to 2,000 mtpd.

Licensor: Uhde GmbH.

Ammonia, PURIFIER_{plus}

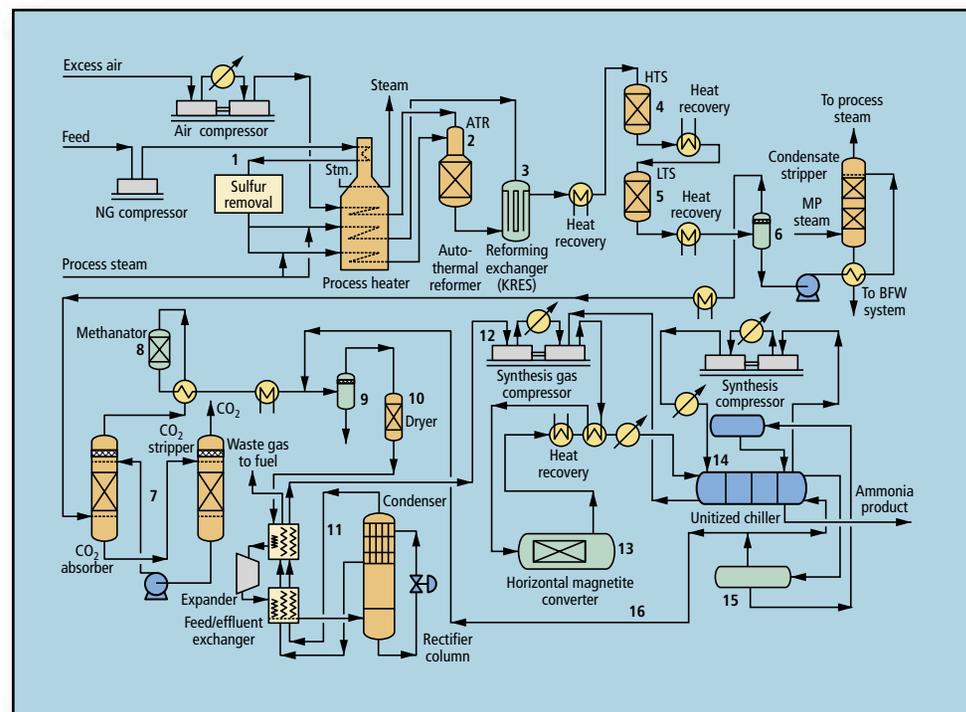
Application: To produce ammonia from hydrocarbon feedstocks using a high-pressure (HP) heat exchange-based steam reforming process integrated with cryogenic purification of syngas.

Description: The key steps in the PURIFIER_{plus} process are reforming using the KBR reforming exchanger system (KRES) with excess air, cryogenic purification of the synthesis gas and synthesis of ammonia over magnetite catalyst in a horizontal converter.

Following sulfur removal (1), the feed is mixed with steam, heated and split into two streams. One stream flows to the autothermal reformer (ATR) (2) and the other to the tube side of the reforming exchanger (3), which operates in parallel with the ATR. Both convert the hydrocarbon feed into raw synthesis gas using conventional nickel catalyst. In the ATR, feed is partially combusted with excess air to supply the heat needed to reform the remaining hydrocarbon feed. The hot autothermal reformer effluent is fed to the shell side of the KRES reforming exchanger, where it combines with the reformed gas exiting the catalyst-packed tubes. The combined stream flows across the shell side of the reforming exchanger where it supplies heat to the reforming reaction inside the tubes.

Shell-side effluent from the reforming exchanger is cooled in a waste-heat boiler, where HP steam is generated, and then flows 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 such as hot potassium carbonate or MDEA (methyl diethanolamine) (7).

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 synthesis gas flows to the cryogenic purifier (11), where it is cooled by feed/effluent heat exchange and fed to a rectifier. The syngas is purified in the rectifier



column, producing a column overhead that is essentially a 75:25 ratio of hydrogen and nitrogen. The column bottoms is a waste gas that contains unconverted methane from the reforming section, excess nitrogen and argon. Both overhead and bottoms are re-heated in the feed/effluent exchanger. The waste gas stream is used to regenerate the dryers and then is burned as fuel in the primary reformer. A small, low-speed expander provides the net refrigeration.

The purified syngas is compressed in the syngas compressor (12), mixed with the loop-cycle stream and fed to the horizontal converter (13). Converter effluent is cooled and then chilled by ammonia refrigeration in a unitized chiller (14). Ammonia product is separated (15)

Ammonia, PURIFIER*plus*, *continued*

from unreacted syngas. Unreacted syngas is recycled back to the syngas compressor. A small purge is scrubbed with water (16) and recycled to the dryers.

Commercial plants: Over 200 large-scale, single-train ammonia plants of KBR design are onstream or have been contracted worldwide. The PURIFIER*plus* ammonia technology provides a low-cost, low-energy design for ammonia plants, minimizes environmental impact, reduces operating requirements and provides enhanced reliability. Two plants use KRES technology and 17 plants use PURIFIER technology.

Licensor: Kellogg Brown & Root, Inc.

Ammonia—Dual pressure process

Application: Production of ammonia from natural gas, LNG, LPG or naphtha. The process uses conventional steam reforming synthesis gas generation in the front-end, while the synthesis section comprises a once-through section followed by a synthesis loop. It is thus optimized with respect to enable ammonia plants to produce very large capacities with proven equipment. The first plant based on this process will be the SAFCO IV ammonia plant in Al-Jubail, Saudi Arabia, which is currently under construction. This concept provides the basis for even larger plants (4,000–5,000 mtpd).

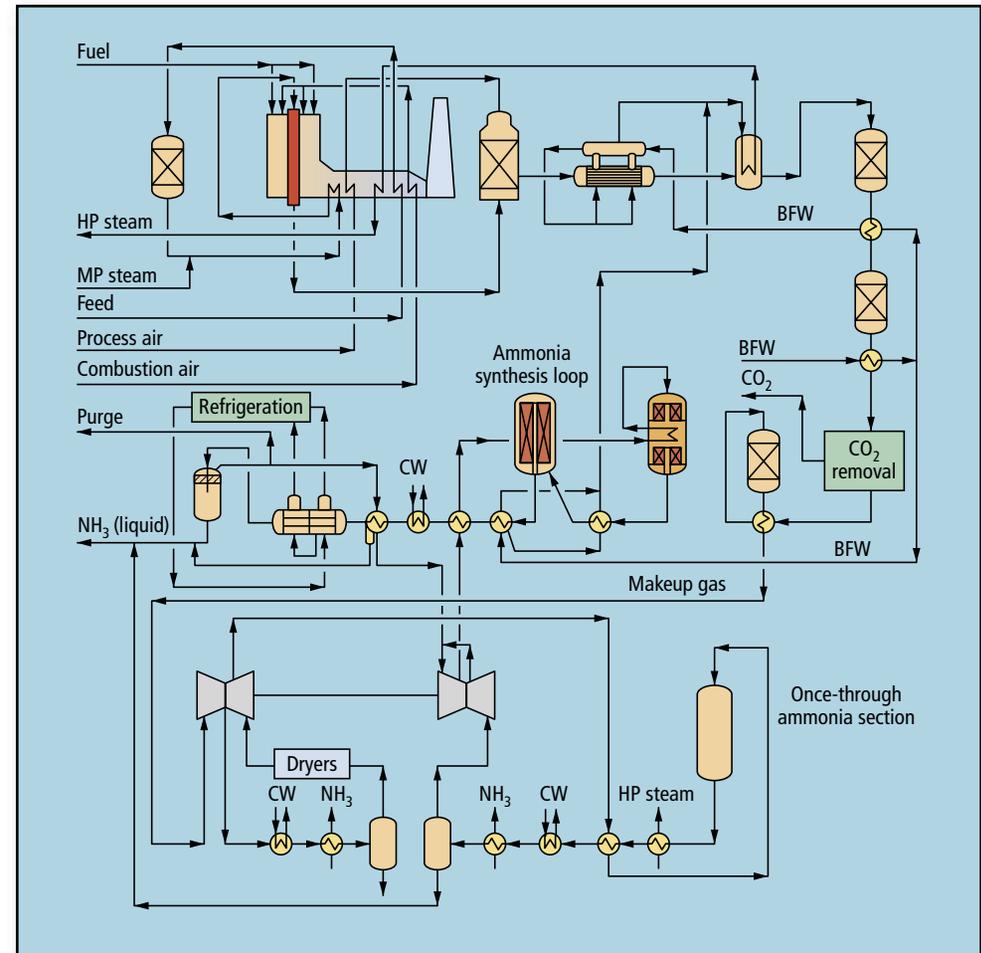
Description: The feedstock (e.g. natural gas) is desulfurized, mixed with steam and converted into synthesis gas over nickel catalyst at approximately 42 bar and 800–850°C in the primary reformer. The Uhde steam reformer is a top-fired reformer with tubes made of centrifugal microalloy steel and a proprietary “cold outlet manifold,” which enhances reliability.

In the secondary reformer, process air is admitted to the syngas via a special nozzle system arranged at the circumference of the secondary reformer head that provides a perfect mixture of air and gas.

Subsequent high-pressure (HP) steam generation and superheating guarantee maximum process heat recovery to achieve an optimized energy efficient process.

CO conversion is achieved in the HT and LT shift over standard catalyst, while CO₂ is removed either in the BASF-aMDEA, the UOP-Benfield or the UOP-Amine Guard process. Remaining carbonoxides are reconverted to methane in catalytic methanation to trace ppm levels.

The ammonia synthesis loop consists of two stages. Makeup gas is compressed in a two-stage inter-cooled compressor, which is the low-pressure casing of the syngas compressor. Discharge pressure of this compressor is about 110 bar. An indirectly cooled once-through converter at this location produces one third of the total ammonia. Effluent from this converter is cooled and the major part of the ammonia produced is separated from the gas.



In the second step, the remaining syngas is compressed to the operating pressure of the ammonia synthesis loop (approx. 210 bar) in the HP casing of the syngas compressor. This HP casing operates at a much lower than usual temperature. The high synthesis loop pressure is achieved by combination of the chilled second casing of the syngas

Ammonia—Dual pressure process, *continued*

compressor and a slightly elevated front-end pressure.

Liquid ammonia is separated by condensation from the once through section, and 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), the remaining gases being used as fuel.

Economics: Typical consumption figures (feed + fuel) range from 6.7 to 7.2 Gcal per metric ton of ammonia and will depend on the individual plant concept as well as local conditions.

Commercial plants: The first plant based on this process will be the SAF-CO IV ammonia plant with 3,300 mtpd, currently under construction in Al-Jubail, Saudi Arabia.

Licensors: Uhde GmbH.

Aniline

Application: A process for the production of high-quality aniline from benzene and nitric acid.

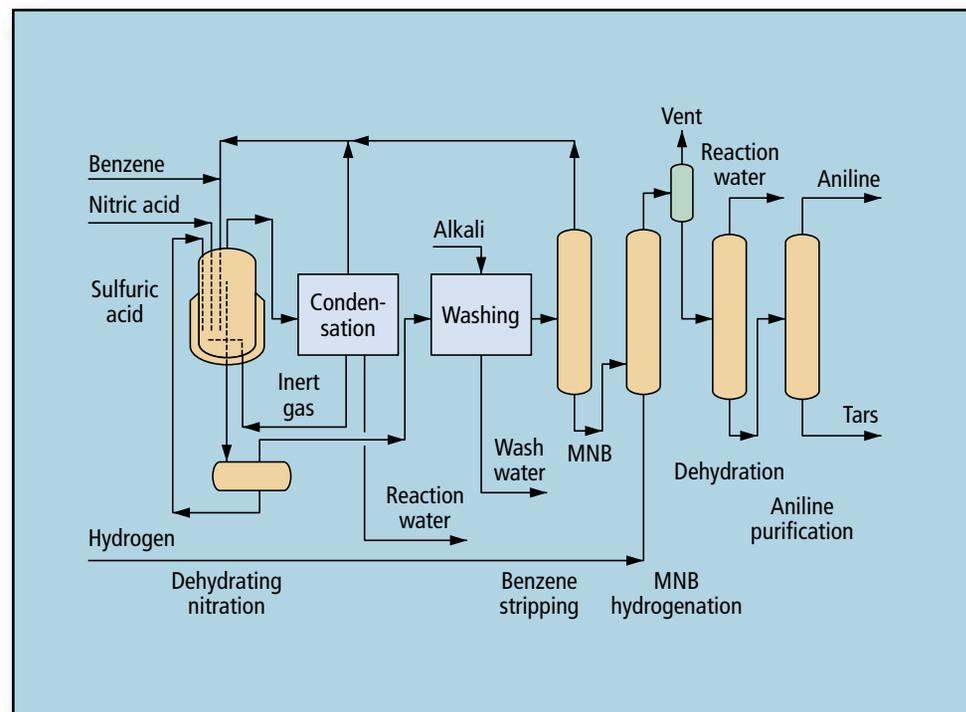
Description: Aniline is produced by the nitration of benzene with nitric acid to mononitrobenzene (MNB) which is subsequently hydrogenated to aniline. In the DuPont/KBR process, benzene is nitrated with mixed acid (nitric and sulfuric) at high efficiency to produce mononitrobenzene (MNB) in the unique dehydrating nitration (DHN) system. The DHN system uses an inert gas to remove the water of nitration from the reaction mixture, thus eliminating the energy-intensive and high-cost sulfuric acid concentration system.

As the inert gas passes through the system, it becomes humidified, removing the water of reaction from the reaction mixture. Most of the energy required for the gas humidification comes from the heat of nitration. The wet gas is condensed and the inert gas is recycled to the nitrator. The condensed organic phase is recycled to the nitrator while the aqueous phase is sent to effluent treatment. The reaction mixture is phase separated and the sulfuric acid is returned to the nitrator.

The crude MNB is washed to remove residual acid and the impurities formed during the nitration reaction. The product is then distilled and residual benzene is recovered and recycled. Purified MNB is fed, together with hydrogen, into a liquid phase plug-flow hydrogenation reactor that contains a DuPont proprietary catalyst. The supported noble metal catalyst has a high selectivity and the MNB conversion per pass is 100%.

The reaction conditions are optimized to achieve essentially quantitative yields and the reactor effluent is MNB-free. The reactor product is sent to a dehydration column to remove the water of reaction followed by a purification column to produce high-quality aniline product.

Commercial plants: DuPont produces aniline using this technology for the merchant market with a total production capacity of 160,000 tpy at



a plant located in Beaumont, Texas. In addition, DuPont's aniline technology is used in three commercial units and one new license was awarded in 2004 with a total aniline capacity of 300,000 tpy.

Licensor: Kellogg Brown & Root, Inc.

Aromatics

Application: The technology produces benzene and xylenes from toluene and C_9 streams. This technology features a proprietary zeolite catalyst and can accommodate varying ratios of feedstock, while maintaining high activity and selectivity.

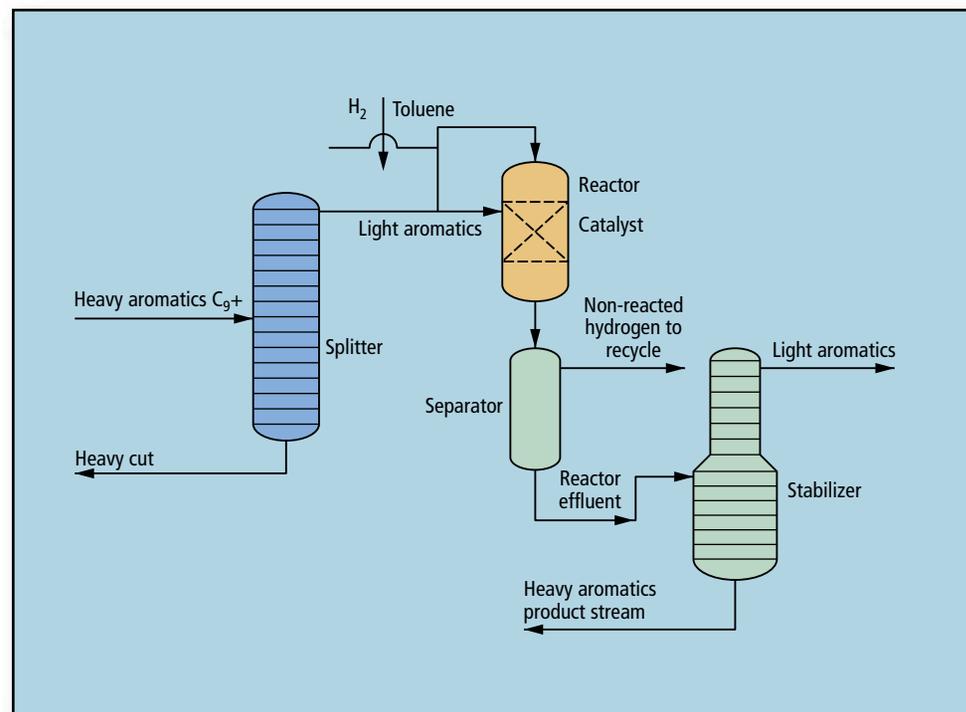
Description: The technology encompasses three main processing areas: splitter, reactor and stabilizer sections. The heavy-aromatics stream (C_9 's feed) is fed to the splitter. The overhead C_9 aromatic product is the feed to the transalkylation reactor section. The splitter bottoms is exchanged with other streams for heat recovery before leaving the system.

The aromatic product is mixed with toluene and hydrogen, vaporized and fed to the reactor. The reactor gaseous product is primarily unreacted hydrogen, which is recycled to the reactor. The liquid product stream is subsequently stabilized to remove further light aromatic components. The resulting aromatics are routed to product fractionation to produce the final benzene and xylenes products.

The reactor is charged with zeolite catalyst, which exhibits both long life and good flexibility to feed stream variations, including substantial C_{10}^+ aromatics. Depending on feed compositions and light components present, the xylene yield can vary from 25% to 32% and C_9 conversion from 53% to 67%.

Process advantages include:

- Simple, low cost fixed-bed reactor design; drop in replacement for other catalysts
- Very high selectivity; benzene purity is 99.9% without extraction
- Physically stable catalyst with long cycle life
- Flexible to handle up to 90+% C_9^+ components in feed with high conversion
- Catalyst is resistant to impurities common to this service
- Operating parameters are moderate
- Decreased hydrogen consumption due to low cracking rates



- Significant decrease in energy consumption due to efficient heat integration scheme.

Commercial plants: Two commercial plants are using GT-TransAlk technology and catalyst.

Licensors: GTC Technology using catalyst manufactured by Sud-Chemie Inc.

Aromatics extraction

Application: The Sulfolane process recovers high-purity C₆–C₉ aromatics from hydrocarbon mixtures, such as reformed petroleum naphtha (reformate), pyrolysis gasoline (pygas), or coke oven light oil (COLO), by extractive distillation with or without liquid-liquid extraction.

Description: Fresh feed enters the extractor (1) and flows upward, countercurrent to a stream of lean solvent. As the feed flows through the extractor, aromatics are selectively dissolved in the solvent. A raffinate stream, very low in aromatics content, is withdrawn from the top of the extractor. The rich solvent, loaded with aromatics, exits the bottom of the extractor and enters the stripper (2). The lighter nonaromatics taken overhead are recycled to the extractor to displace higher molecular weight nonaromatics from the solvent.

The bottoms stream from the stripper, substantially free of nonaromatic impurities, is sent to the recovery column (3) where the aromatic product is separated from the solvent. Because of the large difference in boiling point between the solvent and the heaviest aromatic component, this separation is accomplished easily, with minimal energy input.

Lean solvent from the bottom of the recovery column is returned to the extractor. The extract is recovered overhead and sent on to distillation columns downstream for recovery of the individual benzene, toluene and xylene products. The raffinate stream exits the top of the extractor and is directed to the raffinate wash column (4). In the wash column, the raffinate is contacted with water to remove dissolved solvent. The solvent-rich water is vaporized in the water stripper (5) and then used as stripping steam in the recovery column. The raffinate product exits the top of the raffinate wash column. The raffinate product is commonly used for gasoline blending or ethylene production.

The solvent used in the Sulfolane process was developed by Shell Oil Co. in the early 1960s and is still the most efficient solvent available for recovery of aromatics.

Economics: The purity and recovery performance of an aromatics extraction unit is largely a function of energy consumption. In general, higher solvent circulation rates result in better performance, but at the expense of higher energy consumption. The Sulfolane process demonstrates the lowest solvent-to-feed ratio and the lowest energy consumption of any commercial aromatics extraction technology. A typical Sulfolane unit consumes 275–300 kcal of energy per kilogram of extract produced, even when operating at 99.99 wt% benzene purity and 99.95 wt% recovery.

Estimated inside battery limits (ISBL) costs based on unit processing 158,000 mtpy of BT reformate feedstock with 68 LV% aromatics (US Gulf Coast site in 2003).

Investment, US\$ million	8.5
Utilities (per mt of feed)	
Electricity, kWh	6.2
Steam, mt	0.48
Water, cooling, m ³	13.5

Commercial plants: In 1962, Shell commercialized the Sulfolane process in its refineries in England and Italy. The success of the Sulfolane process led to an agreement in 1965 whereby UOP became the exclusive licensor of the Sulfolane process. Many of the process improvements incorporated in modern Sulfolane units are based on design features and operating techniques developed by UOP. UOP has licensed a total of 134 Sulfolane units throughout the world.

Licensor: UOP LLC.

Aromatics extractive distillation

Application: The Distapex process uses extractive distillation for recovering individual aromatics from a heart cut containing the desired aromatic compound.

Description: The feedstock, i.e., the heart cut with the aromatic component to be recovered, is routed to the middle of the extractive distillation column (1). The solvent, NMP, is supplied at the top of the column. In the presence of the solvent, the aromatic component and the non-aromatics are separated in the column.

The aromatic component passes together with the solvent to the bottom and is routed to the stripper (3). It is separated from the solvent under vacuum. The overhead aromatic component leaves the plant as pure product, and the solvent is circulated to the extractive distillation column (1).

High heat utilization is obtained by intensive heat exchange of the circulating solvent. Necessary additional heat is supplied by medium-pressure steam at 12–14 bar.

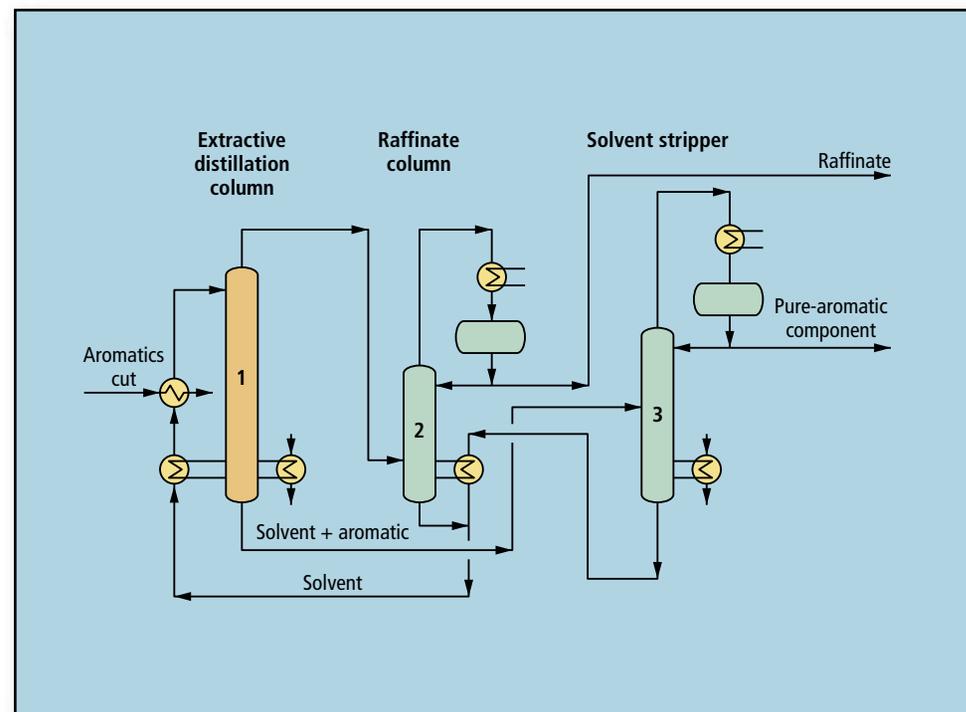
The non-aromatics still containing small quantities of solvent are obtained at the top of the extractive distillation column (1). This solvent is recovered in the raffinate column (2) and returned to the solvent recycle.

Benzene recovery from pyrolysis gasoline is usually above 99.5% at feed concentration above 80%.

Economics: A typical investment for a Distapex plant to recover 200,000 tpy benzene is approximately €8.5 million.

Typical energy consumption figures of the Distapex plant, calculated per ton of benzene produced, are:

Steam (12–14 bar), ton	0.6
Electric power, kWh	4
Water, cooling, m ³	24
Solvent loss, kg	0.01



Installations: The Distapex process is applied in more than 25 reference plants.

Reference: G. Krekel, G. Birke, A. Glasmacher, et al., "Developments in Aromatics Separation," *Erdöl Erdgas Kohle*, May 2000.

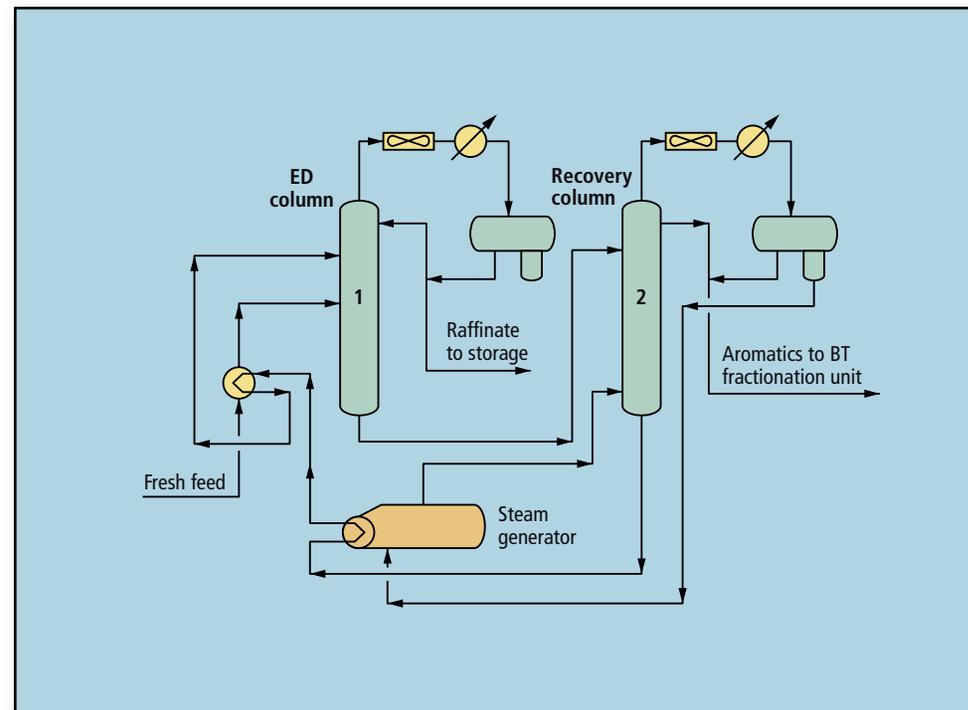
Licensor: Lurgi AG.

Aromatics extractive distillation

Application: The Sulfolane process recovers high-purity aromatics from hydrocarbon mixtures by extractive distillation (ED) with liquid-liquid extraction or with extractive distillation (ED). Typically, if just benzene or toluene is the desired product, then ED without liquid-liquid extraction is the more suitable option.

Description: Extractive distillation is used to separate close-boiling components using a solvent that alters the volatility between the components. An ED Sulfolane unit consists of two primary columns; they are the ED column and the solvent recovery column. Aromatic feed is pre-heated with lean solvent and enters a central stage of the ED column (1). The lean solvent is introduced near the top of the ED column. Non-aromatics are separated from the top of this column and sent to storage. The ED column bottoms contain solvent and highly purified aromatics that are sent to the solvent recovery column (2). In this column, aromatics are separated from solvent under vacuum with steam stripping. The overhead aromatics product is sent to the BT fractionation section. Lean solvent is separated from the bottom of the column and recirculated back to the ED column.

Economics: The solvent used in the Sulfolane process exhibits higher selectivity and capacity for aromatics than any other commercial solvent. Using the Sulfolane process minimizes concern about trace nitrogen contamination that occurs with nitrogen-based solvents. Estimated inside battery limits (ISBL) costs based on a unit processing 158,000 mtpy of BT reformat feedstock with 68 LV% aromatics (US Gulf Coast site in 2003).



Commercial plants: In 1962, Shell commercialized the Sulfolane process in its refineries in England and Italy. The success of the Sulfolane process led to an agreement in 1965 whereby UOP became the exclusive licensor of the Sulfolane process. Many of the process improvements incorporated in modern Sulfolane units are based on design features and operating techniques developed by UOP. UOP has licensed a total of 134 Sulfolane units throughout the world.

Licensor: UOP LLC.

Investment, US\$ million	6.8
Utilities (per mt of feed)	
Electricity, kWh	2.7
Steam, mt	0.35
Water, cooling, m ³	2.5

Aromatics extractive distillation

Application: Recovery of high-purity aromatics from reformat, pyrolysis gasoline or coke-oven light oil using extractive distillation.

Description: In Uhde's proprietary extractive distillation (ED) Morphylane process, a single-compound solvent, N-Formylmorpholine (NFM), alters the vapor pressure of the components being separated. The vapor pressure of the aromatics is lowered more than that of the less soluble nonaromatics.

Nonaromatics vapors leave the top of the ED column with some solvent, which is recovered in a small column that can either be mounted on the main column or installed separately.

Bottom product of the ED column is fed to the stripper to separate pure aromatics from the solvent. After intensive heat exchange, the lean solvent is recycled to the ED column. NFM perfectly satisfies the necessary solvent properties needed for this process including high selectivity, thermal stability and a suitable boiling point.

Economics:

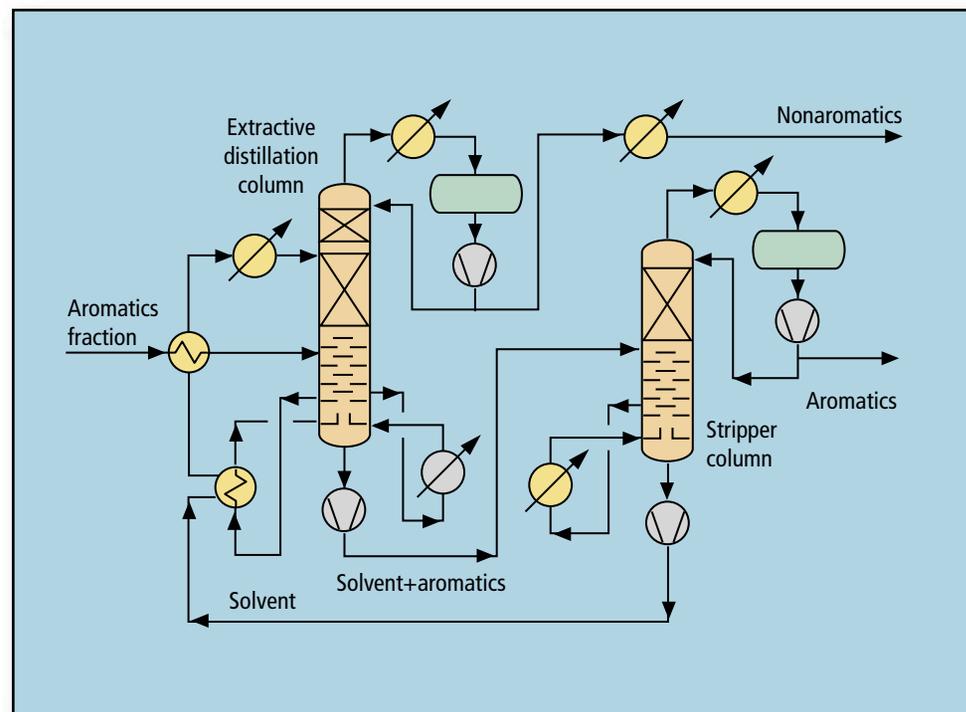
Pygas feedstock:

	Benzene	Benzene/toluene
Production yield		
Benzene	99.95%	99.95%
Toluene	–	99.98%
Quality		
Benzene	30 wt ppm NA*	80 wt ppm NA*
Toluene	–	600 wt ppm NA*
Consumption		
Steam	475 kg/t ED feed	680 kg/t ED feed**

Reformat feedstock with low-aromatics content (20 wt%):

	Benzene
Quality	
Benzene	10 wt ppm NA*
Consumption	
Steam	320 kg/t ED feed

*Maximum content of nonaromatics **Including benzene/toluene splitter



Commercial plants: More than 55 Morphylane plants (total capacity of more than 6 MMt/yr).

References: Emmrich, G., F. Ennenbach and U. Ranke, "Krupp Uhde Processes for Aromatics Recovery," European Petrochemical Technology Conference, June 21–22, 1999, London.

Emmrich, G., U. Ranke and H. Gehrke, "Working with an extractive distillation process," *Petroleum Technology Quarterly*, Summer 2001, p. 125.

Licensors: Uhde GmbH.

Aromatics recovery

Application: Recovery via extraction of high purity C₆–C₉ aromatics from pyrolysis gasoline, reformat, coke oven light oil and kerosene fractions.

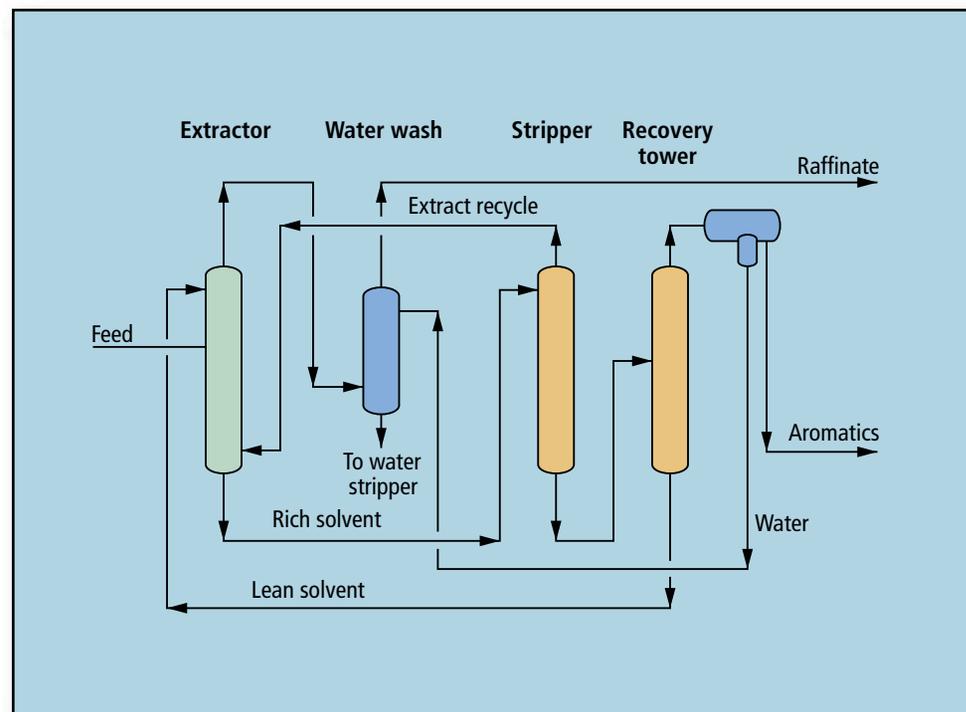
Description: Hydrocarbon feed is pumped to the liquid-liquid extraction column (1) where the aromatics are dissolved selectively in the sulfolane water-based solvent and separated from the insoluble non-aromatics (paraffins, olefins and naphthenes). The non-aromatic raffinate phase exits at the top of the column and is sent to the wash tower (2). The wash tower recovers dissolved and entrained sulfolane by water extraction and the raffinate is sent to storage. Water containing sulfolane is sent to the water stripper.

The solvent phase leaving the extractor contains aromatics and small amounts of non aromatics. The latter are removed in the stripper (3) and recycled to the extraction column. The aromatic-enriched solvent is pumped from the stripper to the recovery tower (4) where the aromatics are vacuum distilled from the solvent and sent to downstream clay treatment and distillation. Meanwhile, the solvent is returned to the extractor and the process repeats itself.

Yields: Overall aromatics' recoveries are > 99% while solvent losses are extremely small, less than 0.006 lb/bbl of feed.

Economics: For 2005 US Gulf Coast location:

Feed	C ₆ –C ₈ pyrolysis gasoline	C ₆ –C ₉ reformat
Feed bpsd	8,000	15,000
Aromatics, wt%	64–88	60–72
Utilities, per bbl feed		
Cooling, 10 ⁶ Btu	0.14–0.16	0.1–0.12
Steam, MP, lb	180–210	188–225
Power, kWh	0.6–0.8	1.1
ISBL Investment, 10 ⁶ US\$	15–18	17–20



Commercial plants: Over 20 licensed units are in operation.

Licensor: Axens, Axens NA.

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. The cryogenic purification of recycle hydrogen to reduce the make-up hydrogen requirement is optional (6).

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 feed, wt%	Xylene
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

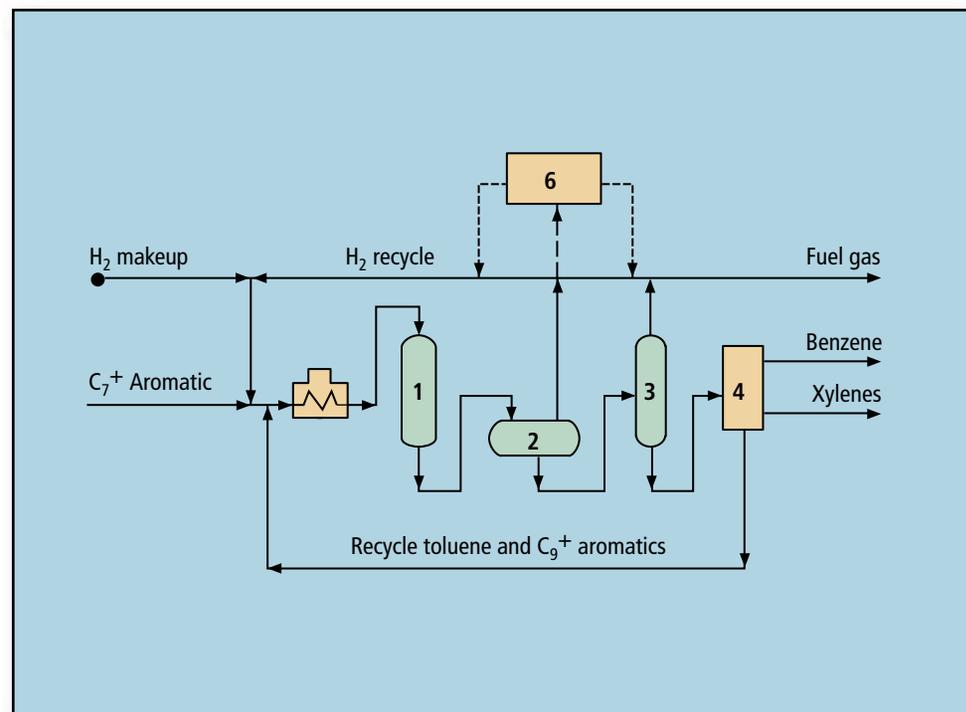
* 5.45°C minimum freeze point

** 1,000 ppm nonaromatics maximum

Economics: Basis of ISBL US Gulf Coast:

Estimated investment, \$/bpsd	6,700
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 gal/y have been licensed.

Licensors: ABB Lummus Global.

Benzene

Application: Produce benzene via the hydrodealkylation of C_7 – C_{11} aromatics.

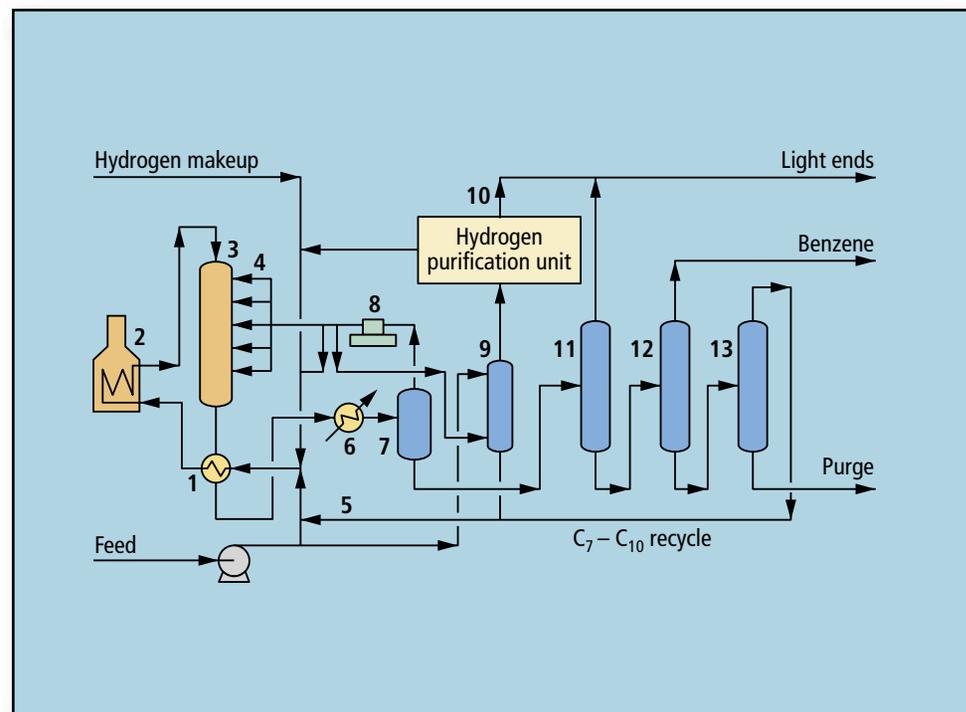
Description: Fresh C_7 – C_8 + (to C_{11}) feed is mixed with recycle hydrogen, makeup hydrogen and C_7 + aromatics from the recycle tower. The mixture is heated by exchange (1) with reactor effluent and by a furnace (2) that also generates high-pressure steam for better heat recovery.

Tight temperature control is maintained in the reactor (3) to arrive at high yields using a multi-point hydrogen quench (4). In this way, conversion is controlled at the optimum level, which depends on reactor throughput, operating conditions and feed composition.

By recycling the diphenyl (5), its total production is minimized to the advantage of increased benzene production. The reactor effluent is cooled by exchange with feed followed by cooling water or air (6) and sent to the flash drum (7) where hydrogen-rich gas separates from the condensed liquid. The gas phase is compressed (8) and returned to the reactor as quench, recycle H_2 .

Part of the stream is washed countercurrently with a feed sidestream in the vent H_2 absorber (9) for benzene recovery. The absorber overhead flows to the hydrogen purification unit (10) where hydrogen purity is increased to 90%+ so it can be recycled to the reactor. The stabilizer (11) removes light ends, mostly methane and ethane, from the flash drum liquid. The bottoms are sent to the benzene column (12) where high-purity benzene is produced overhead. The bottoms stream, containing unreacted toluene and heavier aromatics, is pumped to the recycle column (13). Toluene, C_8 aromatics and diphenyl are distilled overhead and recycled to the reactor. A small purge stream prevents the heavy components from building up in the process.

Yields: Benzene yields are close to the theoretical, owing to several techniques used such as proprietary reactor design, heavy aromatic (diphenyl) recycle and multi-point hydrogen quench.



Economics: Basis: US Gulf Coast 2005:

Toluene feed, metric tpy	120,700
Benzene product, metric tpy	100,000
Power, kW	650
Water, cooling	
Flow, in ³ /hr	208
Temperature differential, °C	11.1
Fuel, heat release, million kcal/hr	8.3
42.0 barg steam production, kg/hr	3,859
ISBL investment, 10 ⁶ USD	40–45

Commercial plants: Thirty-five plants have been licensed worldwide for

Benzene, *continued*

processing a variety of feedstocks including toluene, mixed aromatics, reformat and pyrolysis gasoline.

Licensors: Axens, Axens NA.

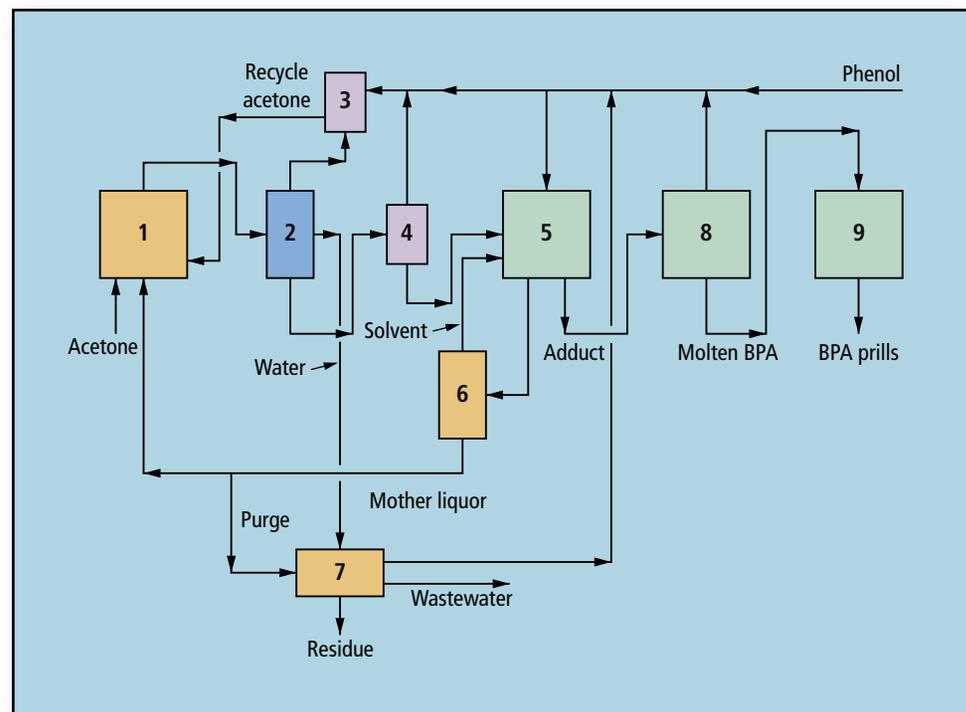
Bisphenol A

Application: The Badger BPA technology is used to produce high-purity bisphenol A (BPA) product suitable for polycarbonate and epoxy resin applications. The product is produced over ion-exchange resin from phenol and acetone in a process featuring proprietary purification technology.

Description: Acetone and excess phenol are reacted by condensation in an ion exchange resin-catalyzed reactor system (1) to produce p,p BPA, water and various byproducts. The crude distillation column (2) removes water and unreacted acetone from the reactor effluent. Acetone and lights are adsorbed into phenol in the lights adsorber (3) to produce a recycle acetone stream. The bottoms of the crude column is sent to the crystallization feed pre-concentrator (4), which distills phenol and concentrates BPA to a level suitable for crystallization.

BPA is separated from byproducts in a proprietary solvent crystallization and recovery system (5) to produce the adduct of p,p BPA and phenol. Mother liquor from the purification system is distilled in the solvent recovery column (6) to recover dissolved solvent. The solvent-free mother liquor stream is recycled to the reaction system. A purge from the mother liquor is sent to the purge recovery system (7) along with the recovered process water to recover phenol. The recovered purified adduct is processed in a BPA finishing system (8) to remove phenol from product, and the resulting molten BPA is solidified in the prill tower (9) to produce product prills suitable for the merchant BPA market.

Process features: The unique crystallization system produces a stable crystal that is efficiently separated from its mother liquor. These plants are extremely reliable and have been engineered to meet the operating standards of the most demanding refining and chemical companies. The catalyst system uses a unique upflow design that is beneficial to catalyst life and performance. High capacity operation has been fully demonstrated.



Product quality: Typical values for BPA quality are:

Freezing point, °C	157
BPA w/w, wt%	99.95
Methanol color, APHA	5

Commercial plants: The first plant, among the largest in the world, began operation in 1992 at the Deer Park (Houston) plant now owned and operated by Resolution Performance Products LLC. Since that time, two other world-scale plants were licensed to the Asia-Pacific market.

Licensor: Badger Licensing LLC.

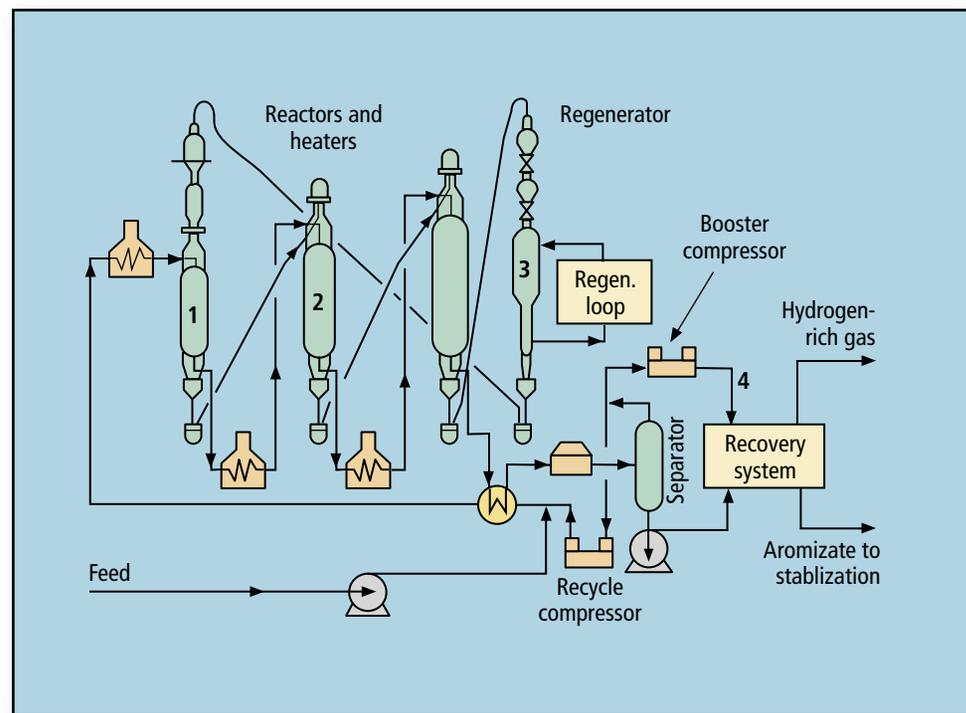
BTX aromatics

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 para-xylene 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 (latest generation AR 501 & 505) 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 Aromizate 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, 2004 Gulf Coast location.

Investment including initial catalyst inventory,*
US\$ million 53

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

BTX aromatics, *continued*

Commercial plants: Sixty-four CCR reforming units have been licensed; including seven plants in operation and four under design.

Licensors: Axens, Axens NA.

BTX aromatics

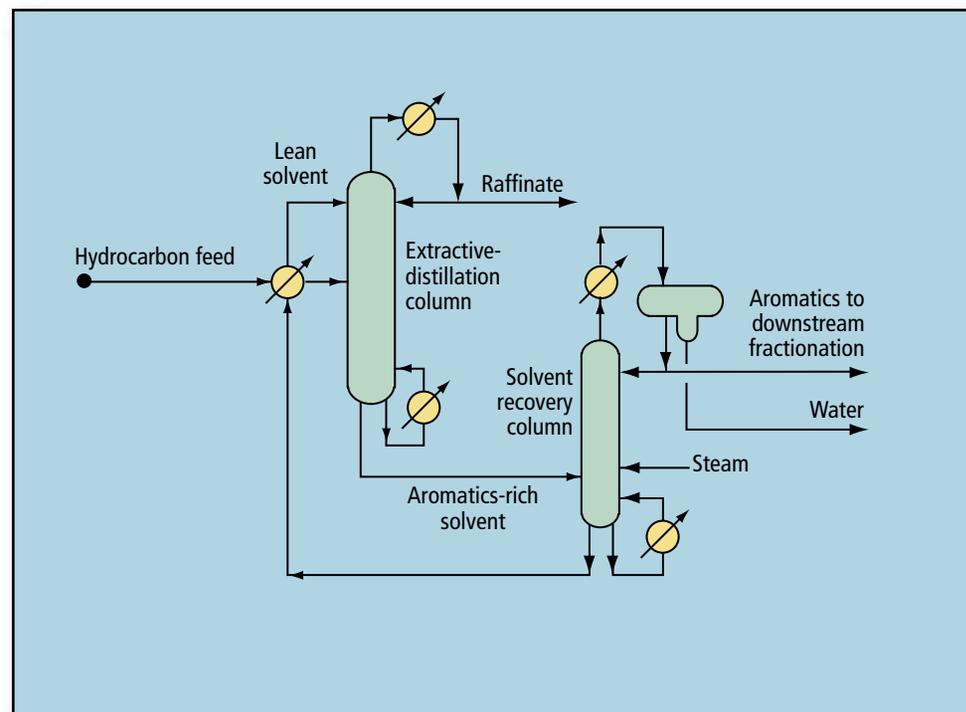
Application: An aromatics process based on extractive distillation, GT-BTX efficiently recovers benzene, toluene and xylenes from refinery or petrochemical aromatics streams, such as catalytic reformat or pyrolysis gasoline.

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: Fourteen commercial licenses are in place.

Reference: "Benzene reduction in motor gasoline—obligation or opportunity," *Hydrocarbon Processing* Process Optimization Confer-

BTX aromatics, *continued*

ence, April 1997. "Improve BTX processing economics," *Hydrocarbon Processing*, March 1998.

Licensors: GTC Technology.

BTX aromatics

Application: To produce reformat, which is concentrated in benzene, toluene and xylenes (BTX) from naphtha and condensate feedstocks via a high-severity reforming operation with a hydrogen byproduct. The CCR Platforming Process is licensed by UOP.

Description: The process consists of a reactor section, continuous catalyst regeneration section (CCR) and product recovery section. Stacked radial flow reactors (1) 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 the endothermic reaction.

Reactor effluent is separated into liquid and vapor products (4). Liquid product is sent to a stabilizer (5) to remove light ends. Vapor from the separator is compressed and sent to a gas-recovery section (6) to separate 90%-pure hydrogen byproduct. A fuel gas byproduct of LPG can also be produced. UOP's latest R-270 series catalyst maximizes aromatics yields.

Yields: Typical yields from lean Middle East naphtha:

H ₂ , wt%	4.3
Benzene, wt%	1.7
Toluene, wt%	29.9
Xylenes, wt%	30.4
A ₉ ⁺ , wt%	13.1

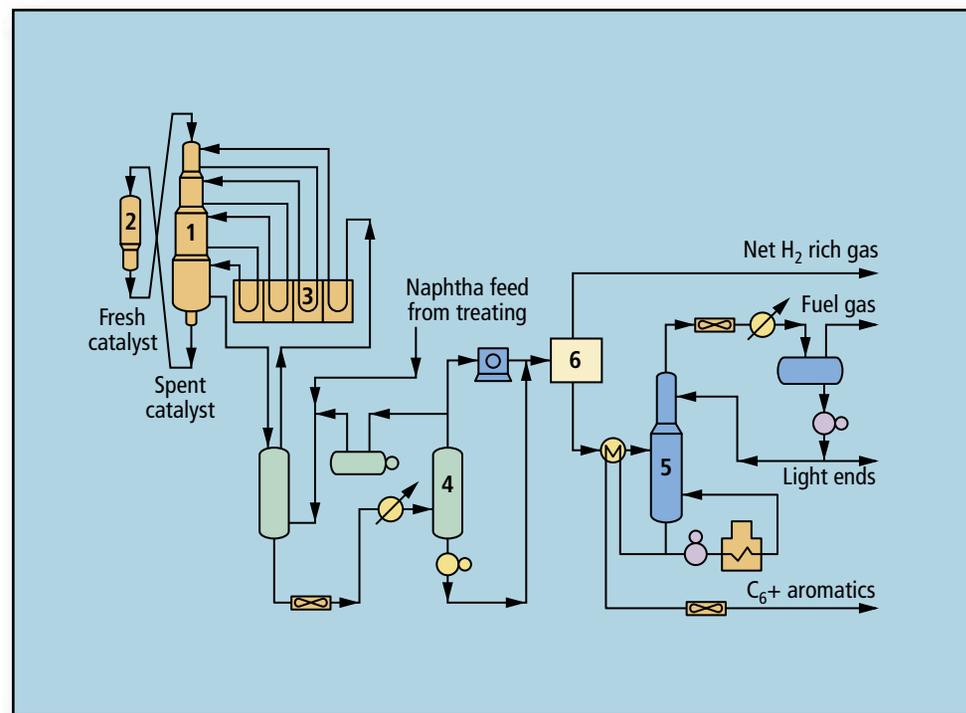
Economics: Capital investment per mtpy of feed:

US\$ 50-75

Utilities per metric ton feedrate

Electricity, kWh	12
Steam, HP, mt	0.16
Water, cooling m ³	20
Fuel, MMkcal	0.13

Commercial plants: There are 173 units in operation and 30 additional



units in design and construction. Total operating capacity represents over 3.9 million bpd.

Licensor: UOP LLC.

BTX aromatics

Application: To produce petrochemical-grade benzene, toluene and xylenes (BTX) 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) section and product-recovery section. Stacked radial-flow reactors (1) facilitate catalyst transfer to and from the CCR catalyst regeneration section (2). A charge heater and interheaters (3) achieve optimum conversion and selectivity for the 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 unit (6). The compressed vapor is then separated into a 95% pure hydrogen coproduct, a fuel-gas stream containing 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 butanes feed. Hydrogen yield is approximately 7 wt% fresh feed. Typical product distribution is 27% benzene, 43% toluene, 22% C_8 aromatics and 8% C_9^+ aromatics.

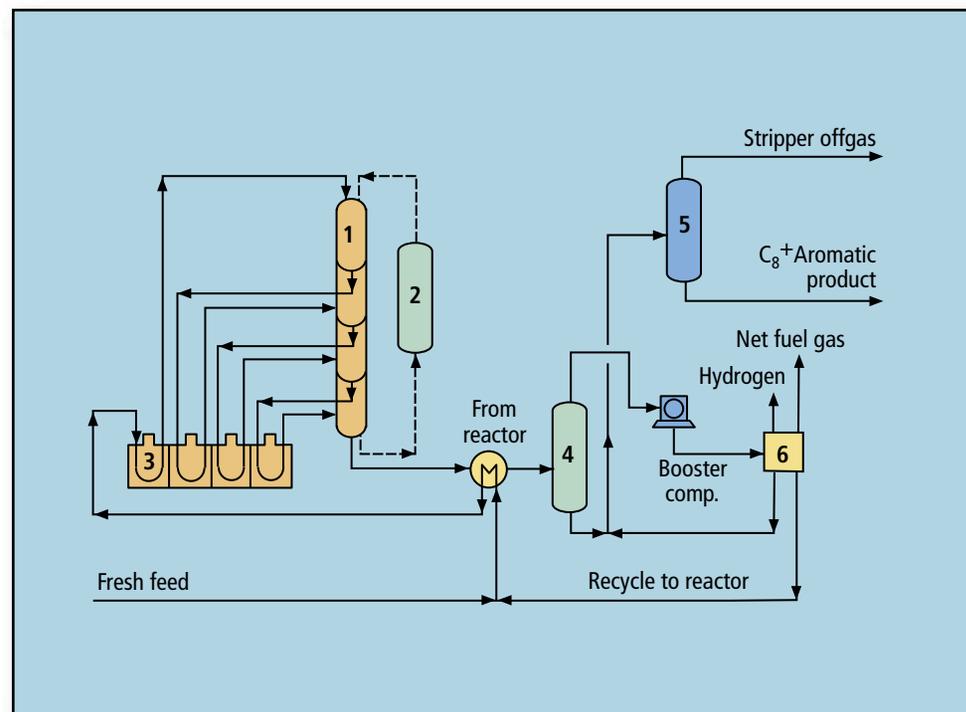
Economics: US Gulf Coast inside battery limits basis, assuming gas turbine driver is used for product compressor.

Investment, US\$ per metric ton (mt) of feed 175–208

Typical utility requirements, unit per mt of feed

Electricity, kWh	0.013
Steam, MP, mt (credit)	(0.7)
Steam, LP, mt	0.13
Water, cooling, mt	19
Fuel, MMkcal	2
Boiler feedwater, mt	0.55

Commercial plants: In 1990, the first Cyclar unit was commissioned at the BP refinery at Grangemouth, Scotland. This unit was designed to



process 1,000 bpd of C_3 or C_4 feedstock at either high- or low-pressure over a wide range of operating conditions. A second unit capable of processing C_3 and C_4 feedstock was commissioned in 2000, and operates at design capacities.

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 LLC.

Butadiene extraction

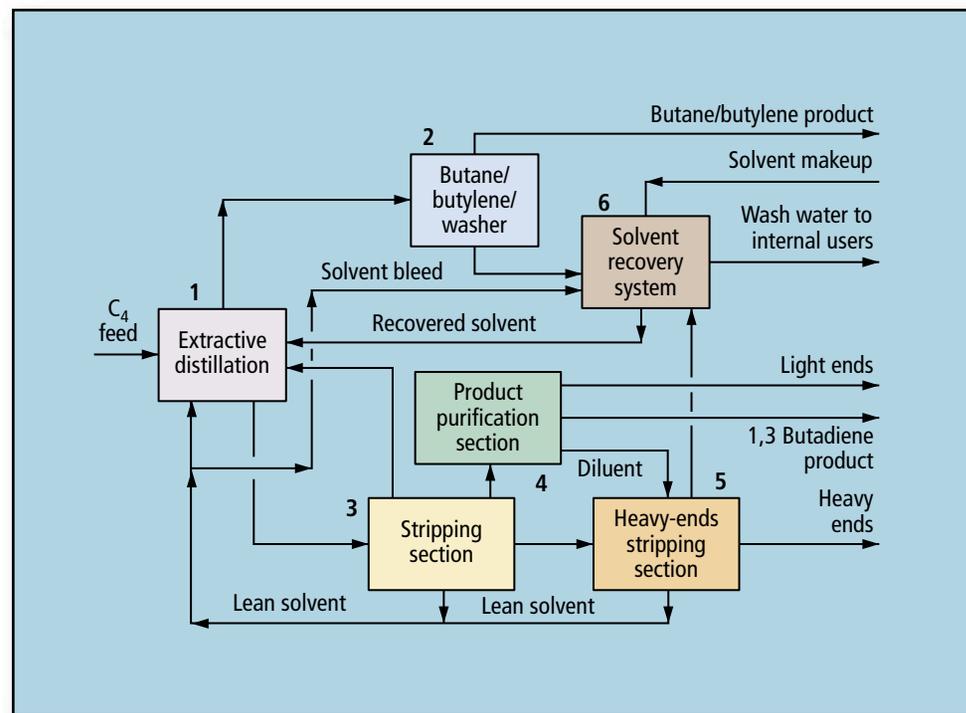
Application: To produce a polymer-grade butadiene product from mixed-C₄ streams by extractive distillation using acetonitrile (ACN) as the solvent.

Description: This butadiene extraction process was originally developed by Shell Chemicals. It is offered under license agreement by Kellogg Brown & Root, who has updated and optimized the process to reduce capital and operating costs.

The process scheme consists of contacting mixed-C₄ feed with lean solvent in the extractive distillation 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). Heavy ends (C₄ acetylenes) are also separated in the stripper system (3) as a side product and further processed in the heavy-ends stripping section (5). The solvent recovery step (6) maintains solvent quality and recovers solvent from various product streams.

Use of acetonitrile is advantageous to other solvent systems for a number of reasons. ACN's lower boiling point results in lower operating temperatures resulting in low fouling rates and long run-lengths. Only low-pressure steam is required for reboilers. The low molecular weight and low molar volume of ACN, combined with its high selectivity to butadiene, result in low solvent circulation rates and smaller equipment sizes. The low viscosity of ACN increases tower efficiencies and reduces column size and cost. ACN is also very stable, noncorrosive and biodegradable. The basic process is noncorrosive and requires only carbon steel materials of construction.

Yields: This process can exceed 98% recovery 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	20	ppm wt maximum
Methyl acetylene	10	ppm wt maximum
Vinyl acetylenes	10	ppm wt maximum
Propadiene	10	ppm wt maximum
1,2-Butadiene	10	ppm wt maximum
C ₅ hydrocarbons	200	ppm wt maximum

Commercial plants: Over 35 butadiene units have been constructed using the Shell ACN technology. Unit capacities range from 20 Mtpy to over 225 Mtpy.

Licensor: Kellogg Brown & Root, Inc.

1,3 Butadiene (Extraction from mixed C₄)

Application: To produce high-purity butadiene from a mixed C₄ stream, typically a byproduct stream from an ethylene plant using liquid feeds (liquids cracker). The BASF/Lummus process uses n-methylpyrrolidone (NMP) as the solvent.

Description: The mixed C₄ feed stream is fed into the first extractive distillation column (1), which produces an overhead butenes stream (raffinate-1) that is essentially free of butadiene and acetylenes.

The bottoms stream from this column is stripped free of butenes in the top half of the rectifier (2). A side stream containing butadiene and a small amount of acetylenic compounds (vinyl and ethyl-acetylene) is withdrawn from the rectifier and fed into the second extractive distillation column (3).

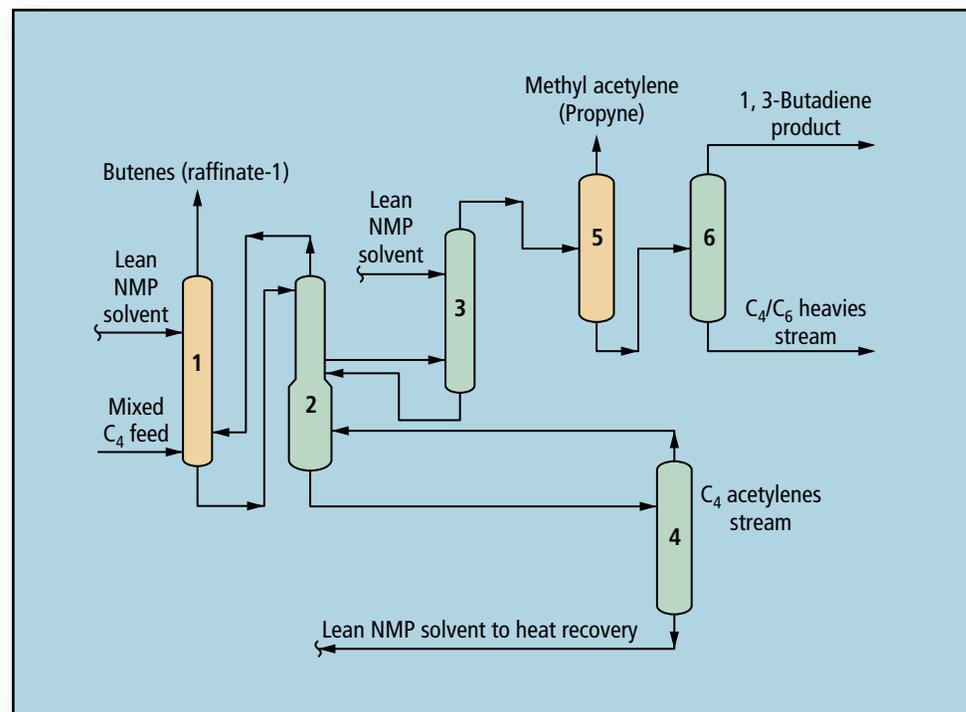
The C₄ acetylenes, which have higher solubilities in NMP than 1,3-butadiene, are removed by the solvent in the bottoms and returned to the rectifier. A crude butadiene (BD) stream, from the overhead of the second extractive distillation column, is fed into the BD purification train. Both extractive distillation columns have a number of trays above the solvent addition point to allow for the removal of solvent traces from the overheads.

The bottoms of the rectifier, containing BD, C₄ acetylenes and C₅ hydrocarbons in NMP, is preheated and fed into the degasser (the solvent stripping column (4)). In this column, solvent vapors are used as the stripping medium to remove all light hydrocarbons from NMP.

The hot-stripped solvent from the bottom of the degasser passes through the heat economizers (a train of heat exchangers) and is fed to the extractive distillation columns.

The hydrocarbons leaving the top of the degasser are cooled in a column by direct contact with solvent (NMP and water) and fed to the bottom of the rectifier via a recycle gas compressor.

Hydrocarbons having higher solubilities in the solvent than 1,3-butadiene accumulate in the middle zone of the degasser and are drawn off as a side stream. This side stream, after dilution with raffinate-1, is



fed to a water scrubber to remove a small amount of NMP from the exiting gases. The scrubbed gases, containing the C₄ acetylenes, are purged to disposal.

In the propyne column (5), the propyne (C₃ acetylene) is removed as overhead and sent to disposal. The bottoms are fed to the second distillation column (the 1,3-butadiene column (6)), which produces pure BD as overhead and a small stream containing 1,2-butadiene and C₅ hydrocarbons as bottoms.

Yield: Typically, more than 98% of the 1,3-butadiene contained in the feed is recovered as product.

1,3 Butadiene (Extraction from mixed C₄), *continued*

Economics: Unit based on a 100,000 metric tpy, ISBL, US Gulf Coast:

Investment, US\$ million	30
Utilities, per ton BD	
Steam, ton	2
Water, cooling, m ³	150
Electricity, kWh	150

Commercial plants: Currently, 27 plants are in operation using the BASF butadiene extraction process. Five additional projects are in the design or construction phase.

Licensor: BASF-AG/ABB Lummus Global.

Butadiene, 1,3

Application: The KLP process selectively hydrogenates acetylenes in crude butadiene streams from steam crackers to their corresponding diene or olefin to recover 1,3-butadiene. The KLP process can be used in new installations to eliminate the costly second-stage extractive distillation step or as a retrofit to increase product quality or throughput.

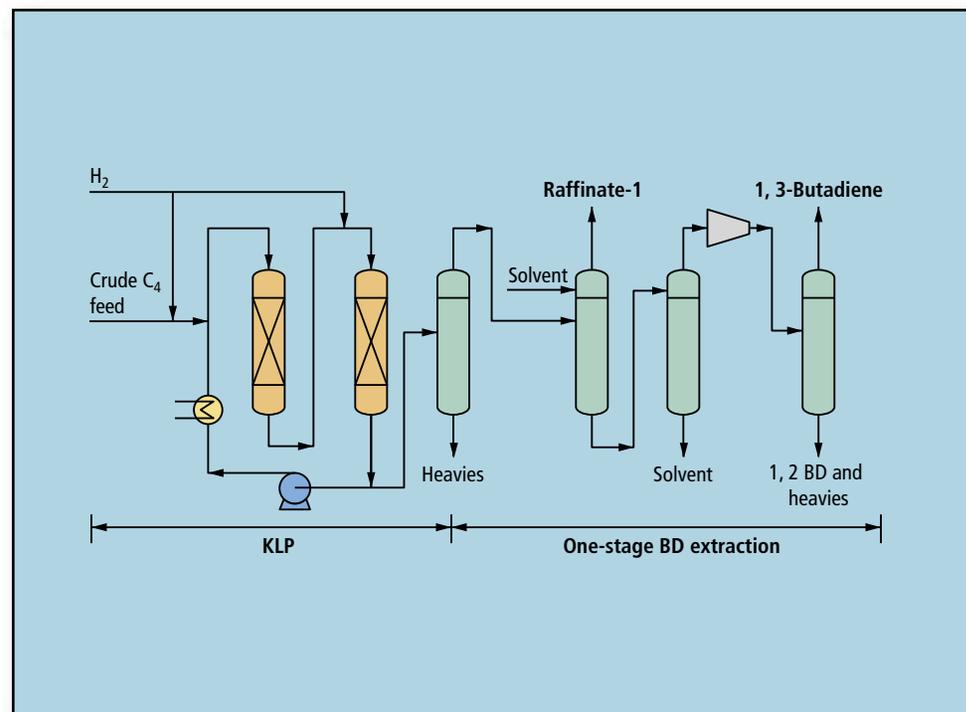
Description: In the KLP process, the C₄ stream is mixed with an essentially stoichiometric amount of hydrogen and fed to two fixed-bed reactors, in series, containing KLP-60 catalyst. The reaction pressure is high enough to maintain the reaction mixture in the liquid phase. The KLP reactor effluent then flows to a distillation column to remove hydrogen and a small amount of heavies formed in the process. The KLP effluent stream is processed in a single-stage extractive distillation unit to separate and recover high-purity 1,3-butadiene.

Yields: The combination of the KLP process with butadiene extraction can provide over 100% recovery of the butadiene contained in the feed as product. The recovery is enhanced by the conversion of vinylacetylene to 1,3-butadiene. Total acetylene levels in the product of less than 10 wt-ppm are achievable. The process also offers improved safety in operations by eliminating concentrated acetylene byproduct streams.

Economics: The capital investment and operating costs for the combination of the KLP process with butadiene extraction are similar or less than two-stage extraction processes.

Commercial plants: Eight KLP units are in operation. These units represent nearly one million metric tpy of operating capacity.

Licensor: UOP LLC.



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 Chemicals has combined its 40 years of experience in fluid-bed oxidation technology with Lurgi AG's 30 years of hydrogenation expertise to jointly develop a direct, dual-reactor process, called GEMINOX.

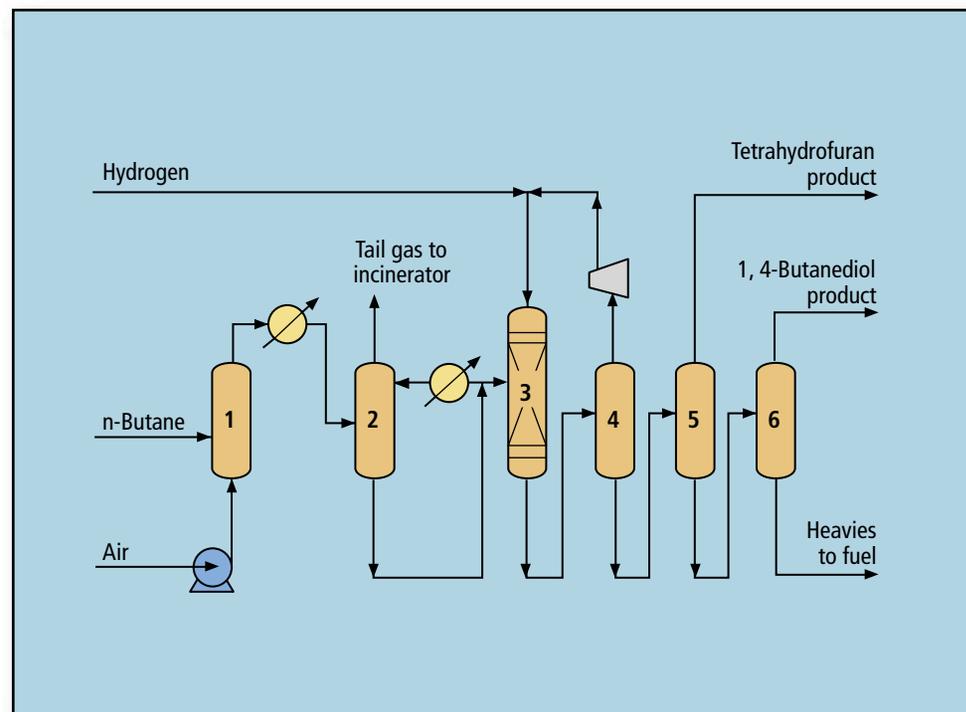
Air and n-butane are introduced into a fluid-bed, catalytic reactor (1). The fluid-bed reactor provides a uniform temperature profile for optimum catalyst performance. Reaction gases are cooled and filtered to remove small entrained catalyst particles and then routed to the recovery section. Reactor effluent is contacted with water in a 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 of the two catalysts is necessary.

Economics: The GEMINOX technology uses fewer processing steps, as found in competing BDO technologies, leading to significant capital



cost savings and lower operating costs. The unique product flexibility afforded by this process also allows the user to quickly meet changing customer and market needs.

Commercial plants: BP's first world-scale 60,000-tpy GEMINOX BDO plant in Lima, Ohio, has been successfully operating since July 2000.

Licensors: BP Chemicals and Lurgi AG.

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.

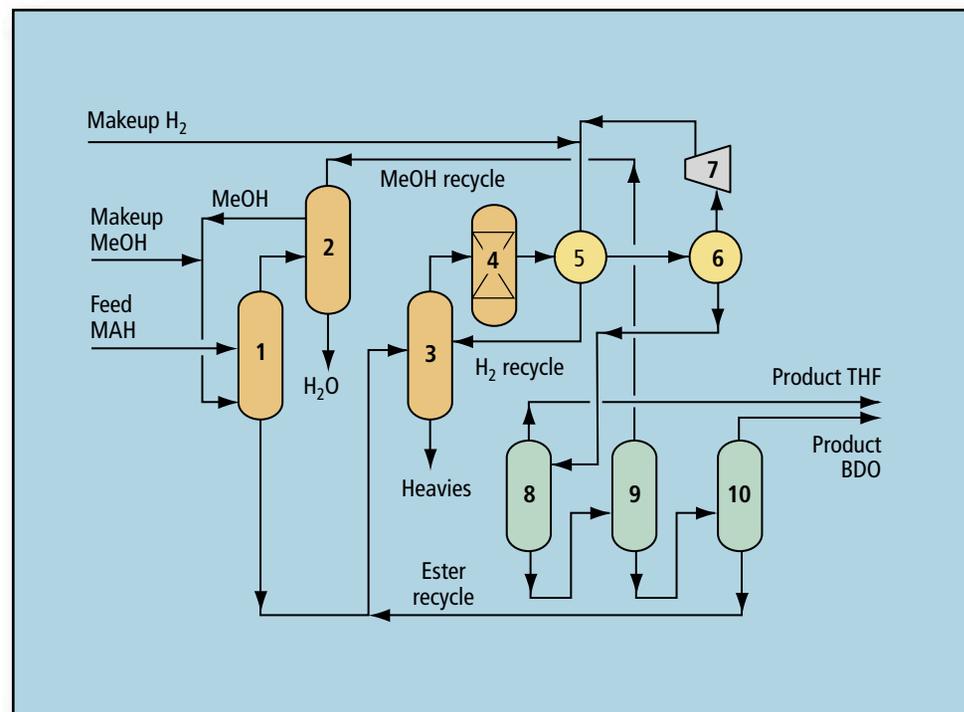
The process can be adapted to produce higher quantities of co-product THF and to extract the GBL as a co-product if required.

Economics: per ton of BDO equivalent:

Maleic anhydride	1.125
Hydrogen	0.116
Methanol	0.050
Electric power, kWh	164
Steam, t	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: Davy Process Technology, UK.



Butene-1

Application: To produce high-purity butene-1 that is suitable for copolymers in LLDPE production via the Alphabutol ethylene dimerization process developed by IFP/Axens 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 catalyst is treated to remove volatile hydrocarbons and recovered.

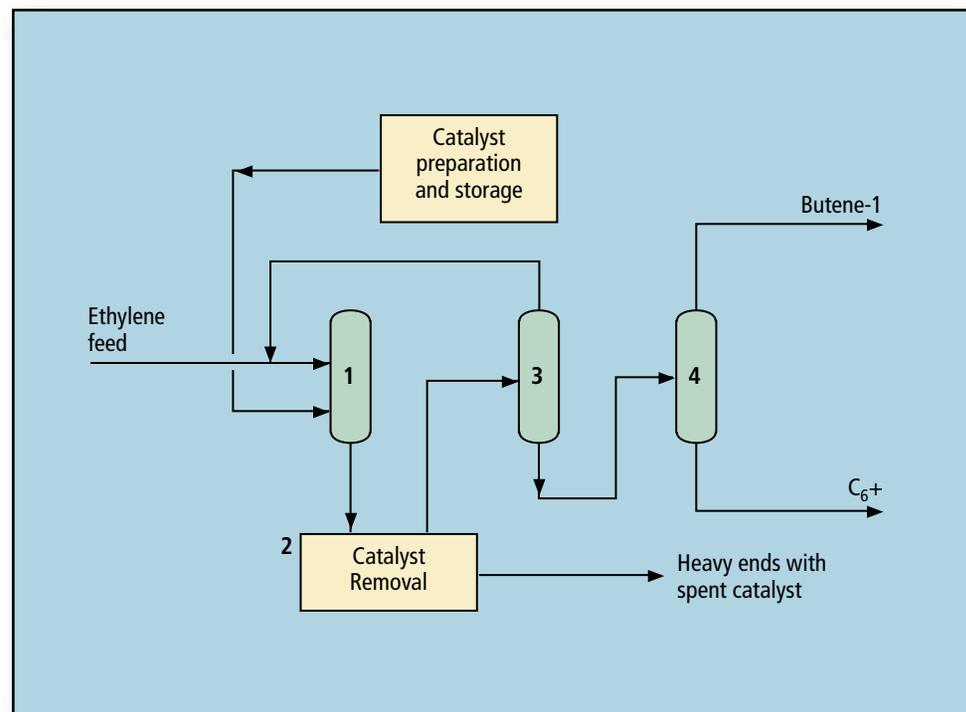
The Alphabutol process features are: simple processing, high turndown, ease of operation, low operating pressure and temperature, liquid-phase operation and carbon steel equipment. The technology has advantages over other production or supply sources: uniformly high-quality product, low impurities, reliable 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 2004 ISBL investment at a Gulf Coast location for producing 20,000-tpy of butene-1 is:

Investment , million US\$	8
Raw material	
Ethylene, tons per ton of butene-1	1.1
Byproducts , C ₆ ⁺ tons per ton of butene-1	0.08
Typical operating cost , US\$ per ton of butene-1	38



Commercial plants: There are 19 licensed units producing 312,000 tpy. Sixteen units are in operation.

Licensors: Axens, Axens NA.

Butyraldehyde, n and i

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

Description: The process reacts propylene with a 1:1 syngas at low pressure (<20 kg/cm²g) in the presence of a rhodium catalyst complexed with a ligand (1). Depending on the desired selectivity, the oxonation reaction produces normal and iso-butyraldehyde with typical n/i ratios of either 10:1 or >22:1. Several different ligand systems are commercially available which can produce selectivity ratios of up to 30:1 and as low as 2:1. The butyraldehyde product is removed from the catalyst solution (2) and purified by distillation (3). N-butyraldehyde is separated from the iso (4).

The SELECTOR Technology 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.

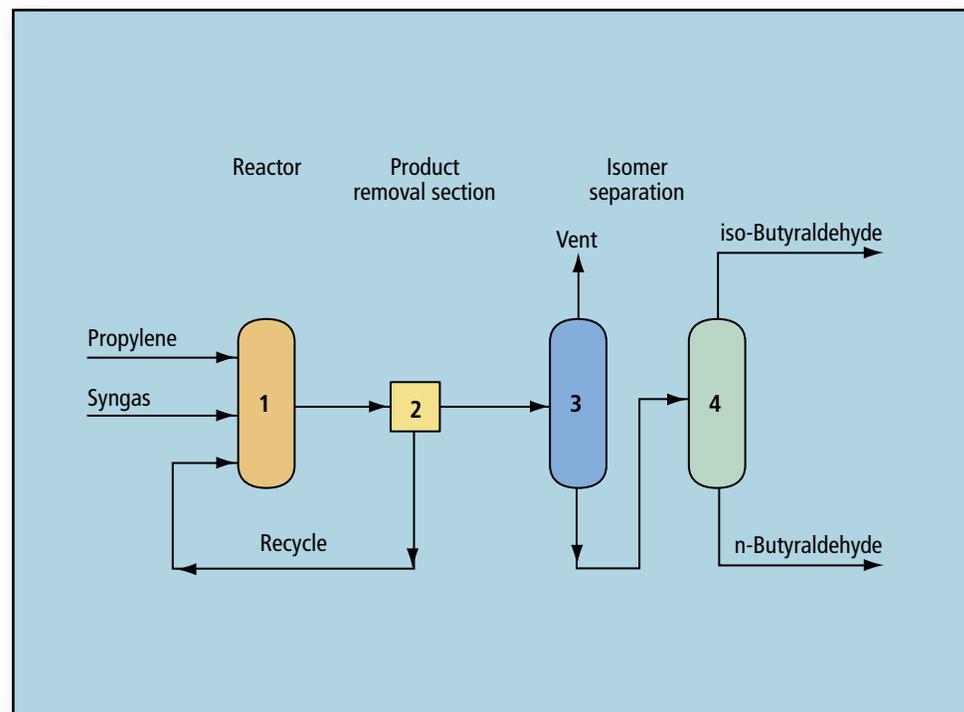
Technology for hydrogenation to normal or iso-butanols or aldolization and hydrogenation to 2-ethylhexanol exists and has been widely licensed. One version of the SELECTOR Technology has been licensed to produce a mixture of alcohols (predominantly 2 propylheptanol) from an n-butene feedstock and another version to produce higher alcohols (up to C15) from Fischer Tropsch produced olefins.

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

Feedstocks

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

Commercial plants: The LP Oxo SELECTOR Technology has been licensed for 23 plants worldwide and is now used to produce more than 60% of the world's butyraldehyde capacity. Plants range in size from 30,000 to 350,000 tpy. The rhodium-based catalyst has a long service 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: Twenty-three worldwide since 1978.

Licensor: Davy Process Technology Ltd., UK, and Union Carbide Corp. (a subsidiary of The Dow Chemical Co., US).

Cumene

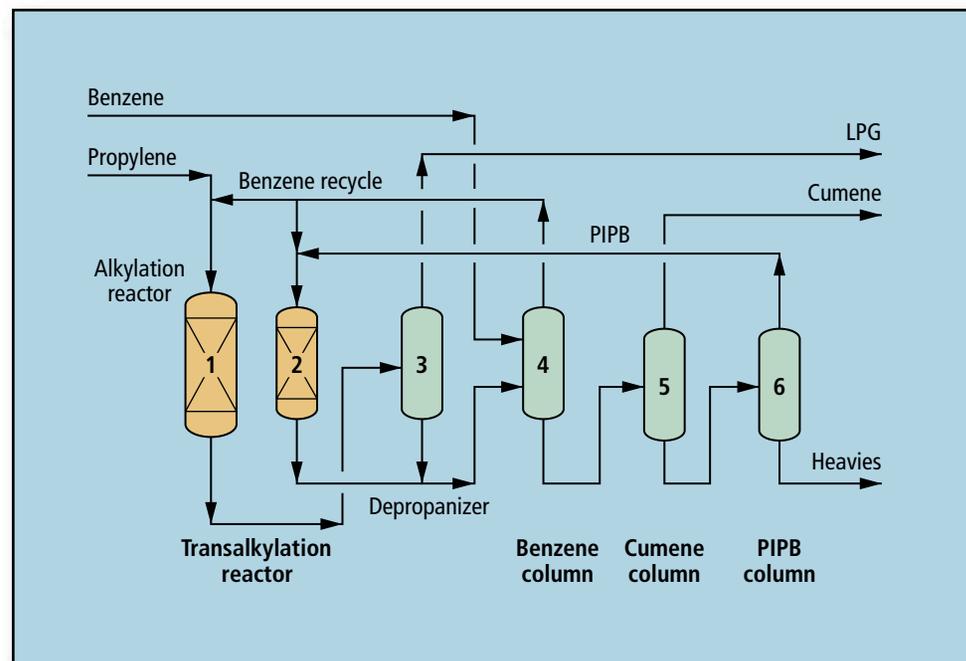
Application: To produce cumene from benzene and any grade of propylene—including lower-quality refinery propylene-propane mixtures—using the Badger process and a new generation of zeolite catalysts from ExxonMobil.

Description: The process includes: 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. Separately, recycled polyisopropylbenzene (PIPB) is premixed with benzene and fed to the transalkylation reactor (2) where PIPB reacts to form additional cumene. The transalkylation and alkylation effluents are fed to the distillation 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 a substantial increase in capacity for existing SPA, $AlCl_3$, or other zeolite 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 the lowest benzene to propylene ratios of any available technology with proven commercial cycle lengths of over seven years. Expected catalyst life is well over five years.

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

Economics: Estimated ISBL investment for a 300,000-mtpy unit on the US Gulf Coast (2004 construction basis), is US\$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 12 plants operating with a combined capacity exceeding 5.2 million mtpy. In addition, four grassroots plants and an $AlCl_3$ revamp are in the design phase. Fifty percent of the worldwide and 75% of zeolite cumene production are from plants using the Badger process.

Licensor: Badger Licensing LLC.

Cumene

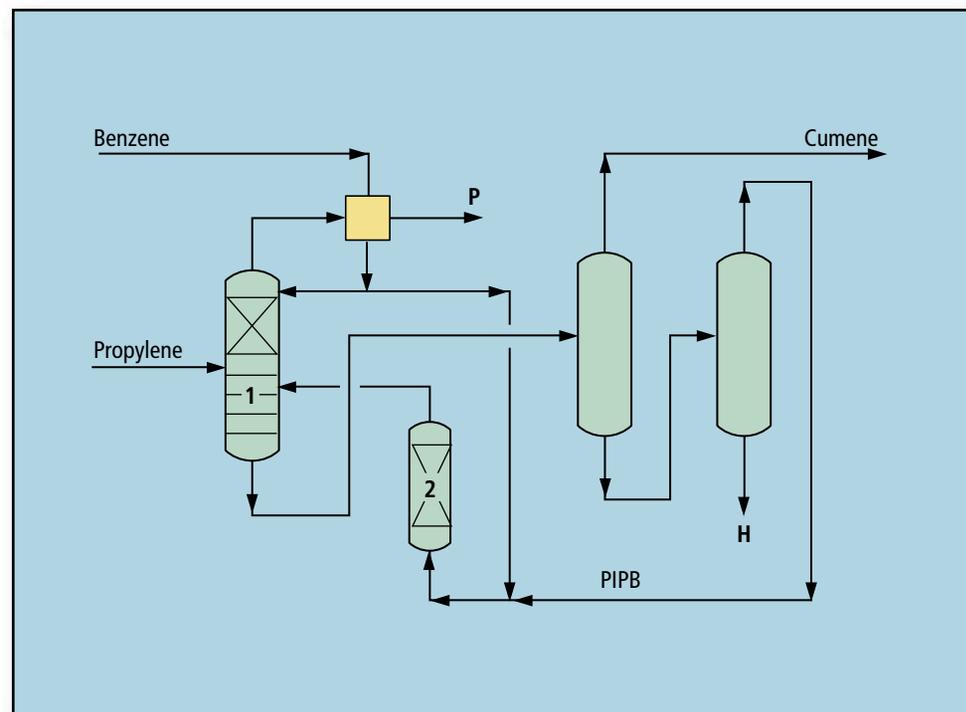
Application: Advanced technology to produce high-purity cumene from propylene and benzene using patented catalytic distillation (CD) technology. The CDCumene process uses a specially formulated zeolite alkylation catalyst packaged in a proprietary CD structure and another specially formulated zeolite 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 6 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 metric tons (mt) of cumene are produced from 65,000 mt of benzene and 35,300 mt of propylene giving a product yield of over 99.7%. Cumene product is at least 99.95% pure and has a Bromine Index of less than 2, without clay treatment.



Economics: Based on a 300,000-mtpy cumene plant located in the US Gulf Coast, the ISBL investment is about US\$15 million.

Typical operating requirements, per metric ton of cumene:

Propylene	0.353
Benzene	0.650
Yield	99.7%
Utilities:	
Electricity, kWh	8
Heat (import), 10 ⁶ kcal	0.5
Steam (export), mt	1.0
Water, cooling, m ³	12

Cumene, *continued*

Commercial plants: Formosa Chemicals & Fibre Corporation, Taiwan—
540,000 mtpy.

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

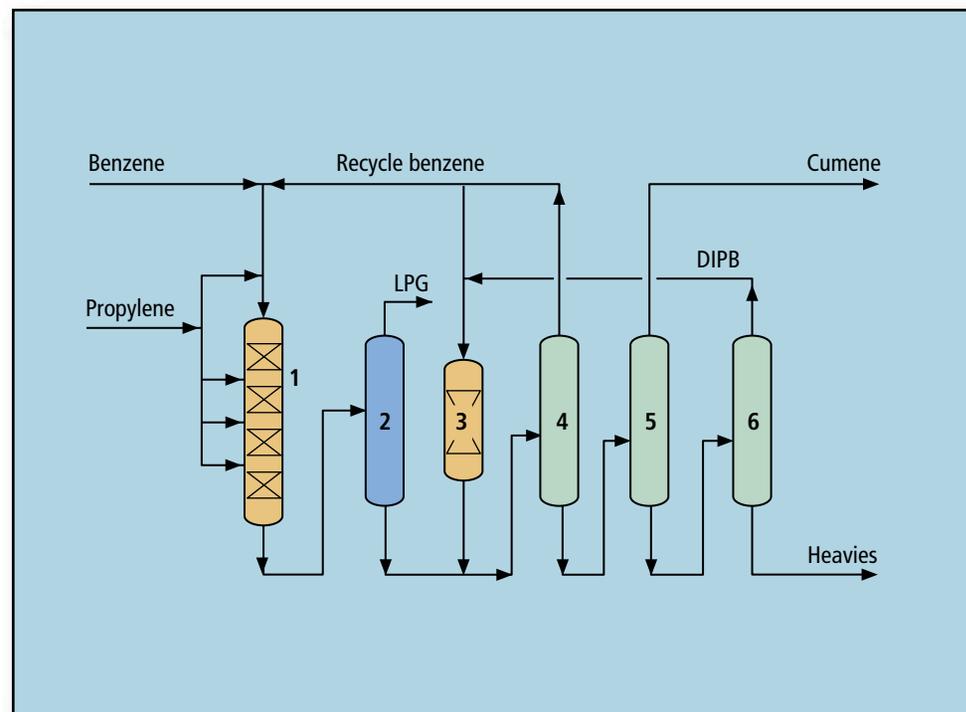
Cumene

Application: To produce high-quality cumene (isopropylbenzene) by alkylating benzene with propylene (typically refinery or chemical grade) using liquid-phase Q-Max process based on zeolitic catalyst technology.

Description: Benzene is alkylated to cumene over a zeolite catalyst in a fixed-bed, liquid-phase reactor. Fresh benzene is combined with recycle benzene and fed to the alkylation reactor (1). The benzene feed flows in series through the beds, while fresh propylene feed is distributed equally between the beds. This reaction is highly exothermic, and heat is removed by recycling a portion of reactor effluent to the reactor inlet and injecting cooled reactor effluent between the beds.

In the fractionation section, propane that accompanies the propylene feedstock is recovered as LPG product from the overhead of the depropanizer column (2), unreacted benzene is recovered from the overhead of the benzene column (4) and cumene product is taken as overhead from the cumene column (5). Di-isopropylbenzene (DIPB) is recovered in the overhead of the DIPB column (6) and recycled to the transalkylation reactor (3) where it is transalkylated with benzene over a second zeolite catalyst to produce additional cumene. A small quantity of heavy byproduct is recovered from the bottom of the DIPB column (6) and is typically blended to fuel oil. The cumene product has a high purity (99.96–99.97 wt%), and cumene yields of 99.7 wt% and higher are achieved.

The zeolite catalyst is noncorrosive and operates at mild conditions; thus, carbon-steel construction is possible. Catalyst cycle lengths are two years and longer. The catalyst is fully regenerable for an ultimate catalyst life of six years and longer. Existing plants that use SPA or AlCl_3 catalyst can be revamped to gain the advantages of Q-Max cumene technology while increasing plant capacity.



Economics: Basis: ISBL US Gulf Coast

Investment, US\$/tpy	40–90
Raw materials & utilities, per metric ton of cumene	
Propylene, tons	0.35
Benzene, tons	0.66
Electricity, kW	12
Steam, tons (import)	0.7
Water, cooling, m ³	3

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 usage in a nearby phenol plant.

Cumene, *continued*

Commercial plants: Seven Q-Max units are in operation with a total cumene capacity of 2.3 million tpy, and two additional units are either in design or under construction.

Licensors: UOP LLC.

Cyclohexane

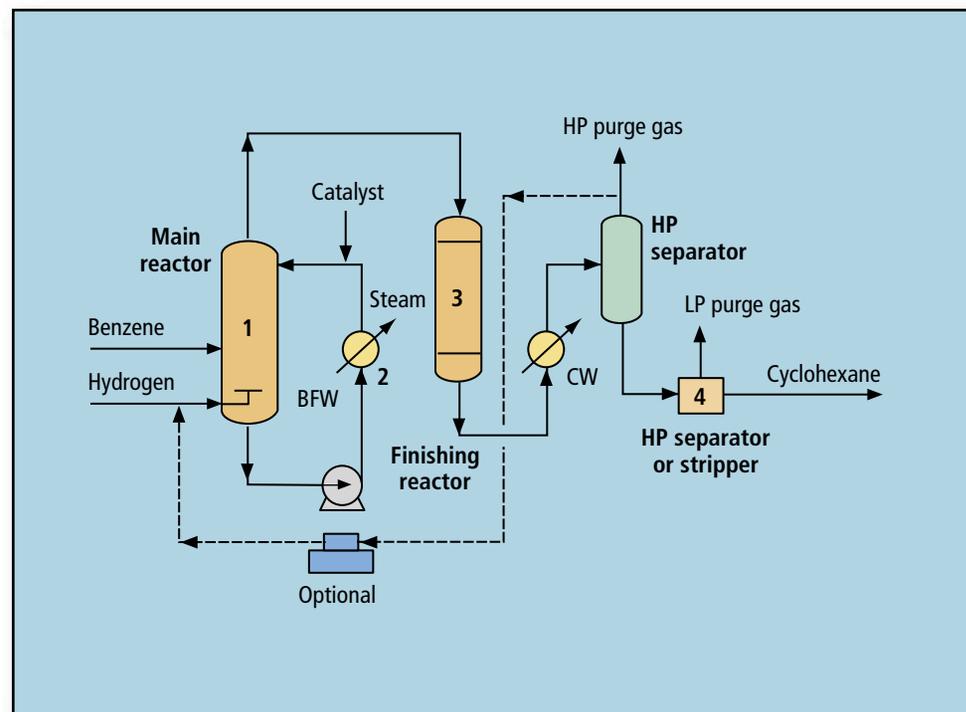
Application: Produce high-purity cyclohexane by liquid-phase catalytic hydrogenation of benzene.

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 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-tpy cyclohexane complex, ISBL 2005 Gulf Coast location with PSA hydrogen is US\$8 million. Catalyst cost is US\$ 1.2/metric ton of product.



Commercial plants: Thirty-three cyclohexane units have been licensed.

Licensor: Axens, Axens NA.

Di-methyl ether (DME)

Application: To produce dimethyl ether (DME) from methanol using Toyo Engineering Corp.'s (TEC's) DME synthesis technology based on methanol dehydration process. Feedstock can be crude methanol as well as refined methanol.

Description: If feed is crude methanol, water is separated out in the methanol column (1). The treated feed methanol is sent to a DME Reactor (2) after vaporization in (3). The synthesis pressure is 1.0–2.0 MPaG. The inlet temperature is 220–250°C, and the outlet is 300–350°C. Methanol one-pass conversion to DME is 70–85% in the reactor. The reactor effluents—DME with byproduct water and unconverted methanol—are fed to a DME column (4) after heat recovery and cooling.

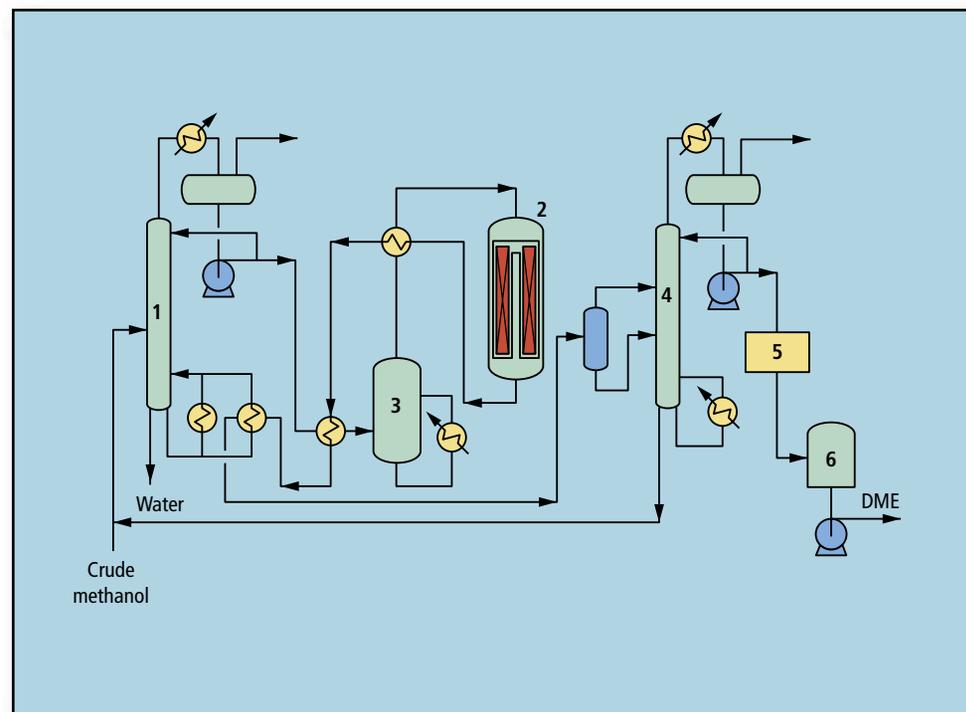
In the DME column (4), DME is separated from the top and condensed. The DME is cooled in a chilling unit (5) and stored in a DME tank (6) as a product. Water and methanol are discharged from the bottom and fed to a methanol column (1) for methanol recovery. The purified methanol from this column is recycled to the reactor after mixing with feedstock methanol.

Economics: The methanol consumption for DME production is approximately 1.4 ton-methanol per ton-DME.

Commercial plants: A 10,000-tpy unit was commissioned in August 2003 in China and is the first fuel DME facility. A second 110,000-tpy facility is scheduled to start up in the third quarter of 2005 in China and will be the largest DME plant.

Reference: Mii, T., "Commercial DME plant for fuel use," First International DME Conference, Paris, France, Oct. 12–14, 2004

Licensors: Toyo Engineering Corp. (TEC).



Dimethyl terephthalate

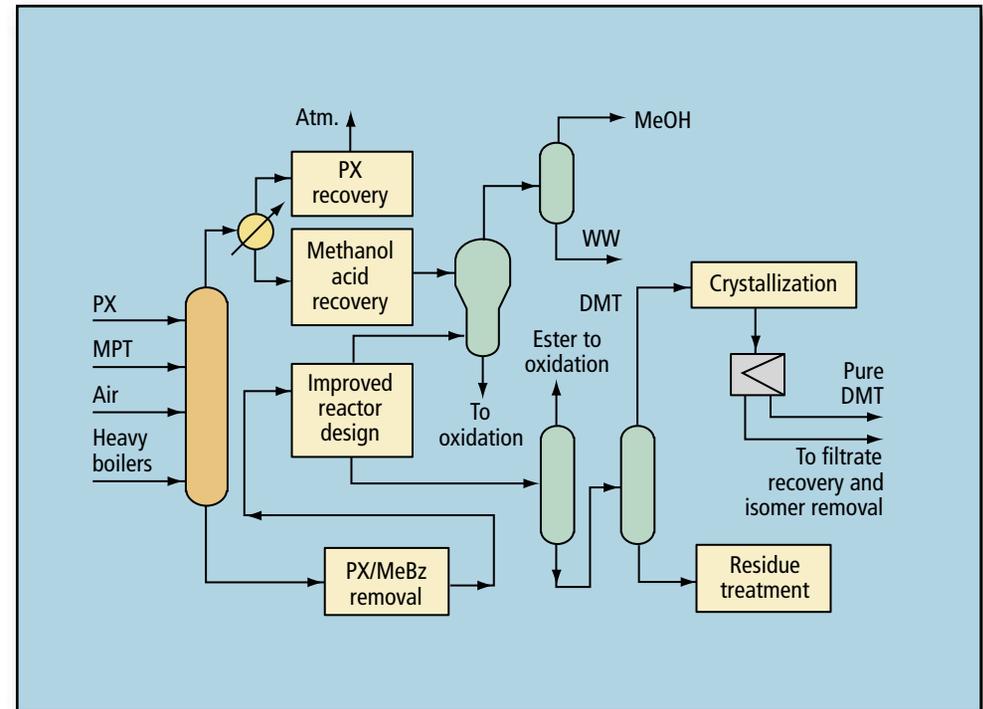
Application: To increase capacity and reduce energy usage of existing or grassroots dimethyl terephthalate (DMT) production facilities using variations of GT-DMT proprietary technology.

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/tpy 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 tons of paraxylene and 360 tons of methanol.

Dimethyl terephthalate, *continued*

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

Licensors: GTC Technology.

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.

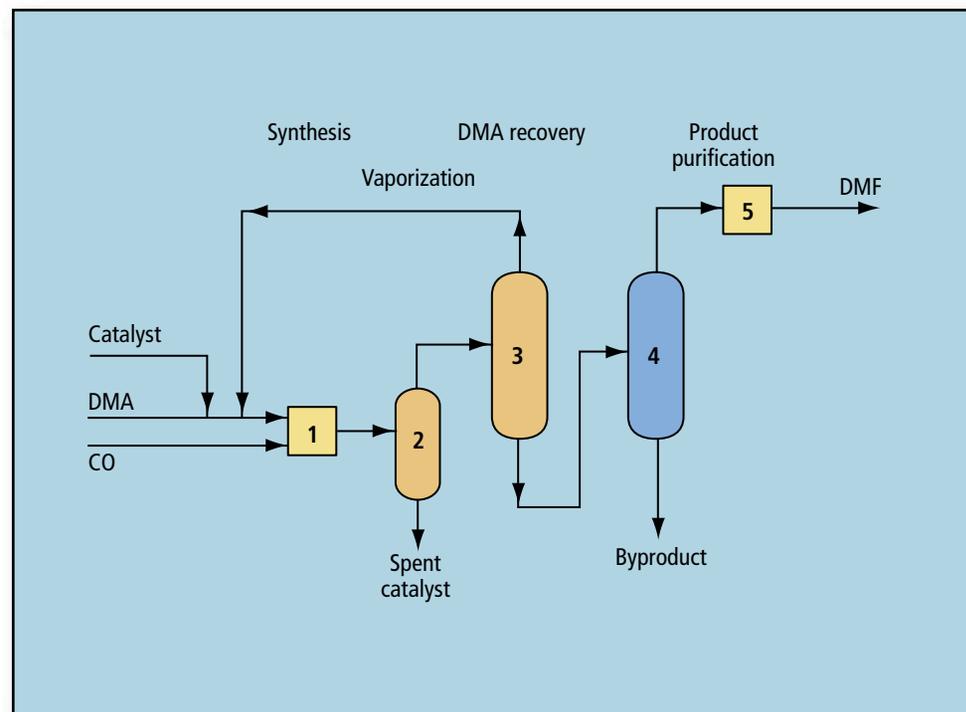
Yields: Greater than 95% on raw materials. CO yield is a function of its quality.

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 mtpy.

Licensor: Davy Process Technology, UK.



EDC via oxygen-lean oxychlorination

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

Oxygen can be supplied from an 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 HCl containing vent streams from direct chlorination, acetaldehyde, monochloroacetic acid and other processes.

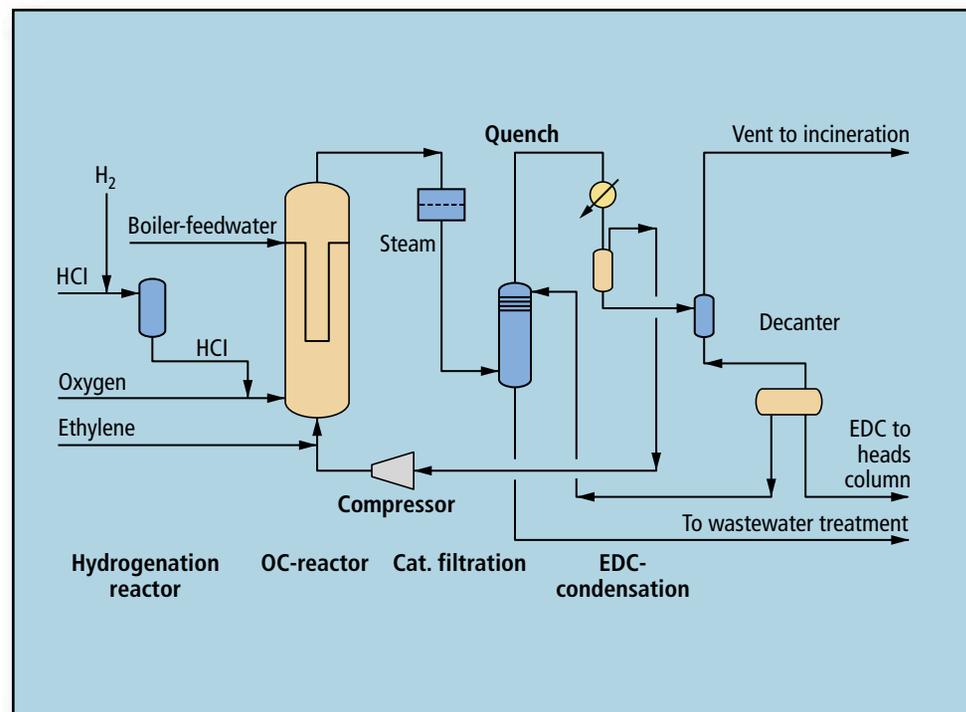
Description: The exothermic reaction is catalyzed by a copper chloride catalyst in a single-step, fluidized-bed reactor at temperatures of 220°C. Heat of reaction is recovered by producing 10 bar g steam or heating other heat-transfer fluids.

The small amount of catalyst fines that pass through the highly efficient cyclone system are removed by 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 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.

Process features and economics are:

Low manufacturing costs: The unlimited catalyst lifetime is combined with the low losses via the highly efficient cyclone system (less than 15g catalyst per metric ton (mton) of EDC produced). High raw-material yields (98.5% ethylene, 99% anhydrous HCl and 94% oxygen), high crude EDC purity (>99.5%) and the possibility of using low-cost oxygen from PSA units ensure a highly competitive process with low production costs.



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

Environment friendly: A highly efficient, hot-gas filtration system separates 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 <5g/t of EDC purification capacity, copper <1g/t of oxychlorination capacity, dioxin-like components <1µg TEQ/t of oxychlorination capacity).

EDC via oxygen-lean oxychlorination, *continued*

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 onstream 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.

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

Commercial plants: The process is used in 20 reactors at 15 sites with annual single reactor capacities up to 320,000 mtons of EDC, alone as HCl-consuming plant or as part of the balanced VCM process. In some cases, it has replaced other oxychlorination technologies from different licensors by replacing existing reactors or existing units. Two new oxychlorination trains were successfully commissioned in September 2004; one oxychlorination unit is under design.

Licensor: Vinnolit.

Contractor: Uhde GmbH.

EDC via high-temperature chlorination

Application: Vinnolit's new high-temperature direct chlorination (DC) reactor provides an energy efficient technology for the production of furnace feed and sales ethylene dichloride (EDC) without distillation from chlorine and ethylene.

Description: The liquid phase reaction of ethylene and chlorine releases approximately 220 kJ/mol of produced EDC.

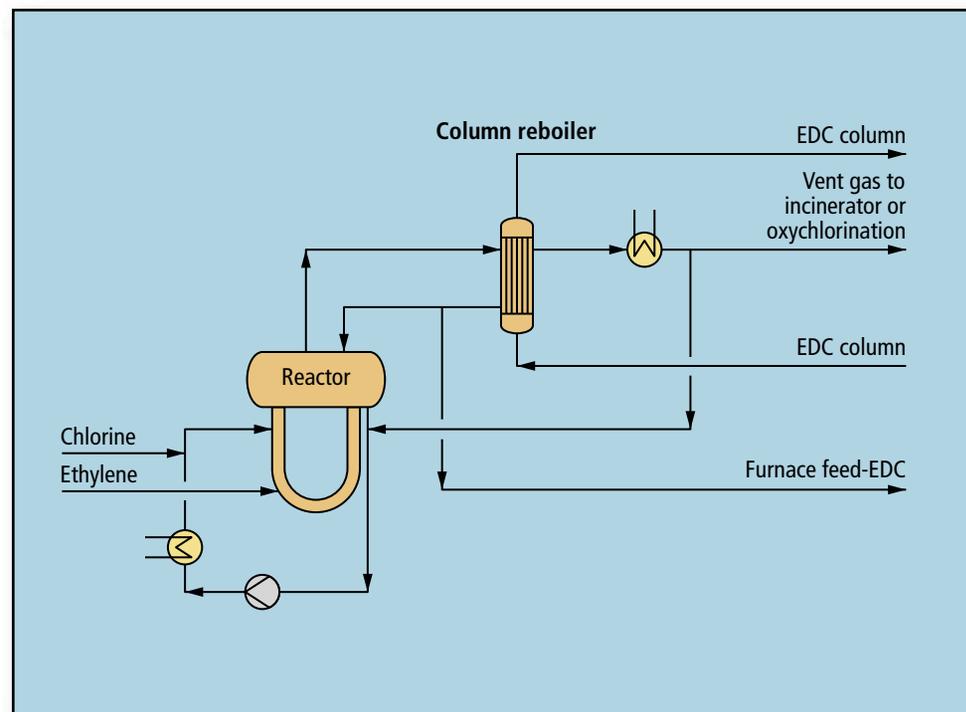
In a simple carbon steel u-shaped loop reactor, chlorine and ethylene are separately dissolved in EDC before the reaction takes place. In combination with the special Vinnolit catalyst this method significantly minimizes byproduct formation.

Downstream of the reaction zone, the lower static pressure permits the reactor content to boil and applies the thermosyphon effect for circulation. EDC vapor leaves the horizontal vessel and either enters the reboiler of a column (e.g., reboiler of high-boil-heads and/or vacuum column) or a heat exchanger, which condenses the EDC vapor. The reaction heat is transferred to the column indirectly. A fraction of the condensed EDC is fed back to the reactor and the rest is directly sent to the EDC cracker without further distillation.

Because of the high yields, the Vinnolit DC reactor can be operated in the stand-alone mode. However, if the reactor is part of a complete VCM plant, offgas can be sent to the oxychlorination reactor to recover the remaining small quantities of ethylene. If sales-EDC specification is the target, only a small stripper column is required to eliminate traces of HCl.

Process features and economics are:

Low manufacturing costs: High raw material yields (99.9% for ethylene and 99.8% for chlorine) and a product quality, which requires no further treatment, ensure a highly competitive process with low production costs. The HTC (high temperature chlorination) boiling reactor is simple, because no EDC washing, wastewater treatment and EDC distillation facilities are necessary.



Low capital costs: A simple design with a minimized number of equipment results in low unit investment costs.

Energy savings: Vinnolit's DC process significantly reduces the steam consumption in a balanced EDC/VCM plant. The saving of steam is approximately 600 kg per metric ton (mton) of EDC produced. The reaction heat can preferably be used in the EDC distillation.

Simple process: The HTC-boiling reactor is simple due to elimination of washing equipment, wastewater treatment and EDC distillation.

New catalyst: The Vinnolit DC catalyst guarantees a furnace feed-EDC quality of > 99.9% without any distillation. Catalyst makeup is not

EDC via high-temperature chlorination, *continued*

required.

Operability and maintainability: A corrosion inhibiting catalyst system and simple equipment without major moving parts keep the maintenance costs low.

Less plot area: The plot area requirement for the DC boiling reactor unit is very small and can be accommodated to customers' needs.

Commercial plants: The DC-process and/or DC-catalyst are used for the annual production of more than 6.5 million mtons of EDC. One unit with an annual capacity of 320,000 mtons of EDC has been successfully commissioned in September 2004. Another unit with the latest plant design is currently under construction.

Licensors: Vinnolit.

Contractor: Uhde GmbH.

Ethanolamines

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

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 NH_3/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 heavies tar byproduct is also produced. Technical grade TEA (85 wt%) can also be produced if required.

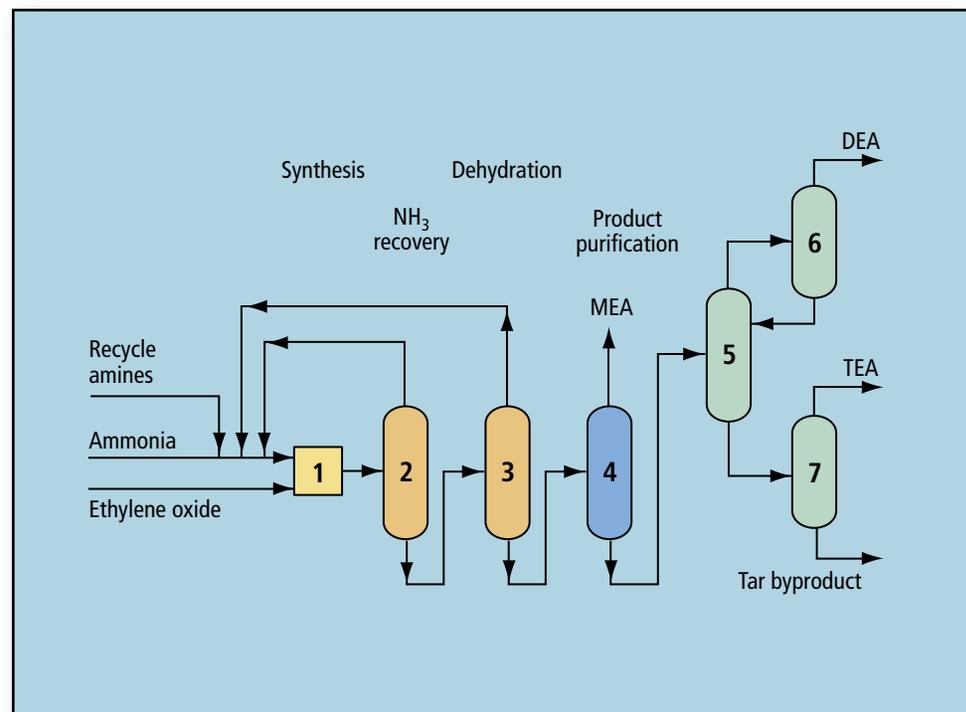
Yields: Greater than 98% on raw materials.

Economics: Typical performance data per ton amines MEA/DEA/TEA product ratio of $\frac{1}{3} : \frac{1}{3} : \frac{1}{3}$

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-mtpy original capacity facility.

Licensor: Davy Process Technology, UK.



Ethers—ETBE

Application: The Uhde (Edeleanu) ETBE process combines ethanol and isobutene to produce the high-octane oxygenate ethyl tertiary butyl ether (ETBE).

Feeds: C₄ cuts from steam cracker and FCC units with isobutene contents ranging from 12% to 30%.

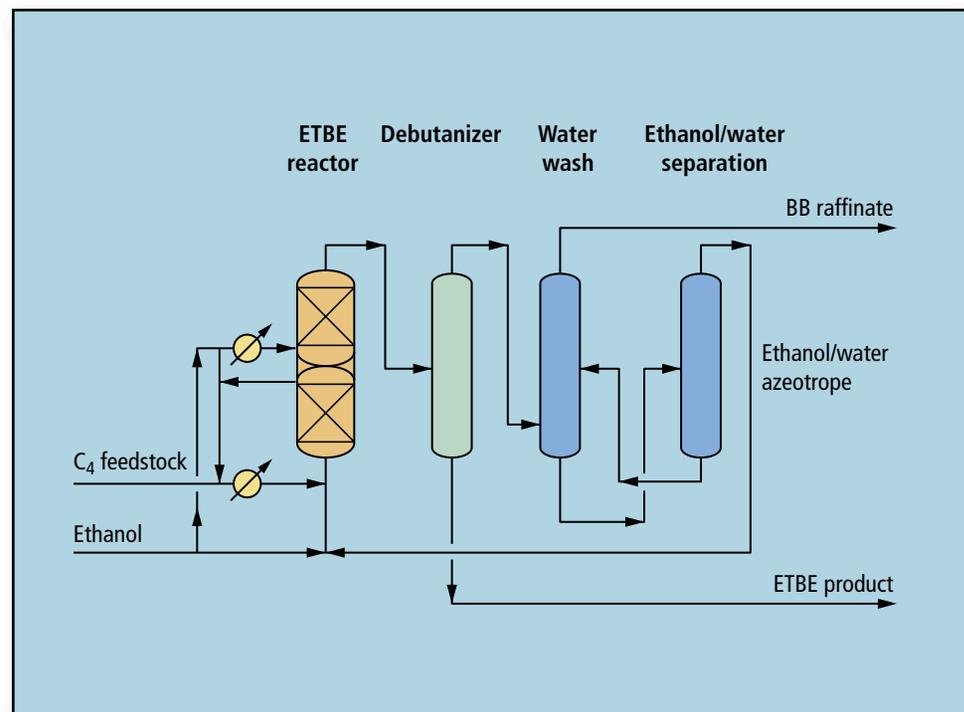
Products: ETBE and other tertiary alkyl ethers are primarily used in gasoline blending as an octane enhancer to improve hydrocarbon combustion efficiency. Moreover, blending of ETBE to the gasoline pool will lower vapor pressure (Rvp).

Description: The Uhde (Edeleanu) technology features a two-stage reactor system of which the first reactor is operated in the recycle mode. With this method, a slight expansion of the catalyst bed is achieved that ensures very uniform concentration profiles in the reactor and, most important, avoids hot spot formation. Undesired side reactions, such as the formation of di-ethyl ether (DEE), are minimized.

The reactor inlet temperature ranges from 50°C at start-of-run to about 65°C at end-of-run conditions. One important feature of the two-stage system is that the catalyst can be replaced in each reactor separately, without shutting down the ETBE unit.

The catalyst used in this process is a cation-exchange resin and is available from several manufacturers. Isobutene conversions of 94% are typical for FCC feedstocks. Higher conversions are attainable when processing steam-cracker C₄ cuts that contain isobutene concentrations of about 25%.

ETBE is recovered as the bottoms product of the distillation unit. The ethanol-rich C₄ distillate is sent to the ethanol recovery section. Water is used to extract excess ethanol and recycle it back to process. At the top of the ethanol/water separation column, an ethanol/water azeotrope is recycled to the reactor section. The isobutene-depleted C₄ stream may be sent to a raffinate stripper or to a molsieve-based unit to remove oxygenates such as DEE, ETBE, ethanol and tert-butanol.



Utility requirements: (C₄ feed containing 21% isobutene; per metric ton of ETBE):

Steam, LP, kg	110
Steam, MP, kg	1,000
Electricity, kWh	35
Water, cooling, m ³	24

Commercial plants: The Uhde (Edeleanu) proprietary ETBE process has been successfully applied in two refineries, converting existing MTBE units. Another MTBE plant is in the conversion stage.

Licensors: Uhde GmbH.

Ethers—MTBE

Application: The Uhde (Edeleanu) MTBE process combines methanol and isobutene to produce the high-octane oxygenate—methyl tertiary butyl ether (MTBE).

Feeds: C₄-cuts from steam cracker and FCC units with isobutene contents range from 12% to 30%.

Products: MTBE and other tertiary alkyl ethers are primarily used in gasoline blending as an octane enhancer to improve hydrocarbon combustion efficiency.

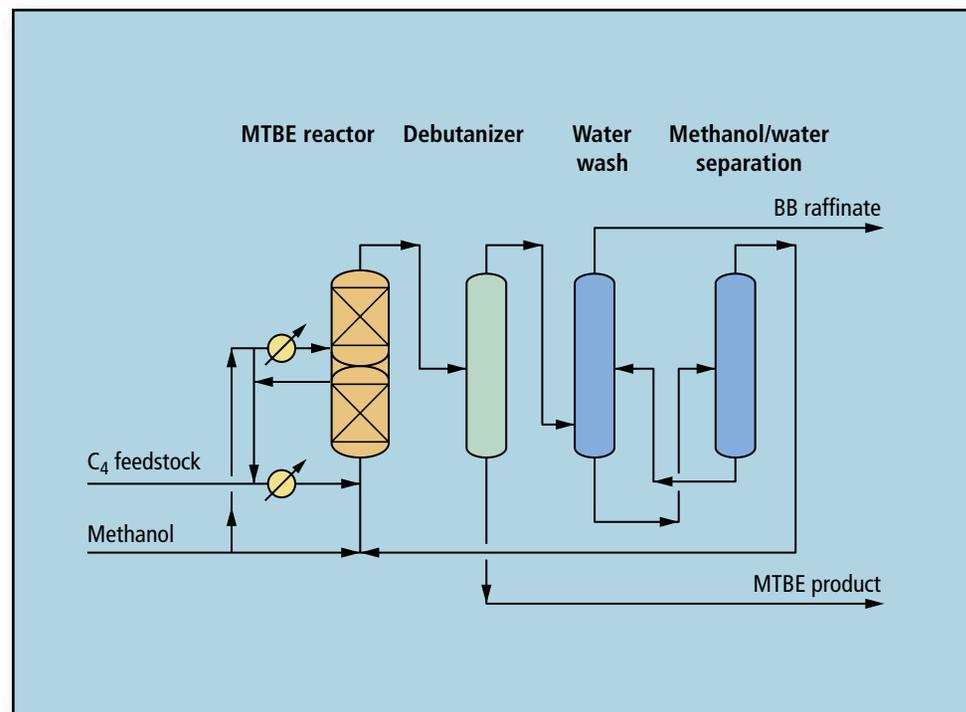
Description: The technology features a two-stage reactor system of which the first reactor is operated in the recycle mode. With this method, a slight expansion of the catalyst bed is achieved which ensures very uniform concentration profiles within the reactor and, most important, avoids hot spot formation. Undesired side reactions, such as the formation of dimethyl ether (DME), are minimized.

The reactor inlet temperature ranges from 45°C at start-of-run to about 60°C at end-of-run conditions. One important factor of the two-stage system is that the catalyst may be replaced in each reactor separately, without shutting down the MTBE unit.

The catalyst used in this process is a cation-exchange resin and is available from several catalyst manufacturers. Isobutene conversions of 97% are typical for FCC feedstocks. Higher conversions are attainable when processing steam-cracker C₄ cuts that contain isobutene concentrations of 25%.

MTBE is recovered as the bottoms product of the distillation unit. The methanol-rich C₄ distillate is sent to the methanol-recovery section. Water is used to extract excess methanol and recycle it back to process. The isobutene-depleted C₄ stream may be sent to a raffinate stripper or to a molsieve-based unit to remove other oxygenates such as DME, MTBE, methanol and tert-butanol.

Very high isobutene conversion, in excess of 99%, can be achieved



through a debutanizer column with structured packings containing additional catalyst. This reactive distillation technique is particularly suited when the raffinate-stream from the MTBE unit will be used to produce a high-purity butene-1 product.

For a C₄ cut containing 22% isobutene, the isobutene conversion may exceed 98% at a selectivity for MTBE of 99.5%.

Utility requirements, (C₄ feed containing 21% isobutene; per metric ton of MTBE):

Steam, LP, kg	900
Steam, MP, kg	100
Electricity, kWh	35
Water, cooling, m ³	15

Ethers—MTBE, *continued*

Commercial plants: The Uhde (Edeleanu) proprietary MTBE process has been successfully applied in five refineries. The accumulated licensed capacity exceeds 1 MMtpy.

Licensors: Uhde GmbH.

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.

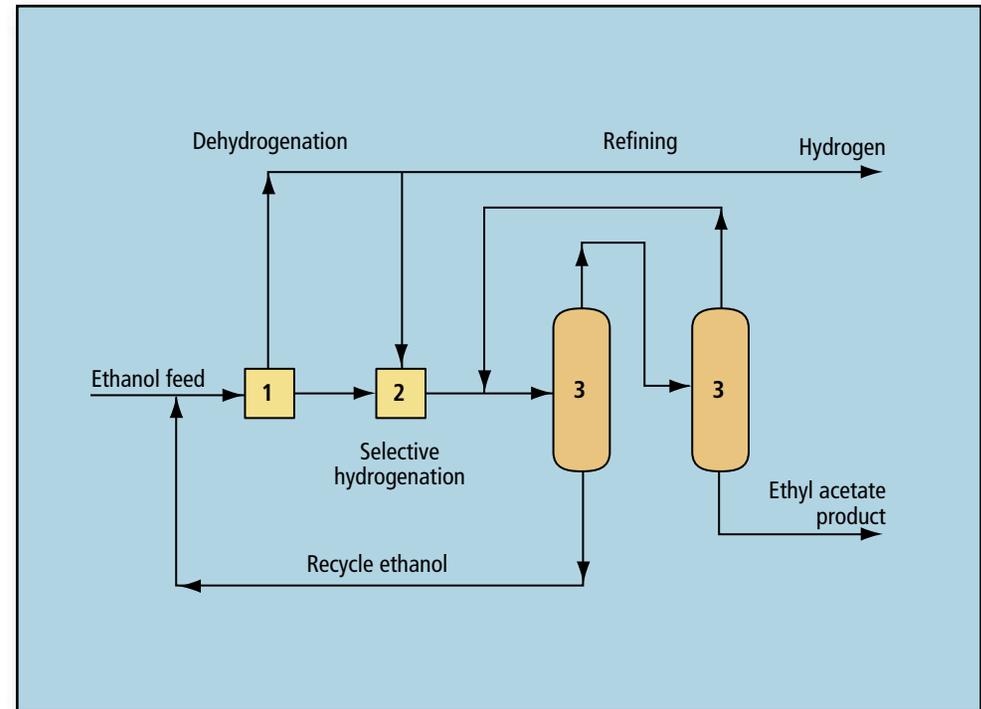
The process is characterized by low-operating temperatures and pressures, which allow all equipment to be constructed from either carbon steel or low-grade stainless steels. It allows ethyl acetate to be made without requiring acetic acid as a feed material. The process is appropriate for both synthetic 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 1990s. The first commercial plant is a 50,000-tpy plant in South Africa, using synthetic ethanol.

Licensees: One since 1998.



Licensor: Davy Process Technology, UK.

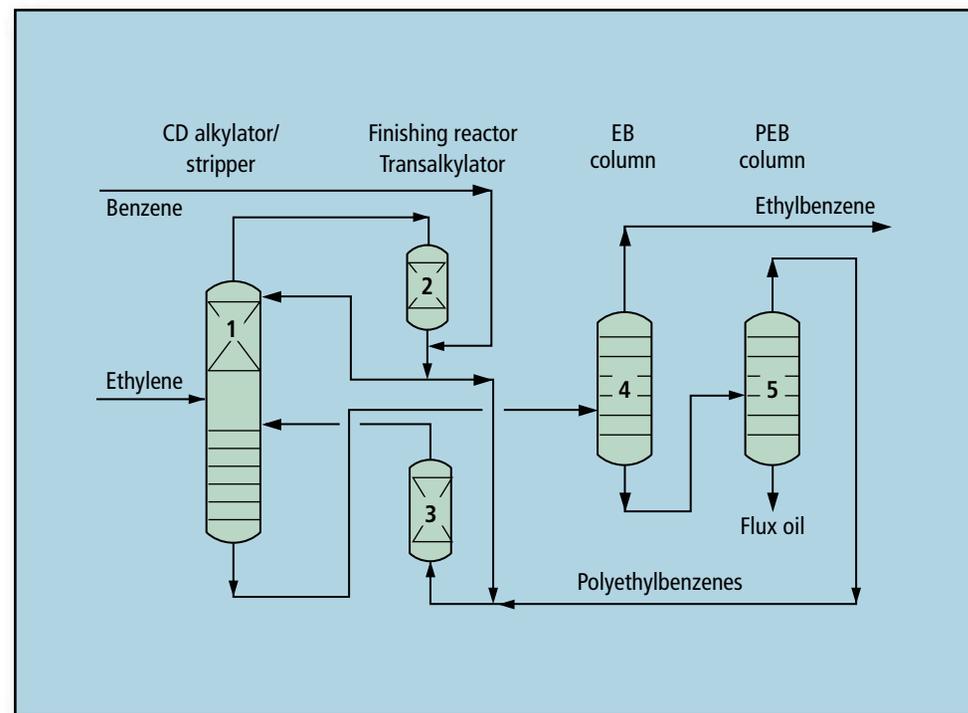
Ethylbenzene

Application: Advanced technology to produce high-purity ethylbenzene (EB) alkylating benzene with ethylene using patented catalytic distillation (CD) technology. The CDTECH EB process uses a specially formulated zeolite alkylation catalyst packaged in a proprietary CD structure. The process is able to handle a wide range in ethylene feed composition—from 10% to 100% ethylene.

Description: The CD alkylator stripper (1) operates as a distillation column. Alkylation and distillation occur in the alkylator 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 (2) where the remaining ethylene reacts over zeolite catalyst pellets. The alkylator stripper bottoms is fractionated (4, 5) into EB product, polyethylbenzenes and flux oil. The polyethylbenzenes are transalkylated with benzene over zeolite catalyst pellets in the transalkylator (3) 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 as in FCC offgas. Reactors are designed for 3 to 6 years of uninterrupted runlength. 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 trans-alkylation reactions are highly selective—producing few byproducts. The EB product has high purity (99.9 wt% minimum) and is suitable for styrene-unit feed. Xylene make is less than 10 ppm. The process has an overall yield of 99.7%.

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



Benzene, kg	738
Electricity, kWh	20
Water, cooling m ³	3
Steam, mtons (export)	1.3
Hot oil, 10 ⁶ kcal	0.6

Commercial plants: Three commercial plants are in operation in Argentina and Canada with capacities from 140,000 to 816,000 mtpy. They process ethylene feedstocks with purities ranging from 75% ethylene to polymer-grade ethylene. An 850,000-mtpy unit using dilute ethylene is currently under construction.

Investment (500,000 tpy, ISBL Gulf Coast), US\$: 17 million

Raw materials and utilities, based on one metric ton of EB:
Ethylene, kg 265

Ethylbenzene, *continued*

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

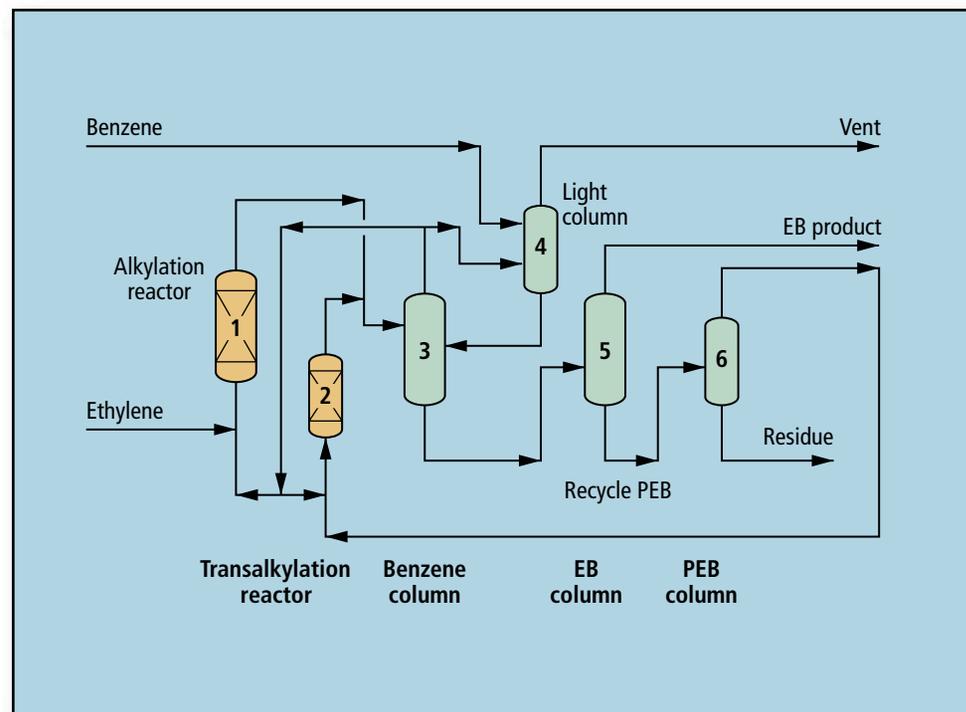
Ethylbenzene

Application: To produce ethylbenzene (EB) from benzene and a polymer-grade ethylene or an ethylene/ethane feedstock using the 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 either a totally liquid-filled or mixed-phase 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 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 small vent stream from the benzene column 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 years are expected for the alkylation and transalkylation catalysts. 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 EB 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	0.265
Benzene	0.739
Steam, high-pressure used	0.98
Steam, medium- and low-pressured generated	1.39

Utilities can be optimized for specific site conditions.

Commercial plants: Since the commercialization of the Badger EB technology in 1980, 45 licenses have been granted. The total licensed capac-

Ethylbenzene, *continued*

ity for the Badger EB technology exceeds 17 million mtpy. The capacity for the EBMax technology exceeds 10.6 million mtpy.

Licensors: Badger Licensing LLC.

Ethylbenzene

Application: State-of-the-art technology to produce high-purity ethylbenzene (EB) by liquid-phase alkylation of benzene with ethylene. The Lummus/UOP EBOne process uses specially formulated, proprietary zeolite catalyst from UOP. The process can handle a wide range of ethylene feed compositions ranging from chemical (70%) to polymer grade (100%).

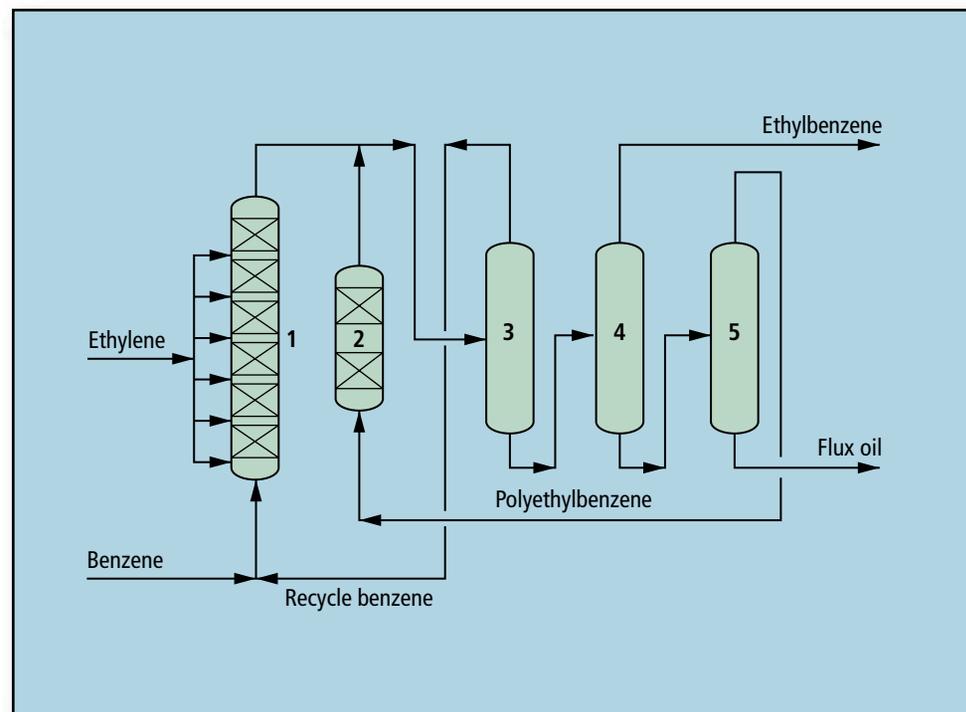
Description: Benzene and ethylene are combined over a proprietary zeolite catalyst in a fixed-bed, liquid-phase reactor. Fresh benzene is combined with recycle benzene and fed to the alkylation reactor (1). The combined benzene feed flows in series through the beds, while fresh ethylene feed is distributed equally between the beds. The reaction is highly exothermic, and heat is removed between the reaction stages by generating steam. Unreacted benzene is recovered from the overhead of the benzene column (3), and EB product is taken as overhead from the EB column (4).

A small amount of polyethylbenzene (PEB) is recovered in the overhead of the PEB column (5) and recycled back to the transalkylation reactor (2) where it is combined with benzene over a second proprietary zeolite catalyst to produce additional EB product. A small amount of flux oil is recovered from the bottom of the PEB column (5) and is usually burned as fuel.

The catalysts are non-corrosive and operate at mild conditions, allowing for all carbon-steel construction. The reactors can be designed for 2–6 year catalyst cycle length, and the catalyst is fully regenerable. The process does not produce any hazardous effluent.

Yields and product quality: Both the alkylation and trans-alkylation 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 10 ppm. The process has an overall yield of 99.7%.

Economics: The EBOne process features consistently high product yields over the entire catalyst life cycle, high-product purity, low-energy consumption, low investment cost, and simple, reliable operation.



Investment, ISBL Gulf Coast, US\$/mtpy 30–45

Raw material and utilities, per metric ton of EB

Ethylene, mtons	0.265
Benzene, mtons	0.738
Utilities, US\$	1

Additional utility savings can be realized via heat integration with downstream Lummus/UOP Classic SM or SMART SM styrene unit.

Commercial plants: Nineteen EBOne units are in operation throughout the world, with a total EB capacity of 5.7 million mtpy. Unit capacities range from 65,000 to 725,000 mtpy. Ethylene feedstock purity ranges from 80 to 100%. Nine additional units are either in design or under construction—the largest unit is 770,000 mtpy.

Ethylbenzene, *continued*

Licensors: ABB Lummus Global and UOP LLC.

Ethylene

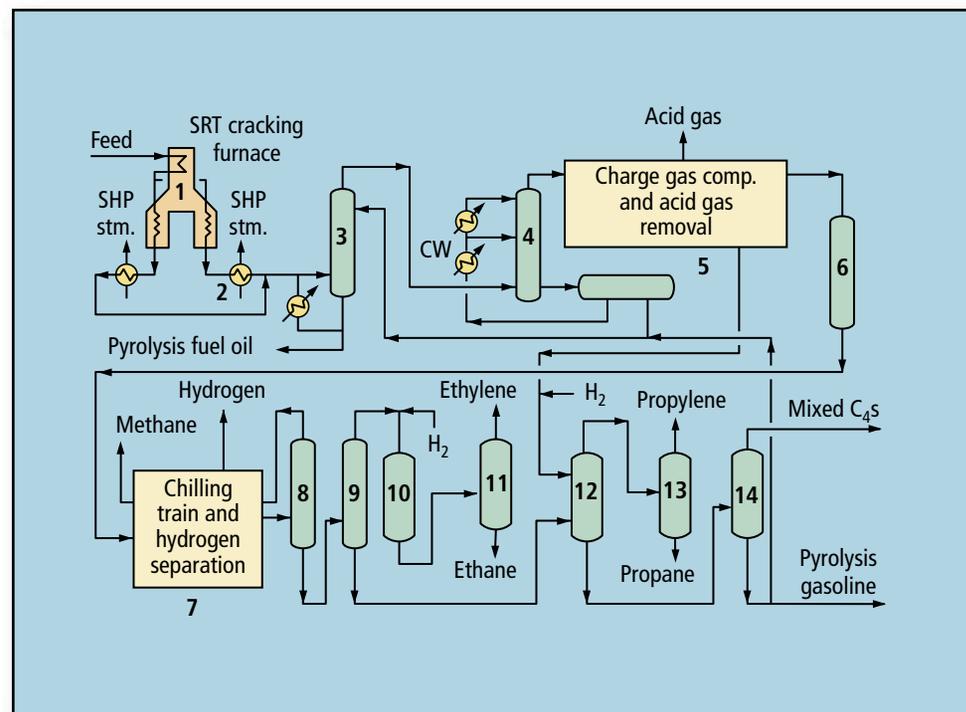
Application: To produce polymer-grade ethylene (99.95 vol%). Major byproducts are propylene (chemical or polymer-grade), a butadiene-rich C₄ stream, C₆ to C₈ aromatics-rich pyrolysis gasoline and high-purity hydrogen.

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).



A revised flow scheme eliminates ~25% of the equipment from this conventional flowsheet. It uses CDHydro hydrogenation for the selective hydrogenation of C₂ through C₄ acetylenes and dienes in a single tower; reduces the cracked-gas discharge pressure to 250 psig; uses a single refrigeration system to replace the three separate systems; and applies metathesis to produce up to 1/3 of the propylene product catalytically rather than by thermal cracking, thereby lowering energy consumption by ~15%.

Energy consumption: Energy consumptions are 3,300 kcal/kg of ethylene produced for ethane cracking and 5,000 kcal/kg of ethylene for naphtha

Ethylene, *continued*

feedstocks. Energy consumption can be as low as 4,000 kcal/kg of ethylene for naphtha feedstocks with gas turbine integration. As noted above, the new flow scheme reduces energy consumption by 14%.

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.

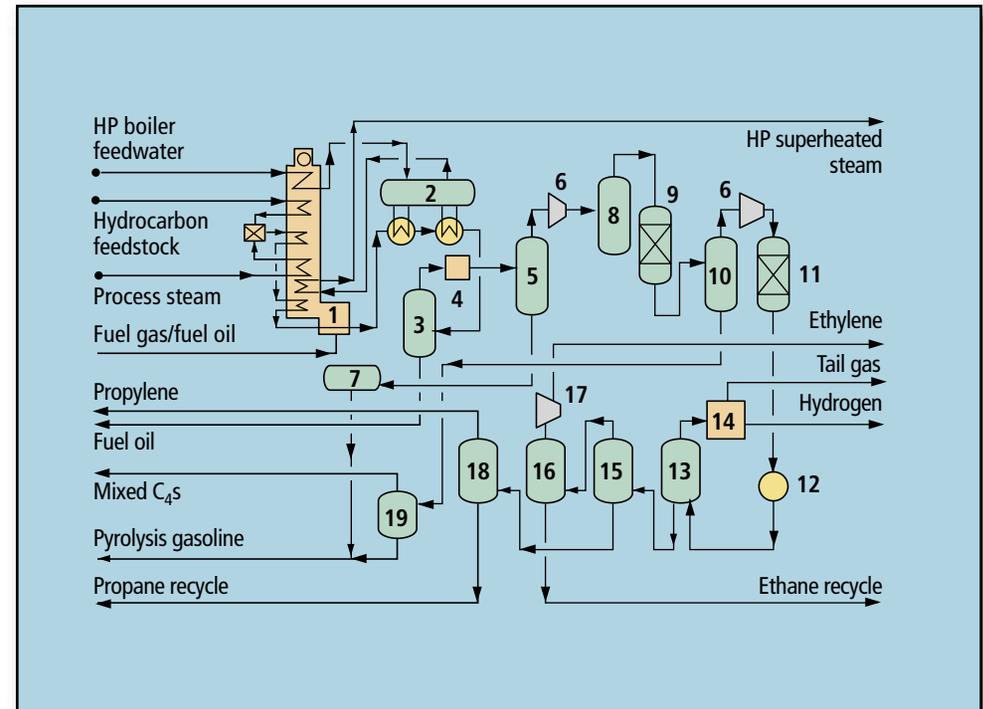
Ethylene

Application: High performance steam-cracking and recovery to produce polymer-grade ethylene and propylene, butadiene-rich mixed C_4 s, aromatic-rich pyrolysis gasoline, hydrogen and fuel streams. Cracking feedstocks range from ethane through vacuum gas oils.

Description: Kellogg Brown & Root's proprietary Selective Cracking Optimum REcovery (SCORE) olefins technology represents 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. ExxonMobil brings innovative technology as well as the benefits of extensive operating experience to further improve operability, reliability, and reduce production costs.

The SCORE pyrolysis furnace portfolio features the straight tube SC-1 design, which has a low reaction time (in the range of 0.1 seconds), and low operating pressures. The design and operating conditions produce higher olefin yields. The portfolio includes a range of designs to satisfy any requirements.

The pyrolysis furnace (1) effluent is processed for heat and product recovery in an efficient, reliable 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 deethanizer-first, depropanizer-first and demethanizer-first configurations are available. The depropanizer-first flow-scheme, primarily applicable to liquid crackers, is shown above. The similar, but simpler, deethanizer-first scheme is appropriate for ethane through ethane/propane gas crackers. These two schemes use front-end acetylene converter systems, which minimize green-oil production, and allow using low-pressure recovery towers. KBR also has extensive experience with the demethanizer-first flow-scheme, which can be offered to clients preferring that technology.



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 C_3 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 C_2 -splitter (16), which produces the polymer-grade ethylene product and the ethane stream, which is typically recycled to the furnaces as a feedstock. The deethanizer bottoms flows to the C_3 -splitter (18) where the polymer-grade propylene is recovered

Ethylene, *continued*

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.

Commercial plants: KBR has been involved in over 140 ethylene projects worldwide with single-train ethylene capacities up to 1.3 million tpy including 21 new grassroots ethylene plants since 1990.

Licensors: Kellogg Brown & Root, Inc.

Ethylene

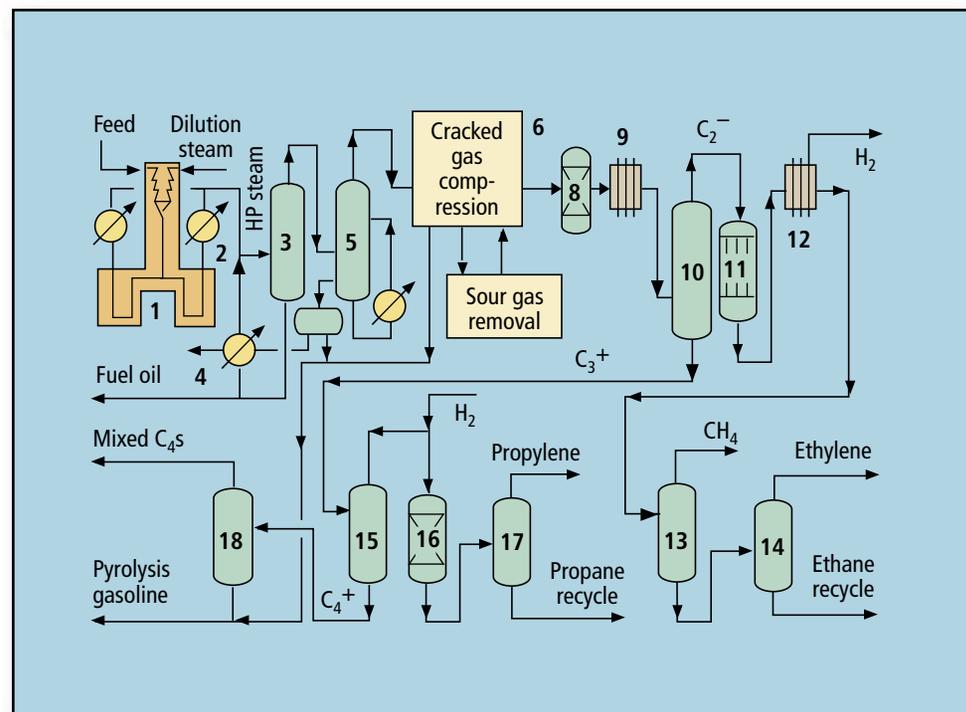
Application: To produce polymer-grade ethylene and propylene by thermal cracking of hydrocarbon fractions—from ethane through naphtha up to hydrocracker residue. Byproducts are a butadiene-rich C_4 stream, a C_6 – C_8 gasoline stream rich in aromatics and fuel oil.

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

The 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 by a water cycle (5) to provide heat to reboilers and process heaters. The cracked 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 before the final compressor stage.

The compressed cracked gas is further cooled (9) and fed to the recovery section: front-end deethanizer (10), isothermal front-end C_2 hydrogenation (11), cold train (12), demethanizer (13) and the heat-pumped low-pressure ethylene fractionator (14), which is integrated with 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).

The C_3 from the deethanizer bottoms (10) is depropanized (15), hydrogenated (16) to remove methyl acetylene and propadiene (16) and fractionated to recover polymer grade propylene. C_4 components are separated from heavier components in the debutanizer (18) to recover a C_4 product and a C_5 stream. The C_5 , together with the



hydrocarbon condensates from the hot section, forms an aromatic-rich gasoline product.

Economics: Ethylene yields vary between 25%, 35%, 45% and 83% for gas oils, naphtha, LPG and ethane respectively. The related specific energy consumption range is 6,000/5,400/4,600 and 3,800 kcal/kg ethylene. Typical installation costs for a world-scale ISBL gas (naphtha) cracker on a Gulf Coast basis are 500 (750) US\$/ton installed ethylene capacity.

Commercial plants: Over 15 million tons of ethylene are produced in more than 40 plants worldwide. Many plants have been expanded in capacity up to 50% and more.

Ethylene, *continued*

Recent awards for world-scale ethylene plants include Borouge in Abu Dhabi, Optimal in Malaysia, Amir Kabir and Marun in Iran and TVK II in Hungary. The Marun plant is one of the world's largest crackers with a capacity of 1.1-million mtpy ethylene and 200,000-mtpy propylene.

Licensors: Linde AG.

Ethylene

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

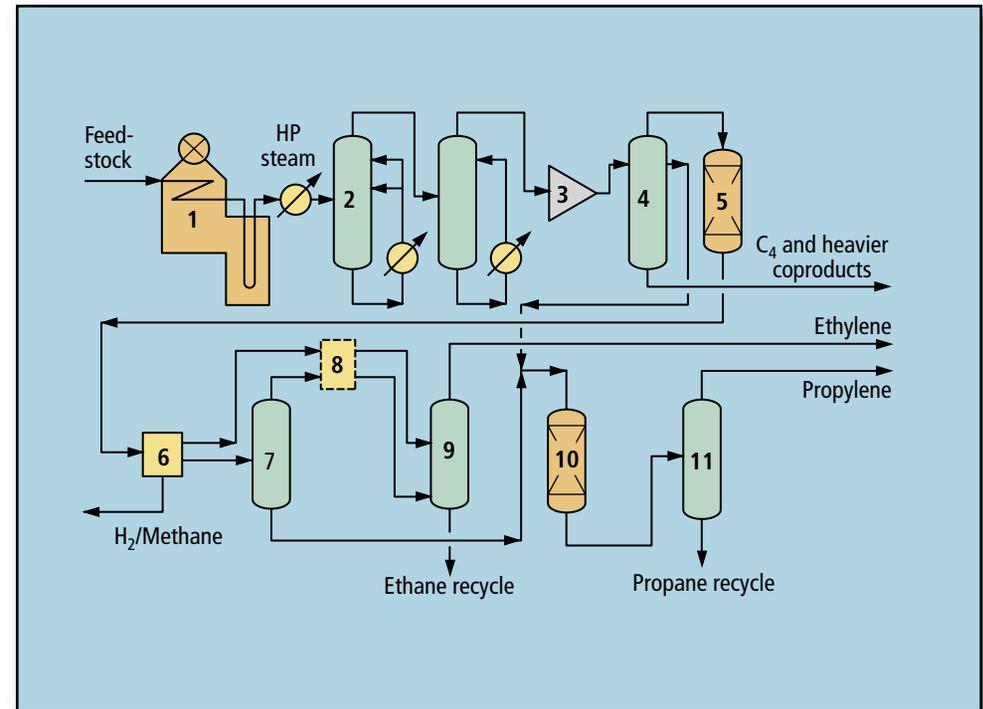
1. USC (ultra selective cracking)—Pyrolysis and quench systems
2. ARS/HRS (advanced recovery system with heat-integrated rectifier simplification)—Cold fractionation.

Plants are characterized by high operational reliability, rapid startups and ability to meet environmental requirements.

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 and pyrolysis fuel oil and gasoline distillate fractionated (2). Cracked gas (C_4 and lighter) is then compressed (3), scrubbed with caustic to remove acid gases and dried prior to fractionation. C_2 and lighter components are separated from the C_4 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/HRS (6).

ARS minimizes refrigeration energy by using distributed distillation and simultaneous heat and mass transfer in the dephlegmator (exclusive arrangement with Air Products) or HRS system. Two C_2 streams of varying composition are produced. Hydrogen and methane are separated overhead.

The heavier C_2 stream is deethanized (7) and C_2 overhead passes to the MP ethylene-ethane fractionator (9) integrated with C_2 refrigeration system. The lighter C_2 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).



C_3 s are combined and hydrogenated to remove methyl acetylene and propadiene (10). Polymer or chemical-grade propylene is then produced overhead from the C_3 superfractionator (11).

C_4 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 due to chilling/prefractionation in the dephlegmator or HRS system, 2. reduced methane content in feed to demethanizer, 3. partial deethanizer bypassing, 4. dual feed ethylene fractionator (lower reflux ratio), and 5. reduced refrigeration demand (approx. 75%).

Ethylene, *continued*

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 120 ethylene units have been built by Stone & Webster. Expansion techniques based on ARS/HRS technology have increased original capacities by as much as 100%.

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

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 transfer-line 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.

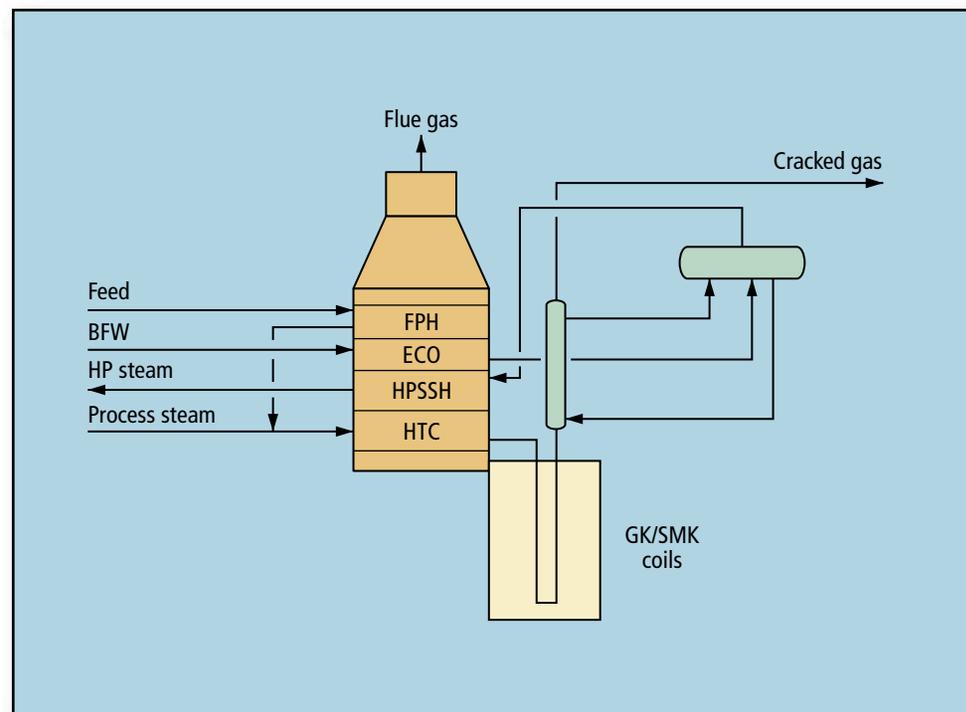
Performance data:

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.

Commercial plants: Over 450 installations since the mid-1960s.

Licensor: Technip.



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 using the T-PAR process for gas separation and product purification from raw cracked gas.

Description: Effluents from cracking furnaces are cooled and processed for tar and heavy-gasoline removal.

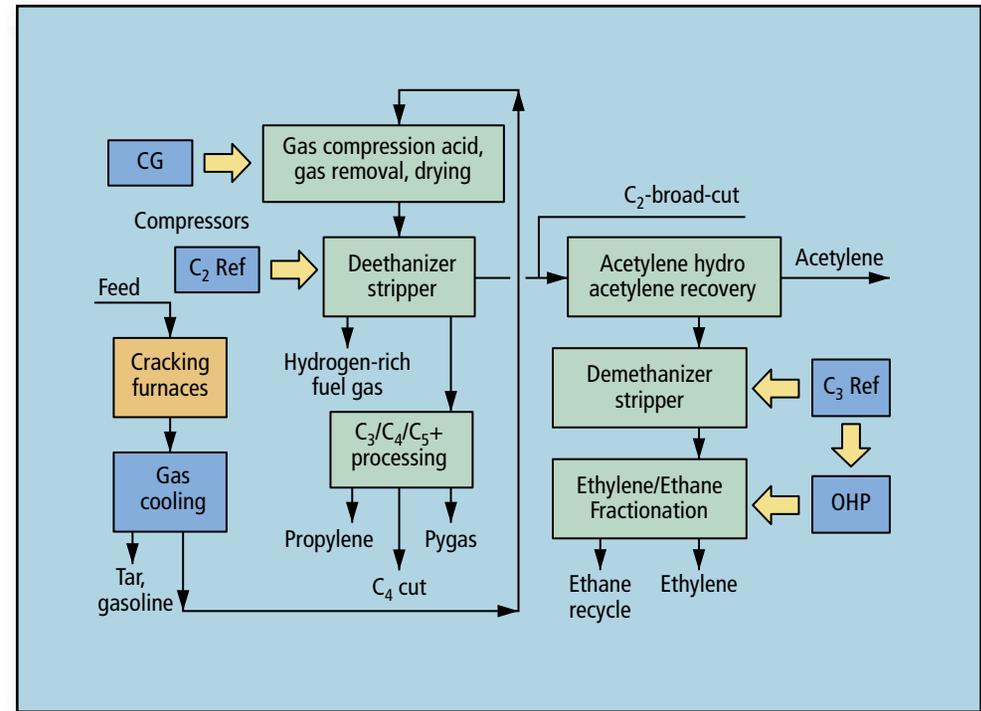
A multistage compressor, driven by a steam turbine, compresses the cooled gas. LP and HP condensates are stripped in two separate strippers where medium gasoline is produced and part of the C_3^+ cut is recovered respectively. A caustic scrubber removes acid gases.

Compressed gas at 450 psig is dried and then chilled. A multi-stream heat exchanger chills the tail gas to -265°F . Liquid condensates are separated at various temperatures, such as -30°F , -65°F , -100°F and -140°F , and are reheated against incoming cracked gas. The partially vaporized streams are sent to a deethanizer stripper operating at about 320 psig. The bottoms C_3^+ stream is sent to propylene and heavys recovery.

The overhead is reheated and enters an adiabatic acetylene hydrogenation reactor, which transforms the acetylene selectively to ethylene and ethane. As an alternate, a solvent-recovery process can be applied without reheating the gas.

Reactor effluent is chilled and light-ends are separated from the C_2 -hydrocarbons. The demethanizer overhead is processed for ethylene recovery while the bottoms is sent to ethylene/ethane separation. An open heat-pump splitter is applied, thus sending ethylene product to the gas pipeline from the discharge of the ethylene-refrigerant compressor.

Dilute ethylene for chemical applications, such as styrene production, can be withdrawn downstream of the hydrogenation reactor. The ethylene content is typically 60 vol%. Catalyst suppliers have tested the hydrogenation step, and commercially available front-end catalysts are suitable for this application.



Economics: The advantages of this process are low equipment costs (viz. the deethanizer system and ethylene/ethane separation) and reliability of the acetylene hydrogenation due to low excess hydrogen at the reactor inlet. The refrigeration compressor benefits from low specific power and suction volume, while the cracked-gas compressor processes above-ambient-temperature gas.

Commercial plants: Technip is commercializing the T-PAR process on a case-by-case basis.

Licensor: Technip.

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 C₅-C₁₁ naphtha into a rich n-paraffins stream and a stream depleted of n-paraffins.

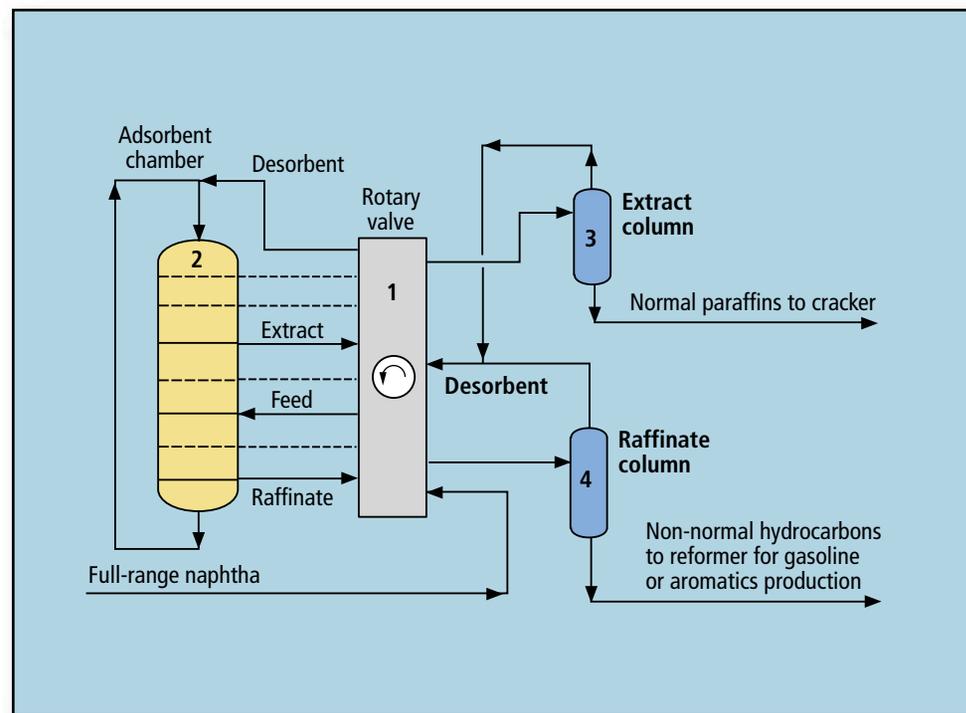
Description: The separation takes place in an adsorption chamber (2) that is divided into a number of beds. Each bed contains proprietary shape-selective adsorbent. Also, each bed in the chamber is connected to a rotary valve (1). The rotary valve is used along with the shape-selective adsorbent to simulate a counter-current moving bed 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: Capital costs and economics depend on feed composition as well as the desired increase in ethylene and propylene production in the steam cracker.

Licensor: UOP LLC.



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 C₂–C₅⁺ cuts. A condensate containing mercury may have negative added-value as a gas field product.

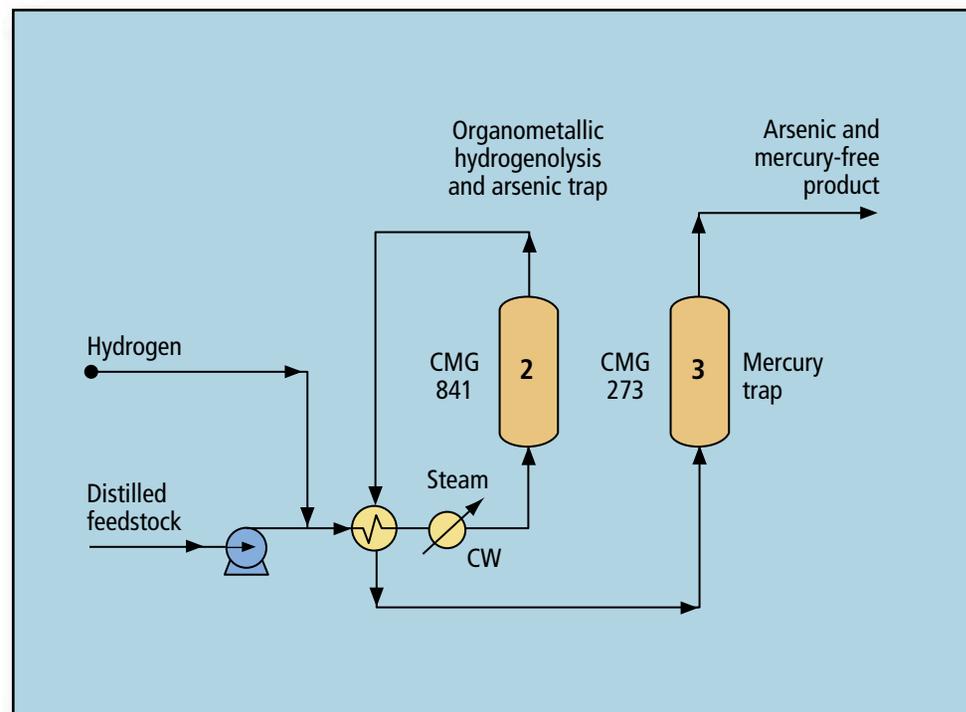
Description: Three RAM processes are available to remove arsenic (RAM I); arsenic, mercury and lead (RAM II); and arsenic, mercury and sulfur from liquid hydrocarbons (RAM III). Described above is the RAM II process. Feed is heated by exchange with reactor effluent and steam (1). It is then hydrolyzed 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 2004 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, US\$/bpd	130	180
Utilities, US\$/bpd	0.08	0.23
Catalyst cost, US\$/bpd	0.03	0.03

Commercial plants: Fifteen 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," Sec-

Ethylene feed pretreatment—mercury, arsenic and lead removal, *continued*

and European Petrochemicals Technology Conference, Prague, 2000.

Licensors: Axens, Axens NA.

Ethylene glycol, mono (MEG)

Application: To produce mono-ethylene glycol (MEG) from ethylene oxide (EO).

Description: EO in an aqueous solution is reacted with CO₂ in the presence of a homogeneous catalyst to form ethylene carbonate (1). The ethylene carbonate subsequently is reacted with water to form MEG and CO₂ (3). The net consumption of CO₂ in the process is nil since all CO₂ converted to ethylene carbonate is released again in the ethylene carbonate hydrolysis reaction. Unconverted CO₂ from the ethylene carbonate reaction is recovered (2) and recycled, together with CO₂ released in the ethylene carbonate hydrolysis reaction.

The product from the hydrolysis reaction is distilled to remove residual water (4). In subsequent distillation columns high-purity MEG is recovered (5) and small amounts of co-produced di-ethylene glycol are removed (6). The homogeneous catalyst used in the process concentrates in the bottom of column 5 and is recycled back to the reaction section.

The process has a MEG yield of 99%+. Compared to the thermal glycol process, steam consumption and wastewater production are relatively low, the latter because no contaminated process steam is generated.

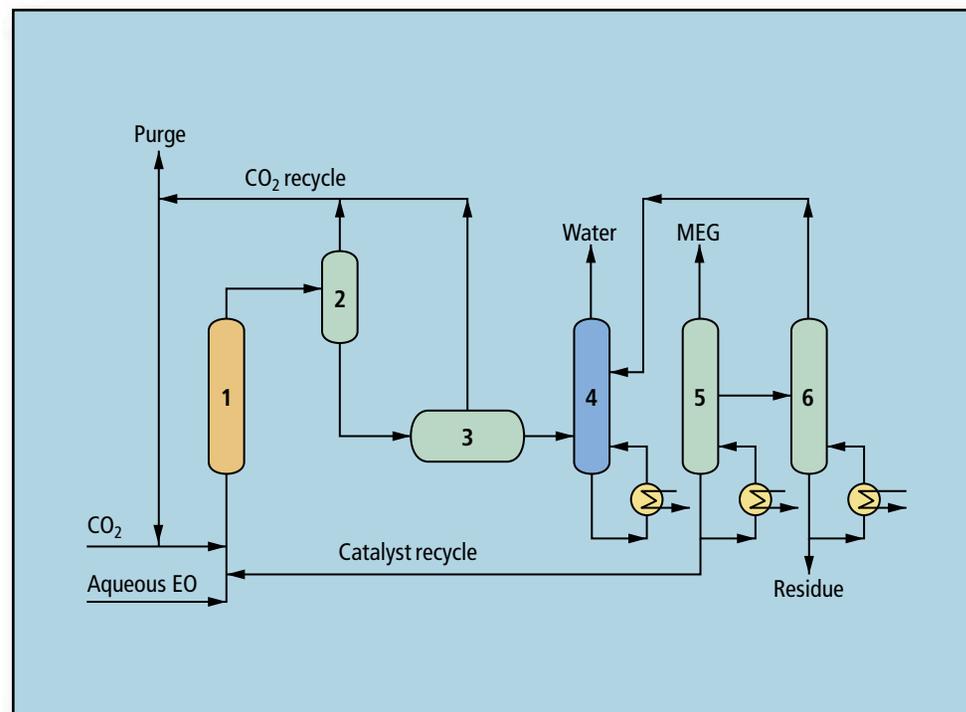
MEG quality and performance of the MEG product in derivatives (polyesters) manufacturing have been demonstrated to be at least as good as and fully compatible with MEG produced via the thermal process.

Commercial plants: The first commercial plant is currently under construction in Taiwan. Two other process licenses have been awarded.

The combination of this process with the Shell EO process is licensed under the name **Shell OMEGA** process.

Licensor: Shell International Chemicals B.V.

Contact: ct-amsterdam@shell.com



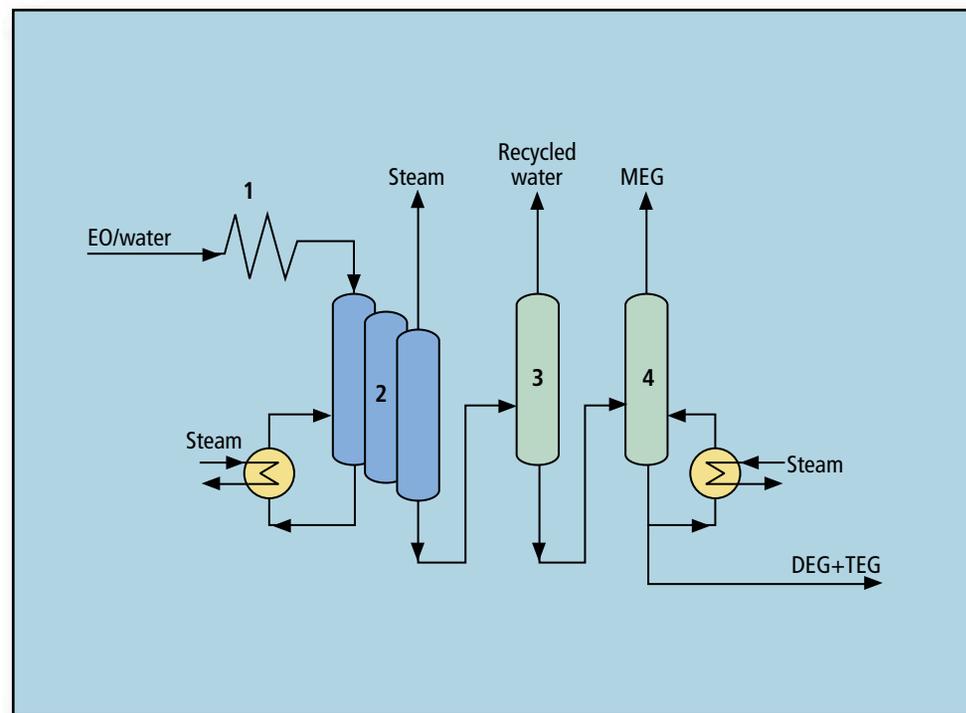
Ethylene glycol

Application: To produce ethylene glycols (MEG, DEG, TEG) from ethylene oxide (EO) using Dow's 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 react 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 (3) 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 heavy glycols. The ability to operate in catalyzed or uncatalyzed mode provides flexibility to the manufacturer to meet changing market demands.



Commercial plants: 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.

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 mono-ethylene glycol (MEG) with di-ethylene glycol (DEG) and tri-ethylene glycol (TEG) as co-products in minor amounts. Excess water, required to achieve a high selectivity to MEG, is evaporated in a multi-stage evaporator (2, 3, 4). The last evaporator produces low-pressure steam that is used as a heating medium at various locations in the plant. The resulting crude glycols mixture is subsequently purified and fractionated in a series of vacuum columns (5, 6, 7, 8).

The selectivity to MEG can be influenced by adjusting the glycol reactor feed composition.

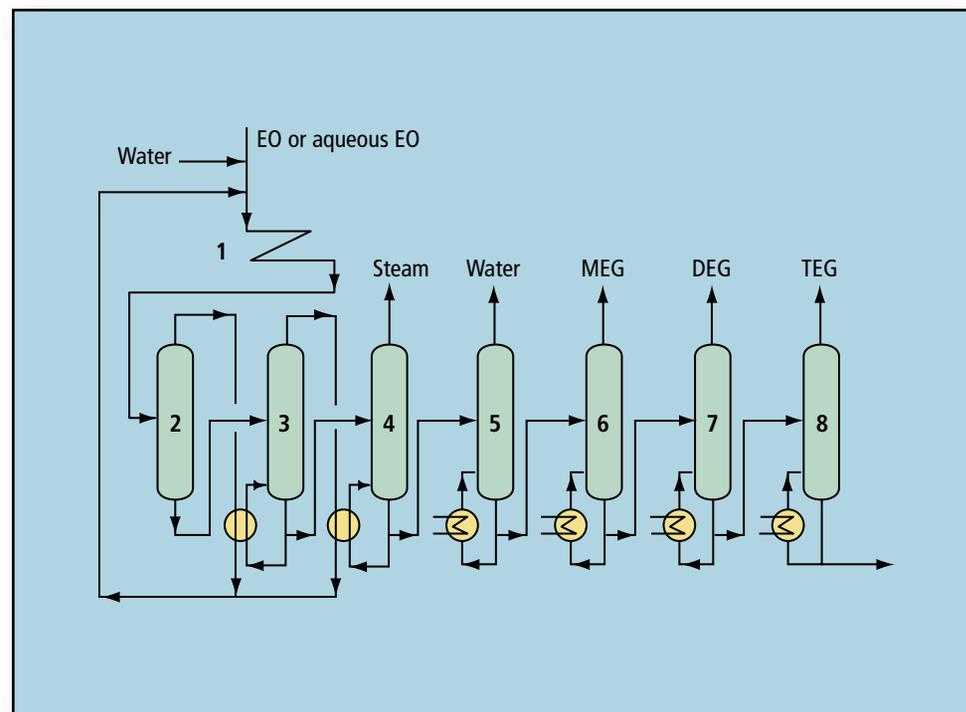
Most MEG plants are integrated with EO plants. In such an integrated EO/MEG facility, the steam system can be optimized to fully exploit the benefits of high-selectivity catalyst applied in the EO plant. However, standalone MEG plants have been designed and built.

The quality of glycols manufactured by this process ranks amongst the highest in the world. It consistently meets the most stringent specifications of polyester fiber and PET producers.

Commercial plants: Since 1958, more than 60 Shell-designed MEG plants have been commissioned or are under construction.

Licensors: Shell International Chemicals B.V.

The combination of this process with the Shell EO process is licensed under the name **Shell MASTER** process.



Ethylene oxide

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

Description: Ethylene and oxygen in a diluent gas made up of a mixture of mainly methane or nitrogen along with carbon dioxide and argon are fed to a tubular catalytic reactor (1). The temperature of reaction is controlled by adjusting the pressure of the steam which is generated in the shell side of the reactor and removes the heat of reaction. The EO produced is removed from the reaction gas by scrubbing with water (2) after heat exchange with the circulating reactor feed gas.

Byproduct CO_2 is removed from the scrubbed reaction gas (3, 4) before it is recompressed and returned to the reaction system where ethylene and oxygen concentrations are restored before returning to the EO reactor.

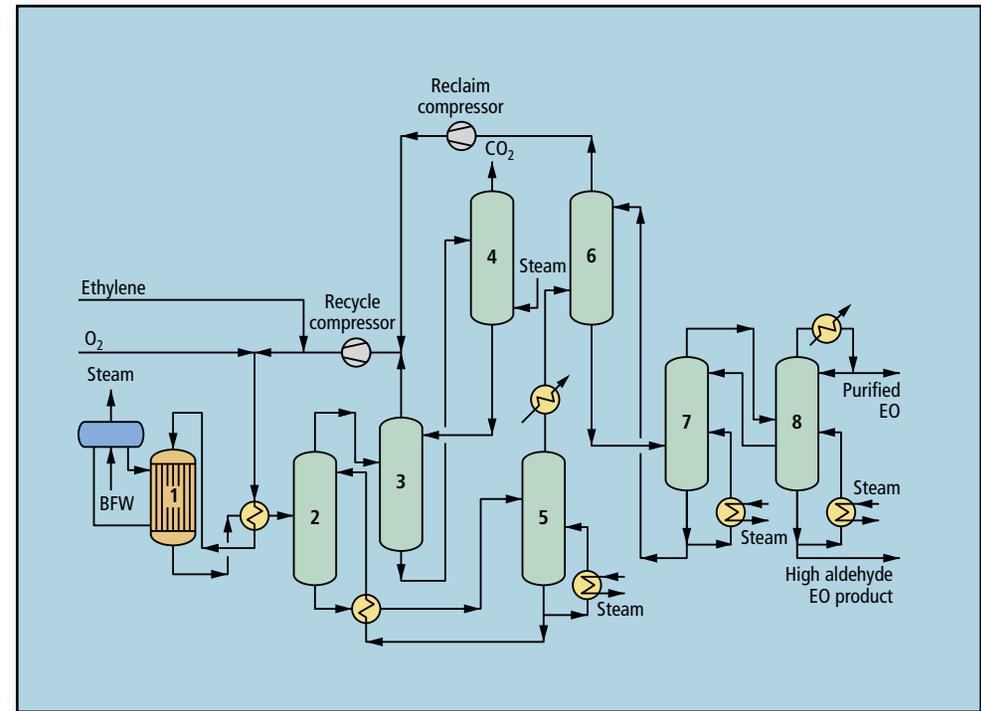
The EO is steam stripped (5) from the scrubbing solution and recovered as a more concentrated water solution (6) for feed to an EO purification system (7, 8) where purified product is made along with a high aldehyde EO product.

Product quality: The EO product meets the low aldehyde specification of 10 ppm maximum, which is required for EO derivatives production.

Product yield: The ethylene yield to purified EO is 1.2 kg per kg ethylene feed. In addition, a significant amount of technical-grade glycol may be recovered by processing waste streams.

Commercial plants: Nearly 50 purified EO projects have been completed or are being designed. This represents a total design capacity of about 4 million metric tons of purified EO with the largest plants exceeding 200,000 mtpy.

Licensors: Scientific Design Company, Inc.



Ethylene oxide

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

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-containing high-selectivity catalyst is used that has been improved significantly over the years. Methane is used as ballast gas. Heat generated by the reaction is recovered by boiling water at elevated pressure on the reactor's shell-side; the resulting high-pressure steam is used for heating purposes at various locations within the process.

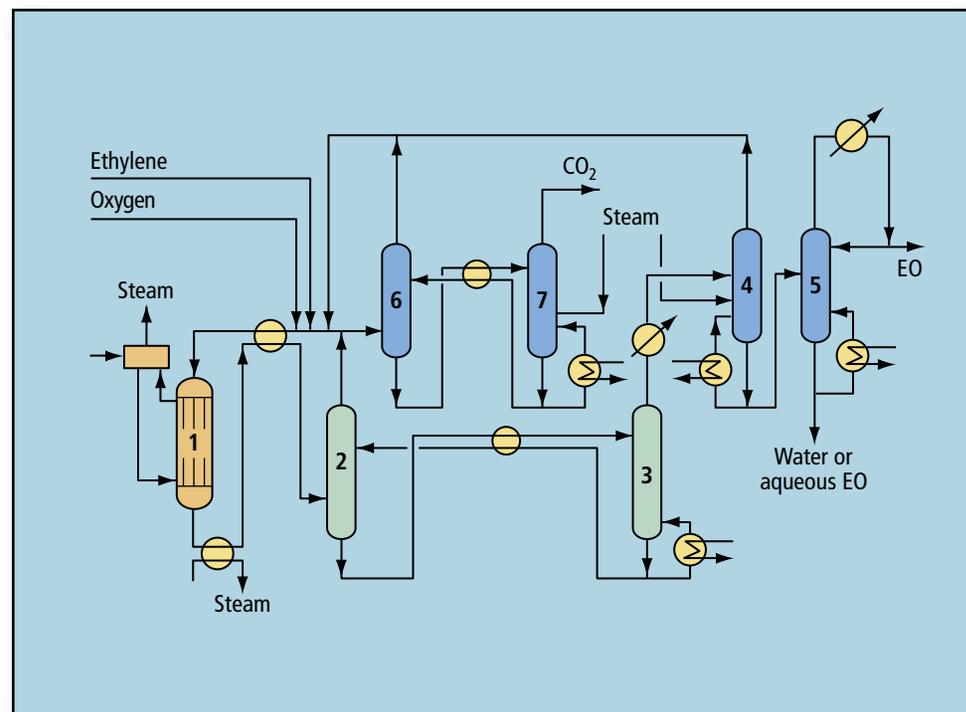
EO contained in the reactor product-gas is absorbed in water (2) and further concentrated in a stripper (3). Small amounts of co-absorbed ethylene and methane are recovered from the crude EO (4) and recycled back to the EO reactor. The crude EO can be further concentrated into high-purity EO (5) or routed to the glycols plant (as EO/water feed).

EO reactor product-gas, after EO recovery, is mixed with fresh feed and returned to the EO reactor. Part of the recycle gas is passed through an activated carbonate solution (6, 7) to recover CO₂, a byproduct of the EO reaction that has various commercial applications.

Most EO plants are integrated with fiber-grade mono-ethylene glycol (MEG) production facilities. In such an integrated EO/MEG facility, the steam system can be optimized to fully exploit the benefits of high-selectivity catalyst.

When only high-purity EO is required as a product, a small amount of technical-grade MEG inevitably is co-produced.

Yields: Modern plants are typically designed for and operate at a molar EO catalyst selectivity approaching 90% with fresh catalyst and 86–87% as an average over 3 years catalyst life, resulting in an average EO production of about 1.4 tons per ton of ethylene. However, the technology is flexible and the plant can be designed tailor-made to customer requirements or different operating time between catalyst changes.



Commercial plants: Since 1958, more than 60 Shell-designed plants have been commissioned or are under construction. Approximately 40% of the global capacity of EO equivalents is produced in Shell-designed plants.

Licensors: Shell International Chemicals B.V.

The Shell EO process is licensed under the name **Shell MASTER** process when combined with the Shell ethylene glycols process, and under the name **Shell OMEGA** process when combined with the Shell process for selective MEG production via ethylene carbonate intermediate.

Ethylene oxide

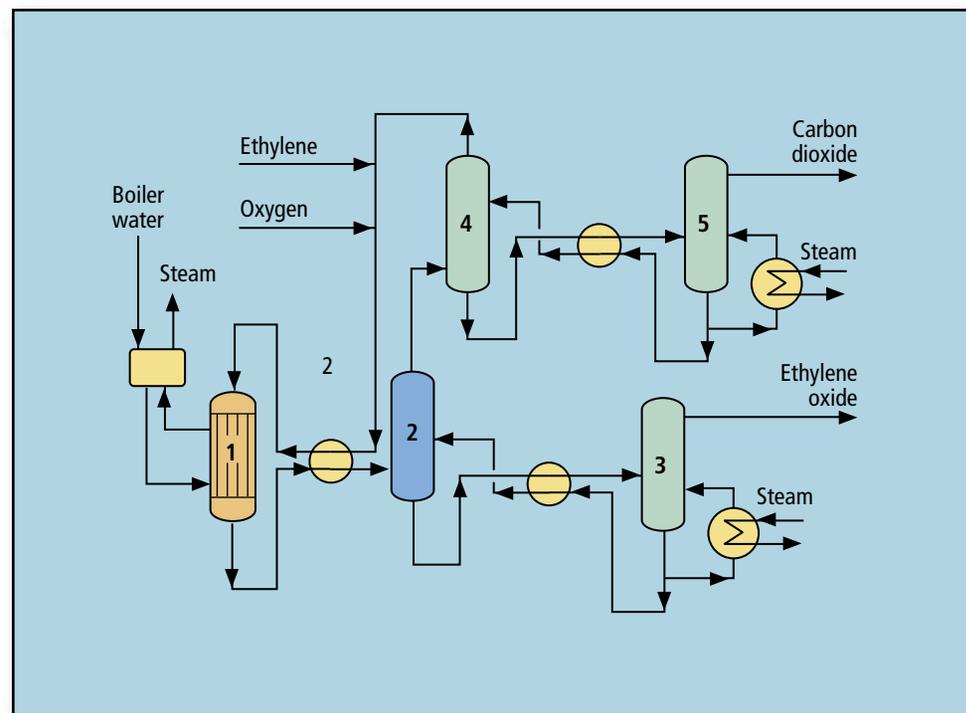
Application: To produce ethylene oxide (EO) from the direct oxidation of ethylene using the Dow Meteor process.

Description: The Meteor Process, a technology first commercialized 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 with lower facility investment costs.

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 provide 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.



Commercial plants: Union Carbide was the first to commercialize the direct oxidation process for EO in the 1930s. Since 1954, 18 Union Carbide-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 Union Carbide-designed plants.

Licensor: Union Carbide Corp., a subsidiary of The Dow Chemical Co.

Ethylene oxide/Ethylene glycols

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

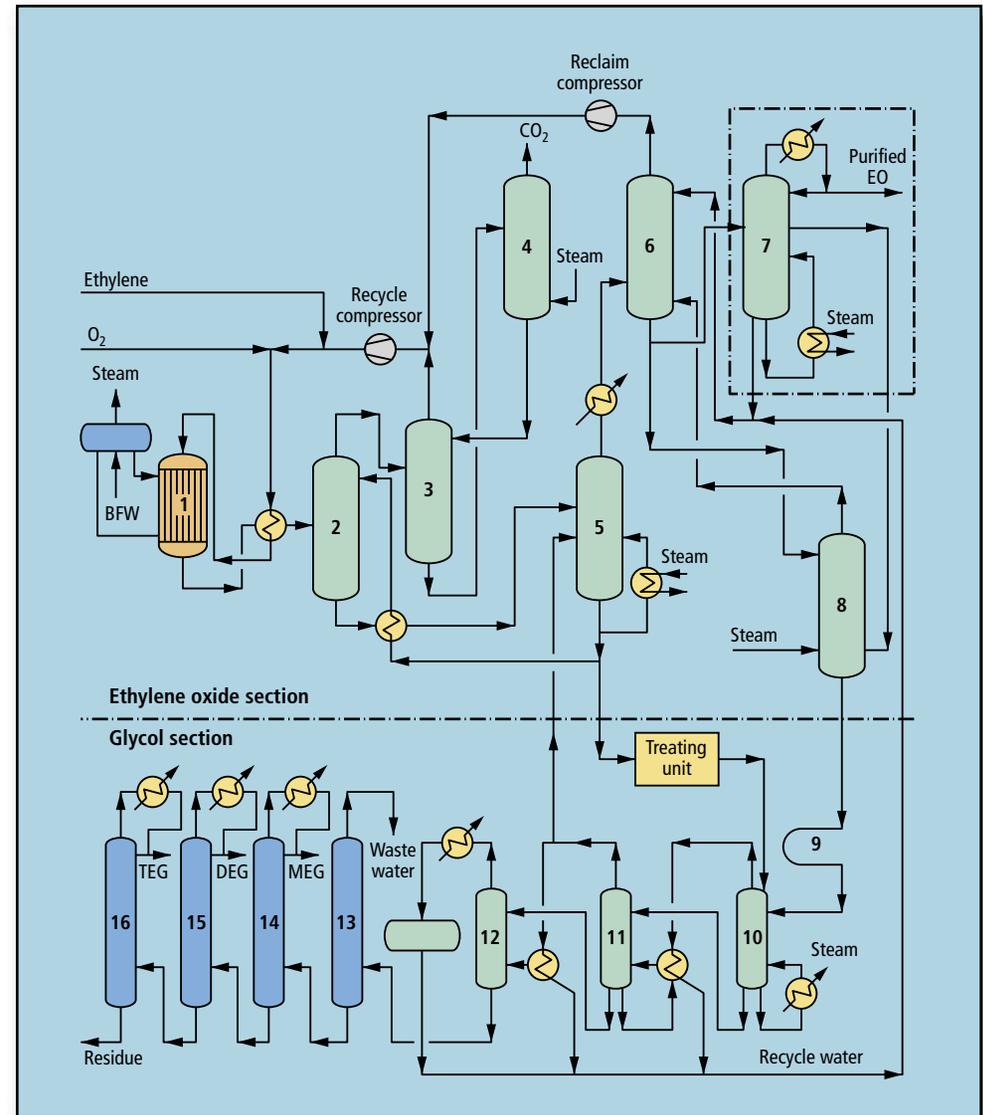
Modern EO/EG plants are highly integrated units where EO produced in the EO reaction system can be recovered as glycols (MEG, DEG and TEG) with a co-product of purified EO, if desired. Process integration allows for a significant utilities savings as well as the recovery of all bleed streams as high-grade product, which would otherwise have been recovered as a lesser grade product. The integrated plant recovers all MEG as fiber-grade product and EO product as low-aldehyde product. The total recovery of the EO from the reaction system is 99.7% with only a small loss as heavy glycol residue.

Description: Ethylene and oxygen in a diluent gas made up of a mixture of mainly methane or nitrogen along with carbon dioxide (CO₂) and argon are fed to a tubular catalytic reactor (1). The temperature of reaction is controlled by adjusting the pressure of the steam which is generated in the shell side of the reactor and removes the heat of reaction. The EO produced is removed from the reaction gas by scrubbing with water (2) after heat exchange with the circulating reactor feed gas.

Byproduct CO₂ is removed from the scrubbed reaction gas (3, 4) before it is recompressed and returned to the reaction system where ethylene and oxygen concentrations are restored before returning to the EO reactor.

The EO is steam stripped (5) from the scrubbing solution and recovered as a more concentrated water solution (6) that is suitable for use as feed to a glycol plant (8) or to an EO purification system (7). The stripped water solution is cooled and returned to the scrubber.

The glycol plant feed along with any high aldehyde EO bleeds from the EO purification section are sent to the glycol reactor (9) and then to a multi-effect evaporation train (10, 11, 12) for removal of the bulk of the water from the glycols. The glycols are then dried (13) and sent to the glycol distillation train (14, 15, 16) where the MEG, DEG and TEG products are recovered and purified.



Ethylene oxide/Ethylene glycols, *continued*

Product quality: The SD process has set the industry standard for fiber-grade MEG quality. When EO is produced as a co-product it meets the low aldehyde specification requirement of 10-ppm aldehyde maximum, which is required for EO derivative units.

Yield: The ethylene yield to glycols is 1.81 kg of total glycols per kg of ethylene. The ethylene yield for that portion of the production going to purified EO is 1.31 kg of EO product / kg of ethylene.

Commercial plants: Over 90 EO/EG plants using SD technology have been built. The world's largest MEG plant with a capacity of 700,000 mtpy of MEG is presently in design and follows the startup of a 600,000-mtpy plant in October 2004.

Licensors: Scientific Design Company, Inc.

Formaldehyde

Application: To produce aqueous formaldehyde (AF) or urea formaldehyde precondensate (UFC) from methanol using the *Haldor Topsøe Formaldehyde SR process* comprising two reactors in series.

Description: Air and recycle gas are compressed by the blower (1) and then mixed with liquid methanol that is injected through spray nozzles. The mixture is preheated to about 200°C by heat exchange with hot circulating oil in the heat exchanger (2) after which the gas is successively passed to the two series reactors (3 and 4).

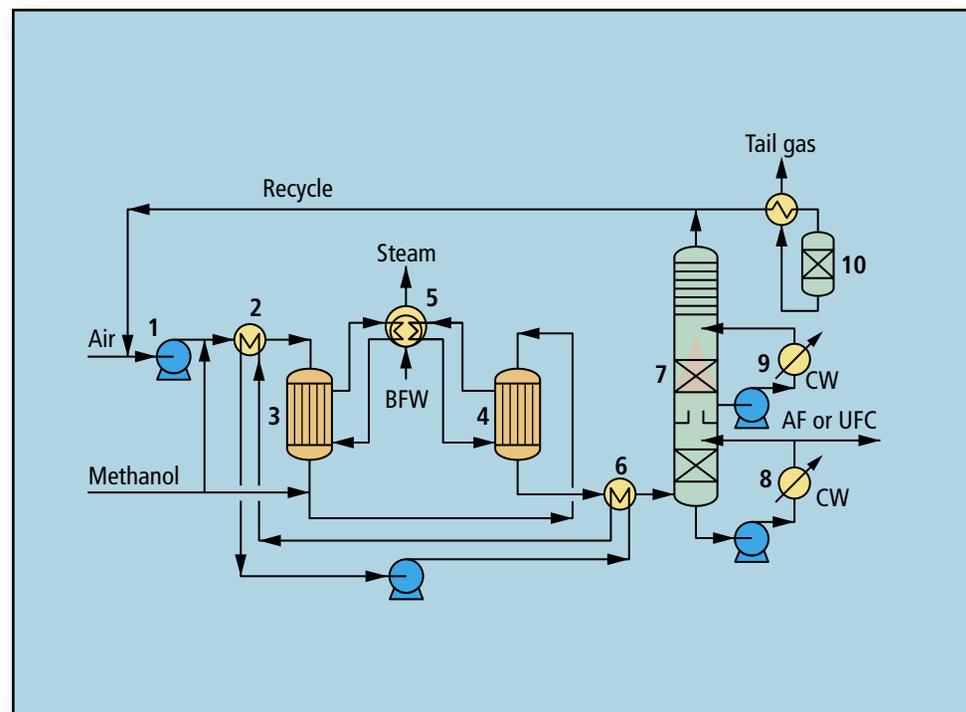
Additional methanol is injected into the gas between the two reactors. The reactors contain many tubes filled with FK-2 catalyst, where methanol and oxygen react to make formaldehyde. Reaction heat is removed by a bath of boiling heat-transfer oil. Hot oil vapor is condensed in the waste-heat boiler (5), thus generating steam at up to 40 bar pressure. Before entering the absorber (7), the reacted gas is cooled in the after cooler (6) and reheats the circulating oil from the process-gas heater (2).

In the absorber, the formaldehyde is absorbed in water or urea solution. Heat is removed by one or two cooling circuits (8, 9). From the lower circuit (8), product in the form of either AF or UFC is withdrawn. Scrubbed gas from the absorber is split in two streams—recycle gas and tail gas. The tail gas is vented after any organic impurities are catalytically incinerated in the reactor (10). Thus, the tail-gas purity conforms to the environmental standards for any country.

With regard for the catalyst, the percentage of methanol that can be added to a formaldehyde reactor is limited to about 9-vol%. Using two reactors in series higher production yields are achievable with the same gas flow than what would be possible in a plant with only one reactor (or a plant with two reactors in parallel).

Advantages of series reactors vs. single or parallel reactors are:

- Lower capital cost due to reduced size of equipment and piping



- Longer catalyst life: 30–36 months in reactor I, 18 months in reactor II
- Lower electricity consumption and higher steam production
- Higher conversion of methanol, therefore less methanol in product
- The *Haldor Topsøe Formaldehyde SR process* is well-suited to expand existing formaldehyde plants—up to 100% capacity increase may be achieved.

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

Formaldehyde, *continued*

Product	55 wt% AF	85 wt% UFC
Methanol, kg	420–425	425–430
70% urea solution, kg	–	220
Process water, kg	250	72
Water, cooling, m ³	42	38
Electricity, kWh	49	52

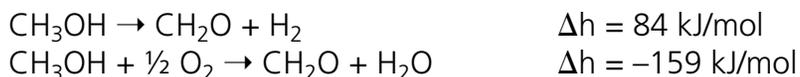
Commercial plants: Three commercial SR units built, all are operating successfully. Three additional units are under construction.

Licensors: Haldor Topsøe A/S.

Formaldehyde

Application: Formaldehyde as a liquid solution of 37–52 wt% is primarily used in the production of polyoxymethylene (POM) and hexamethylenetetramine as well as synthetic resins in the wood industry.

Description: Formaldehyde solutions are produced by oxidation with methanol in the air. In the UIF process, the reaction occurs on the surface of a silver-crystal catalyst at temperatures of 620°C–680°C, where the methanol is dehydrated and partly oxidized:



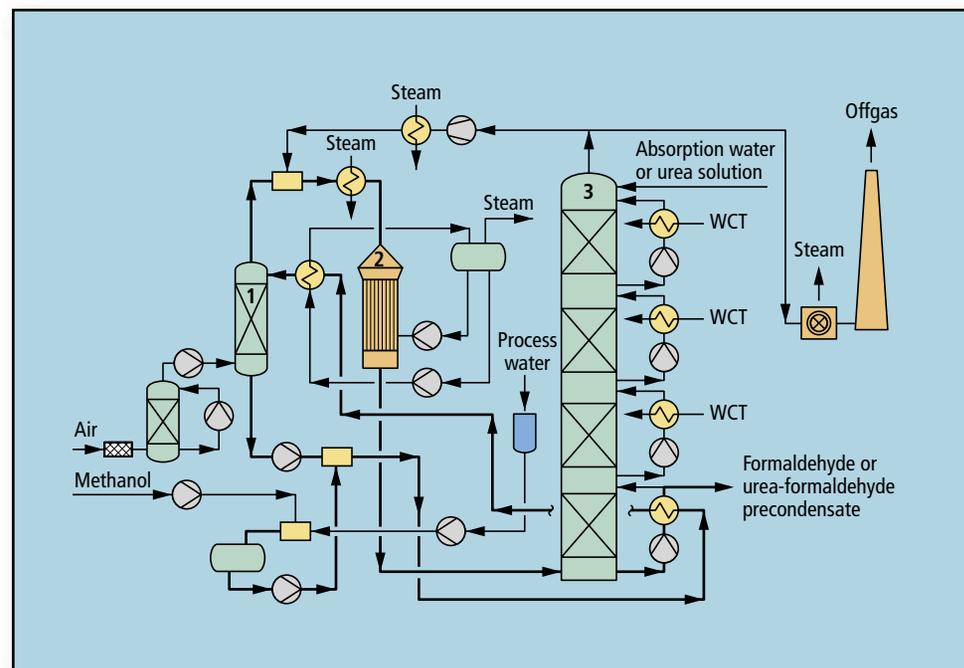
The methanol/water mixture, adjusted for density balance and stored in the preparation tank, is continuously fed by pump to the methanol evaporator (1). The required process air is sucked in by a blower via a filter and air scrubber into the methanol evaporator.

From here the methanol/water/air mixture enters the reactor (2) where the conversion of methanol to formaldehyde occurs. Because the reaction is exothermic, the required temperature is self-maintained once the ignition has been executed.

The reaction gases emerging from catalysis contain formaldehyde, water, nitrogen, hydrogen and carbon dioxide as well as nonconverted methanol. They are cooled to 150°C in a waste-heat boiler directly connected to the reactor. The amount of heat released in the boiler is sufficient for heating the methanol evaporator. The reaction gases enter a 4-stage absorption tower (3), where absorption of formaldehyde occurs in counter-flow via aqueous formaldehyde solution and cold demineralized water. The final formaldehyde solution is removed from the first absorption stage.

Waste gas from the absorption tower with a heating value of approximately 2000 kJ/m³ is burned in a post connected thermal combustion unit. The released heat can be used to produce high-pressure steam or thermal oil heating.

By recycling a part of waste gas to the reactor, formaldehyde concentrations up to 52 wt% in the final solution can be reached.



To produce urea/formaldehyde precondensate, an aqueous urea solution in place of absorption water is fed into the absorption tower.

Economics: Due to the waste-gas recycling system, the methanol content in the formaldehyde solution can be reduced to less than 1 wt.% and formic acid less than 90 ppm.

Typical consumption figures per 1,000 kg of formaldehyde solution (37 wt%) are:

Methanol, kg	445
Water, kg	390
Electricity, kWh	38
Water, cooling, m ³	40

Licensor: Uhde Inventa-Fischer.

Hydrogen

Application: Production of hydrogen (H_2) from hydrocarbon (HC) feedstocks by steam reforming.

Feedstocks: Ranging from natural gas to heavy naphtha as well as potential refinery offgases. Many recent refinery hydrogen plants have multiple feedstock flexibility, either in terms of backup or alternative or mixed feed. Automatic feedstock change-over has also successfully been applied by Technip in several modern plants with multiple feedstock flexibility.

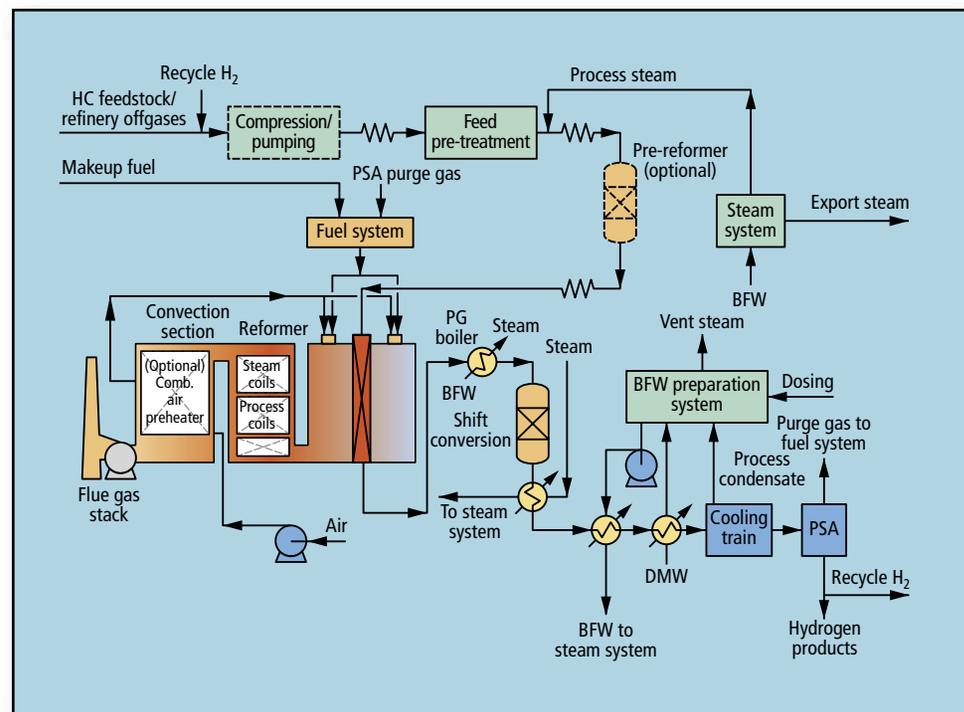
Description: The generic flowsheet consists of feed pre-treatment, pre-reforming (optional), steam-HC reforming, shift conversion and hydrogen purification by pressure swing adsorption (PSA). However, it is often tailored to satisfy specific requirements.

Feed pre-treatment normally involves removal of sulfur, chlorine and other catalyst poisons after preheating to 350–400°C.

The treated feed gas mixed with process steam is reformed in a fired reformer (with adiabatic pre-reformer upstream, if used) after necessary super-heating. The net reforming reactions are strongly endothermic. Heat is supplied by combusting PSA purge gas, supplemented by make-up fuel in multiple burners in a top-fired furnace.

Reforming severity is optimized for each specific case. Waste heat from reformed gas is recovered through steam generation before the water-gas shift conversion. Most of the carbon monoxide (CO) is further converted to hydrogen. Process condensate resulting from heat recovery and cooling is separated and generally reused in the steam system after necessary treatment. The entire steam generation is usually on natural circulation, which adds to higher reliability. The gas flows to the PSA unit that provides high-purity hydrogen product (up to < 1 ppm CO) at near inlet pressures.

Typical specific energy consumption based on feed + fuel – export steam ranges between 3 Gcal/ KNm^3 and 3.5 Gcal/ KNm^3 (330–370 Btu/scf) LHV, depending upon the feedstock, plant capacity, optimization



criteria and steam export requirements. Recent advances include integration of hydrogen recovery and generation and recuperative (post-) reforming, also for capacity retrofits.

Commercial plants: Technip has been involved in over 240 hydrogen plants worldwide.

Licensors: Technip.

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.

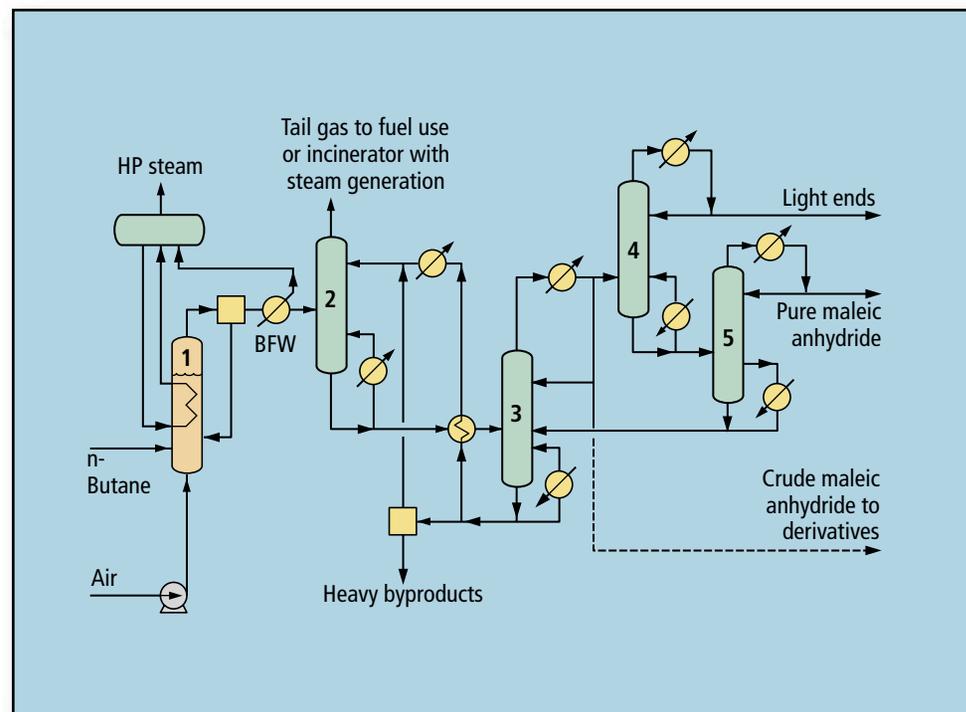
Description: N-butane and air are fed to a fluid-bed catalytic reactor (1) to produce maleic anhydride. The fluid-bed reactor eliminates hot spots and permits operation at close to the stoichiometric reaction mixture. This results in a greatly reduced air rate relative to fixed-bed processes and translates 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 nonaqueous product recovery system results in superior product quality and large savings in steam consumption. It also 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 with a total capacity of 200,000 mtpy. The largest commercial installation is Lonza's 55,000-mtpy plant in Ravenna, Italy. Second generation process optimizations and catalyst have elevated the plant performances since 1998.

Licensor: ABB Lummus Global/Lonza Group.



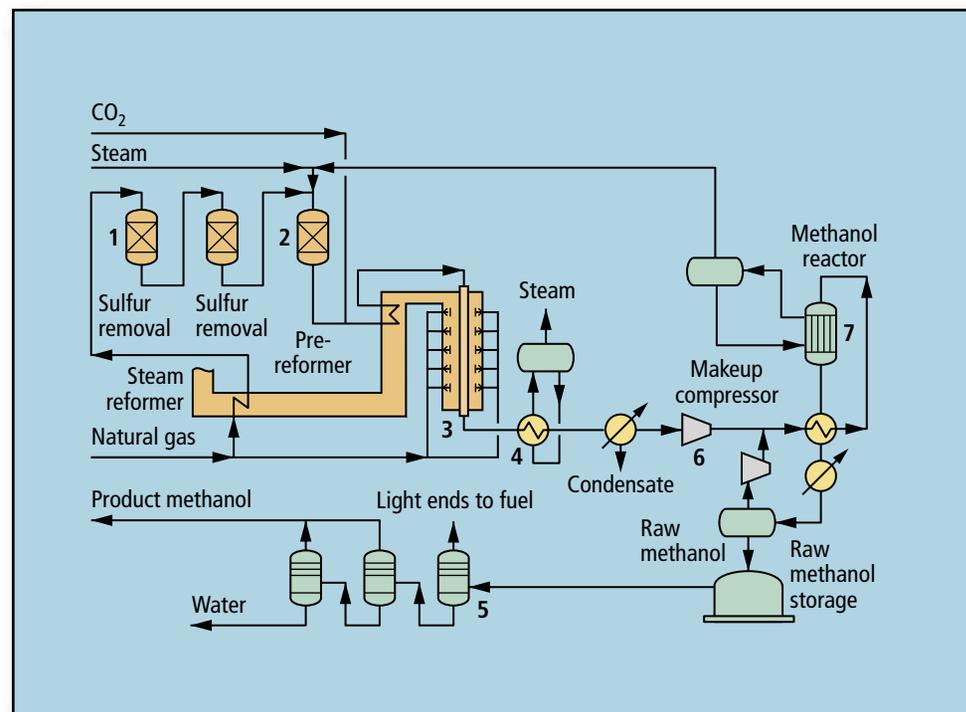
Methanol—steam-methane reforming

Application: To produce methanol from natural or associated gas feedstocks using advanced tubular reforming followed by boiling water reactor synthesis. This technology is an option for capacities up to approximately 3,000 mtpd methanol for cases where carbon dioxide (CO_2) is available. Topsøe also offers technology for larger-scale methanol facilities up to 10,000 mtpd per production train and technology to modify ammonia capacity into methanol production.

Description: The gas feedstock is compressed (if required), desulfurized (1) and process steam is added. Process steam used is a combination of steam from the process condensate stripper and superheated medium pressure steam from the header. The mixture of natural gas and steam is preheated, prereformed (2) and sent to the tubular reformer (3). The prereformer uses waste heat from the flue-gas section of the tubular reformer for the reforming reaction, thus reducing the total load on the tubular reformer. Due to high outlet temperature, exit gas from the tubular reformer has a low concentration of methane, which is an inert in the synthesis. The synthesis gas obtainable with this technology typically contains surplus hydrogen, which will be used as fuel in the reformer furnace. If CO_2 is available, the synthesis gas composition can be adjusted, hereby minimizing the hydrogen surplus. Carbon dioxide can preferably be added downstream of the prereformer.

The flue gas generated in the tubular reformer is used for preheat of reformer and prereformer feed, natural gas preheat, steam superheat and preheat of combustion air. The synthesis gas generated in the tubular reformer is cooled by high-pressure steam generation (4), preheat of boiler feed water and reboiling in the distillation section (5).

After final cooling by air or cooling water, the synthesis gas is compressed (6) and sent to the synthesis loop (7). The synthesis loop is comprised of a straight-tubed boiling water reactor, which is more efficient than adiabatic reactors. Reaction heat is removed from the reactor by generating MP steam. This steam is used for stripping of process condensate and thereafter as process steam. Preheating the



reactor feed cools effluent from the synthesis reactor. Further cooling is obtained by air or water cooling. Raw methanol is separated and sent directly to the distillation section (5) featuring a very efficient three-column layout. Recycle gas is sent to the recirculator compressor (8) after a small purge to remove inert compound buildup.

Topsøe supplies a complete range of catalysts for methanol production. The total energy consumption for this process scheme is about 7.2 Gcal/ton methanol without CO_2 addition. With CO_2 addition, the total energy consumption can be reduced to 7.0 Gcal/ton methanol.

Methanol—steam-methane reforming, *continued*

Economics: Tubular reforming technology is attractive at capacities >2,500–3,000 mtpd methanol, where the economy of scale of alternative technologies such as two-step or autothermal reforming cannot be fully utilized.

Commercial plants: The most recent plant is a 3,030-mtpd methanol facility with CO₂ import. The plant was commissioned in 2004.

Licensors: Haldor Topsøe A/S.

Methanol—autothermal reforming (ATR)

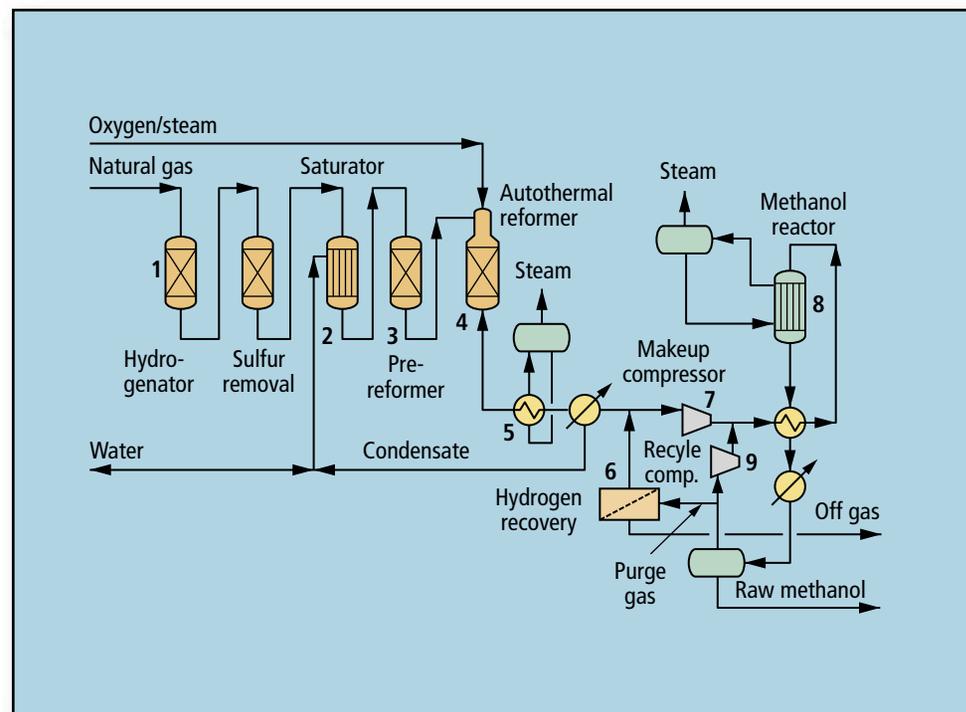
Application: To produce methanol from natural or associated gas feedstocks using autothermal reforming (ATR) followed by boiling water reactor synthesis. This technology is well suited for very large-scale plants as well as for the production of methanol to olefins or fuel-grade methanol. Topsøe also offers technology for smaller methanol facilities 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 the natural gas is saturated with process condensate and excess water from the distillation section. Recycling of process condensate and excess water minimizes the water requirement. Low-grade medium-pressure steam is used in the saturator, thus saving high-pressure steam. The mixture of natural gas and steam is preheated, prereformed (3) and sent to the autothermal reformer (4). Autothermal reforming features a stand-alone oxygen-fired reformer and, thus, the cost-intensive primary tubular reformer may be omitted completely. The autothermal reformer can operate at any pressure. The operating pressure is normally selected between 30 and 40 kg/cm²g.

Synthesis gas generated in the autothermal reformer is cooled by high-pressure steam generation (5), preheat of boiler feed water, reboiling in the distillation section and preheat of demineralized water.

The synthesis gas obtainable with this technology is typically deficient in hydrogen. Therefore, the synthesis gas composition must be adjusted by recycling recovered hydrogen (6) from the synthesis loop. After final cooling by air or cooling water, the recycle hydrogen is added to the synthesis gas, which is compressed in a single-step compressor (7) and sent to the synthesis loop (8).

The synthesis loop is comprised of a straight-tubed boiling water reactor, which is more efficient than adiabatic reactors. Reaction heat is removed from the reactor by generation of medium-pressure steam. This steam is used for heating in the saturator (2). Preheating the



reactor feed cools effluent from the synthesis reactor. Further cooling is by air or water cooling. Raw methanol is separated and sent directly to the distillation section featuring a very efficient three-column layout. Recycle gas is sent to the recirculator compressor (9) after a purge to remove inert compound buildup. The purge is sent to a hydrogen recovery unit where hydrogen is separated and recycled to the synthesis gas compressor.

Topsøe supplies a complete range of catalysts for methanol production. The total energy consumption for this process scheme is about 7.1 Gcal/ton methanol. Total energy consumption for production of fuel grade methanol is approximately 6.8 Gcal/ton methanol.

Methanol—autothermal reforming (ATR), *continued*

Economics: For large-scale plants, the total investment, including an oxygen plant, is approximately 10% lower than for a conventional plant based on tubular steam reforming.

Licensors: Haldor Topsøe A/S.

Methanol—two-step reforming

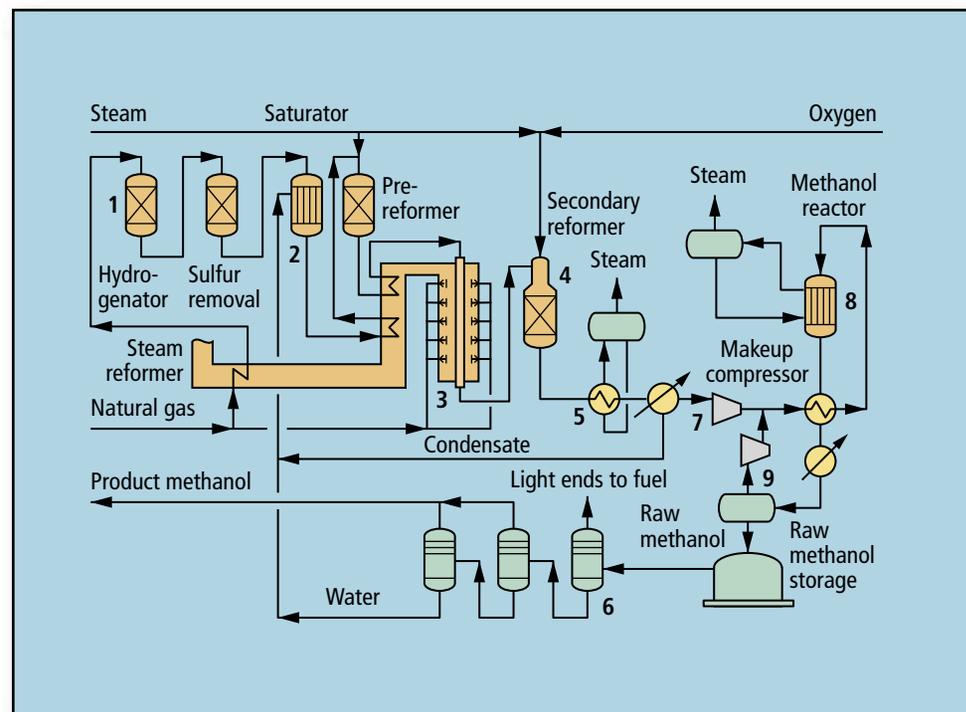
Application: To produce methanol from natural or associated gas feedstocks using two-step reforming followed by low-pressure synthesis. This technology is well suited for world-scale plants. Topsøe also offers technology for smaller as well as very large methanol facilities up to 10,000 tpd, and technology 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' 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 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. This plant was commissioned in 2004.

Licensors: Haldor Topsøe A/S.

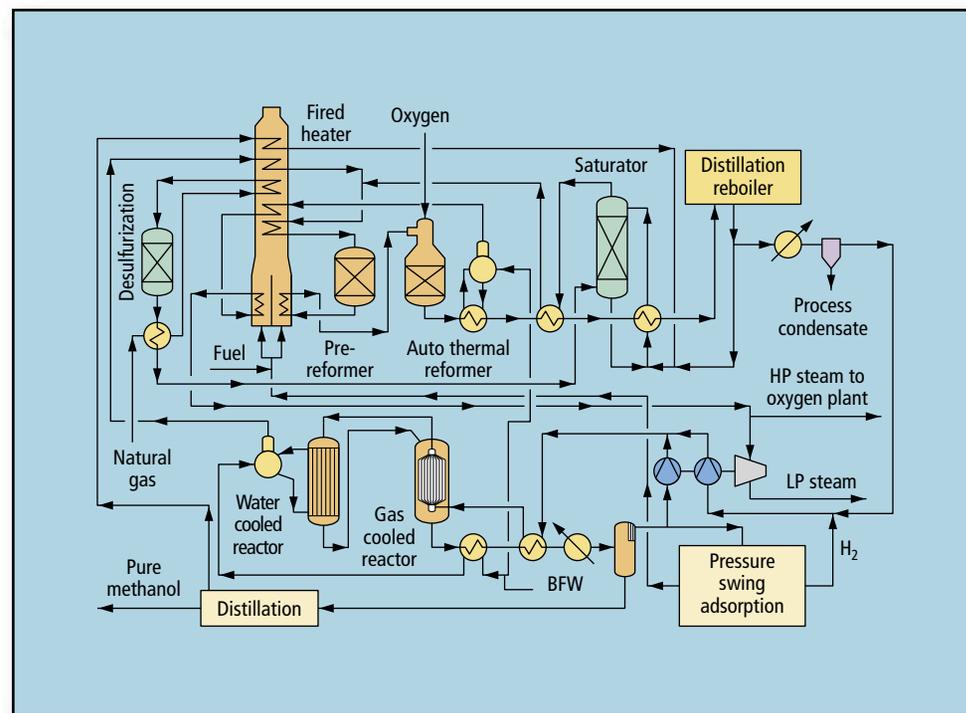
Methanol

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 H_2 , CO_2 and CH_4 . Final preheating of the gas is achieved in the fired heater. In the autothermal reformer, the gas is reformed with steam and O_2 . The product gas contains H_2 , CO , CO_2 and a small amount of unconverted CH_4 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 $40^{\circ}C$ 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

Methanol, *continued*

the tank farm, and the process water is preheated in the fired heater and used as makeup 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 US\$350 million, depending on location.

Commercial plants: Thirty-five methanol plants have been built using Lurgi's Low-Pressure methanol technology. One MegaMethanol plant is in operation, two are under construction and three MegaMethanol contracts have been awarded with capacities up to 6,750 mtpd of methanol.

Licensors: Lurgi AG.

Methanol

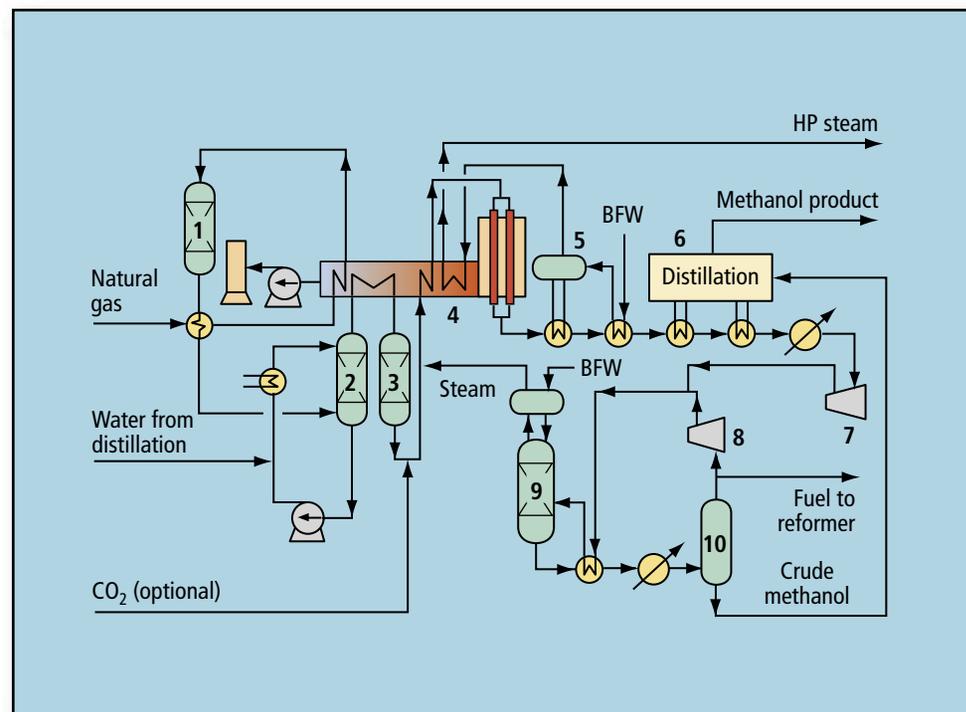
Application: The One Synergy process is improved low-pressure methanol process to produce methanol. The new method produces methanol from natural or associated gas using two-stage steam reforming followed by compression, synthesis and distillation. Capacities, ranging from 5,000 to 7,000 mtpd, are practical 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 the 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) and 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 7.2–7.8 Gcal/ton. A guideline figure to construct a 5,000-mtpd plant is US\$370–400 million.

Methanol, *continued*

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 Syntex LPM methanol technology. Two 5,000-mtpd plants are under construction.

Licensors: One Synergy, a consortium of Davy Process Technology, Johnson Matthey Catalysts, and Aker Kvaerner.

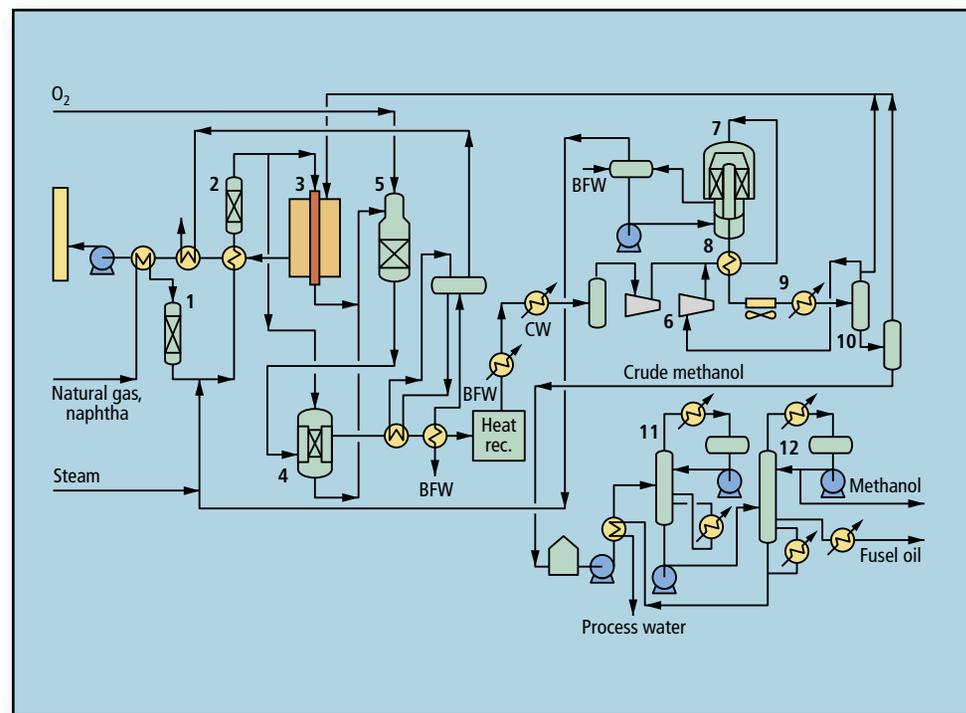
Methanol

Application: To produce Federal-Grade AA refined methanol from natural gas-based synthesis gas and naphtha using Toyo Engineering Corp.'s (TEC's) Synthesis Gas Generation technologies and proprietary MRF-Z reactor incorporated in the Johnson Matthey's (JM's) process. In a natural gas-based plant, the synthesis gas is produced by reforming natural gas with steam and/or oxygen using high-activity steam reforming "ISOP" catalyst.

Description: Syngas preparation section. The feedstock is first preheated and sulfur compounds are removed in a desulfurizer (1). Steam is added, and the feedstock-steam mixture is preheated again. A part of the feed is reformed adiabatically in pre-reformer (2). The half of feedstock-steam mixture is distributed into catalyst tubes of the steam reformer (3) and the rest is sent to TEC's proprietary heat exchanger reformer, "TAF-X" (4), installed in parallel with (3) as the primary reforming. The heat required for TAF-X is supplied by the effluent stream of secondary reformer (5). Depending on plant capacity, the TAF-X (4) and/or the secondary reformer (5) can be eliminated.

Methanol synthesis section. The synthesis loop is comprised of a circulator combined with compressor (6), "MRF-Z" reactor (7), feed/effluent heat exchanger (8), methanol condenser (9) and separator (10). Currently, MRF-Z reactor is the only reactor in the world capable of producing 5,000–6,000 t/d methanol in a single-reactor vessel. The operation pressure is 5–10 MPa. The syngas enters the MRF-Z reactor (7) at 220–240°C and leaves at 260–280°C normally.

JM proprietary methanol synthesis catalyst is packed in the shell side of the reactor. Reaction heat is recovered and used to efficiently generate steam in the tube side. Reactor effluent gas is cooled to condense the crude methanol. The crude methanol is separated in a separator (10). The unreacted gas is circulated for further conversion. A purge is taken from the recycling gas used as fuels in the reformer (3).



Methanol purification section. The crude methanol is fed to a two-column distillation system, which consists of a small topping column (11) and a refining column (12) to obtain high-purity Federal Grade AA methanol.

Economics: In typical natural gas applications, approximately 30 GJ/ton-methanol, including utilities, is required.

Installations: Toyo has accumulated experience with the licensing of 20 methanol plant projects.

Reference: US Patent: 6100303.

Licensor: Toyo Engineering Corp. (TEC)/Johnson Matthey PLC.

Methanol, *continued*

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

Licensors: Uhde GmbH is a licensee of Johnson Matthey Catalysts' Low-Pressure Methanol (LPM) Process.

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, 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 the 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.

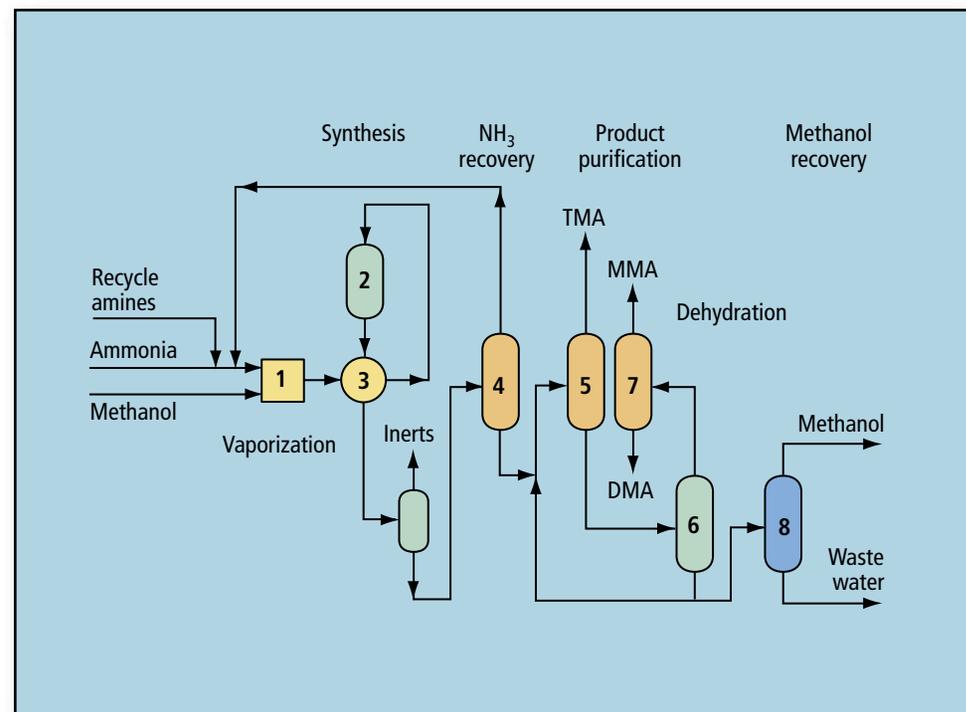
Methanol recovery (8) improves efficiency and extends catalyst life by allowing greater methanol slip exit from the converter. Addition of a methanol-recovery column to existing plants can help to increase production rates.

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 $\frac{1}{3} : \frac{1}{3} : \frac{1}{3}$

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 mtpy.

Licensor: Davy Process Technology, UK.

Mixed xylenes

Application: To convert C_9^+ heavy aromatics, alone or in conjunction with toluene or benzene co-feed, primarily to mixed xylenes using ExxonMobil Chemical's TransPlus process.

Description: Fresh feed, ranging from 100% C_9^+ aromatics to mixtures of C_9^+ aromatics with either toluene or benzene, are converted primarily to xylenes in the TransPlus process. Co-boiling C_{11} aromatics components, up to 435°F NBP, can be included in the C_9^+ 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).

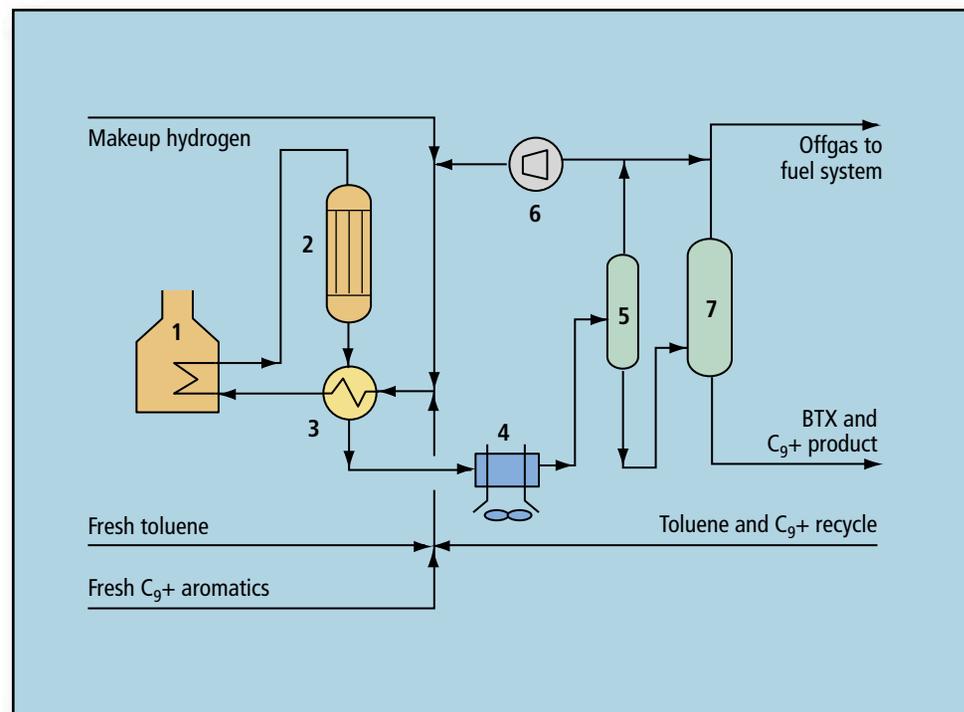
Primary reactions occurring are the dealkylation of alkylaromatics, transalkylation and disproportionation, producing benzene/toluene and C_8 aromatics containing over 95% xylenes. The thermodynamic equilibrium of the resulting product aromatics is mainly dependent on the ratio of methyl groups to aromatic rings in the reactor feed. Hydrogen-rich gas from the high-pressure separator (5) is recycled back to the reactor with makeup hydrogen (6). Unconverted toluene and C_9^+ aromatics are recycled to extinction.

The ability of TransPlus to process feeds rich in C_9^+ aromatics enhances the product slate toward 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 retrofit applications.

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

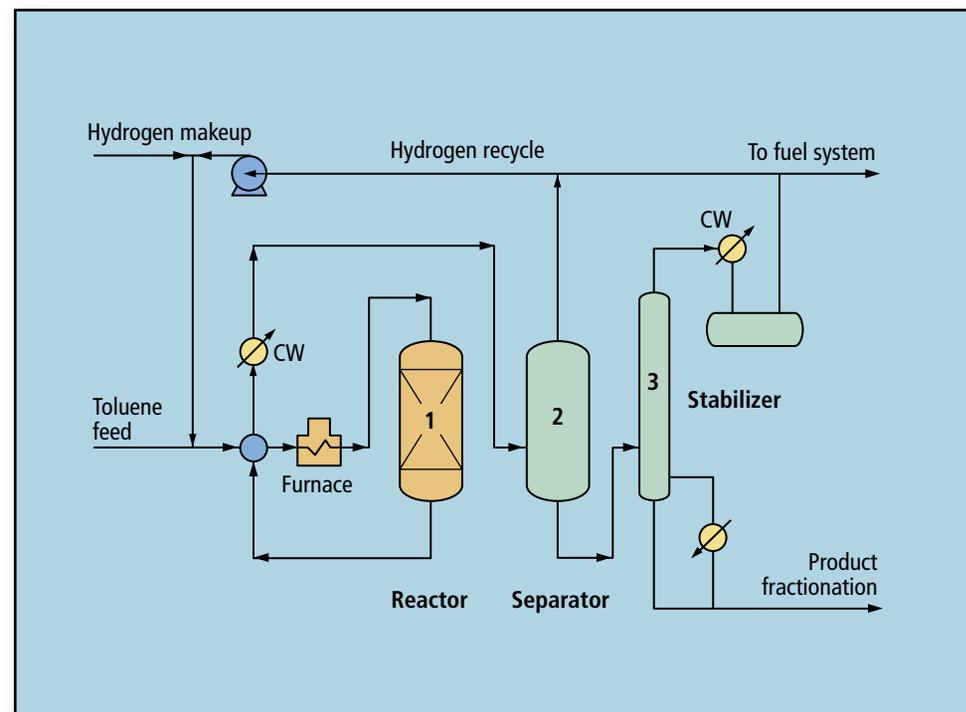
Licensor: ExxonMobil Chemical Technology Licensing LLC, (retrofit applications); Axens, Axens NA (grassroots applications).



Mixed xylenes

Application: To selectively convert toluene to mixed xylene and high-purity benzene using ExxonMobil Chemical'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
	100.0	100.0
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 US 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	1.53 10 ²⁵
Maintenance, per year as % of investment	2.0

Commercial plants: Four MTDP-3 licensees since 1995.

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

Licensors: ExxonMobil Chemical Technology Licensing LLC (retrofit applications); Axens, Axens NA (grassroots applications).

Mixed xylenes

Application: To convert C_9^+ heavy aromatics, alone or in conjunction with toluene or benzene co-feed, primarily to mixed xylenes using ExxonMobil Chemical's TransPlus process.

Description: Fresh feed, ranging from 100% C_9^+ aromatics to mixtures of C_9^+ aromatics with either toluene or benzene, are converted primarily to xylenes in the TransPlus process. Co-boiling C_{11} aromatics components, up to 435°F NBP, can be included in the C_9^+ 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).

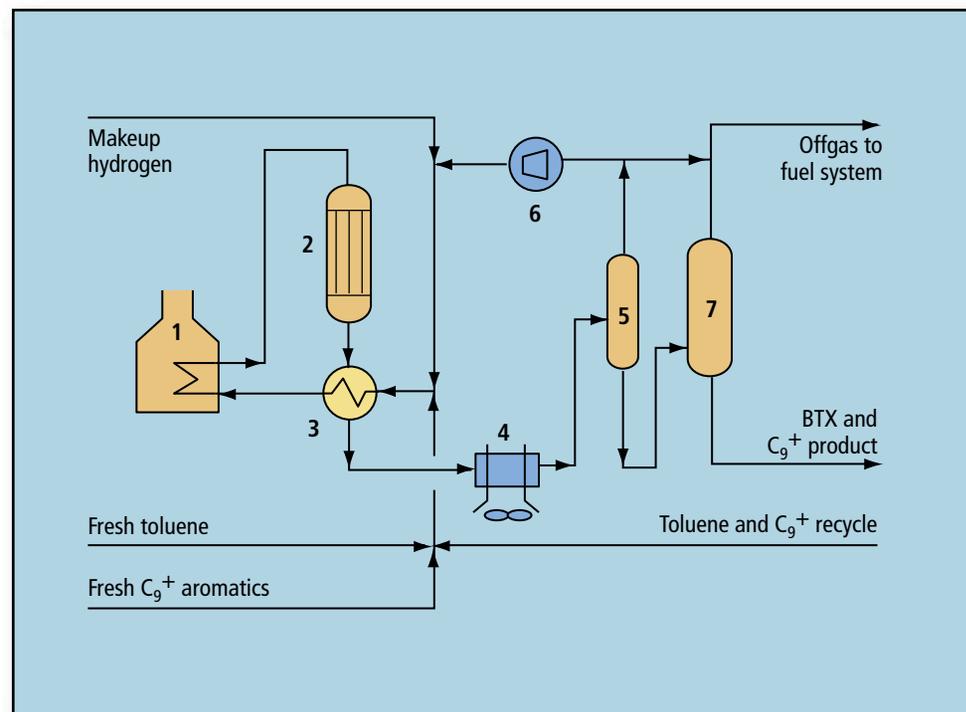
Primary reactions occurring are the dealkylation of alkylaromatics, transalkylation and disproportionation, producing benzene/toluene and C_8 aromatics containing over 95% xylenes. The thermodynamic equilibrium of the resulting product aromatics is mainly dependent on the ratio of methyl groups to aromatic 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 C_9^+ aromatics are recycled to extinction.

The ability of TransPlus to process feeds rich in C_9^+ aromatics enhances the product slate toward 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 retrofit applications.

Commercial plants: The first commercial unit was started up in Taiwan in 1997. There are five TransPlus references.

Licensor: ExxonMobil Chemical, (retrofit applications); Axens, Axens NA (grassroots applications).



Mixed xylenes

Application: In a modern UOP aromatics complex, the TAC9 process is integrated into the flow scheme to selectively convert C_9 – C_{10} aromatics into xylenes rather than sending them to the gasoline pool or selling them as a solvent.

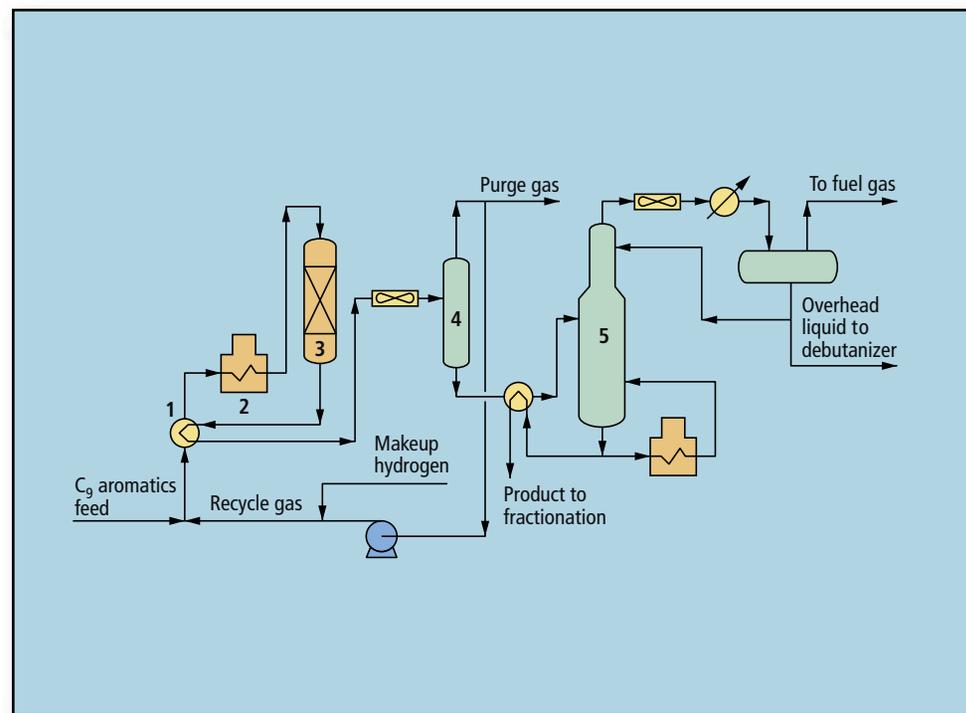
Description: The TAC9 process consists of a fixed-bed reactor and product separation section. The feed is combined with hydrogen-rich recycle gas, preheated in a combined feed exchanger (1) and heated in a fired heater (2). The hot feed vapor goes to a reactor (3). The reactor effluent is cooled in a combined feed exchanger and sent to a product separator (4). Hydrogen-rich gas is taken off the top of the separator, mixed with makeup hydrogen gas, and recycled back to the reactor. Liquid from the bottom of the separator is sent to a stripper column (5). The stripper overhead gas is exported to the fuel gas system. The overhead liquid may be sent to a debutanizer column or a stabilizer. The stabilized product is sent to the product fractionation section of the UOP aromatics complex.

Economics: The current generation of TAC9 catalyst has demonstrated the ability to operate for several years without regeneration. ISBL costs based on a unit processing 306,400 mtpy of feed consisting of 100 wt% C_9 – C_{10} (US Gulf Coast site in 2003):

Investment, US\$ million	11.6
Utilities (per mt of feed)	
Electricity, kWh	3.1
Steam, mt	0.07
Water, cooling, m ³	1.6
Fuel, MMkcal	0.13

Commercial plants: Three commercial units have been brought on-stream, with feed rates ranging from 210,000 mtpy to 850,000 mtpy.

Licensor: UOP LLC.



Mixed xylenes

Application: The Tatoray process produces mixed xylenes and petrochemical grade benzene by disproportionation of toluene and transalkylation of toluene and C₉+ aromatics.

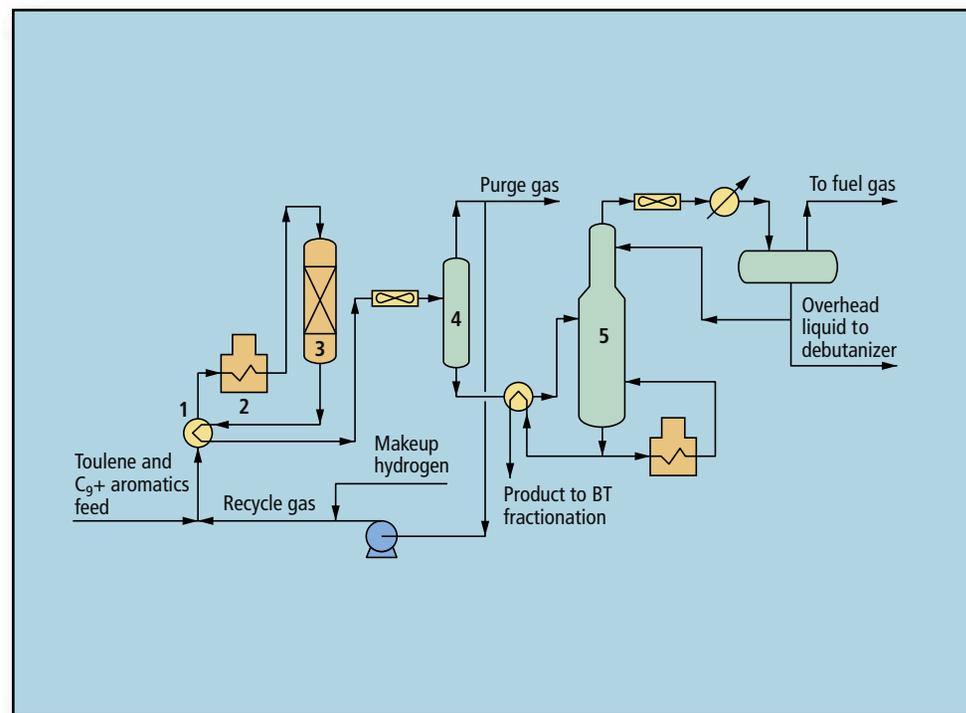
Description: The Tatoray process consists of a fixed-bed reactor and product separation section. The fresh feed is combined with hydrogen-rich recycle gas, preheated in a combined feed exchanger (1) and heated in a fired heater (2). The hot feed vapor goes to the reactor (3). The reactor effluent is cooled in a combined feed exchanger and sent to a product separator (4). Hydrogen-rich gas is taken off the top of the separator, mixed with makeup hydrogen gas and recycled back to the reactor. Liquid from the bottom of the separator is sent to a stripper column (5). The stripper overhead gas is exported to the fuel gas system. The overhead liquid may be sent to a debutanizer column. The products from the bottom of the stripper are recycled back to the BT fractionation section of the aromatics complex.

The Tatoray process unit is capable of processing feedstocks ranging from 100 wt% toluene to 100 wt% A₉⁺. The optimal concentration of A₉⁺ in the feed is typically 40–60 wt%. The Tatoray process provides an ideal way to produce additional mixed xylenes from toluene and heavy aromatics.

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Economics: The process is designed to function at a much higher level of conversion per pass. This high conversion minimizes the size of the BT columns, and the size of Tatoray process unit, as well as the utility consumption of all of these units. Estimated ISBL costs based on a unit processing feed capacity of 355,000 mtpy (US Gulf Coast site in 2003):

Investment, US\$ million	11.3
Utilities (per mt of feed)	
Electricity, kWh	17.5
Steam, mt	0.11
Water, cooling, M ³	2.5
Fuel, MMkcal	0.04



Commercial plants: UOP has licensed a total of 44 Tatoray units; 40 of these units are in operation and 4 are in various stages of construction.

Licensors: UOP LLC.

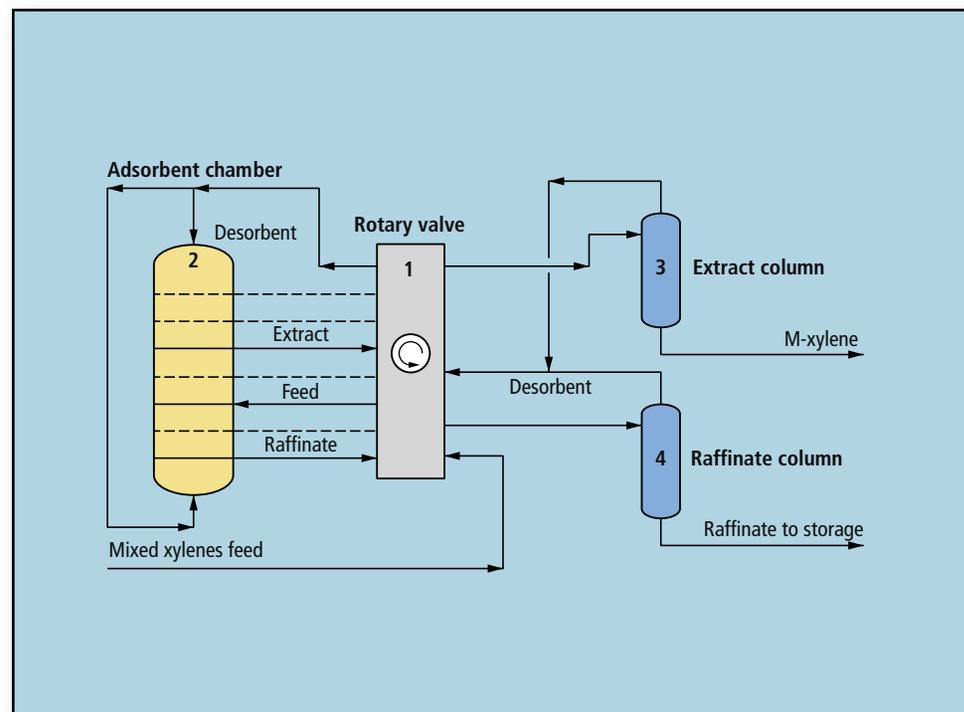
m-Xylene

Application: The MX Sorbex process recovers *meta*-xylene (*m*-xylene) from mixed xylenes. UOP's innovative Sorbex technology uses adsorptive separation for highly efficient and selective recovery, at high purity, of molecular species that cannot be separated by conventional fractionation.

Description: The process simulates a moving bed of adsorbent with continuous counter-current flow of liquid feed over a solid bed of adsorbent. Feed and products enter and leave the adsorbent bed continuously, at nearly constant compositions. A rotary valve is used to periodically switch the positions of the feed-entry and product-withdrawal points as the composition profile moves down the adsorbent bed.

The fresh feed is pumped to the adsorbent chamber (2) via the rotary valve (1). *M*-xylene is separated from the feed in the adsorbent chamber and leaves via the rotary valve to the extract column (3). The dilute extract is then fractionated to produce 99.5 wt% *m*-xylene as a bottoms product. The desorbent is taken from the overhead and recirculated back to the adsorbent chamber. All the other components present in the feed are rejected in the adsorbent chamber and removed via the rotary valve to the raffinate column (4). The dilute raffinate is then fractionated to recover desorbent as the overhead product and recirculated back to the adsorbent chamber.

Economics: The MX Sorbex process has been developed to meet increased demand for purified isophthalic acid (PIA). The growth in demand for PIA is linked to the copolymer requirement for PET bottle resin applications, a market that continues to rapidly expand. The process has become the new industry standard due to its superior environmental safety and lower cost materials of construction. Estimated ISBL costs based on unit production of 50,000 mtpy of *m*-xylene (US Gulf Coast site in 2003).



Investment, US\$ million	30.0
Utilities (per mt of <i>m</i> -xylene produced)	
Electricity, kWh	87
Steam, mt	4.0
Water, cooling, m ³	3.8

Commercial plants: Five MX Sorbex units are currently in operation and another unit is in design. These units represent an aggregate production of 335,000 mtpy of *m*-xylene.

Licensor: UOP LLC.

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 olefin 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 toward octenes are about 85%. The typical C₈ product is a mixture having a minimum of 98.5% octene isomers with the following distribution:

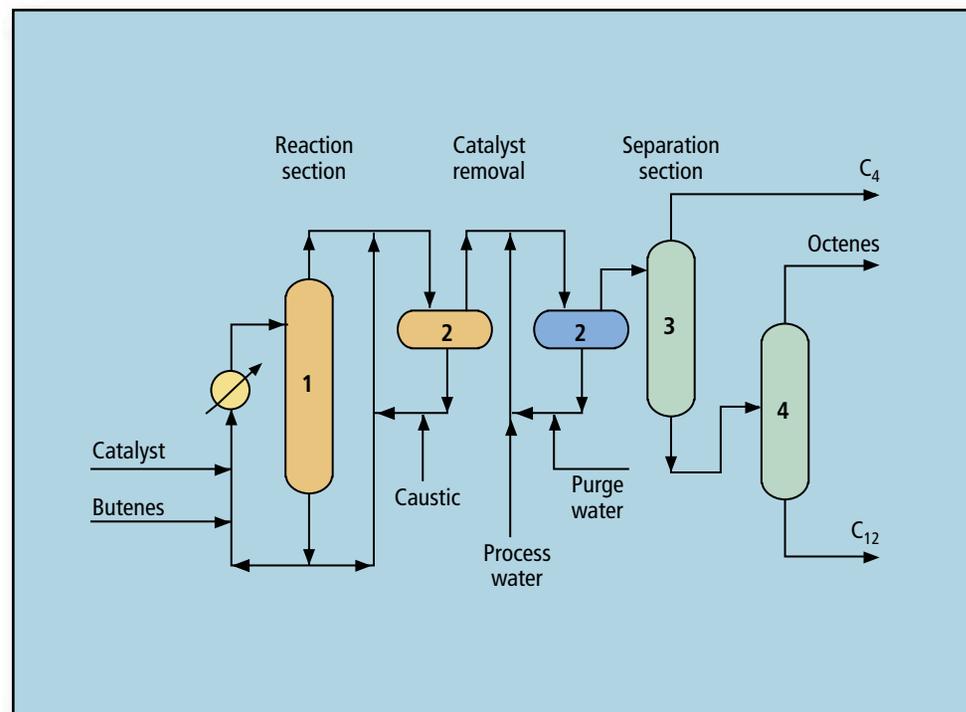
n-Octenes	7%
Methyl-heptenes	58%
Dimethyl-hexenes	35%

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

Economics: Basis: ISBL 2004 for a Gulf Coast location using 50,000 tpy of a raffinate-2 C₄ cut containing 75% n-butenes.

Investment, US\$ million	6
Typical operating cost, US\$	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 tpy up to 90,000 tpy.



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

Licensor: Axens, Axens NA.

Olefins—progressive separation for olefins recovery and raw cracked-gas purification

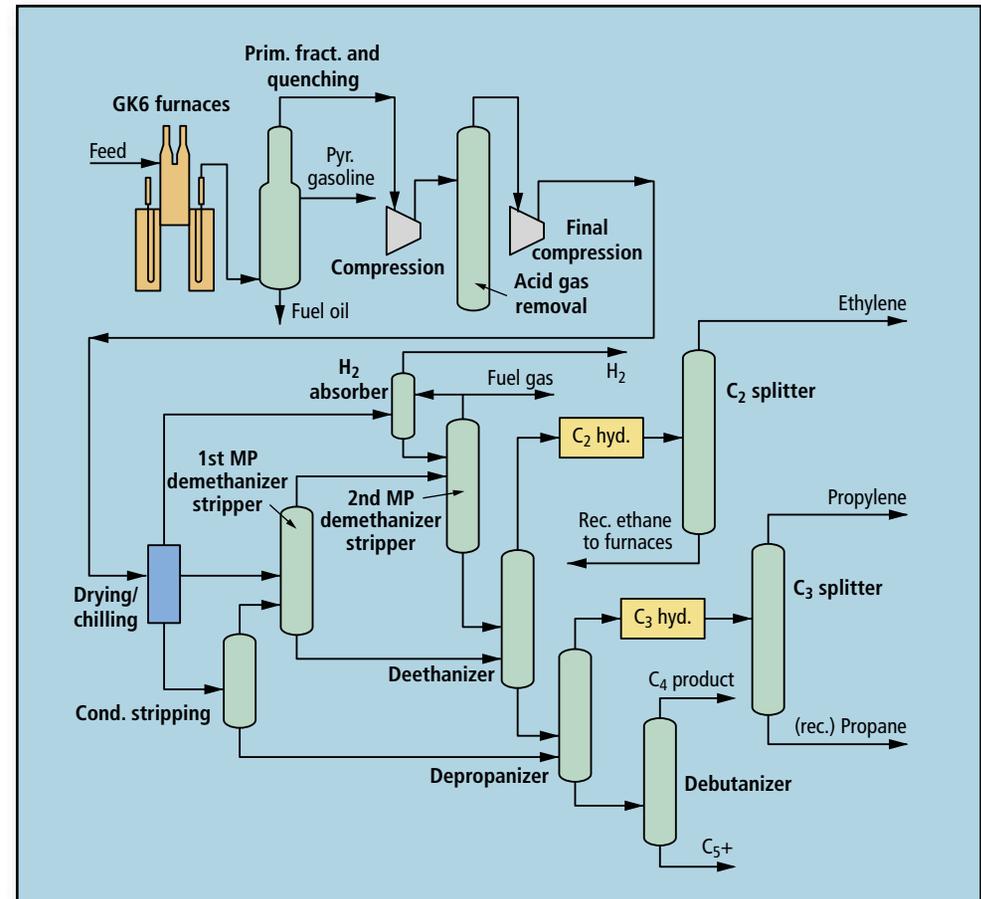
Application: To produce polymer-grade ethylene and propylene, a butadiene-rich C_4 cut, an aromatic C_6 – C_8 rich raw pyrolysis gasoline, and a high-purity hydrogen by steam pyrolysis of hydrocarbons ranging from ethane to vacuum gas oils.

Feedstocks: 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. This method allows producing olefins at low energy consumption with particularly low environmental impact.

Hydrocarbon feedstocks are preheated (also to recover heat) and then cracked by combining with steam in tubular Pyrolysis Furnace (1) at an outlet temperature ranging from 1,500°F to 1,600°F. The furnace technology can be either an SMK type (for gas cracking) or GK type (for liquid cracking). The GK type design can be oriented to a high-olefins yield with very flexible propylene/ethylene ratios (GK6 TYPE) or to a high BTX production (GK3 type). This specific 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 (2) (TLE or SLE), generating high-pressure steam. In liquid crackers, cracked gas flows to a primary fractionator (3) after direct quench with oil, where fuel oil is separated from gasoline and lighter components, and then to a quench water tower (4) 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 (5,6) where medium gasoline is produced and part of the C_3^+ cut is recovered respectively. A caustic scrubber (7) removes acid gases.



Compressed gas at 450 psig is dried and chilled. A double demethanizing stripping system (8,9) operating at medium pressure and reboiled by cracked gas minimizes the refrigeration required (heat integration) as well as the investment cost for separating methane (top) and C_2^+ cut (bottoms). A dual column concept—absorber (10) concept—is applied between the secondary demethanizer overheads and the chilled cracked

Olefins—progressive separation for olefins recovery and raw cracked-gas purification, *continued*

that minimizes the ethylene losses with a low energy requirement. High-purity hydrogen is produced in a cold box (11).

The bottoms from the two demethanizers (of different quality) are sent to the deethanizer (12). The Technip progressive separation allows the deethanizer reflux ratio to be reduced. The deethanizer overhead is selectively hydrogenated for acetylene conversion prior to the ethylene splitter (13) 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 (14,15) for C₃ cut separation from the C₄ cut and heavies, thus giving a low fouling tendency at minimum energy consumption.

The methyl-acetylene and propadiene in the C₃ cut are hydrogenated to propylene in a liquid-phase reactor. Polymer-grade propylene is separated from propane in a C₃ splitter (16). The residual propane is either recycled for further cracking, or exported. C₄s and light gasoline are separated in a debutanizer (17).

Gas expansion (heat recovery) and external cascade using ethylene and propylene systems supply refrigeration. The main features of Technip's patented technology are:

- Optimization of olefins yields and selection of feedstocks
- Reduced external refrigeration in the separation sections
- Auto-stable process, heat integration acts as feed forward system.

Simple process control; large usage of stripper/absorbers towers (single specification) instead of distillation tower (antagonistic top & bottom specifications).

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 & propylene) from 84% (ethane) to 38% (vacuum gas oils), and 49% for an intermediate full-range naphtha. The specific energy consumption range is 3,100 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 four ethylene plants ranging from 500 kty up to 1,400 kty using either ethane or liquid feedstocks. While over 300 cracking furnaces have been built, and 15 units operate worldwide, numerous expansions over the nominal capacity based on progressive separation techniques are under way, with up to an 80% increase in capacity. For ethane cracking, front-end hydrogenation scheme is also available.

Licensors: Technip.

Olefins—butenes extractive distillation

Application: Separation of pure C₄ olefins from olefinic/paraffinic C₄ mixtures via extractive distillation using a selective solvent. BUTENEX is the Uhde technology to separate light olefins from various C₄ feedstocks, which include ethylene cracker and FCC sources.

Description: In the extractive distillation (ED) process, a single-compound solvent, N-Formylmorpholine (NFM), or NFM in a mixture with further morpholine derivatives, alters the vapor pressure of the components being separated. The vapor pressure of the olefins is lowered more than that of the less soluble paraffins. Paraffinic vapors leave the top of the ED column, and solvent with olefins leaves the bottom of the ED column.

The bottom product of the ED column is fed to the stripper to separate pure olefins (mixtures) from the solvent. After intensive heat exchange, the lean solvent is recycled to the ED column. The solvent, which can be either NFM or a mixture including NFM, perfectly satisfies the solvent properties needed for this process, including high selectivity, thermal stability and a suitable boiling point.

Economics:

Consumption per metric ton of FCC C₄ fraction feedstock:

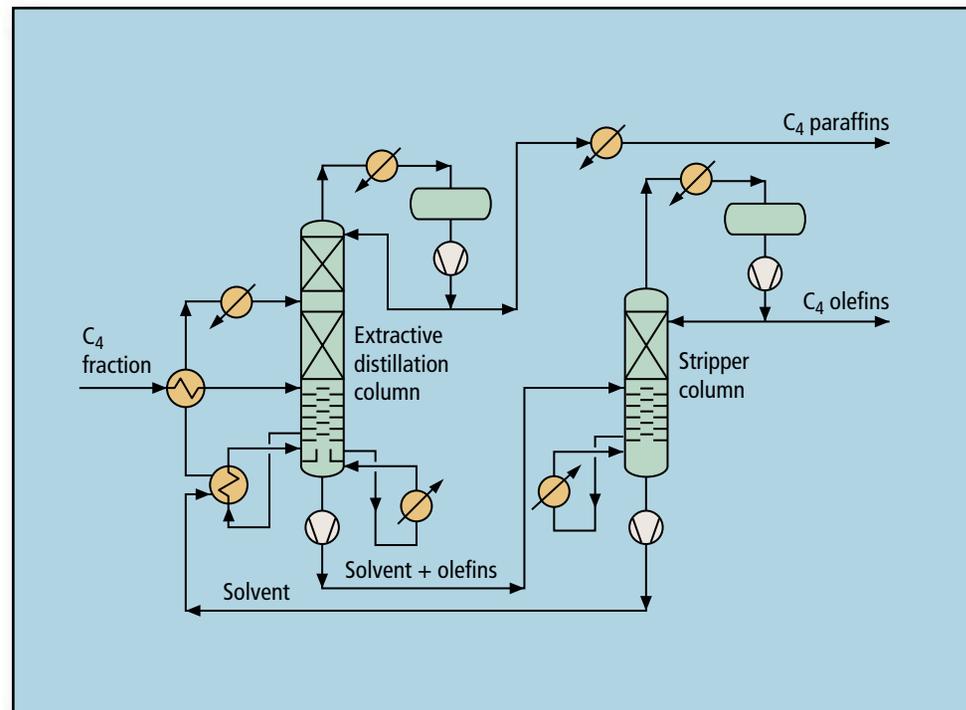
Steam, t/t	0.5–0.8
Water, cooling ($\Delta T = 10^\circ\text{C}$), m ³ /t	15.0
Electric power, kWh/t	25.0

Product purity:

n-Butene content	99.+ wt.-% min.
Solvent content	1 wt.-ppm max.

Commercial plants: Two commercial plants for the recovery of n-butenes have been installed since 1998.

Licensor: Uhde GmbH.



Olefins by dehydrogenation

Application: The Uhde STeam Active Reforming STAR process produces (a) propylene as feedstock for polypropylene, propylene oxide, cumene, acrylonitrile or other propylene derivatives, and (b) butylenes as feedstock for methyl tertiary butyl ether (MTBE), alkylate, isooctane, polybutylenes or other butylene derivatives.

Feed: Liquefied petroleum gas (LPG) from gas fields, gas condensate fields and refineries.

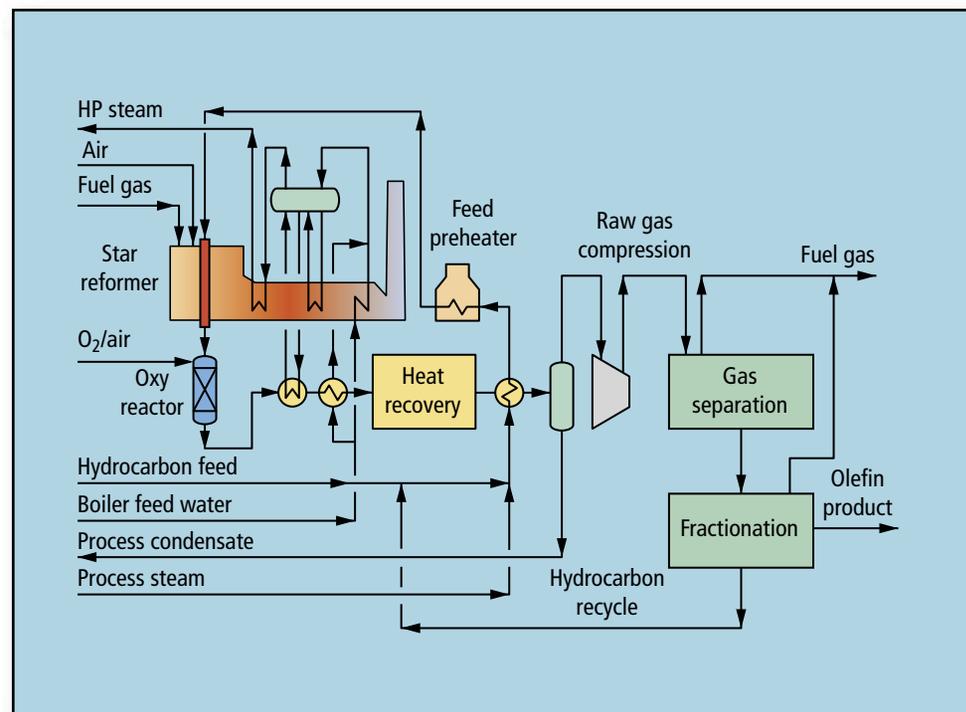
Product: Propylene (polymer- or chemical-grade); isobutylene; n-butylenes; high-purity hydrogen (H_2) may also be produced as a byproduct.

Description: The fresh paraffin feedstock is combined with paraffin recycle and internally generated steam. After preheating, the feed is sent to the reaction section. This section consists of an externally fired tubular fixed-bed reactor (Uhde reformer) connected in series with an adiabatic fixed-bed oxyreactor (secondary reformer type). In the reformer, the endothermic dehydrogenation reaction takes place over a proprietary, noble metal catalyst.

In the adiabatic oxyreactor, part of the hydrogen from the intermediate product leaving the reformer is selectively converted with added oxygen or air, thereby forming steam. This is followed by further dehydrogenation over the same noble-metal catalyst. Exothermic selective H_2 conversion in the oxyreactor increases olefin product space-time yield and supplies heat for further endothermic dehydrogenation. The reaction takes place at temperatures between 500°C – 600°C and at 4 bar–6 bar.

The Uhde reformer is top-fired and has a proprietary “cold” outlet manifold system to enhance reliability. Heat recovery utilizes process heat for high-pressure steam generation, feed preheat and for heat required in the fractionation section.

After cooling and condensate separation, the product is subsequently compressed, light-ends are separated and the olefin product is



separated from unconverted paraffins in the fractionation section.

Apart from light-ends, which are internally used as fuel gas, the olefin is the only product. High-purity H_2 may optionally be recovered from light-ends in the gas separation section.

Economics: Typical specific consumption figures (for polymer-grade propylene production) are shown (per metric ton of propylene product, including production of oxygen and all steam required):

Propane, kg/metric ton	1,200
Fuel gas, GJ/metric ton	6.4
Circul. cooling water, m ³ /metric ton	220
Electrical energy, kWh/metric ton	180

Olefins by dehydrogenation, *continued*

Commercial plants: Two commercial plants using the STAR process for dehydrogenation of isobutane to isobutylene have been commissioned (in the US and Argentina). More than 60 Uhde reformers and 25 Uhde secondary reformers have been constructed worldwide.

References: Heinritz-Adrian, M., N. Thiagarajan, S. Wenzel and H. Gehrke, "STAR—Uhde's dehydrogenation technology (an alternative route to C₃- and C₄-olefins)," ERTC Petrochemical 2003, Paris, France, March 2003.

Thiagarajan, N., U. Ranke and F. Ennenbach, "Propane/butane dehydrogenation by steam active reforming," Achema 2000, Frankfurt, Germany, May 2000.

Licensors: Uhde GmbH.

Olefins

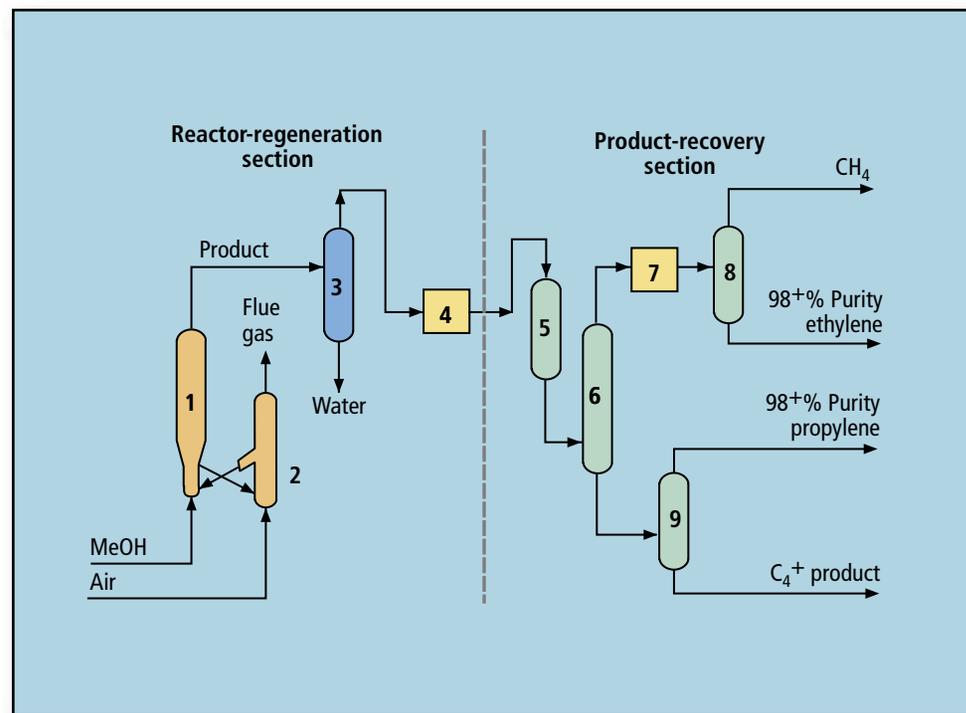
Application: To produce ethylene, propylene and butenes from natural gas or equivalent, via methanol, using the UOP/Hydro MTO (methanol to olefins) process.

Description: This 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 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 polymer-grade ethylene and propylene by adding simple fractionation 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 feedrate to an MTO plant:

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

The process is flexible. Ethylene to propylene product weight ratio can be modified between the range of 0.75 to 1.3 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: Hydro operated a demonstration unit that was installed in Norway in 1995. The first commercial MTO unit is planned for startup in 2008 in Nigeria.

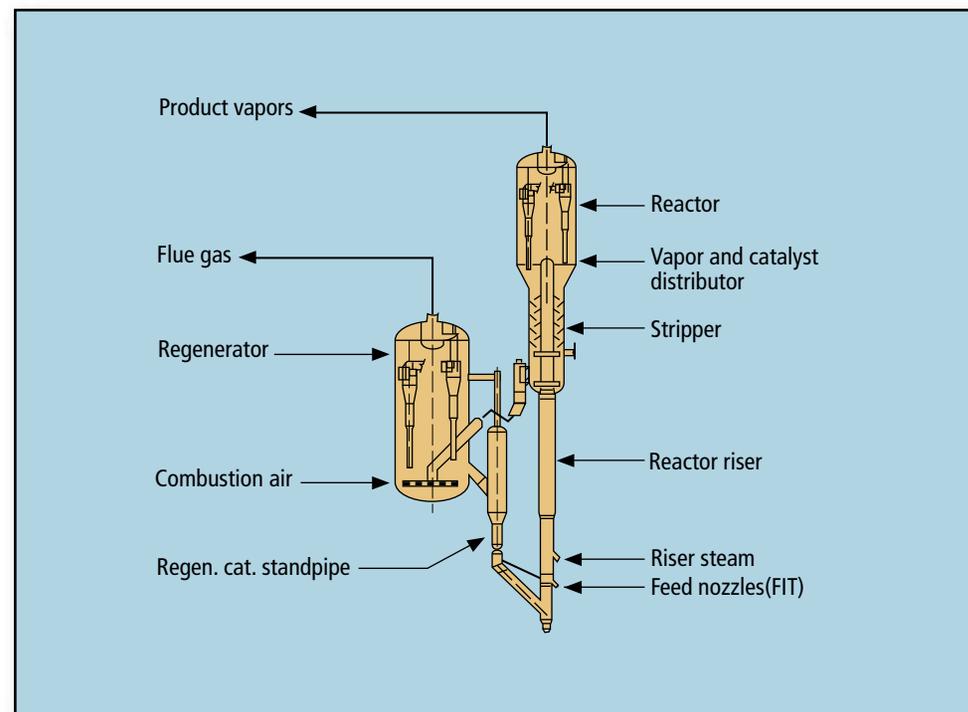
Licensor: UOP LLC/Hydro.

Olefins — catalytic

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 traditional 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.



Reference: Dharra, et al., "Increase light olefins production," *Hydrocarbon Processing*, April 2004.

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

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 grassroots applications.

Commercial plants: Currently eight units are in operation, seven in China and one in Thailand. Another plant for Saudi Aramco, presently in design, will be the largest DCC unit in the world..

Normal paraffins, C₁₀–C₁₃

Application: The Molex process recovers normal C₁₀–C₁₃ paraffins from kerosine using UOP's innovative Sorbex adsorptive separation technology.

Description: Straight-run kerosine is fed to a stripper (1) and a rerun column (2) to remove light and heavy materials. The remaining heart-cut kerosine is heated in a charge heater (3) and then treated in a Union-finishing reactor (4) to remove impurities. The reactor effluent is sent to a product separator (5) to separate gas for recycle, and then the liquid is sent to a product stripper (6) to remove light ends. The bottoms stream from the product stripper is sent to a Molex unit (7) to recover normal paraffins.

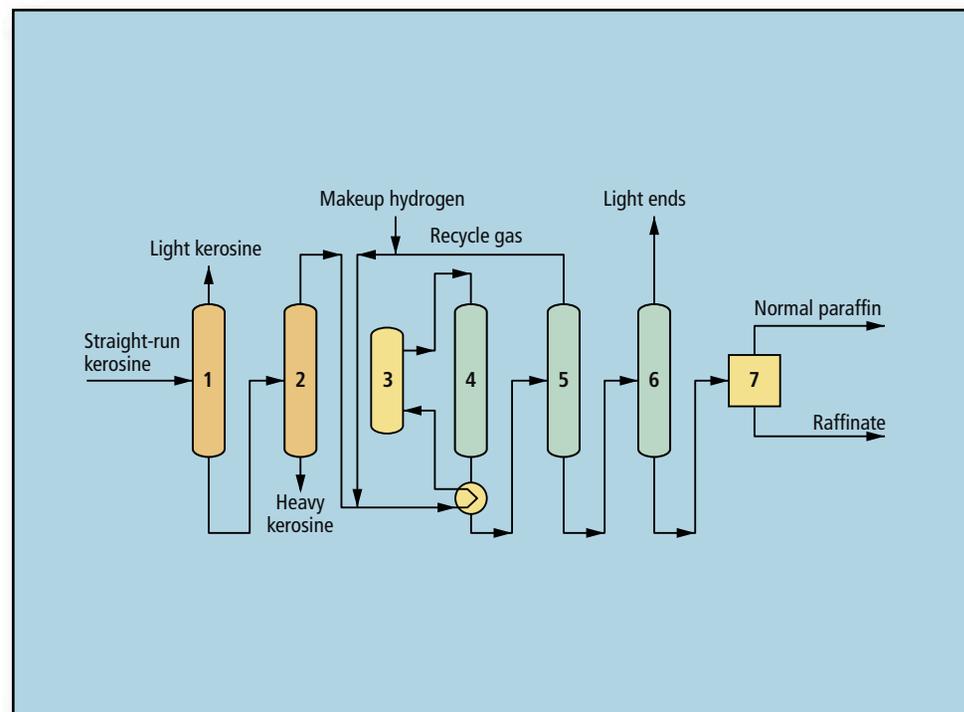
Feedstock is typically straight-run kerosine with 18–50% normal paraffin content. Product purity is typically greater than 99 wt%.

Economics: Investment, US Gulf Coast battery limits for the production of 100,000 tpy of normal paraffins: 700 \$/tpy

Commercial plants: Twenty-eight Molex units have been built.

Reference: McPhee, A., "Upgrading Kerosene to Valuable Petrochemicals," 24th Annual DeWitt World Petrochemical Review, Houston, Texas, US, March 1999.

Licensor: UOP LLC.



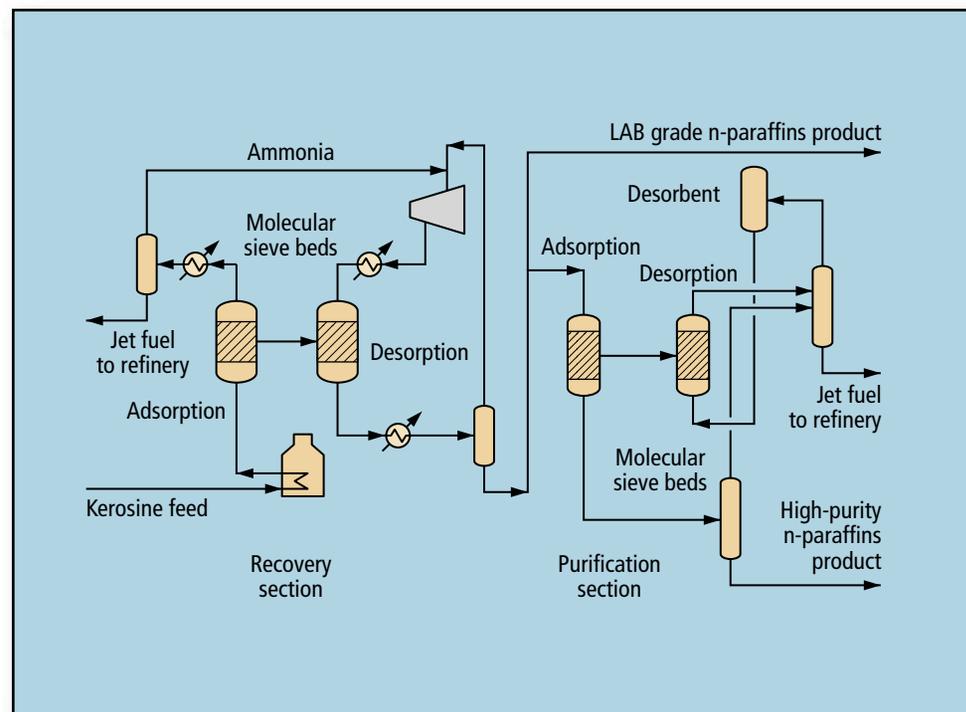
Paraffin, normal

Application: Efficient low-cost recovery and purification processes for the production of LAB-grade and/or high-purity n-paraffin products from kerosine.

Description: The ExxonMobil Chemical (EMC) process offers commercially proven technologies for efficient recovery and purification of high-purity n-paraffin from kerosine feedstock. Kerosine feedstocks are introduced to the recovery section where the n-paraffins are efficiently recovered from the kerosine stream in a vapor-phase fixed-bed molecular sieve adsorption process. In the process, the n-paraffins are selectively adsorbed on a molecular sieve and subsequently desorbed with a highly effective desorbent.

The non n-paraffin hydrocarbons are rejected and returned to the refinery. The process provides a unique environment allowing the solid adsorbent to be very tolerant of sulfur compounds, which are typically present in kerosine feedstock. The adsorbent is therefore able to last long cycle lengths with a total life up to 20 years, as commercially demonstrated by ExxonMobil. In most cases, due to the high sulfur tolerance, the kerosine feedstock will not require hydrotreating pretreatment, which significantly reduces capital investment and operating cost. The recovery section produces LAB-grade n-paraffin product.

High-purity, specialty-grade n-paraffin products are produced in the ExxonMobil Purification process. The LAB-grade product from the recovery process is further processed in a purification section, where residual aromatics and other impurities are further reduced. Purification is accomplished in a liquid-phase, fixed-bed adsorption system. The impurities are selectively adsorbed on a molecular sieve, and subsequently removed with a hydrocarbon desorbent. The high-purity n-paraffins product is the highest quality available in the market. ExxonMobil commercially produces and markets n-paraffin product with aromatics content below 100 wtppm. The ExxonMobil n-paraffin technologies offer the industry's lowest capital and operating cost solutions and highest purity products for n-paraffin producers.



Product quality: Typical properties of high-purity n-paraffin product:

Purity, wt%	99
Aromatics, wt ppm	100
Bromine Index, mg/100g	<20
Sulfur, wt ppm	<1

Yield: Typically, over 99% of the n-paraffin contained in the kerosine stream is recovered.

Commercial plants: ExxonMobil Chemical has 40 years of experience in the production of n-paraffins and is the second largest producer in the

Paraffin, normal, *continued*

world. ExxonMobil's n-paraffin plant at Baytown, Texas, produces high-purity product in a single train at a nameplate capacity of 250,000 tpy.

Licensors: Kellogg Brown & Root, Inc.

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

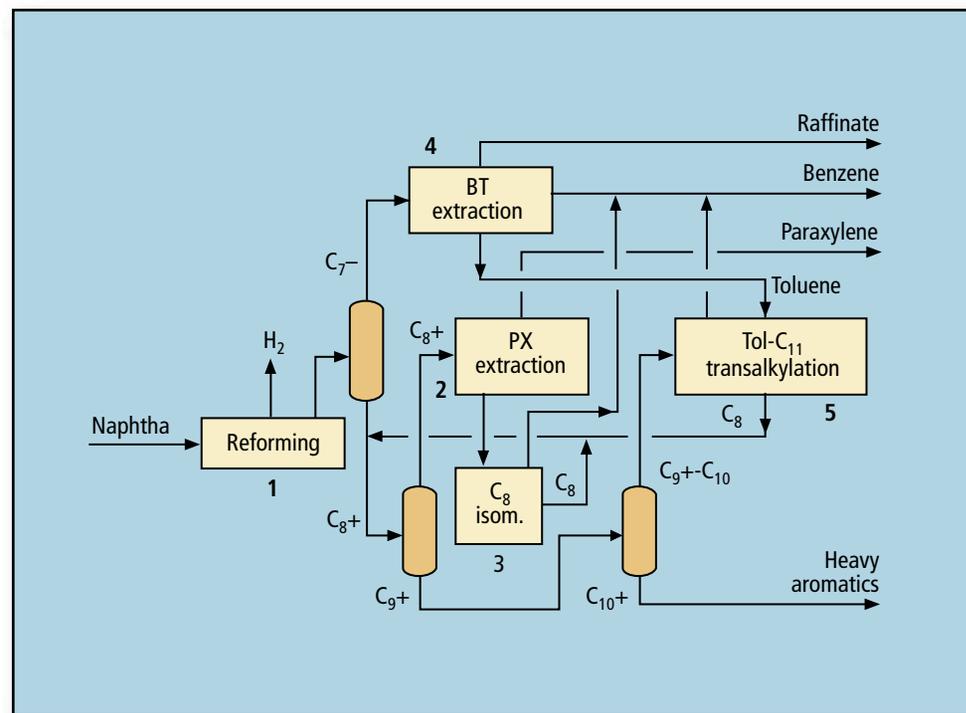
Eluxyl technology has the industrially proven ability to meet ultimate single train PX purity and capacities as high as 750,000 mtpy. Proprietary hybrid Eluxyl configurations integrate an intermediate purity adsorption section with a single-stage crystallization, ideal for retrofits. Axens is the licensor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

* Mobil and ** Uhde technologies licensed by Axens for grassroots applications

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

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

Economics: The ISBL 2004 Gulf Coast location erected cost, including first load of catalysts and chemicals, with 30% allowance for offsites.



Investment, million US\$	430
Annual utilities, catalyst and chemical operating cost (million US\$/yr)	41

Commercial plants: Eight Eluxyl units have been licensed, accounting for 3 million tpy of paraxylene and three units that are in operation. Six isomerization units use the Oparis catalyst and 19 ExxonMobil EB dealkylating units have been put into operation. Three TransPlus units are currently in operation.

Reference: Dupraz, C., et al., "Maximizing paraxylene production with ParamaX."; Hotier, G., and Methivier, A., "Paraxylene Production with

Paraxylene, *continued*

the Eluxyl Process." AIChE 2002 Spring Meeting, New Orleans, March 2002.

Licensors: Axens, Axens NA.

Paraxylene

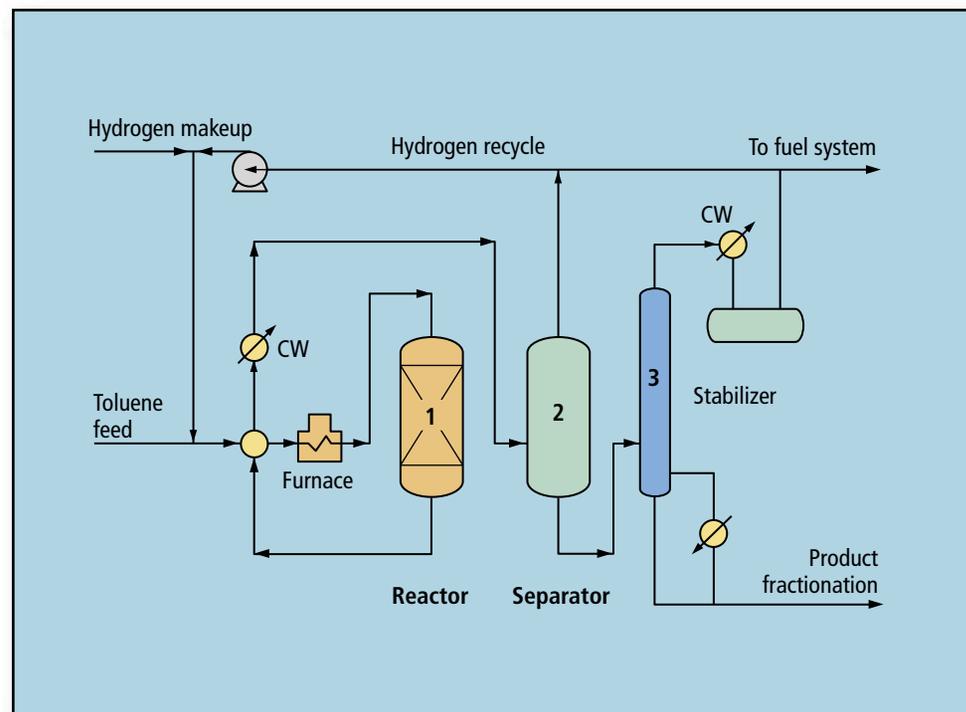
Application: To selectively convert toluene to high-purity (90%+) paraxylene-rich (PX) xylenes and benzene using ExxonMobil Chemical's technologies—PxMax and ASTDP.

Description: Dry toluene feed and hydrogen-rich recycle gas are pumped through feed/effluent exchangers and charge heater and into the 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 effluent 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.

The PxMax technology uses catalyst which is ex-situ selectivated by pretreatment during catalyst manufacture. The ASTDP technology uses catalyst which is in-situ coke selectivated. 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 PxMax and ASTDP.

Operating conditions: PxMax 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 PxMax version of this technology results in simplified operation and lower capital costs. Both catalysts offer long operating cycles and are regenerable.

Commercial plants: There are seven MSTDP units (predecessor technology to PxMax), and ASTDP and four units using PxMax technology. The first two PxMax units started up in 1996 and 1997 at Chalmette Refining's Louisiana Refinery and Mobil Chemical's Beaumont plant, respectively.



Licensor: ExxonMobil Chemical (retrofit applications); Axens, Axens NA (grassroots applications).

Paraxylene

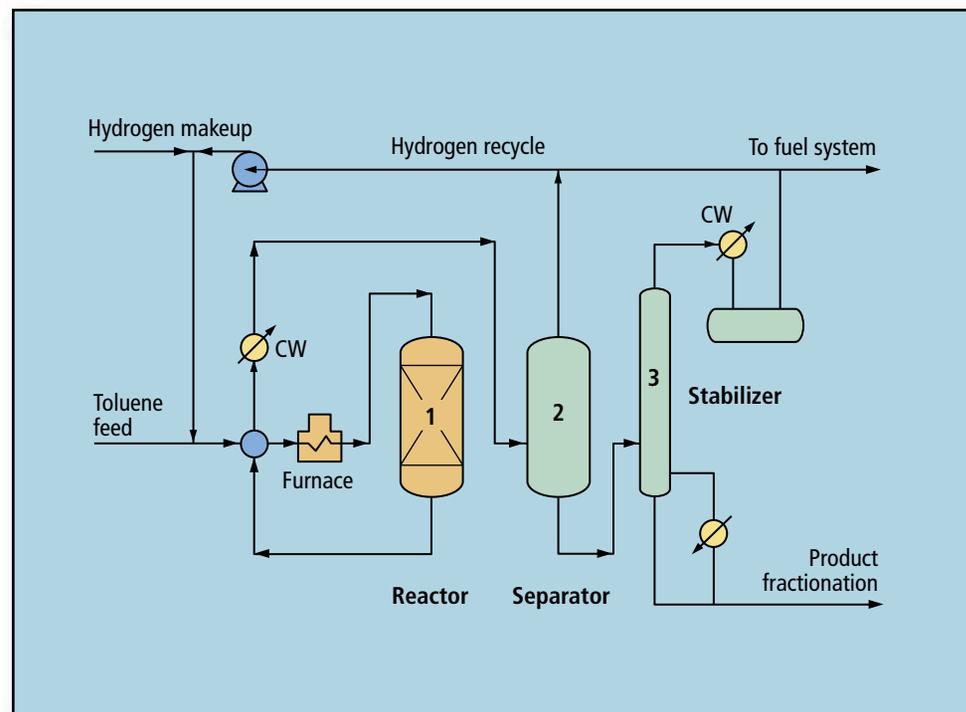
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Licensor: ExxonMobil Chemical Technology Licensing LLC (retrofit applications); Axens, Axens NA (grassroots applications).

Paraxylene

Application: A UOP aromatics complex is a combination of process units which are used to convert petroleum naphtha and pyrolysis gasoline into the basic petrochemical intermediates: benzene, toluene, paraxylene and/or ortho-xylene.

Description: The configuration of an aromatics complex depends upon the available feedstock, the desired product slate, and the balance between performance and capital investment. A fully integrated modern complex contains a number of UOP process technologies.

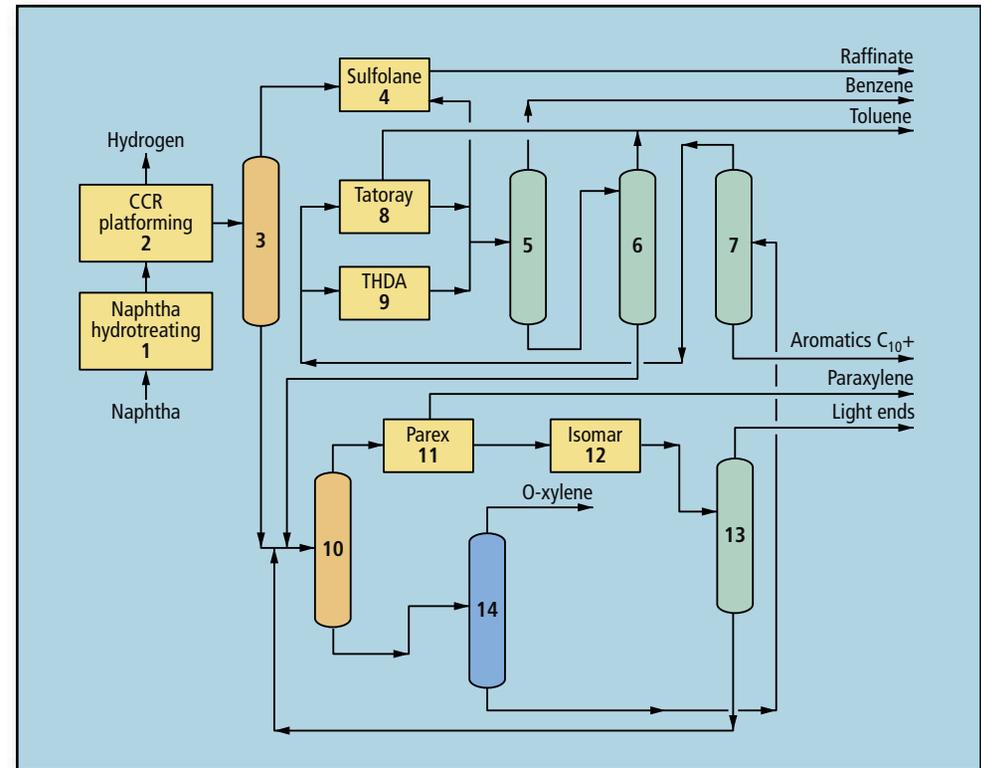
The naphtha feed is first sent to a UOP naphtha hydrotreating unit (1) to remove sulfur and nitrogen compounds and then sent to a CCR Platforming unit (2) to reform paraffins and naphthenes to aromatics.

The reformate produced in the CCR Platforming unit is sent to a debutanizer column, which strips off the light ends. The debutanizer bottoms are sent to a reformate splitter (3). The C_7 fraction from the overhead of the reformate splitter is sent to a Sulfolane unit (4). The C_8^+ fraction from the bottom of the reformate splitter is sent to a xylene fractionation section. The Sulfolane unit extracts the aromatics and then individual high-purity benzene and toluene products are recovered in a BT fractionation section (5 & 6).

Toluene is usually blended with C_9^+ aromatics (A_9^+) from the overhead of the heavy aromatics column (7) and charged to a Tatoray unit (8) for production of additional xylenes and benzene. Toluene and heavy aromatics can also be charged to a THDA unit (9) for production of additional benzene.

The C_8^+ fraction from the bottom of the reformate splitter is charged to a xylene splitter column (10). The bottom of the xylene splitter column is sent to the o-xylene column (14) to separate high-purity o-xylene product and the bottoms are sent to the heavy aromatics column (7).

The xylene splitter overhead is sent directly to a Parex unit (11), where 99.9 wt% pure paraxylene is recovered by adsorptive separation



at very high recovery. The raffinate from the Parex unit is almost entirely depleted of paraxylene and is sent to an Isomar unit (12). In the Isomar unit, additional paraxylene is produced by re-establishing an equilibrium distribution of xylene isomers. The effluent from the Isomar unit is sent to a deheptanizer column (13). The bottoms from the deheptanizer are recycled back to the xylene splitter column.

Economics: A summary of the investment cost and the utility consumption for a typical para-xylene aromatics complex to process 1.336 million mtpy of naphtha feed is indicated below. The estimated ISBL erected

Paraxylene, *continued*

cost for the unit assumes construction on a US Gulf coast site in 2003.

Investment, US\$ million	274
Products, mtpy	
Benzene	226,000
paraxylene	700,000
Pure hydrogen	47,000
Utilities, per mt of feed	
Electricity, kWh	64.3
Steam, mt	0.2
Water, cooling, m ³	35.9
Fuel, Gcal	2.5

Commercial plants: UOP is the world's leading licensor of process technology for aromatics production. UOP has licensed more than 600 separate process units for aromatics production, including over 200 CCR Platforming units, 134 Sulfolane units, 80 Parex units, 61 Isomar units, 44 Tatoray units and 38 THDA units.

UOP has designed 80 integrated aromatics complexes which produce both benzene and paraxylene. These complexes range in paraxylene production capacity from 21,000 to 1.2 million mtpy.

Licensor: UOP LLC.

Paraxylene

Application: To produce a desired xylene isomer (or isomers) from a mixture of C₈ aromatics using the UOP Isomar and Parex processes.

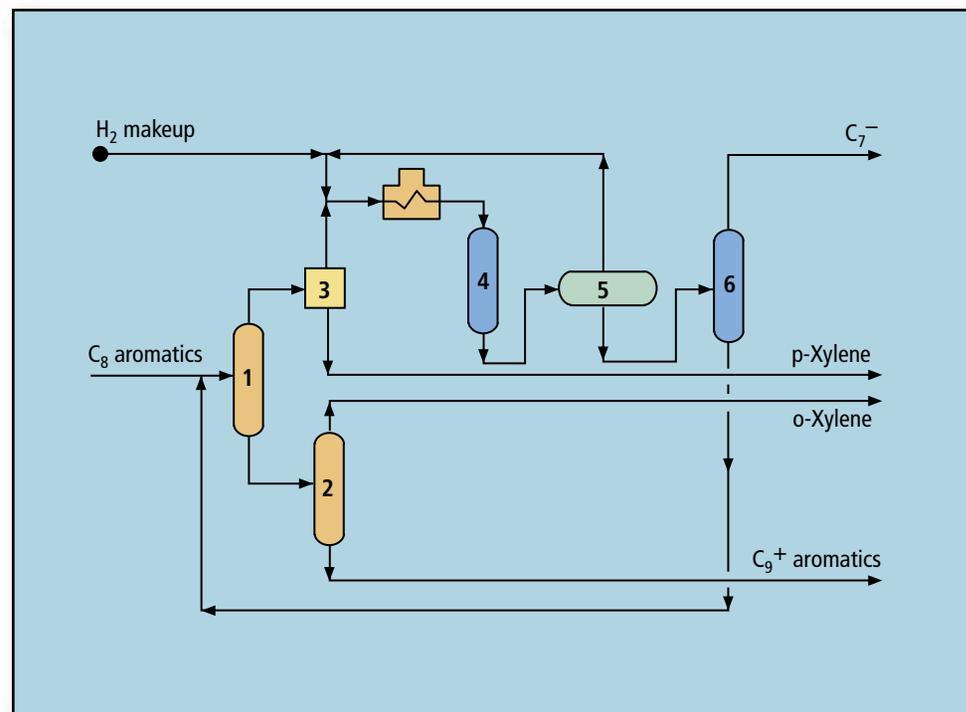
Description: Fresh feed containing an equilibrium mixture of C₈ aromatic isomers is fed to a xylene splitter (1). Bottoms from the splitter are then separated (2) into an overhead product of o-xylene and a byproduct of C₉⁺ aromatics. Overhead from the splitter is sent to a UOP Parex process unit (3) to recover 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 C₈ aromatic isomers. Hydrogen-rich recycle gas is separated (5) from the reactor effluent before fractionation (6) to remove light-cracked byproducts overhead. The remaining C₈ aromatics are then combined with the fresh feed and sent to the xylene splitter (1).

The feedstock consists of a mixture of C₈ 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 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 capable of producing 99.9% pure p-xylene with per pass recovery greater than 97%.

Operating conditions: Moderate temperature and pressure requirements permit using carbon and low-alloy steel and conventional process equipment.

Yields: Typical mass balance for the Parex-Isomar 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 which includes the xylene splitter column and the o-xylene column, US Gulf Coast fourth quarter 2002.

Investment, US\$ per mt of feed	94–108
Utilities, US\$ per mt of p-xylene product	30

Paraxylene, *continued*

Commercial plants: Since 1971, UOP has licensed 80 Parex units and 61 Isomar units.

Licensors: UOP LLC.

Paraxylene

Application: The PX-Plus XP Process converts toluene to paraxylene and benzene. The paraxylene is purified to 99.9+ wt% via single-stage crystallization and a wash column. The benzene purity is 545-grade by fractionation.

Description: The PX-Plus XP Process is composed of three processing steps:

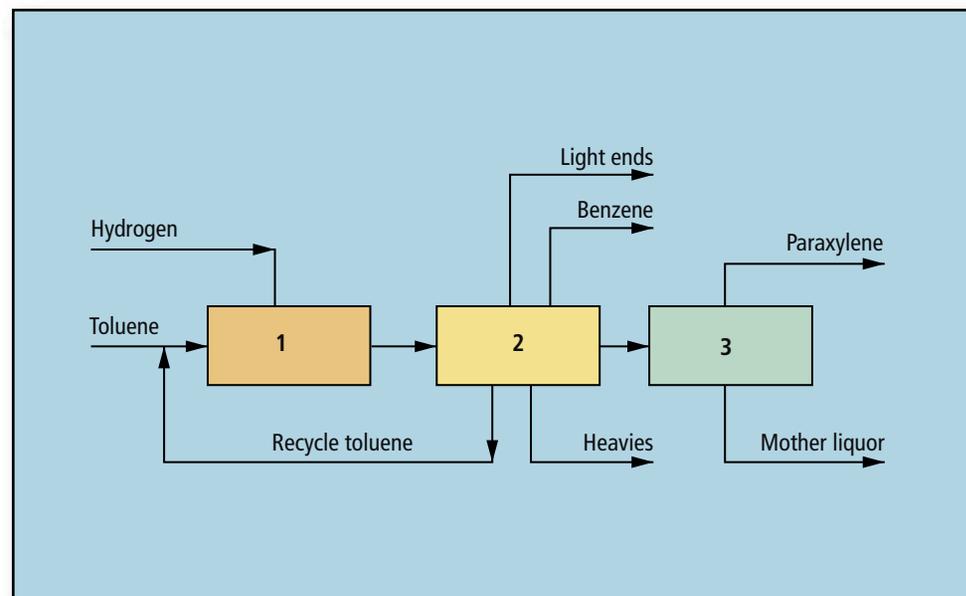
- (1) Selective toluene disproportionation, via the PX-Plus Process
- (2) Fractionation for recovery of recycle toluene and benzene product
- (3) The Badger/Niro paraxylene crystallization process, where single-stage crystallization and crystal wash columns are used.

In the PX-Plus technology, fresh toluene is combined with recycle gas, heated and fed to a fixed-bed reactor. The para-selective catalyst produces xylene product with 90% paraxylene in the xylenes. Reactor effluent flows to a separator, where the recycle gas is recovered, and the liquid product is sent to a stripper.

In the fractionation section, stripper bottoms are fed to a benzene column, where the benzene product is recovered and the unconverted toluene is fractionated for recycle. The toluene column bottoms are sent to a rerun column where the paraxylene concentrated fraction is taken overhead.

In the Badger/Niro crystallization unit, the xylenes are fed to a single-stage crystallization section that uses continuous suspension crystallization. In this section, the paraxylene is purified with a single refrigerant compressor system, and the mother liquor rejected. The purified paraxylene is fed to a Niro wash column section where ultra-high-purity paraxylene is produced by countercurrent crystal washing.

Components of this flexible technology are especially suited for capacity expansion of existing paraxylene production facilities.



Yields:

Toluene conversion per pass	30%
Paraxylene yield, wt%	40
Benzene yield, wt%	45
Light ends, wt%	<6
Paraxylene recovery	93.5%
Paraxylene purity, wt%	99.9

Economics: Capital investment per mty of paraxylene product

EEC, US\$	200
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Utilities per mt of paraxylene product

Electricity, kWh	87
Steam, HP, mt	0.7
Steam, LP, mt	0.07
Water, cooling, m ³	15
Fuel, MMkcal	1.2

Paraxylene, *continued*

Commercial plants: Two PX-Plus units are in operation; another unit is in design and construction. Two Badger/Niro licensed and process packages were produced for three Badger/Niro crystallization projects.

Licensors: UOP LLC, Stone & Webster, Inc., and Niro Process Technology B.V.

Paraxylene crystallization

Application: CrystPX is suspension crystallization technology to improve production of paraxylene, increasing capacities, increasing purity levels achievable, simplifying operation scheme, and significantly lowering capital investment. The technology optimizes current equipment and design techniques to deliver efficient and reliable production utilizing flexible, attainable equipment and feed streams.

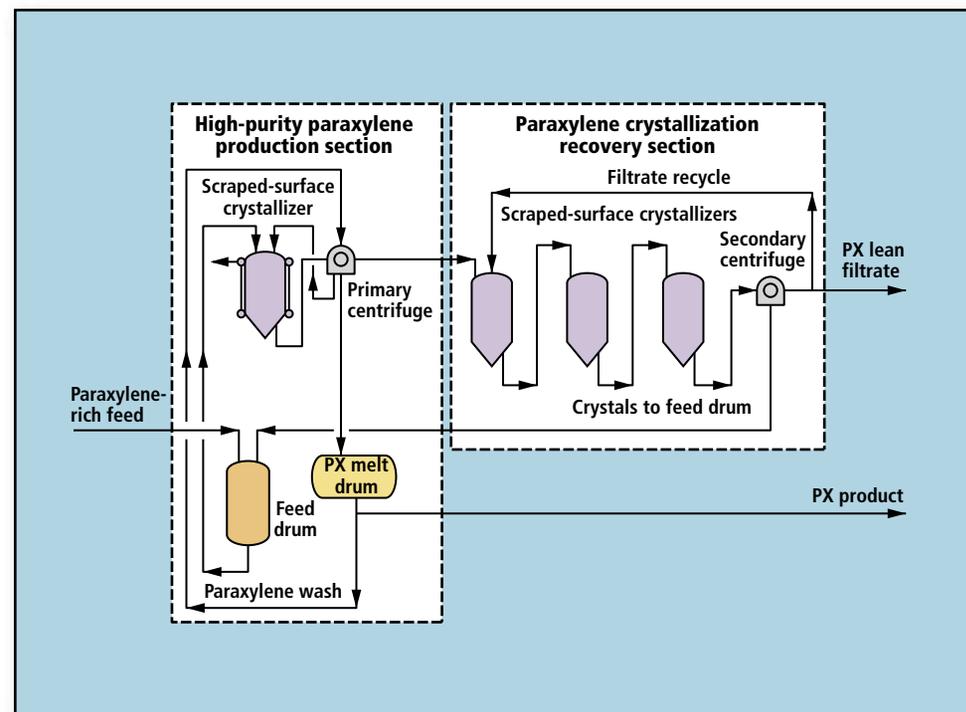
Description: Suspension crystallization of paraxylene (PX) in the xylene isomer mixture is used to produce paraxylene crystals. The technology uses an optimized arrangement of equipment to obtain the required recovery and product purity. Washing the paraxylene crystal with the final product in a high efficiency pusher-centrifuge system produces the paraxylene product.

When paraxylene content in the feed is enriched above equilibrium, for example, streams originating from selective toluene conversion processes, the proprietary crystallization process technology is even more economical to produce high-purity paraxylene product at high recoveries. The process technology takes advantage of recent advances in crystallization techniques and improvements in equipment to create this economically attractive method for paraxylene recovery and purification.

Design uses only crystallizers and centrifuges in the primary operation. This simplicity of equipment promotes low maintenance costs, easy incremental expansions, and controlled flexibility. High-purity paraxylene is produced in the front section of the process at warm temperatures, taking advantage of the high concentration of paraxylene already in the feed. At the back end of the process, high paraxylene recovery is obtained through a series of crystallizers operated successively at colder temperatures. This scheme minimizes the need for recycling excessive amounts of filtrate, thus reducing overall energy requirements.

Process advantages include:

- High paraxylene purity and recovery (99.8+ wt% purity at up to 95% recovery)



- Crystallization equipment is simple, easy to procure and operationally trouble free
- Compact design requires small plot size, and lowest capital investment
- System is flexible to meet market requirements for paraxylene purity
- System is easily amenable to future requirement for incremental capacity increases
 - Feed concentration of paraxylene is used efficiently
 - Technology is flexible to process a range of feed concentrations (75–95 wt% paraxylene) in a 1-stage refrigeration system

Paraxylene crystallization, *continued*

- Design variations are used to recover paraxylene efficiently from feedstocks (~22% PX) in a multi-stage system, competitive with adsorption-based systems.

Economics: Techno-economic comparison of CrystPX to conventional technologies; basis: 90% PX feed purity, 400,000 tpy of 99.8 wt% PX.

	CrystPX	Other crystallization technologies
Investment cost, \$MM	26.0	40.0
Paraxylene recovery, %	95	95
Electricity consumption, kWh/ton PX	50	80
Operation mode	Continuous	Batch

Licensors: GTC Technology in alliance with Lyondell Chemical Co.

Phenol

Application: Improved technology to produce highest quality phenol and acetone from cumene. Refined alpha methyl styrene (AMS) production is optional. High yield is achieved at low operating and capital costs without tar cracking.

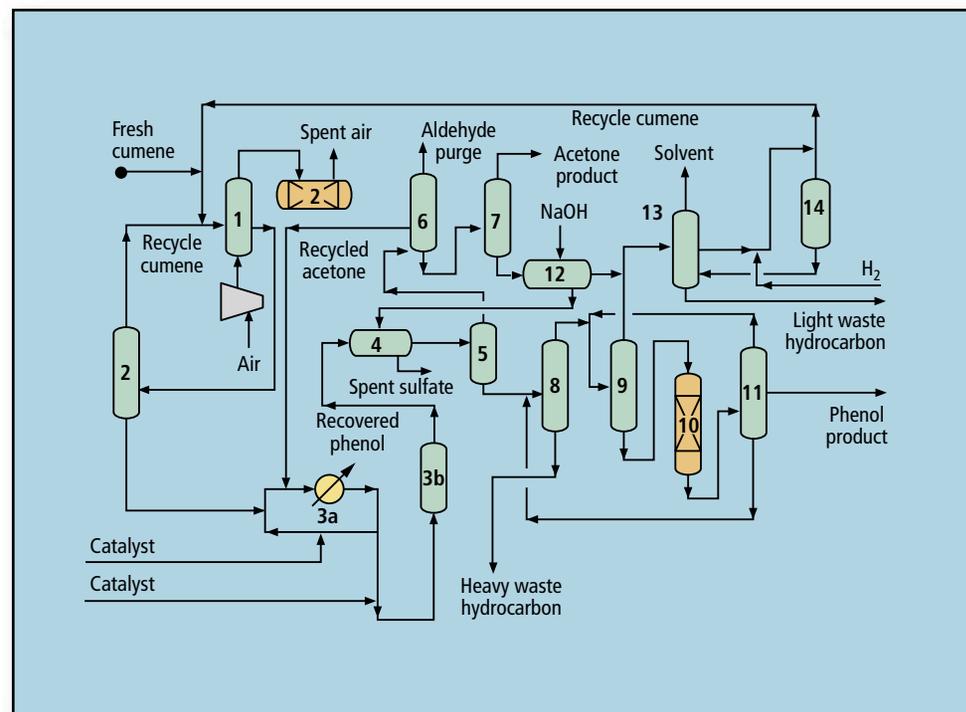
Description: Fresh and recycle cumene is oxidized (1) with air to form cumene hydroperoxide (CHP) using new oxidizer treatment technology to reduce organic acid formation and improve selectivity. Overhead vapors are cooled and condensed to recover cumene. Spent air is treated to absorb and recover residual hydrocarbons.

Oxidate is concentrated in a multistage cumene stripping system (2). Concentrated CHP flows directly to the cleavage unit where it is decomposed under precisely controlled conditions using new two-stage Advanced Cleavage Technology (3a and 3b). Cleavage conditions are optimized to permit CHP decomposition without producing heavy byproducts. Cleavage effluent is neutralized (4) before the mixture is fractionated.

Neutralized cleavage effluent is first split into separate acetone/cumene/AMS/water and phenol/heavier fractions (5). Overheads from the splitter are then fractionated to remove aldehydes (6) and cumene/AMS/water (7) to produce high-purity acetone (99.75+ wt%). Splitter bottoms is fractionated under vacuum to produce a crude phenol distillate (8) and a heavy waste hydrocarbon stream. Hydrocarbon impurities are removed from the crude phenol by hydroextractive distillation (9) followed by catalytic phenol treatment (10) and vacuum distillation (11) to produce ultra-high-purity phenol (+99.99 wt%).

Phenol is recovered from the acetone finishing column bottoms (12) by extraction with caustic. AMS in the raffinate is then concentrated (13), hydrogenated (14) and recovered as cumene for recycle to oxidation. Refined AMS production is optional.

Yields: 100,000 tons of phenol and 61,500 tons of acetone are produced from 131,600 tons of cumene, giving a product yield of over 99%.



Commercial plants: GE Plastics, Mt. Vernon, Indiana (300,000 metric tons/yr [mtpy], revamped in 1992); Formosa Chemicals & Fibre Corporation, Taiwan (400,000 mtpy, revamped in 2001 to double the original plant capacity). Lummus has more than 50 years of phenol-plant design experience.

Licensor: ABB Lummus Global/GE Plastics/Illa International.

Phenol

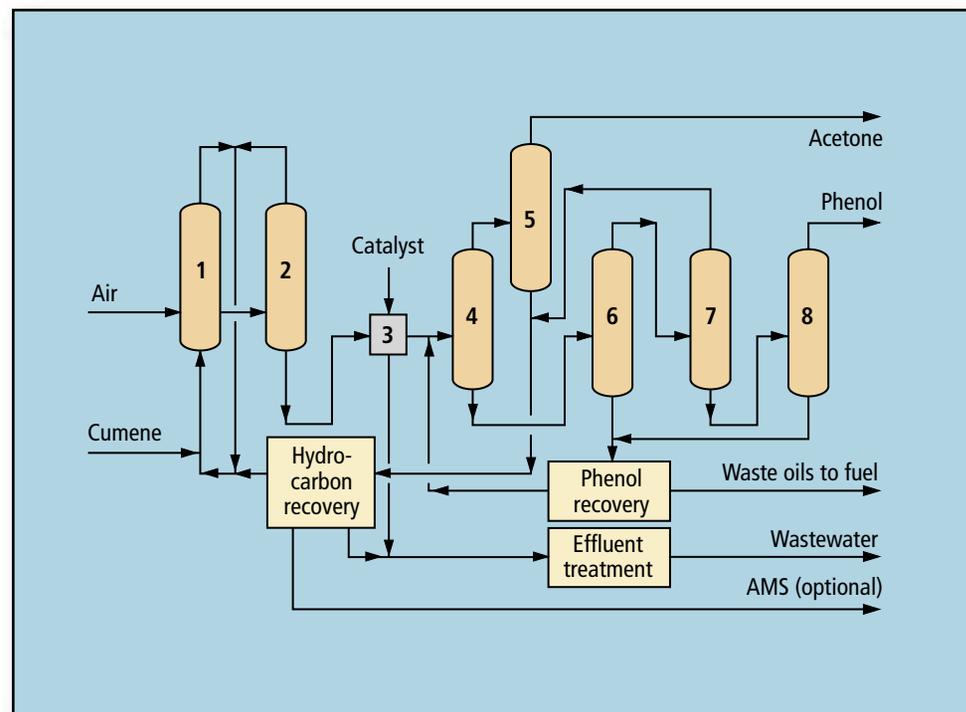
Application: A high-yield process to produce high-purity phenol and acetone from cumene with optional byproduct recovery of alpha methylstyrene (AMS) and acetophenone (AP).

Description: Cumene is oxidized (1) with air at high efficiency (+95%) to produce cumene hydroperoxide (CHP), which is concentrated (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 high-quality phenol and acetone products with very little heavy and light-end byproducts. 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 of over 2.8 MMtpy. KBR has licensed 7 grassroots plants in 10 years with a total capacity of 1.0 MMtpy. Three new licenses were awarded in 2004 with two startups scheduled for 2005. More than 50% of the world's phenol is produced via the KBR process.

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

Licensors: Kellogg Brown & Root, Inc.



Phenol

Application: The Sunoco/UOP phenol process produces high-quality phenol and acetone by liquid-phase peroxidation of cumene.

Description: Key process steps:

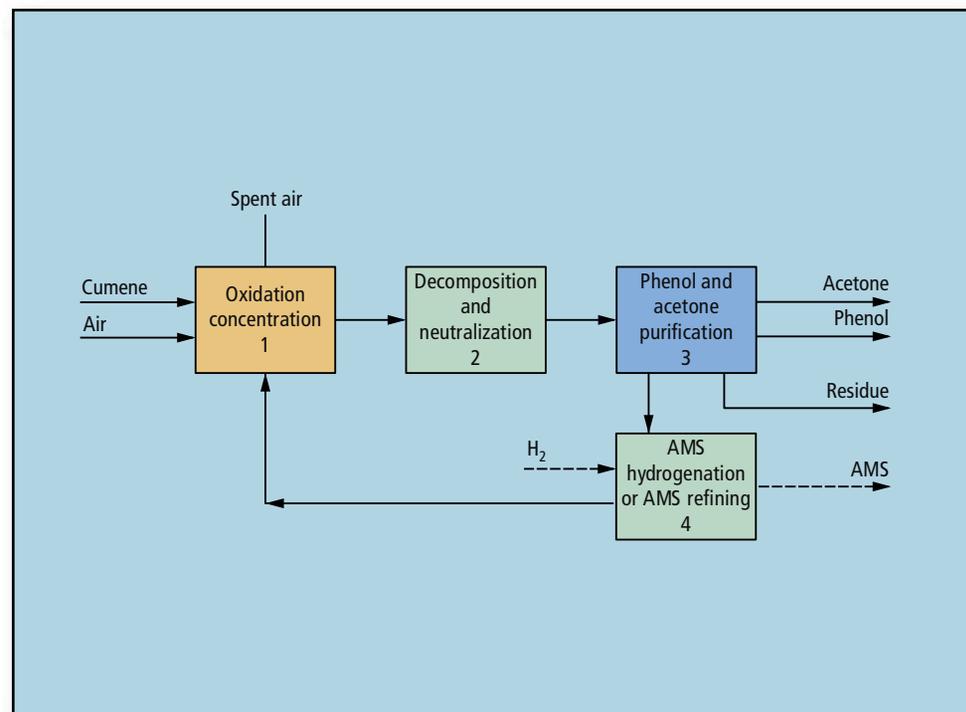
Oxidation and concentration (1): Cumene is oxidized to cumene hydroperoxide (CHP). A small amount of dimethylphenylcarbinol (DMPC) is also formed, but low-pressure and low-temperature oxidation results in very high selectivity of CHP. CHP is then concentrated and unreacted cumene is recycled back to the oxidation section.

Decomposition and neutralization (2): CHP is decomposed to phenol and acetone, accompanied by dehydration of DMPC to alphas-methylstyrene (AMS), catalyzed by mineral acid. This unique design achieves a very high selectivity to phenol, acetone and AMS without using recycle acetone. The high total yields from oxidation and decomposition combine to achieve 1.31 wt cumene/wt phenol without tar cracking. Decomposed catalyst is neutralized.

Phenol and acetone purification (3): Phenol and acetone are separated and purified. A small amount of byproduct is rejected as heavy residue.

AMS hydrogenation or AMS refining (4): AMS is hydrogenated back to cumene and recycled to oxidation, or AMS is refined for sale.

Cumene peroxidation is the preferred route to phenol, accounting for more than 90% of world production. The Sunoco/UOP Phenol process features low feedstock consumption (1.31 wt cumene/wt phenol) without tar cracking, avoiding the expense and impurities associated with tar cracking. High phenol and acetone product qualities are achieved through a combination of minimizing impurity formation and efficient purification techniques. Optimized design results in low investment cost along with low utility and chemicals consumption for low variable cost of production. Design options for byproduct alphas-methylstyrene (AMS) allow producers to select the best alternative for their market: hydrogenate AMS back to cumene, or refine AMS for sale. No acetone



recycle to the decomposition (cleavage) section, simplified neutralization, and no tar cracking make the Sunoco/UOP Phenol process easier to operate.

Commercial plants: The Sunoco/UOP Phenol process is currently used in 11 plants worldwide having total phenol capacity of more than 1 million mtpy. Four additional process units, with a total design capacity of 600,000 mtpy, are in design and construction.

Licensor: Sunoco and UOP LLC.

Phthalic anhydride

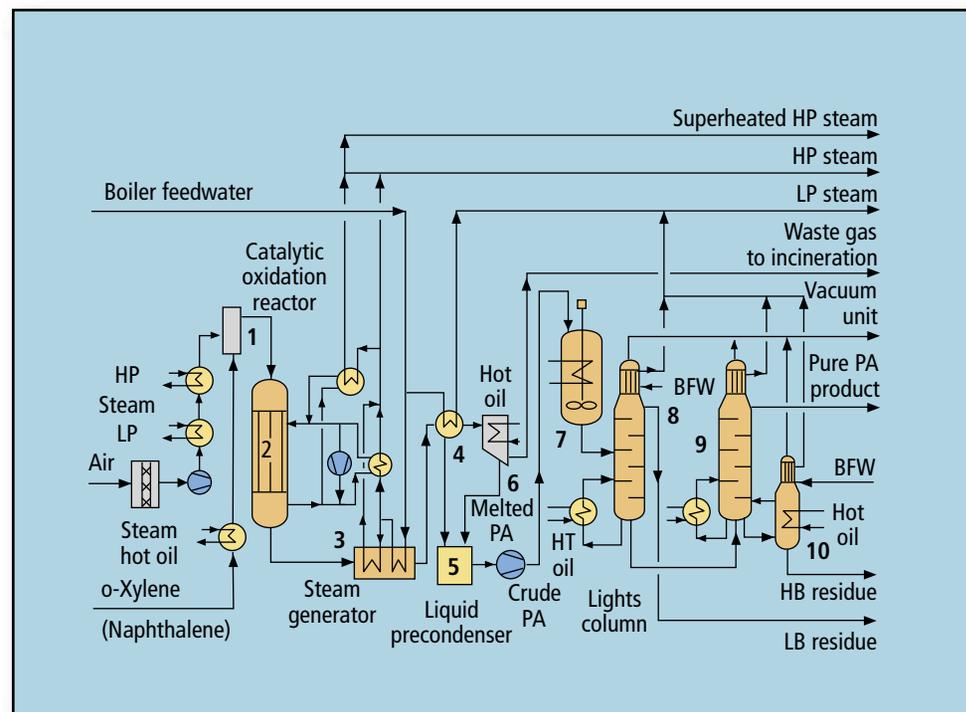
Application: To produce phthalic anhydride (PA) from o-xylene, naphthalene or mixtures of both feedstocks using a fixed-bed vapor phase process, originally known as the von Heyden Process.

Description: Air is heated and loaded with evaporated (1) o-xylene and/or naphthalene. The hydrocarbon/air mixture enters a multitubular 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. The loadings of 100 g/Nm³ air in an adiabatic post-reactor is recommended, which is installed in the enlarged gas cooler casing (3). Reactor effluent gas is precooled in a gas cooler (3) before part of the PA vapor is condensed to a liquid in the precondenser (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 from 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 naphthalene 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.

Licensor: BASF AG and Lurgi AG.

Polyalkylene terephthalates—(PET, PBT, PTT, PEN)

Application: New process to produce polyesters from the polyalkylene terephthalate family from terephthalic acid (PTA) or dimethyl terephthalate (DMT) and diols using the UIF proprietary two-reactor (2R) process consisting of tower reactor ESPREE and DISCAGE finisher or, alternatively a solid-state finishing.

Description: A slurry composed of a dicarboxylic acid and a diol is prepared at a low mole ratio. The slurry is fed to the tower reactor's bottom where the main esterification occurs under pressure or under vacuum at temperatures ranging between 170°C to 270°C. This reaction may be catalyzed or autocatalyzed.

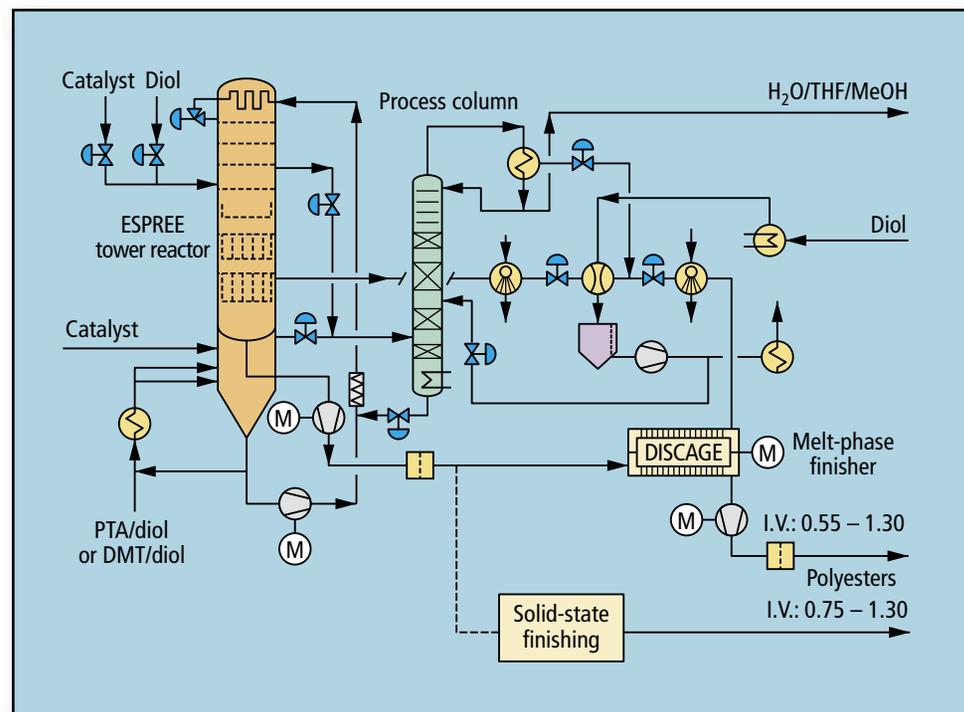
Monomer is transferred via a pressurized pipe to the reactor top where reaction side products are flashed out. Higher conversion rates (97–99%) are achieved by a cascade of four to six reaction cups at decreasing pressures and increasing temperatures.

Stirring and intermix are done by reaction vapors while passing through the cups. A precondensate with i.V.s of 0.28 to 0.35 is obtained after surface-active film evaporation—done as a twin assembly, under vacuum and higher temperature.

The prepolymer may be finished in the melt phase with UIF's DISCAGE reactor or in a solid-stating unit to obtain the required end-product features.

A process column separates side reaction low boilers from the diol, which is then recycled back to the reaction. Spray condensers and vacuum units recover unreacted feedstock and recycle the diol, thus improving the economics of this process.

Economics: This new process reduces conversion cost by more than 25% as compared to conventional/historical processes by its compact design, low energy input, short-term reaction and agitator-less design. A product yield of more than 99.5% is attainable.



Energy cost can be reduced by more than 20%. Additionally, the end-product's quality is improved due to eliminating intermediate product lines; it offers narrow residence time distribution as well as intensive surface renewal and fast reaction.

Commercial plants: Four commercial units with a total operating capacity of 1,000 mtpd and one pilot unit of 1 mtpd.

References: "Compact continuous process for high viscosity PBT," Polyester 2000 Fifth World Congress, Zürich.

Polyalkylene terephthalates—(PET, PBT, PTT, PEN),

continued

“2R single-stream PET process: A new highly economic polyester technology,” *International Fibre Journal*, vol. 19/2004, issue 4, pp. 64–67.

Licensors: Uhde Inventa-Fischer.

Polycaproamide

Application: Uhde 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 elevated 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).

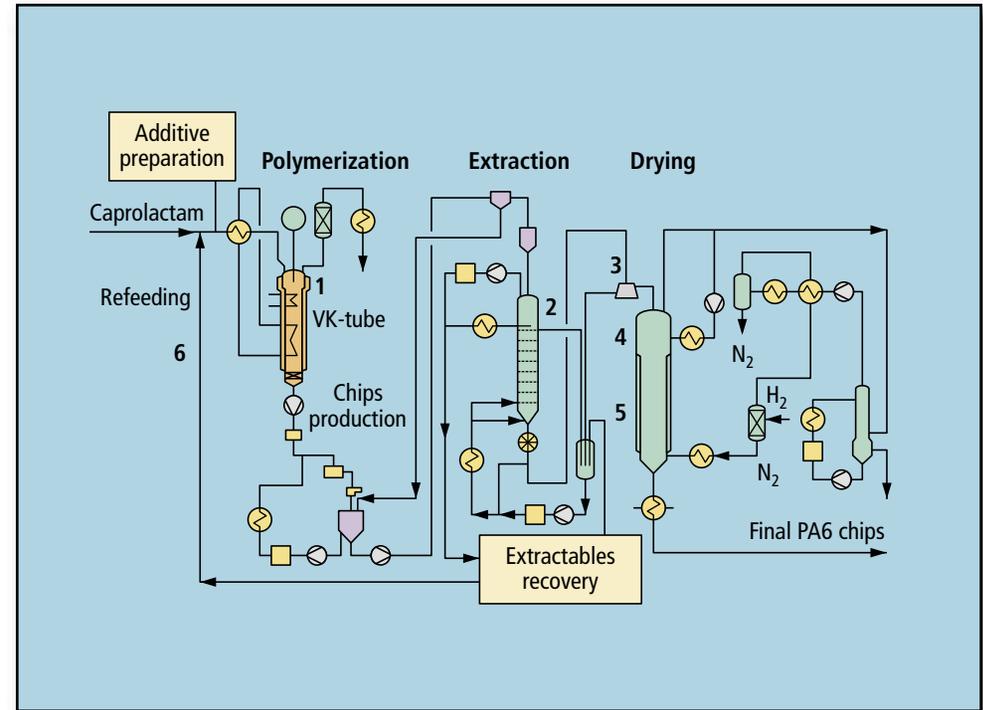
The chips—containing about 9% of monomer and cyclic oligomers—are treated with hot water in the extraction column. The extractables are removed, to a very large extent, to achieve a good polymer quality and high performance when processed further.

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 via a heat exchanger.

The drying unit can be extended to a solid-state postcondensation, i.e., drying and solid-state postcondensation occurs in one process stage. Thus, high viscosity chips for industrial yarns, films and extrusion molded parts 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. Extract water is concentrated and directly re-fed (6) to the polymerization unit. Alternatively, the concentrated extract is fed to a separate, specially designed, continuous repolymerization 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: Uhde Inventa-Fischer.

Polyesters (polyethylene terephthalate)

Application: To produce polyesters for resin and textile applications from terephthalic acid (PTA) or dimethyl terephthalate (DMT) and diols [ethylene glycol (EG) or others], using the UIF-proprietary four-reactor(4R)-process including DISCAGE-finisher.

Description: A slurry composed of PTA and EG, or molten DMT and EG is fed to the first esterification/ester-interchange reactor (1) in which main reaction occurs at elevated pressure and temperatures (200°C–270°C). Reaction vapors—water or methanol—are sent to a low/high boiler separation column. High boilers are reused as feedstock.

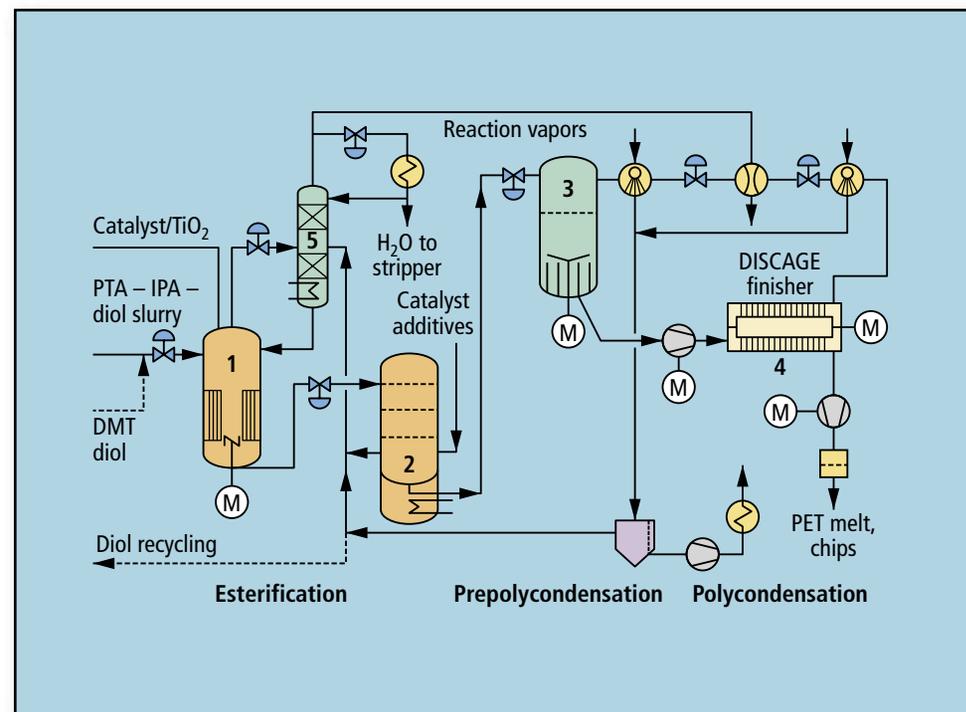
The oligomer is sent to a second cascaded, stirred reactor (2) operating at a lower pressure and a higher temperature. The reaction conversion continues to more than 97%. Catalyst and additives may be added. Reaction vapors are sent to the process column (5). The oligomer is then prepolymerized by a third cascaded reactor (3) under sub-atmospheric pressure and increased temperature to obtain a degree of polycondensation >20. Final polycondensation up to intrinsic viscosities of $i. V. = 0.9$ is done in the DISCAGE-finisher (4). Pelletizing or direct melt conversion usage is optional.

EG is recovered by condensing process vapors at vacuum conditions. Vacuum generation may be done either by water vapor as a motive stream or by the diol (EG). The average product yield exceeds 99%.

Economics: Typical utility requirements per metric ton of PET are:

Electricity, kWh	55.0
Fuel oil, kg	61.0
Nitrogen, Nm ³	0.8
Air, Nm ³	9.0

Commerical plants: Thirteen lines with processing capacities ranging from 100 to 700 mtpd are operating; more than 50 polyester CP plants



have been built worldwide. Presently, 700 mtpd lines are in operation as single-train lines, including a single finisher.

Licensor: Uhde Inventa-Fischer.

Polyethylene, HDPE

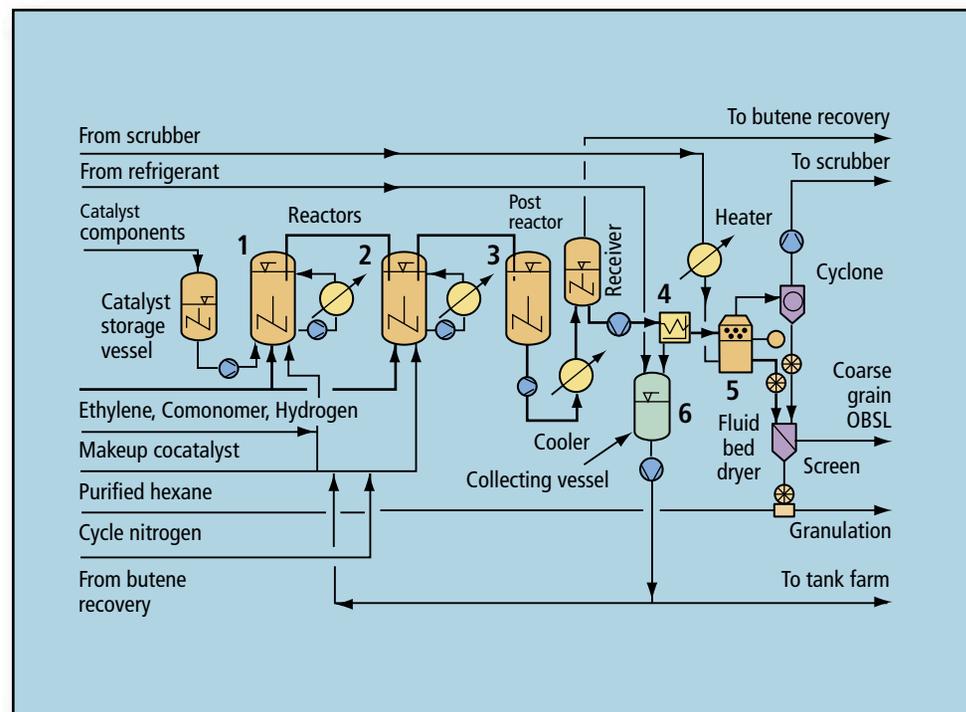
Application: To produce high-density polyethylene (HDPE) using the stirred-tank, heavy-diluent *Hostalen* process.

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

Polymerization occurs in a dispersing medium, such as n-hexane, using a very high-activity Ziegler catalyst. 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, the dispersing medium, monomer and hydrogen are fed to the reactor (1, 2) where polymerization occurs. In the case of bimodal grade production, the catalyst is only fed to the first reactor (1); the second step 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 (2). Reactor conditions are controlled continuously, thus a 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, and no monomer recycling is needed. In the decanter (4), the polymer is separated from the dispersing medium. The polymer containing the remaining hexane is dried in a fluidized bed dryer (5) and then pelletized in the extrusion section. The separated and collected dispersing medium of the fluid separation step (6) with the dissolved co-catalyst 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 the manufacturing of tailor-made products with a definite MWD from narrow to broad MWD. The melt flow index may vary from 0.2 (bimodal product) to over 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, waste bins, transport containers).

Economics: Consumption, per metric ton of PE (based on given product mix):

Ethylene and comonomer, t	1.015
Electricity, kWh	500
Steam, kg	450
Water, cooling water, $\Delta T = 10^\circ\text{C}$, mt	175

Commercial plants: There are 33 *Hostalen* plants in operation or under

Polyethylene, HDPE, *continued*

construction, with a total licensed capacity of nearly 5.5 million tpy. Individual capacity can range up to 400,000 tpy for a single-line installation.

Licensors: Basell Polyolefins.

Polyethylene, LDPE

Application: The high-pressure *Lupotech* TS or TM tubular reactor process is used to produce low-density polyethylene (LDPE) homopolymers and EVA copolymers. Single-train capacity of up to 400,000 tpy can be provided.

Description: Ethylene, initiator and, if applicable, comonomers are fed to the process and compressed to pressures up to 3,100 bar before entering the tubular reactor. In the TS mode, the complete feed enters the reactor at the inlet after the preheater; in the TM mode, part of the gas is cooled and quenches the reactor contents at various points of injection.

The polymer properties (MI, ρ , MWD) are controlled by the initiator, pressure, temperature profile and comonomer content. After the reactor, excess ethylene is recovered and recycled to the reactor feed stream. The polymer melt is mixed with additives in an extruder to yield the final product.

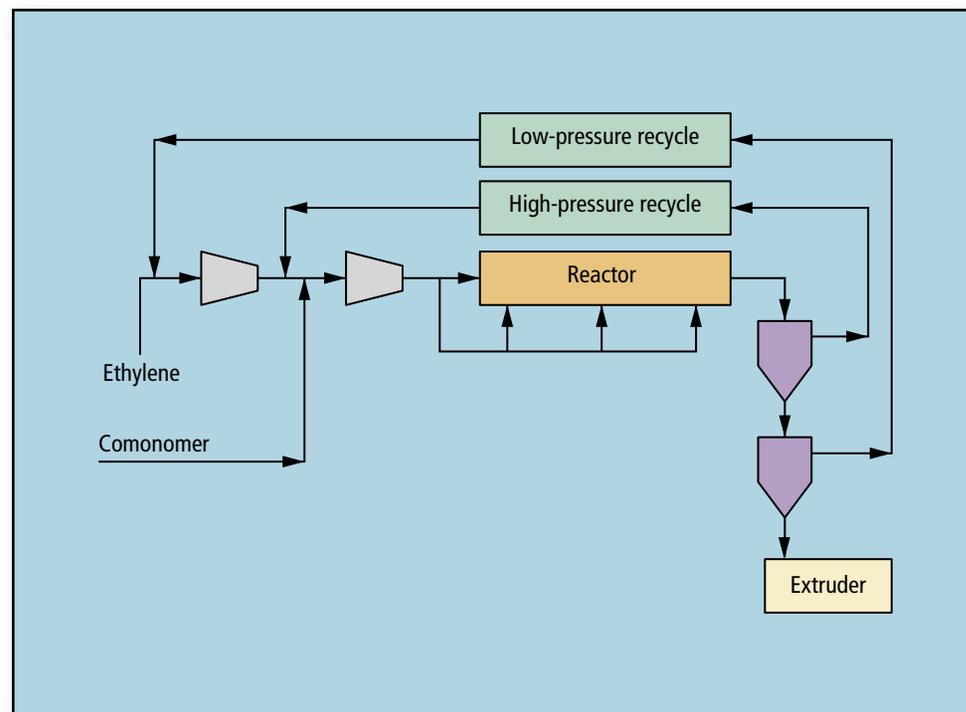
A range of products can be obtained using the *Lupotech* T process, ranging from standard LDPE grades to EVA copolymers or N-butyl-acrylate modified copolymer. The products can be applied in (shrink) film extrusion, injection molding, extrusion blow molding, pipe extrusion, pipe coating, tapes and monofilaments.

There is no limit to the number of reactor grades that can be produced. The product mix can be adjusted to match market demand and economical product ranges. Advantages for the tubular reactor design with low residence time are easy and quick transitions, startup and shut-down.

Reactor grades from MI 0.15 to ≥ 50 and from density 0.917 to 0.934 g/cm³, with comonomer content up to 30% can be prepared.

Economics: Consumption, per metric ton of PE:

Ethylene, t	1.010
Electricity, kWh	700–1,000
Steam, t	-1.2 (export credit)
Nitrogen, Nm ³	4



Commercial plants: Many *Lupotech* T plants have been installed after the first plant in 1955, with a total licensed capacity of 4.4 million tons. Basell operates LDPE plants in Europe with a total capacity of close to 1 million tpy. The newest state-of-the-art *Lupotech* TS unit at Basell's site in Aubette, France, was commissioned in 2000; with a capacity of 320 thousand tons, it is the largest single-line LDPE plant.

Licensors: Basell Polyolefins.

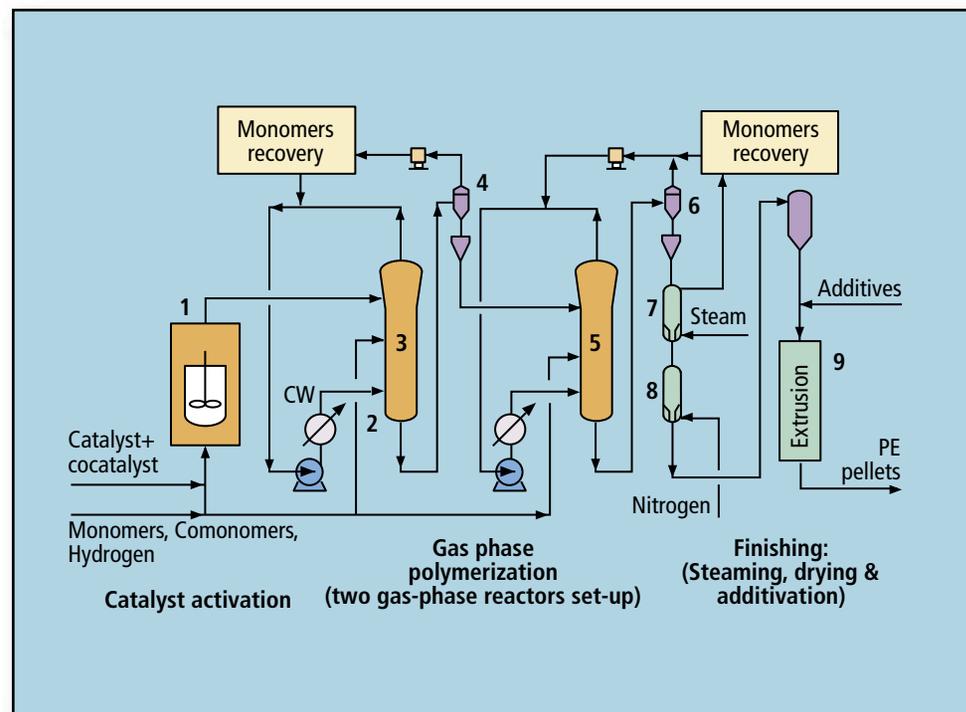
Polyethylene

Application: New generation *Spherilene* gas-phase technology with simplified process flow scheme, to produce linear-low-density polyethylene (LLDPE), medium density polyethylene (MDPE) and high-density polyethylene (HDPE) of narrow, unimodal molecular weight distribution as well as bimodal molecular weight distribution, using only a single Ziegler-Natta titanium-based catalyst family, with full online swing capability without shutdowns.

Description: Catalyst components are mixed and fed directly to a pre-contact vessel (1), where the catalyst is activated under controlled conditions. The activated catalyst system flows continuously into the first gas-phase reactor (GPR) (3). A cooler on the circulation gas loop (2) removes the reaction heat.

Product containing still active catalyst is continuously discharged from the first GPR via a proprietary device to a second GPR (5) with similar configuration. Resultant discharged gas is recovered, and no gas from the first GPR enters the second GPR, due to a proprietary "lock-hopper" system (4). The second GPR is independently supplied with necessary monomer, comonomer and hydrogen to maintain reaction conditions truly independent from the first GPR. This gives *Spherilene* process the ability to produce truly bimodal HDPE grades and the added freedom to obtain "inverse" comonomer distribution in the final product by selectively feeding comonomer only where necessary. Pressure and temperature in the GPRs are also independently controlled; while no additional feed of catalytic components to the second GPR is required.

The polymer, in spherical form with particle size ranging from approximately 0.5 mm to 3 mm, is then discharged in a receiver recovering the resultant gas (6) and to a proprietary unit for monomer stripping and neutralization of any remaining catalyst activity (7). Residual hydrocarbons in the polymer are stripped out and recycled back to reaction. The polymer is dried by a closed-loop nitrogen system (8) and with no volatile substances, is sent to liquid and/or solid additives incorporation step before extrusion (9).



Products: Product density range is very wide, from approximately 0.915 g/cc (LLDPE) to > 960 g/cc (HDPE), including full access to the MDPE range (0.930 to 0.940 g/cc). Melt index (MI) capability ranges from 0.01 to > 100 g/10 min. Because of the dual GPR set-up, *Spherilene* technology enables production of premium bimodal grades (MI, density) in gas phase with "inverse" comonomer distribution, hitherto available only via more investment-intensive slurry technologies. Commercially proven grades include bimodal HDPE for pressure pipe markets with PE100 certification and bimodal HDPE grades for high-strength film markets. Traditional HDPE grades for injection molding and extrusion applications, a

Polyethylene, *continued*

full range of LLDPE products for cast and blown film, extrusion coating and injection molding applications as well as MDPE products for rotomolding, geomembranes, textile and raffia are available.

Economics: Consumption, per metric ton of LLDPE:

Ethylene and comonomer, t	1.005
Electricity, kWh	410
Steam, kg	200
Water, cooling, $\Delta T = 10^{\circ}\text{C}$, mt	150

Commercial plants: Licensed from 1992, nine plants using *Spherilene* process and technology have been licensed, with a total capacity of 1.8 million tpy. Single-line capacities in operation range from 100,000 to 300,000 tpy, with current process design available for plants up to 400,000 tpy in single-line capacity.

Licensor: Basell Polyolefins.

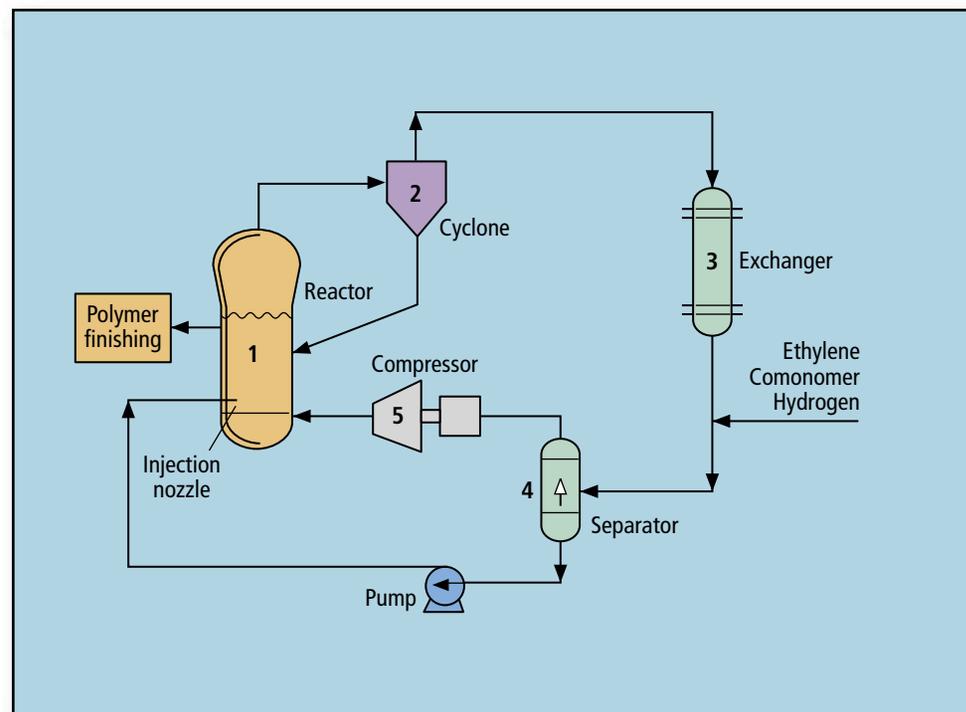
Polyethylene

Application: The Innovene G (gas phase) process produces linear-low-density polyethylene (LLDPE) and high-density polyethylene (HDPE) using either Ziegler-Natta, chromium or metallocene catalysts.

Description: Ziegler-Natta and metallocene catalysts are directly injected into the reactor from storage whereas chromium catalysts are injected following activation of the catalyst via BP proprietary technology. The BP catalyst portfolio enables the production of a full-range of PE products with the same swing reactor using these three main catalyst families.

Accurate control of all the product properties, such as density and melt index, 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 between 75°C and 110°C. Polymer particles grow in the 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), which are unique to the Innovene gas-phase technology and recycled to the reactor. This feature ensures that fine particles do not circulate in the reaction loop, where they could foul the compressor, exchanger and reactor grid. The cyclones also prevent product contamination during transitions. Unreacted gas is cooled (3) and separated from any 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 via 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.



Economics: The low-pressure technology and ease of operation ensures that the Innovene process is inherently safe, best-in-class environmentally and economically attractive with regard to both investment capex and opex.

Products: A wide range of LLDPE and HDPE products can be produced within the same reactor. LLDPE is used in film, injection molding and extrusion applications and can be made using either butene or hexene as the comonomer. Narrow molecular weight HDPE provides superior injection molding and rotational molding grades whereas broad molecular weight HDPE is used for blow molding, pipe, film and other extrusion applications.

Polyethylene, *continued*

Commercial plants: Thirty-five reactor lines are operating, in design or under construction worldwide representing around 6 MMtpy production with capacities ranging from 50,000 tpy to 350,000 tpy. Designs up to 450,000 tpy are also available.

Licensors: BP.

Polyethylene

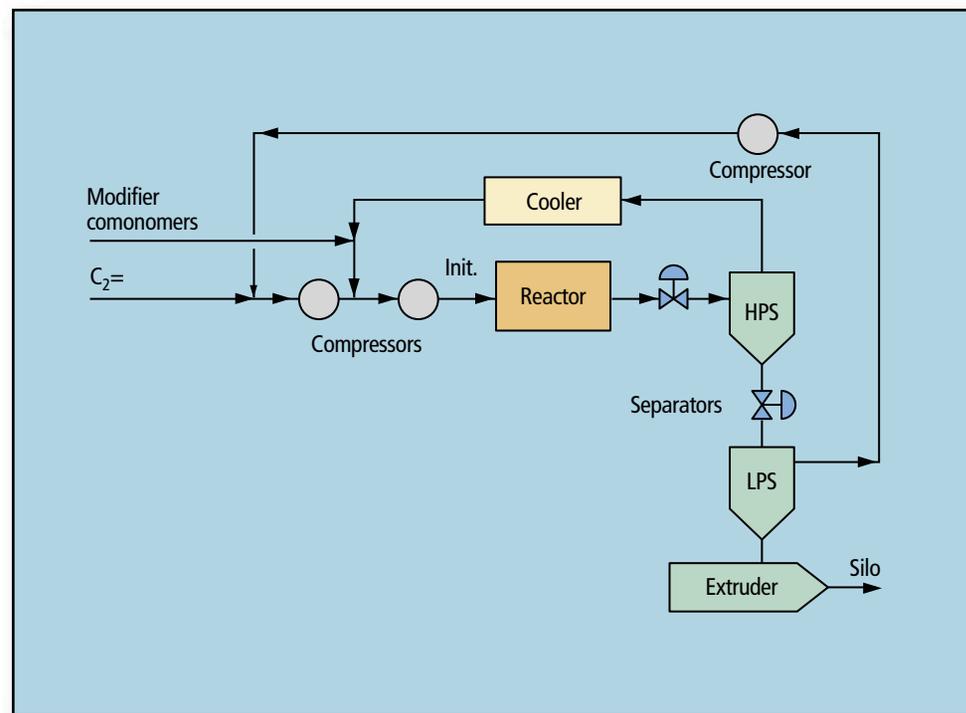
Application: To produce low-density polyethylene (LDPE) homopolymers and EVA copolymers using the high-pressure free radical process. Large-scale tubular reactors with a capacity in the range of 130–400 Mtpy, as well as stirred autoclave reactors with capacity around 100 Mtpy can be used.

Description: A variety of LDPE homopolymers and copolymers can be produced on these large reactors for various applications including films, molding and extrusion coating. 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 reactors are typically used to produce 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 other PE processes are short residence time and the ability to switch from homopolymers to copolymers incorporating polar comonomers in the same reactor. The high-pressure process produces long-chain, branched products from ethylene without expensive comonomers that are required by other processes to reduce product density. 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: Affiliates of ExxonMobil Chemical Technology Licensing LLC operate 22 high-pressure reactors on a worldwide basis with a capacity of approximately 1.4 MMtpy. Homopolymers and a variety of copolymers are produced. Since 1996, ExxonMobil Chemical Technology Licensing LLC has sold licenses with a total installed capacity (either

Polyethylene, *continued*

in operation or under construction) of approximately 1 million tpy.

Licensors: ExxonMobil Chemical Technology Licensing LLC.

Polyethylene

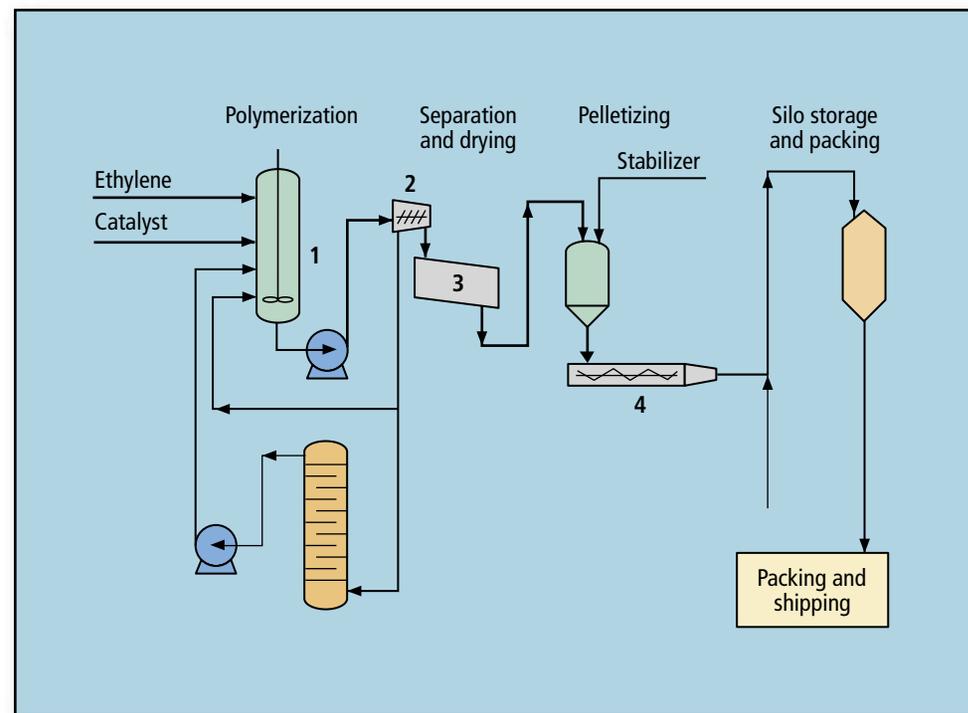
Applications: To produce high density polyethylene (HDPE) and medium density polyethylene (MDPE) under low-pressure slurry process—"CX process."

Description: The CX process uses two polymerization reactors in series. The products have bimodal molecular-weight distribution (MWD), where MWD and composition distribution is freely and easily controlled by adjusting the operating conditions of two reactors without changing the catalyst.

This process produces a wide melt index range by applying innovative catalyst chemistry combined with a sophisticated polymerization process. An all-round catalyst and simple polymerization operation provide easy product changeover that reduces transition time and yields negligible off-spec product from the transition. Mitsui has also developed new catalyst that contributes better morphology of the polymer powder and ethylene consumption.

Ethylene, hydrogen, co-monomer and a super-high activity catalyst are fed into the reactors (1). Polymerization reaction occurs under a slurry state. The automatic polymer property control system plays a very effective role in product-quality control. Slurry from the reactors is pumped to the separation system (2). The wetcake is dried into powder in the dryer system (3). As much as 90% of the solvent is separated from the slurry and is directly recycled to the reactors without any treatment. The dry powder is pelletized in the pelletizing system (4) along with required stabilizers.

Products: Broad range of homo-polymer and copolymer can be produced including PE100+ pipe grade.



Economics: Typical consumption per metric ton of natural HDPE pellets:

Ethylene and co-monomer, kg	1,004
Electricity, kWh	345
Steam, kg	340
Water, cooling, t	190

Commercial plants: Forty-one reaction lines of CX process are in operation or construction worldwide with a total production capacity of over 4.5 million tpy.

Licensor: Mitsui Chemicals, Inc.

Melt index
Molecular-weight distribution
Comonomer distribution
Density



0.01 to > 50
Freely controlled from
narrow to very wide
0.93 to 0.97

Polyethylene

Application: The SCLAIRTECH¹ technology (PE) process can produce linear-low-density, medium-density and high-density polyethylene (PE) with narrow to broad molecular weight distribution using either Ziegler-Natta (ZN) or proprietary single-site catalyst (SSC).

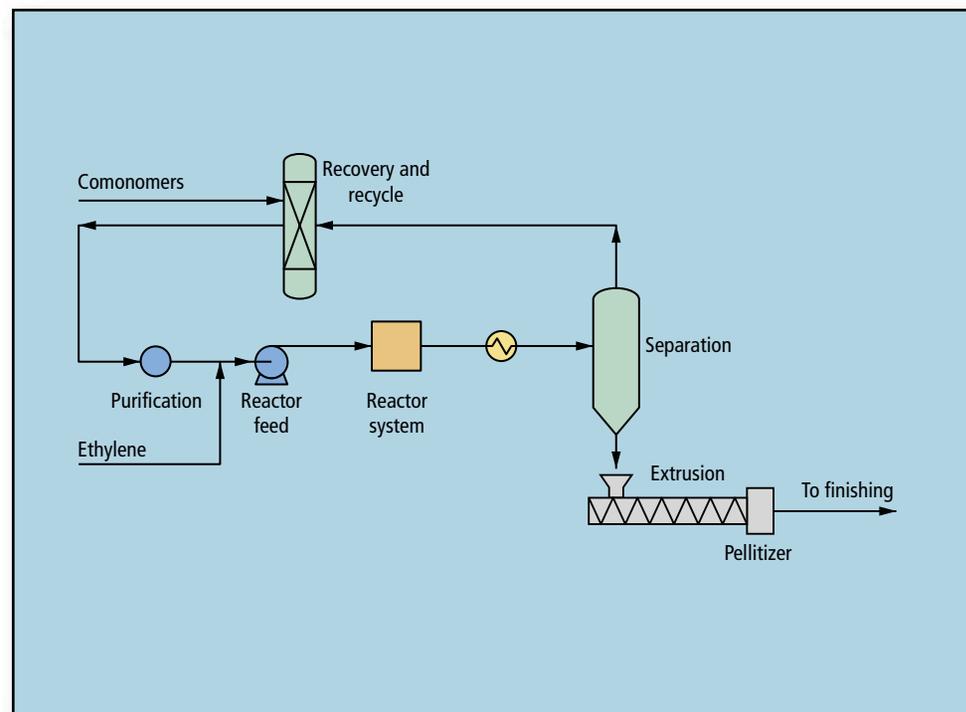
Description: Ethylene and comonomer are dissolved in solvent then fed into a reactor. Butene-1, octene-1 or both together can be used as comonomer. The reactor system operates in a solution phase, and, due to inherent low residence time (less than 2 minutes), it offers a tremendous flexibility for grade transitions and significant versatility for meeting product needs of a diverse market.

High conversions maximize production and eliminate any potential for runaway reactions. A hydrocarbon solvent is used to keep the contents of the reactor in solution and also aids in heat removal. The solvent is flashed and recovered, along with the energy captured from the heat of reaction, and circulated back to the reactor. Molten polymer is sent to a simple extruder and pelletizer assembly.

Products: SCLAIRTECH process can produce PE products with density range of 0.905–0.965 kg/m³, melt index (MI) from 0.2 to in excess of 150, and narrow to broad molecular weight distribution (MWD). This allows producers to participate in the majority of the polyethylene market segments including among low-, medium- and high-density films, rotational, injection and blow molding applications.

Products made with this technology offer exceptional quality as measured by low gel, superior opticals and lot-to-lot consistency, along with high performance characteristics for demanding applications.

Economics: This technology offers advantaged economics for producers desirous of participating in a broad range of market segments and/or niche applications, due to its ability to transition quickly and cover a large product envelope on a single line. An ability to incorporate como-



nomers such as octene-1 allows producers to participate in premium markets resulting in higher business returns.

Commercial plants: The first SCLAIRTECH plant was built in 1960. Currently, more than 12 plants worldwide are either operating, in design, or under construction with this technology, representing about 3 million tpy total capacity.

Licensors: NOVA Chemicals (International) S.A.

¹SCLAIRTECH is a trademark of NOVA Chemicals.

Polyethylene

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

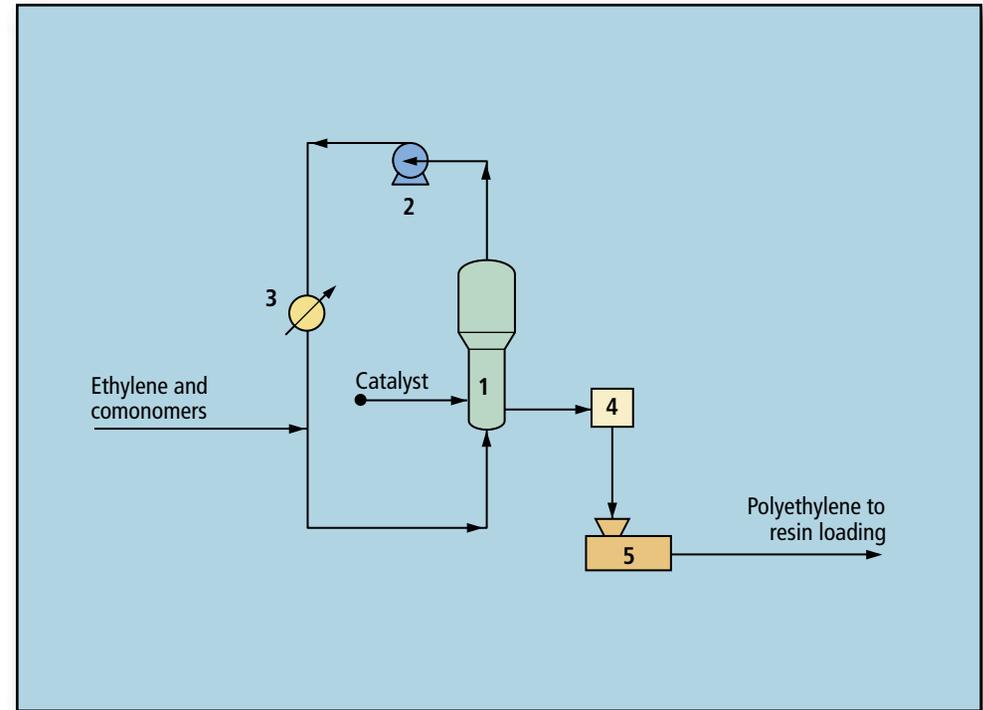
Description: A wide range of polyethylenes is made in a gas-phase, fluidized-bed reactor using proprietary solid and slurry catalysts. The product is in a dry, free-flowing granular form substantially free of fines as it leaves the reactor and is converted to pellet form for sale. Melt index and molecular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



row or broad. Melt index may be varied from less than 0.1 to greater than 200. Grades suitable for film, blow-molding, pipe, roto-molding and extrusion applications are produced.

Commercial plants: Ninety-six 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.

Licensors: Univation Technologies.

Polypropylene

Application: *Spheripol* process technology produces propylene-based polymers including homopolymer PP and many families of random and heterophasic impact and specialty impact copolymers.

Description: In the *Spheripol* process, homopolymer and random copolymer polymerization takes place in liquid propylene within a tubular loop reactor (1). Heterophasic impact copolymerization can be achieved by adding a gas-phase reactor (3) 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 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 typical polymerization-grade (99.5%).

Yields: Polymer yields of 40,000–60,000 kg/kg of supported catalyst are obtained. The polymer has a controlled particle size distribution and an isotactic index of 90–99%.

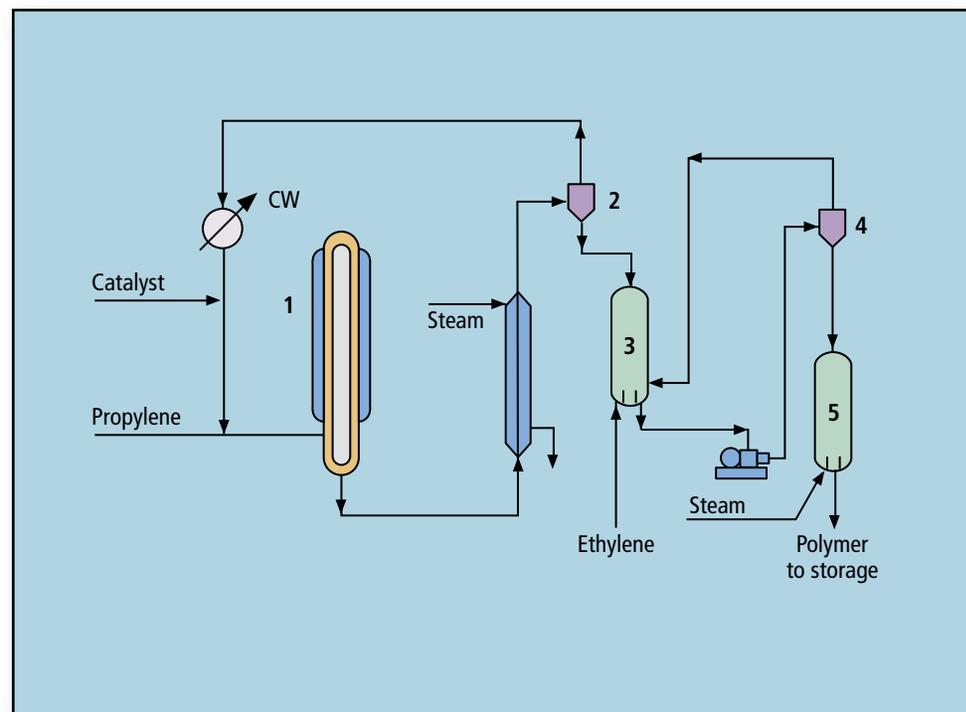
Economics: The *Spheripol* process offers a broad range of products with excellent quality and low-capital and operating costs.

Consumption, per metric ton of PP:

Propylene and comonomer, t	1.002–1.005
Catalyst, kg	0.016–0.025
Electricity, kWh	80*
Steam, kg	280
Water, cooling, mt	90

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

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



Commercial plants: *Spheripol* technology is used for about 50% of the total global PP capacity. There are 94 *Spheripol* process plants operating worldwide with total capacity of about 17 million tpy. Single-line design capacity is available in a range from 40,000 to 550,000 tpy.

Licensors: Basell Polyolefins.

Polypropylene

Application: To produce polypropylene-based polymers, including homopolymer polypropylene, random, heterophasic impact and specialty dual composition copolymers, using *Spherizone* process technology.

Description: The *Spherizone* process is Basell's new proprietary gas-loop reactor technology based on a Multi-Zone Circulating Reactor (MZCR) concept. Inside the reactor (1) the growing polymeric granule is continuously recirculating between two interrelated zones, where two distinct and different fluidynamic regimes are realized.

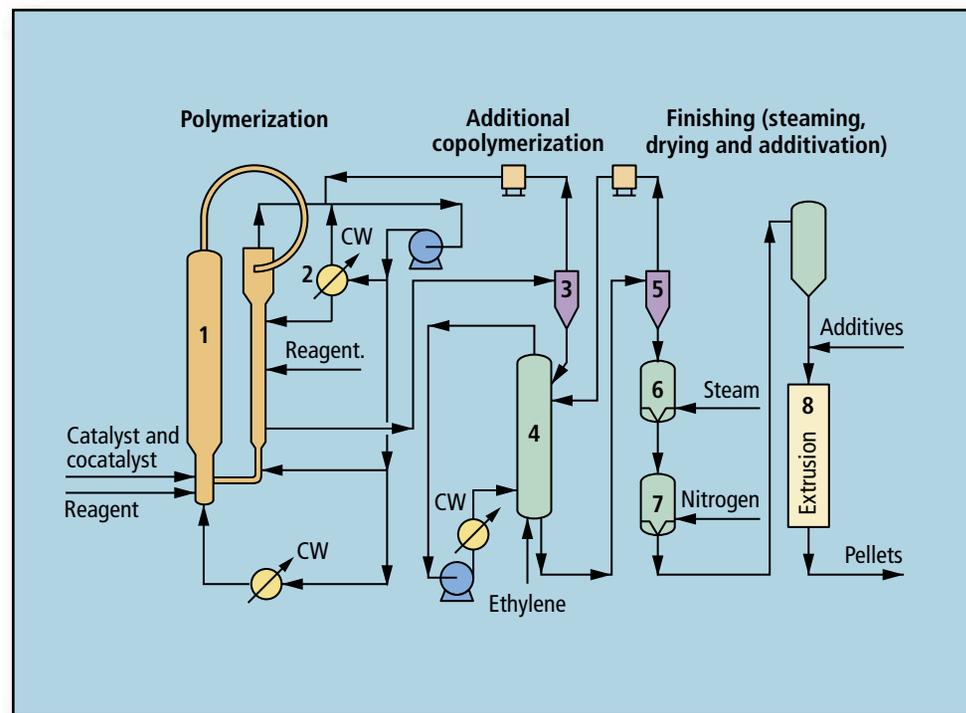
In the first zone (1a), the polymer is kept in a fast fluidization regime; when leaving this zone, the gas is separated and the polymer crosses the second zone (1b) in a packed bed mode and is then reintroduced in the first zone. A complete and massive solid re-circulation is obtained between the two zones.

The fluidynamic peculiar regime of the second zone, where the polymer enters as dense phase in plug flow, altering the gas composition with respect to the chain terminator (hydrogen) and to the comonomer. This is accomplished by injecting monomers from the external system (2) in one or more points of the second zone (1b) and so two or more different polymers (MFR and/or comonomer type and content) can grow on the same granule.

While the granules recycle through the multiple zones, different polymers are generated in an alternate and cyclic way via continuous polymerization. This allows the most intimate mixing of different polymers, giving a substantial homogeneity of the final product.

Unreacted monomer is flashed at intermediate pressure (3) and recycled back to the loop reactor, while polymer can be fed to a fluidized gas-phase reactor (4) operated in series (optional) where additional copolymer can be added to the product from the gas loop.

From the intermediate separator/second reactor, the polymer is discharged to a receiver (5), the unreacted gas is recovered, while the polymer is sent to a proprietary unit for monomer steam stripping and catalyst deactivation (6). The removed residual hydrocarbons are recycled



to the reaction. While the polymer is dried by a closed-loop nitrogen system (7) and, now free from volatile substances, the polymer is sent to additives incorporation step (8).

Economics: Raw material and utility requirements per metric ton of product:

Propylene (plus comonomer for copolymers), kg	1,002–1,005
Catalyst, kg	0.025
Electricity, kWh	120*
Steam, kg	120
Water, cooling, m ³	85

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

Polypropylene, *continued*

Products: The process can produce a broad range of propylene-based polymers, including mono- and bimodal (medium/wide/very wide molecular weight distribution) homopolymer PP, high stiffness homopolymers, random copolymers and terpolymers, high-clarity random copolymers as well as two compositions (homopolymer/random copolymer, twin-random or random/heterophasic copolymer). Conventional heterophasic impact copolymers (with improved stiffness/impact balance) can be produced with the second additional gas phase reactor, with ethylene/propylene rubber content up to 40%.

Commercial plants: A retrofitted 160,000 tpy plant is in operation at the Basell site in Brindisi since 2002, and 3 licenses for a total capacity of 1 million ton have been granted during 2004. The largest unit license is a 450,000-tpy single-line plant.

Technology owner: Basell Polyolefins.

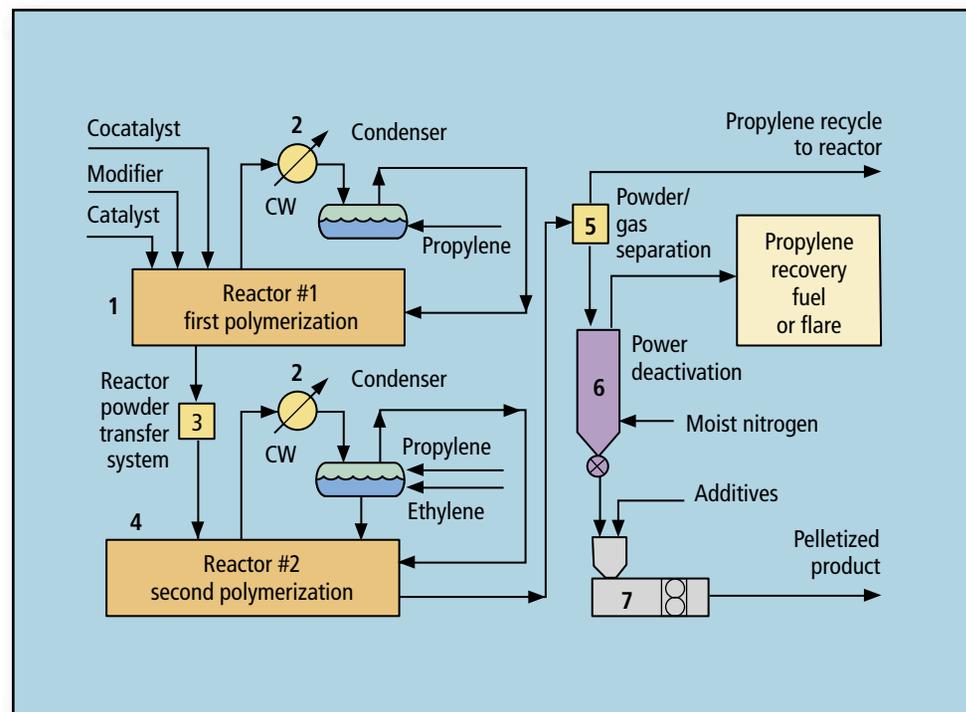
Polypropylene

Application: To produce polypropylene (PP) homopolymer, random copolymer and impact copolymer using the BP Innovene 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 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 applications, including injection molding, blow molding, thermoforming, film, extrusion, sheet and fiber. Impact copolymer produced using this process exhibits a superior balance of stiffness and impact resistance over a broad temperature range.

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

Licensors: BP.

Polypropylene

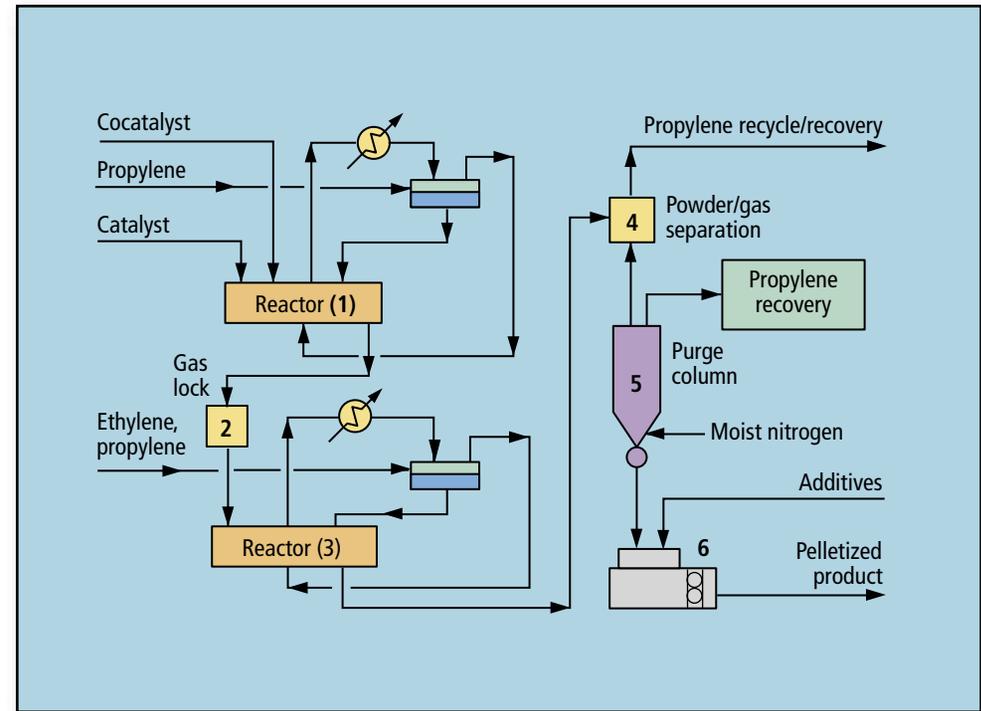
Application: A process to produce homopolymer polypropylene and ethylene-propylene random and impact co-polymers using Chisso Gas-Phase Technology utilizing horizontal plug-flow reactor.

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 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 wide range of polymer design, especially for comonomer products.

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: Ten polypropylene plants are in operation or under construction, with capacities ranging from 65,000 tpy to 360,000 tpy.



Chisso offers processing designs for single-production with capacities reaching 400,000 tpy.

Licensor: Japan Polypropylene Corp.

The rights to license this technology were given from Chisso to Japan Polypropylene Corp., which is a PP joint venture between Chisso and Mitsubishi Chemical Corp.

Polypropylene

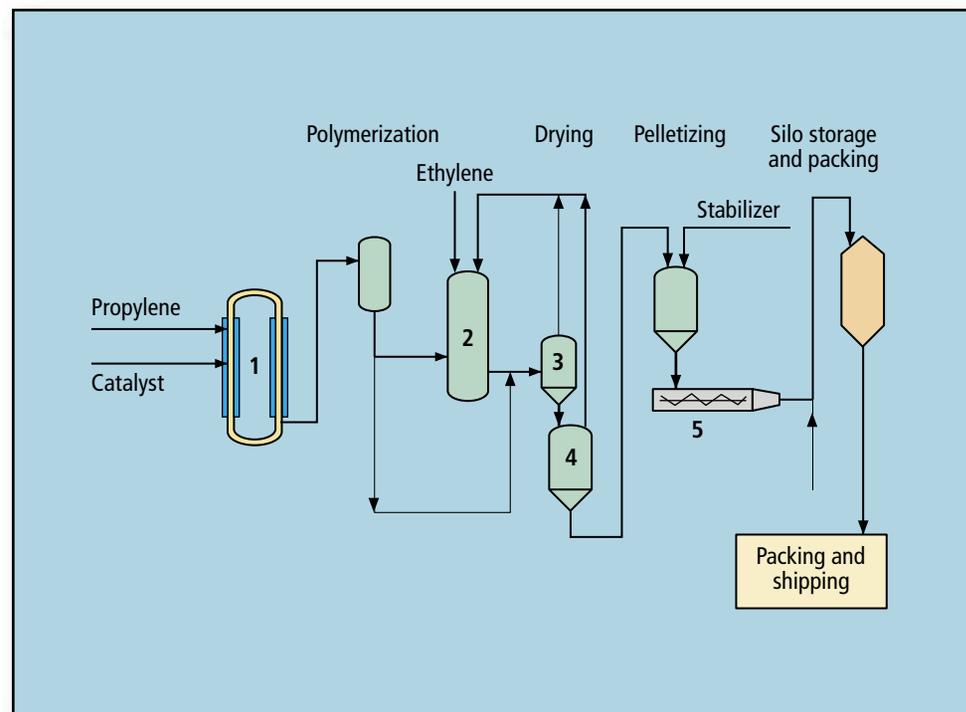
Applications: To produce polypropylene (PP) including homo-polymer, random copolymer and impact copolymer.

Description: The process, with a combination of the most advanced high-yield and high-stereospecificity catalyst, is a nonsolvent, nondeashing process. It eliminates atactic polymers and catalyst residue removal. The process can produce various grades of PP 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%.

With new catalysts based on di-ether technology (5th generation catalyst, RK-Catalyst and RH-Catalyst), wider melt-index ranged polymers can be produced (compare with those produced with 4th generation catalyst) due to the high hydrogen response of RK/RH-Catalyst.

The reactor polymer has narrow and controlled particle size distribution that stabilizes plant operation and also permits easy shipment as powder. Due to the proprietary design of the gas-phase reactor, no fouling is observed during the operation, and, consequently, reactor cleaning after producing impact copolymer is not required. In addition, combination of the flexibility of the gas-phase reactor and high-performance catalysts allow processing impact copolymer with a high-ethylene content.

In the process, homopolymer and random copolymer polymerization occurs in the loop-type reactor (or vessel-type reactor) (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 by the separator and recycled to the reactor system. The polymer powder is then transferred to the dryer system (4) where remaining propylene is removed and recovered. The dry powder is pelletized by the pelletizing system (5) along with required stabilizers.



Product: The process can produce a broad range of polypropylene polymers, including homo-polymer, random copolymer and impact copolymer, which become high-quality grades that can cover various applications.

Economics: Typical consumption per metric ton of natural propylene homopolymer pellets:

Propylene (and ethylene for copolymer),kg	1,005
Electricity, kWh	320
Steam, kg	310
Water, cooling, t	100

Polypropylene, *continued*

Commercial plants: Twenty-five reactor lines are in operation, engineering design or construction worldwide with a total production capacity of over 2.5 MMtpy.

Licensors: Mitsui Chemicals, Inc.

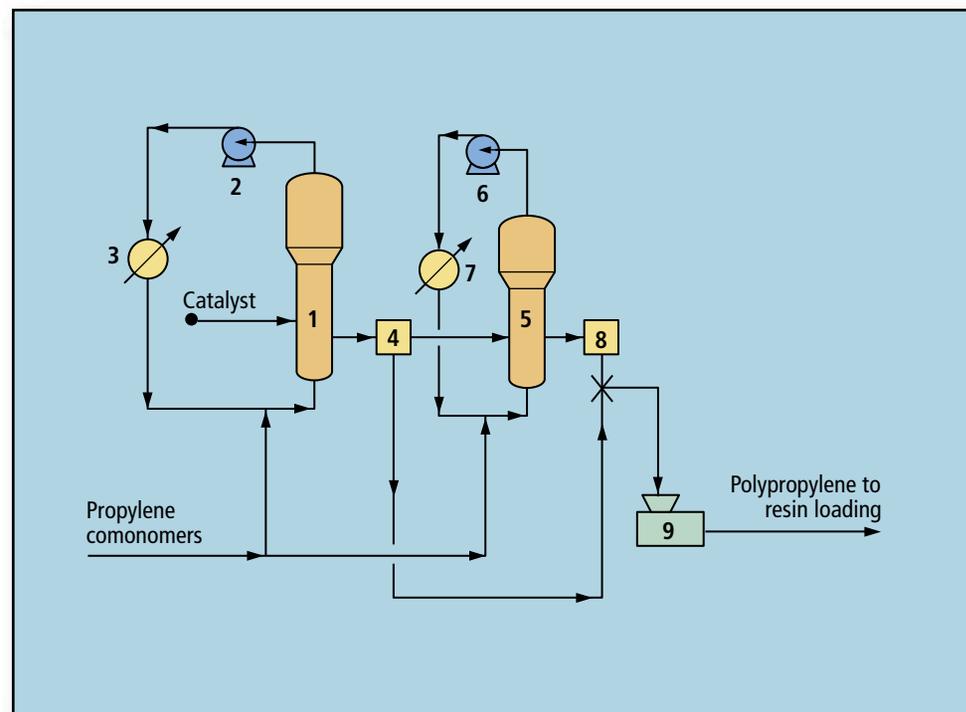
Polypropylene

Application: To produce homopolymer, random copolymer and impact copolymer polypropylene using the Dow 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 yet capable design results in low investment and operating costs, low environmental impact, 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), unreacted gas is separated from the product and returned to the reactor.

To make impact copolymers, the polypropylene resin formed in the first reactor (1) is transferred into the second reactor (5). Gaseous propylene and ethylene, with no additional catalyst, are fed into the second reactor to produce the polymeric rubber phase within the existing polypropylene particles. The second 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. Polypropylene product 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 systems available from multiple vendors (9). Dow has ongoing development programs with these suppliers to optimize their systems for UNIPOL PP resins, guaranteeing low energy input and high product quality. Controlled rheology, high melt-flow grades are produced in the pelletizing system through the addition of selected peroxides.

Products: Homopolymers can be produced with melt flows from less than 0.1 to 3,000 dg/min and isotactic content in excess of 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 dg/min). A

Polypropylene, *continued*

full range of impact copolymers can be polymerized with excellent stiffness for even the most demanding applications. Products from narrow to broad molecular-weight distribution can be manufactured in grades proven advantage for film injection, molding, blow molding, extrusion and textile applications.

Commercial plants: Nearly 40 reaction lines are in operation, with capacities ranging from 80,000 to 260,000 tpy, and plants in design up to 500,000 tpy. Total worldwide production of polypropylene with this technology is nearly 6 million tpy.

Licensor: The Dow Chemical Co. Univation Technologies is the licensor of the UNIPOL PE process.

Polystyrene, expandable

Application: To produce expandable polystyrene (EPS) via the suspension process using BP Chemicals/ABB Lummus Global technology.

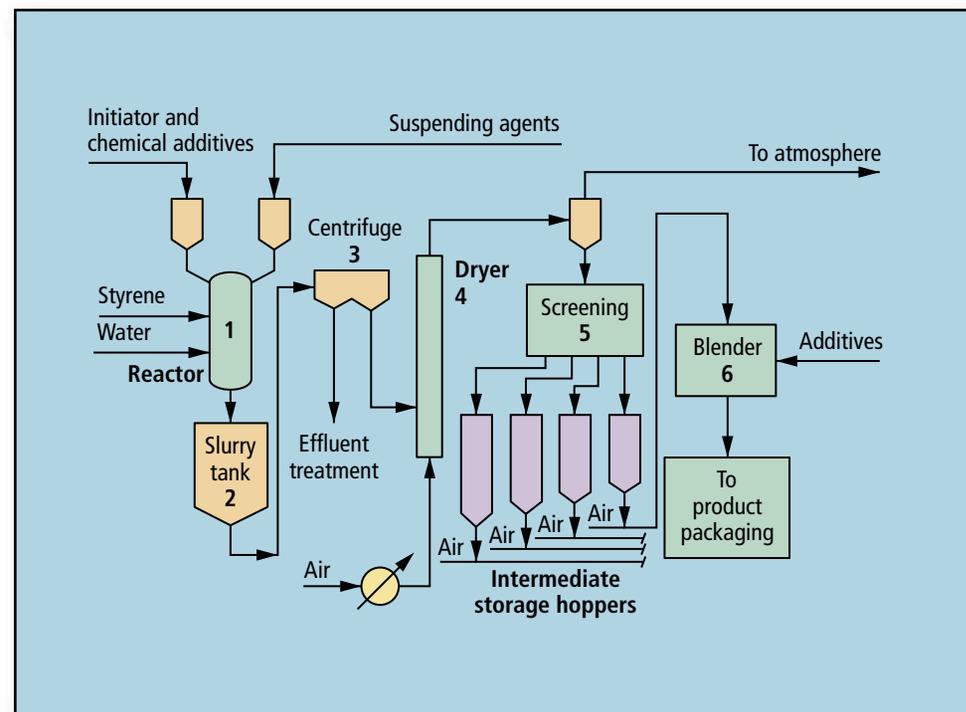
Description: The BP/Lummus styrene polymerization technology for the manufacture of regular and flame-retardant grades of EPS is a one-step batch suspension reaction followed by continuous dewatering, drying and size classification.

Styrene monomer, water, initiators, suspending agents, nucleating agents and other minor ingredients are added to the reactor (1). The contents are then subjected to a time-temperature profile under agitation. The suspending agent and agitation disperse the monomer to form beads. At the appropriate time, a premeasured quantity of pentane is introduced into the reactor. Polymerization is then continued to essentially 100% conversion. After cooling, the EPS beads and water are discharged to a holding tank (2).

From this point, the process becomes continuous. The bead/water slurry is centrifuged (3) where most of the "mother liquor" is removed. The beads are conveyed to a pneumatic dryer (4) where the remaining moisture is removed.

The dry beads are then screened (5), yielding as many as four product cuts. External lubricants are added in a proprietary blending operation (6) and the finished product is conveyed to shipping containers.

Economics: The BP/Lummus process is one of the most modern technologies for EPS production. Computer control is used to produce product uniformity while minimizing plant energy requirements. BP provides ongoing process research for product improvement and new product potential.



Commercial plants: Three commercial production units are in operation: one in France, one in Germany, and one in China for a total capacity of 200,000 metric tons.

Licensors: ABB Lummus Global/BP Chemicals.

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

Styrene and pentane, kg	1,000–1,015
Process chemicals, kg	25–49
Demineralized water, kg	1,000
Electricity, kWh	150
Steam, mt	0.42
Water, cooling, m ³	120

Polystyrene, high impact

Application: To produce a wide range of general purpose and high-impact polystyrenes (PS) via the bulk continuous process using the BP Chemicals/ABB Lummus Global technology.

Description: The production of general purpose PS (GPPS) and high-impact PS (HIPS) is essentially the same with the exception of the initial, rubber-dissolution step for HIPS.

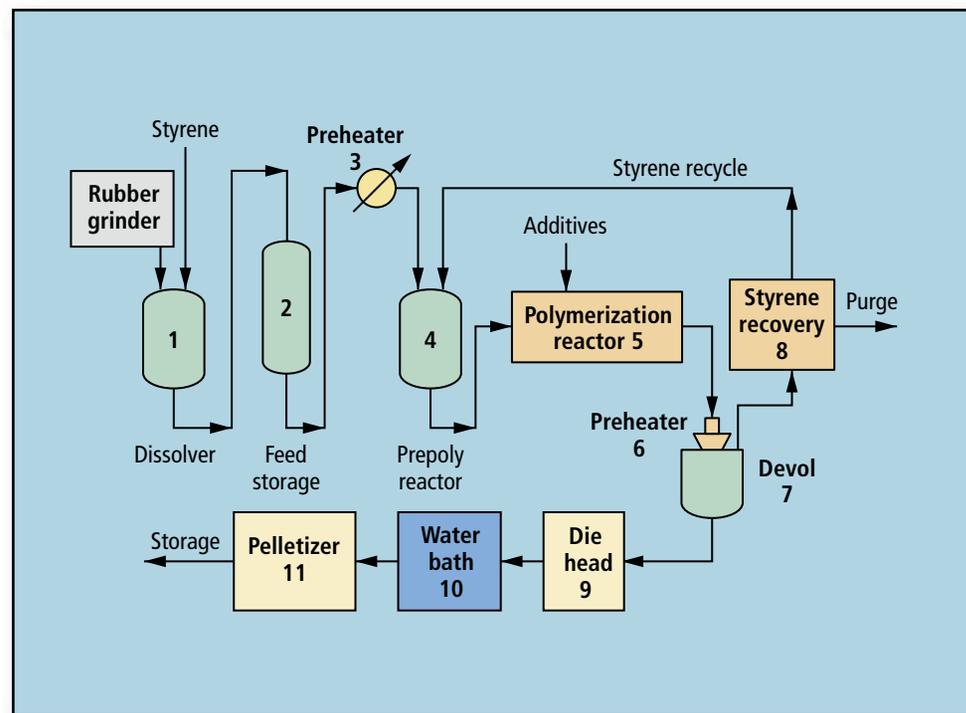
The production of HIPS begins with the granulating and dissolving of rubber and other additives in styrene monomer (1) and then transferring the rubber solution to a storage tank (2). For general-purpose product, controlled amounts of ingredients are fed directly to the feed preheater (3).

From this point on, the production steps for GPPS and HIPS are the same. The feed mixture is preheated (3) and continuously fed to the prepolymerizer (4) where the rubber morphology is established.

Following prepolymerization, the polymer mixture is pumped to the polymerization reactor (5) of proprietary design. At the exit of the reactor, the polymerization is essentially complete. The mixture is then preheated (6) in preparation for devolatilization.

The devolatilizer (7) is held under a very high vacuum to remove unreacted monomer and solvent from the polymer melt. The monomer is distilled in the styrene recovery unit (8) and recycled back to the prepolymerizer. The polymer melt is then pumped through a die head (9) to form strands, a waterbath (10) to cool the strands, a pelletizer (11) to form pellets and is screened to remove large pellets and fines. The resultant product is air-conveyed to bulk storage and packaging facilities.

Economics: The BP/Lummus process offers one of the most modern technologies for GPPS and HIPS production. A broad product line is available with a consistently high product quality. BP provides ongoing process research for product improvement and new product potential.



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

	GPPS	HIPS
Styrene and mineral oil, kg	1,011	937
Rubber, kg	-	73
Additives	1	2
Electricity, kWh	97	110
Fuel, 10 ³ kcal	127	127
Water, cooling, m ³	46	26
Steam, LP, kg	6	6

Commercial plants: Plants in France, Germany, and Sweden are in operation with a total capacity of approximately 450,000 mtpy of GPPS and HIPS. Another 300,000 mtpy GPPS and HIPS unit will start up in China in 2005.

Polystyrene, high impact, *continued*

Licensors: ABB Lummus Global/BP Chemicals.

Polystyrene, general purpose (GPPS)

Application: To produce a wide range of general purpose polystyrene (GPPS) with excellent high clarity and suitable properties to process PS foam via direct injection extrusion by the continuous bulk polymerization process using Toyo Engineering Corp. (TEC)/Mitsui Chemicals Inc. technology.

Description: Styrene monomer, a small amount of solvent and additives are fed to the specially designed reactor (1) where the polymerization is carried out. The polymerization temperature of the reactor is carefully controlled at a constant level to keep the desired conversion rate. The heat of polymerization is easily removed by a specially designed heat-transfer system.

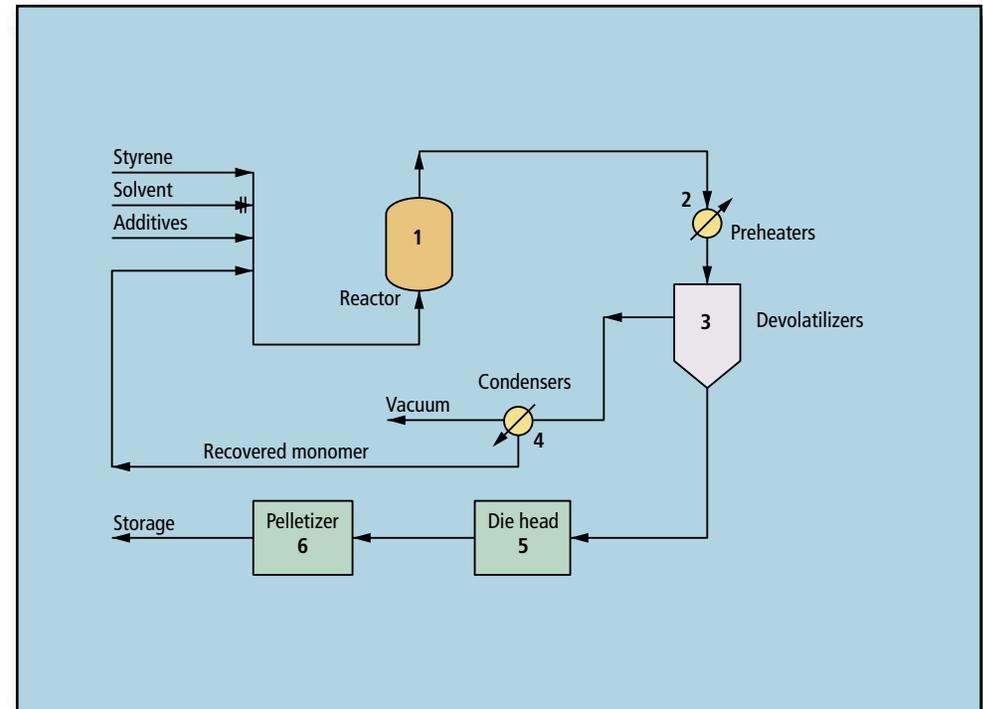
At the exit of the reactor, the polymerization is essentially complete. The mixture is then preheated (2) and transferred to the devolatilizers (3) where volatile components are separated from the polymer solution by evaporation under vacuum. The residuals are condensed (4) and recycled back to the process. The molten polymer is pumped through a die (5) and cut into pellets by a pelletizer (6).

Economics: Basis: 50,000 mtpy GPPS, US Gulf Coast:

Investment, million US\$	14
Raw materials consumption per one metric ton of GPPS, kg	1,009
Utilities consumption per one metric ton of GPPS, US\$	10.5

Installations: Six plants in Japan, Korea, China, India and Russia are in operation with a total capacity of 200,000 metric tpy.

Licensor: Toyo Engineering Corp.(TEC) / Mitsui Chemicals Inc.



Polystyrene, high-impact (HIPS)

Application: To produce a wide range of high-impact polystyrene (HIPS) with well-balanced mechanical properties and processability via the continuous bulk polymerization process using Toyo Engineering Corp. (TEC)/Mitsui Chemicals Inc. technology. The process has a swing production feature and is also capable of producing general purpose polystyrene (GPPS).

Description: Styrene monomer, ground rubber chips and small amount of additives are fed to the rubber dissolver (1). The rubber chips completely dissolved in styrene. This rubber solution is sent to a rubber-solution-feed tank (2). The rubber solution from the tank is sent to the prepolymerizer (3) where it is prepolymerized, and the rubber morphology is established.

The prepolymerized solution is then polymerized in specially designed reactors (4) arranged in series. The polymerization temperature of the reactors is carefully controlled at a constant level to maintain the desired conversion rate. The heat of the polymerization is easily removed by a specially designed heat-transfer system.

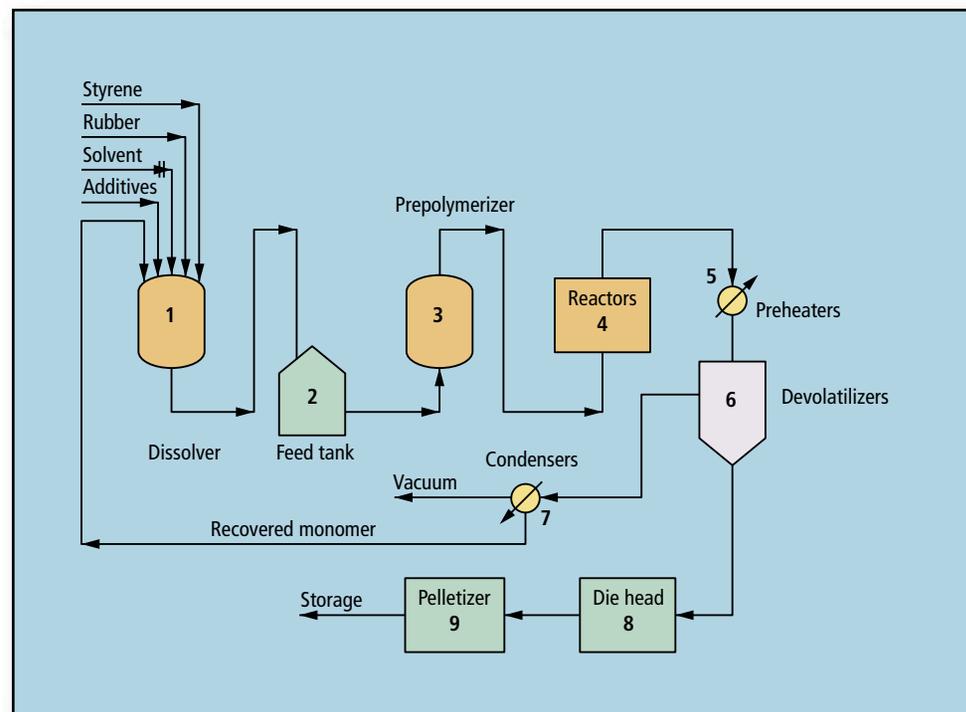
The polymerization product, a highly viscous solution, is preheated (5) and transferred to the devolatilizers (6). Volatile components are separated from the polymer solution by evaporation under vacuum. The residuals are condensed (7) and recycled to the process. The molten polymer is pumped through a die (8) and cut into pellets by a pelletizer (9).

Economics: Basis: 50,000-metric tpy HIPS unit, US Gulf Coast:

Investment, million US\$	21
Raw materials consumption per one metric ton of HIPS, kg	1,009
Utilities consumption per one metric ton of HIPS, US\$	8

Installations: Six plants in Japan, Korea, China and India are in operation with a total capacity of 190,000 metric tpy.

Licensor: Toyo Engineering Corp. (TEC)/Mitsui Chemicals Inc.



Propylene (and isobutylene)

Application: Technology for dehydrogenation of propane (or isobutane) to make high-purity propylene (or isobutylene). The CATOFIN process uses specially formulated proprietary catalyst from Süd-Chemie.

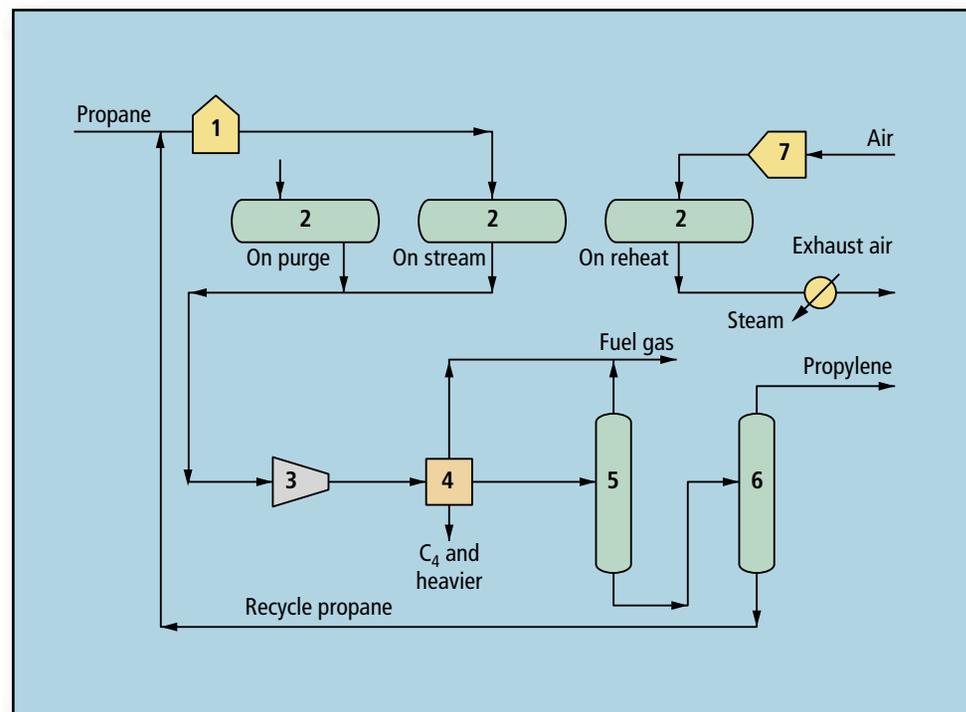
Description: The CATOFIN reaction system consists of parallel fixed-bed reactors and a regeneration air system. The reactors are cycled through a sequence consisting of reaction, regeneration and evacuation/purge steps. Multiple reactors are used so that the reactor feed/product system and regeneration air system operate in a continuous manner.

Fresh propane feed is combined with recycle feed from the bottom of the product splitter (6), vaporized, raised to reaction temperature in a charge heater (1) and fed to the reactors (2). Reaction takes place at vacuum conditions to maximize feed conversion and olefin selectivity.

After cooling, the reactor effluent gas is compressed (3) and sent to the recovery section (4), where inert gases, hydrogen, and light hydrocarbons are separated from the compressed reactor effluent and C₄ and heavier are rejected. The ethane, propane and propylene components are then sent to the product purification section deethanizer (5) and product splitter (6), where propylene product is separated from unreacted propane. The propane is recycled to the reactors.

After a suitable period of onstream operation, feed to an individual reactor is discontinued and the reactor is reheated/regenerated. Reheat/regeneration air heated in the regeneration air heater (7) is passed through the reactors. The regeneration air serves to restore the temperature profile of the bed to its initial onstream condition in addition to burning coke off the catalyst. When reheat/regeneration is completed, the reactor is re-evacuated for the next onstream period.

Yields and product quality: Propylene produced by the CATOFIN process is typically used for the production of polypropylene, where purity demands are the most stringent (>99.95%). The consumption of propane (100%) is 1.17 metric ton (mt) per mt of propylene product.



Economics: Where a large amount of low value LPG is available, the CATOFIN process is the most economical way to convert it to high value product. The large single-train capacity possible with CATOFIN units (the largest to date is for 455,000 mtpy propylene) minimizes the investment cost/mt of product.

Investment: ISBL Gulf Coast, US\$/mtpy	400–500
Raw material and utilities, per mt of propylene	
Propane, mt	1.17–1.18
Power, kWh	60
Fuel, MWh	2.5–3.0

Propylene (and isobutylene), *continued*

Commercial plants: Currently, 11 CATOFIN dehydrogenation plants are onstream producing over 2,600,000 mtpy of isobutylene and 700,000 mtpy of propylene.

Licensors: ABB Lummus Global.

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 isomerizes 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. A variation of OCT—Automet Technology—can be used to generate ethylene, propylene and the comonomer—hexene-1—by metathesis of n-butenes.

Yields: OCT 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.

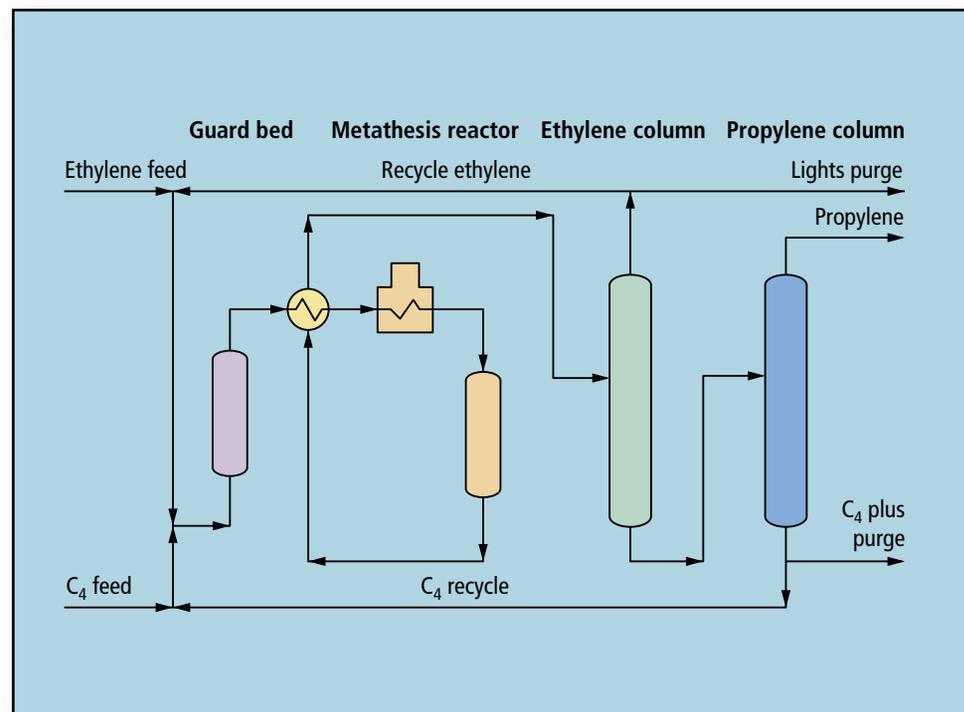
In the Automet Technology, butenes yield about 10% ethylene, 38% propylene and 47% hexene-1. The balance is C₆ and heavier material.

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

Investment, total direct field cost, US\$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, US\$ 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. Two plants have recently started up: a 690 MM lb/yr unit for BASF Fina Petrochemical in Port Arthur, Texas and a 320 MM lb/yr unit for Mitsui Petrochemical in Osaka, Japan. Six other plants are under design or construction, bringing

Propylene, *continued*

the worldwide propylene capacity via OCT to over 2 million mtpy. The Automet Technology is in operation on a semi-commercial scale at the Tianjin Petrochemical Co. in Tianjin, China.

Licensors: ABB Lummus Global.

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

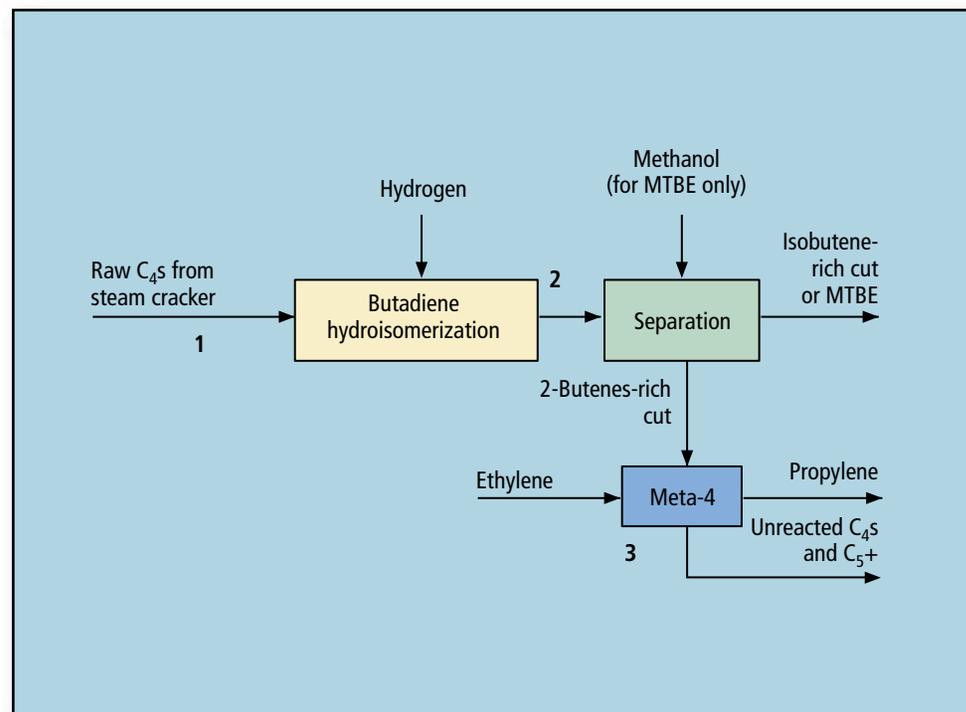
The hydroisomerization step features: complete C₄ acetylenes and butadiene conversion to butenes, maximum 2-butenes production, flexibility to process different feeds, polymer-free product and no residual hydrogen. The second step separates isobutylene either by conventional distillation, or by reacting 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 2004 investment for a Gulf Coast location of a Meta-4 process producing 180,000 tpy propylene is US\$19 million. Typical operating cost is \$18 per metric ton of propylene.

Commercial plants: Over 100 C₄ hydrogenation units have been built using Axens 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 Axens CCR Octanizing and Aromizing reformers.

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

Licensor: Axens, Axens NA.

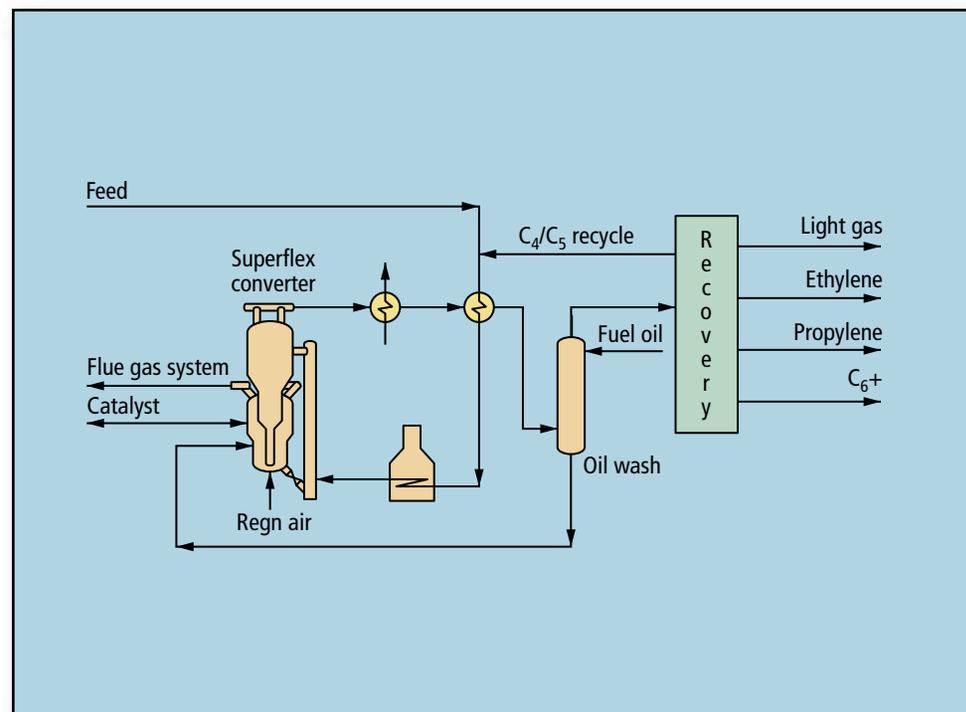
Propylene

Application: To produce propylene and ethylene from low-value, light hydrocarbon streams from ethylene plants and refineries with feeds in the carbon number range of C_4 to C_8 , such as steam cracker C_4/C_5 olefins, cat-cracker naphthas, 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 worldwide for license by Kellogg Brown & Root. It uses a fluidized catalytic reactor system with a proprietary catalyst to convert low-value feedstocks to predominately 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 raffinates, C_5 olefin-rich streams removed from motor gasolines, and Fischer-Tropsch light liquids.

The fluidized reactor system is similar to a refinery FCC unit and consists of a fluidized 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 competing fixed-bed reactors so that a substantial portion of the paraffins, as well as olefins, are converted. This allows for flexibility in the amounts of paraffins in the feeds to SUPERFLEX and the ability to recycle unconverted feed to extinction.

The cooled reactor effluent can be processed for the ultimate production of polymer-grade olefins. Several design options are available, including fully dedicated recovery facilities; recovery in a nearby, existing ethylene plant recovery section to minimize capital investment; or processing in a partial recovery unit to recover recycle streams and concentrate olefin-rich streams for further processing in nearby plants.



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		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	19.7	22.9	16.8	15.6

* Ultimate yield with C_4 s and C_5 s recycled.

Propylene, *continued*

Commercial plants: The first SUPERFLEX licensee with a propylene production of 250,000 mtpy is Sasol Technology. Engineering is underway and completion of the unit in South Africa is scheduled for 2005.

Licensors: Kellogg Brown & Root, Inc.

Propylene—methanol to propylene (MTP)

Application: To produce propylene from natural gas via methanol. This route delivers dedicated propylene from nonpetroleum sources, i.e., independently from steam crackers and FCCs.

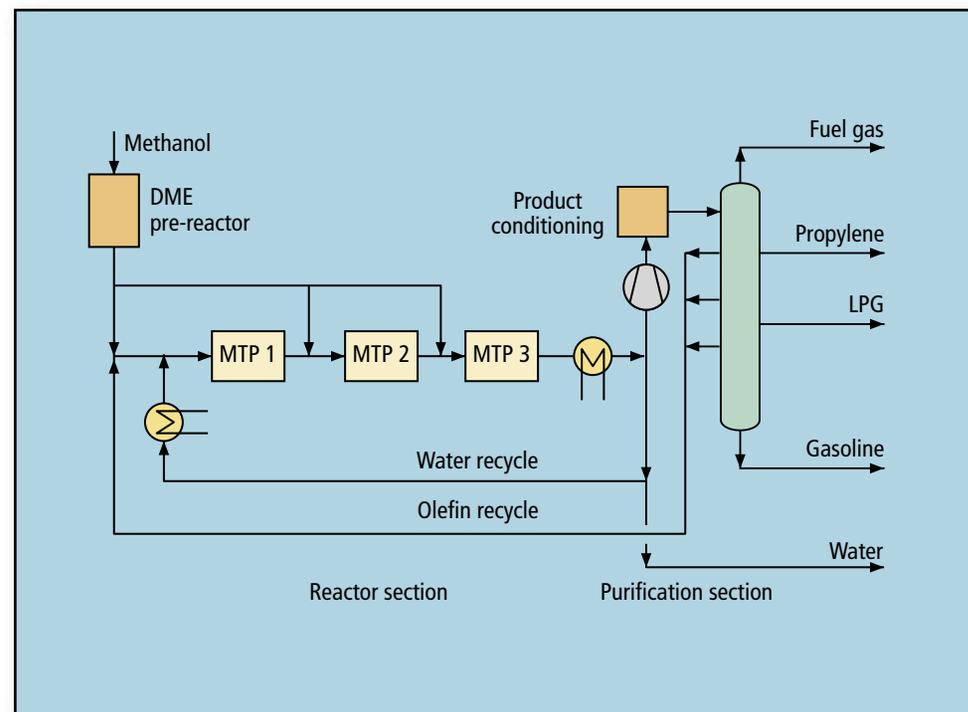
Description: Methanol feed from a MegaMethanol plant is sent to an adiabatic DME pre-reactor where methanol is converted to DME and water. The high-activity, high-selectivity catalyst nearly achieves thermodynamic equilibrium. The methanol/water/DME stream is routed to the first MTP reactor stage where the steam is added. Methanol/DME are converted by more than 99%, with propylene as the predominant hydrocarbon product. Additional reaction proceeds in the second and third MTP reactor stages. Process conditions in the three MTP reactor stages are chosen to guarantee similar reaction conditions and maximum total propylene yield. The product mixture is then cooled, and product gas, organic liquid and water are separated.

The product gas is compressed, and traces of water, CO₂ and DME are removed by standard techniques. The cleaned gas is then further processed yielding chemical- or polymer-grade propylene as specified. Several olefin-containing streams are recycled to the MTP reactor as additional propylene sources. To avoid accumulation of inert materials within the loop, a small purge removes light-ends, further purge streams of C₄ and C₅/C₆. High-grade gasoline is produced as a byproduct.

Water is recycled to steam generation; excess water from the methanol conversion is purged. This process water can be used for irrigation after appropriate and inexpensive treatment.

Economics: Current studies and projects are based on a combined MegaMethanol/MTP plant with a capacity of 5,000 mtpd of methanol (1.667 million mtpy), yielding approximately 519,000 mtpy of propylene and 143,000 mtpy of gasoline.

Based on a natural gas cost of 0.5 \$/MMBtu, net production cost for propylene will be 166 \$/mt. (Including owner's cost, capitalized



interest and depreciation, assuming a moderate credit of 160 \$/mt for the byproduct gasoline.)

Technology status: From January 2002 until March 2004, a demonstration unit was operating at the Statoil methanol plant at Tjeldbergodden, Norway. This unit has confirmed the lab results. The catalyst is commercially available. Lurgi offers the process on commercial terms.

References: Koempel, H., W. Liebner and M. Wagner, "MTP—An economical route to dedicated propylene," Second ICIS-LOR World Olefin Conference, Amsterdam, Feb. 11–12, 2003.

Koempel, H., W. Liebner and M. Rothaemel, "Progress report on

Propylene—methanol to propylene (MTP), *continued*

MTP with focus on DME, " AIChE Spring National meeting, New Orleans, April 25–29, 2004.

Licensors: Lurgi AG.

Propylene

Applications: To primarily produce propylene from C_4 to C_8 olefins supplied by steam crackers, refineries and/or methanol-to-olefins (MTO) plants via olefin cracking.

Description: The ATOFINA/UOP Olefin Cracking Process was jointly developed by Total Petrochemicals (formerly ATOFINA) and UOP to convert low-value C_4 to C_8 olefins to propylene and ethylene. The process features fixed-bed reactors operating at temperatures between 500°C and 600°C and pressures between 1 and 5 bars gauge.

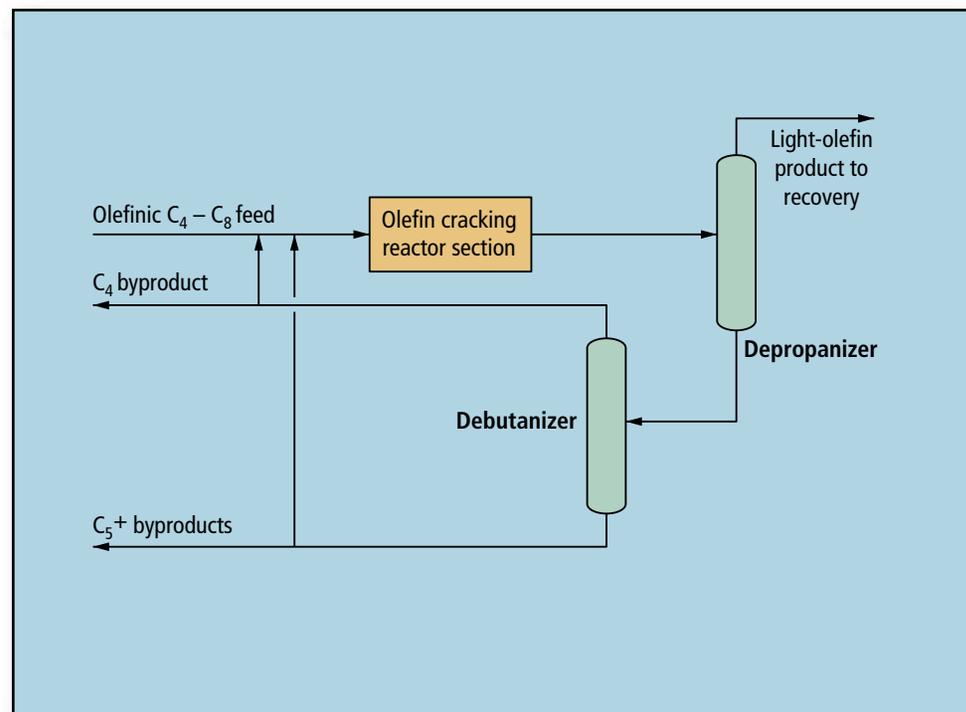
This process uses a proprietary zeolitic catalyst and provides high yields of propylene. Usage of this catalyst minimizes reactor size and operating costs by allowing operation at high-space velocities, and high conversions and selectivities without requiring an inert diluent stream. A swing-reactor system is used for catalyst regeneration. Separation facilities depend on how the unit is integrated into the processing system.

The process is designed to utilize olefinic feedstocks from steam crackers, refinery FCC and coker units, and MTO units, with typical C_4 to C_8 olefin and paraffin compositions. The catalyst exhibits little sensitivity to common impurities such as dienes, oxygenates, sulfur compounds and nitrogen compounds.

Economics: Capital and operating costs depend on how the process is integrated with steam cracking, refinery or other facilities.

Yields: Product yields are dependent on feedstock composition. The process provides propylene/ethylene production at ratios of nearly 4:1. Case studies of olefin cracking integration with naphtha crackers have shown 30% higher propylene production compared to conventional naphtha-cracker processing.

Reference: Vermeiren, W., J. Andersen, R. James, D. Wei, "Meeting the changing needs of the light olefins market," *Hydrocarbon Engineering*, October 2003.



Commercial plants: Total Petrochemicals operate a demonstration unit that was installed in an affiliated refinery in Belgium in 1998. Engineering is in progress for the first commercial unit.

Licensors: UOP LLC

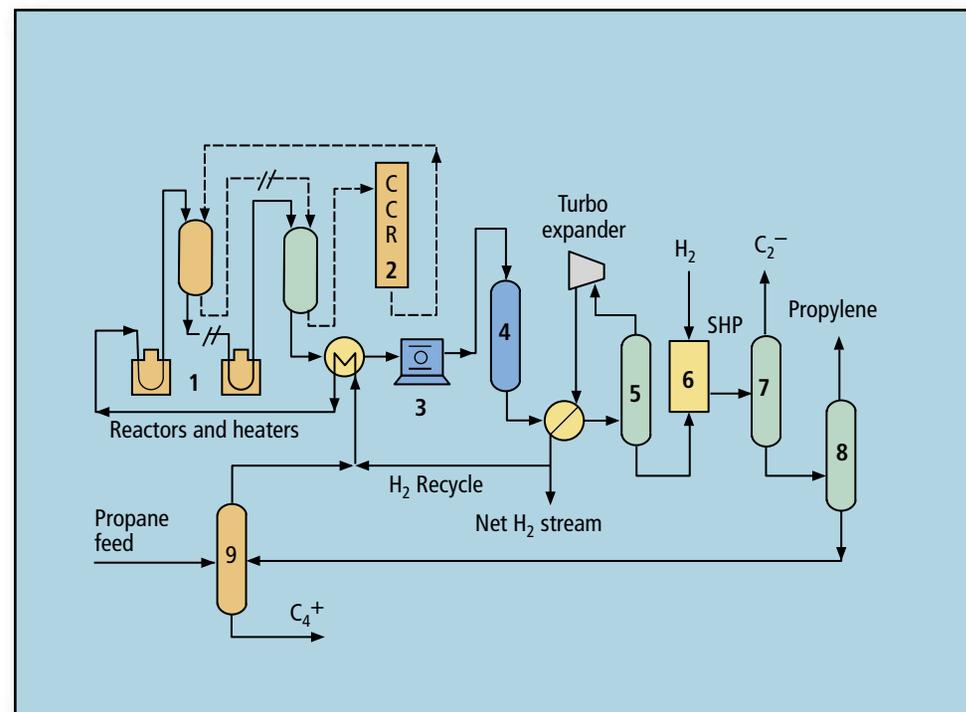
Propylene

Application: To produce polymer-grade propylene from propane using the 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: US 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.



Commercial plants: Eleven Oleflex units are in operation to produce propylene and isobutylene. Six of these units produce propylene. These units represent 1.25 million mtpy of propylene production. Three additional Oleflex units for propylene production are in design or under construction.

Licensor: UOP LLC.

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, m³ 50

Net fuel gas, MMkcal (export credit) 1.2

Catalyst and chemical cost, \$/metric ton product 14

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.

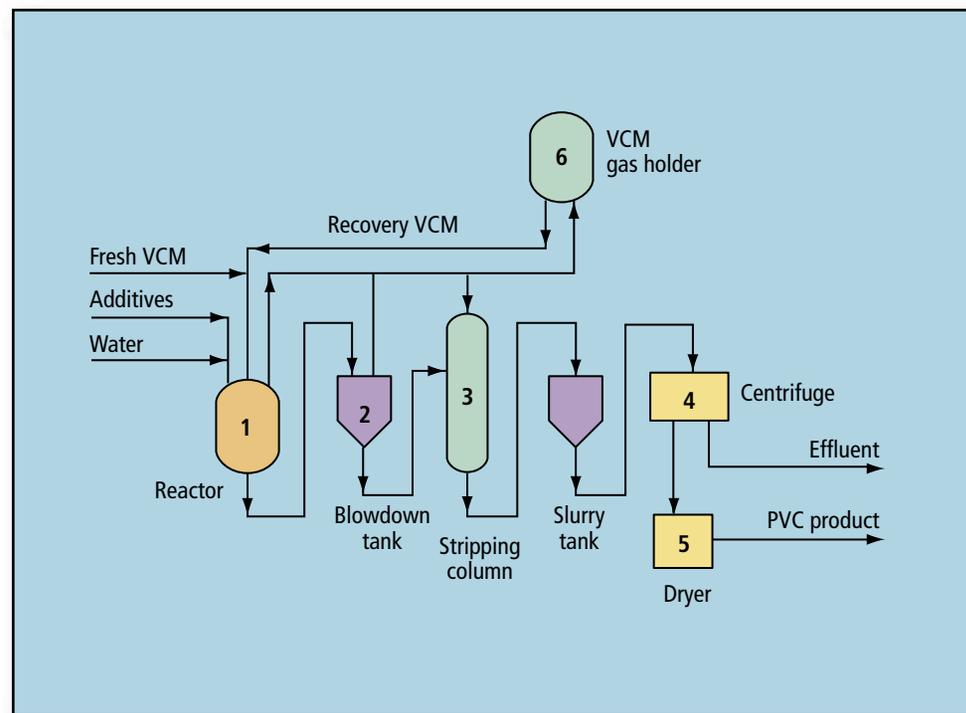
Recovered VCM is held in a gas holder (6), then compressed, cooled and condensed to be reused for the following polymerization batch.

Economics:

Raw materials and utilities, per ton of PVC:

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

Commercial plants: The process has been successfully licensed 15 times worldwide. Total capacity of the Chisso process in the world is more than 1.5 million tpy. In addition, Chisso VCM removal technology has been licensed to many PVC producers worldwide.



Licensor: Chisso Corp.

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 150 m³. 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).

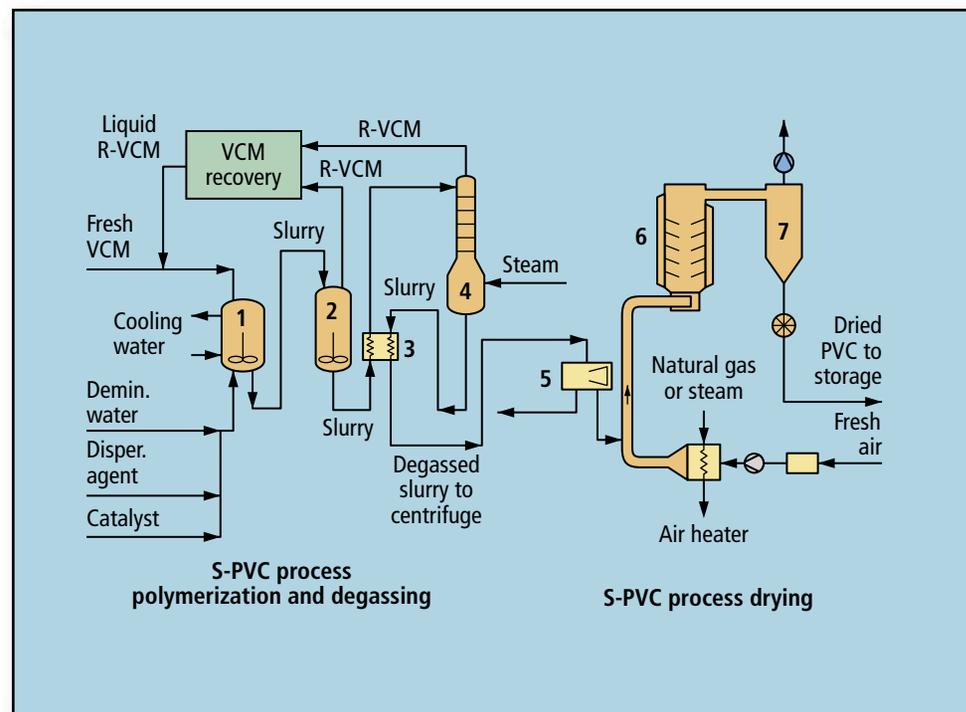
The batch-wise polymerization occurs in the following operation sequence:

- Prepare the reactor, which includes applying a highly effective anti-fouling 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 flashed 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 metric ton of PVC:

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

Commercial plants: Vinnolit is producing up to 650,000 PVC metric tpy. Total capacity of the Vinnolit process in the world is about one million metric tpy. Vinnolit cyclone dryer has been licensed to many PVC producers worldwide.

PVC (suspension), *continued*

Licensors: Vinnolit.

Contractor: Uhde GmbH.

Upgrading pyrolysis gasoline

Application: Increase the value of steam cracker pyrolysis gasoline (pygas) using conversion, distillation and selective hydrogenation processes. Pygas, the C₅–C₉ fraction issuing from steam crackers, is a potential source of products such as dicyclopentadiene (DCPD), isoprene, cyclopentane, benzene, toluene and xylenes.

Description: To produce DCPD and isoprene, pygas is depentanized and the C₅ fraction is processed thermally to dimerize cyclopentadiene to DCPD which separates easily (1) from the C₅s via distillation. Isoprene can be recovered by extractive distillation and distillation. The remaining C₅s and the C₆–C₉ cut are fed to the first stage (2) catalytic hydrogenation unit where olefins and diolefins are eliminated.

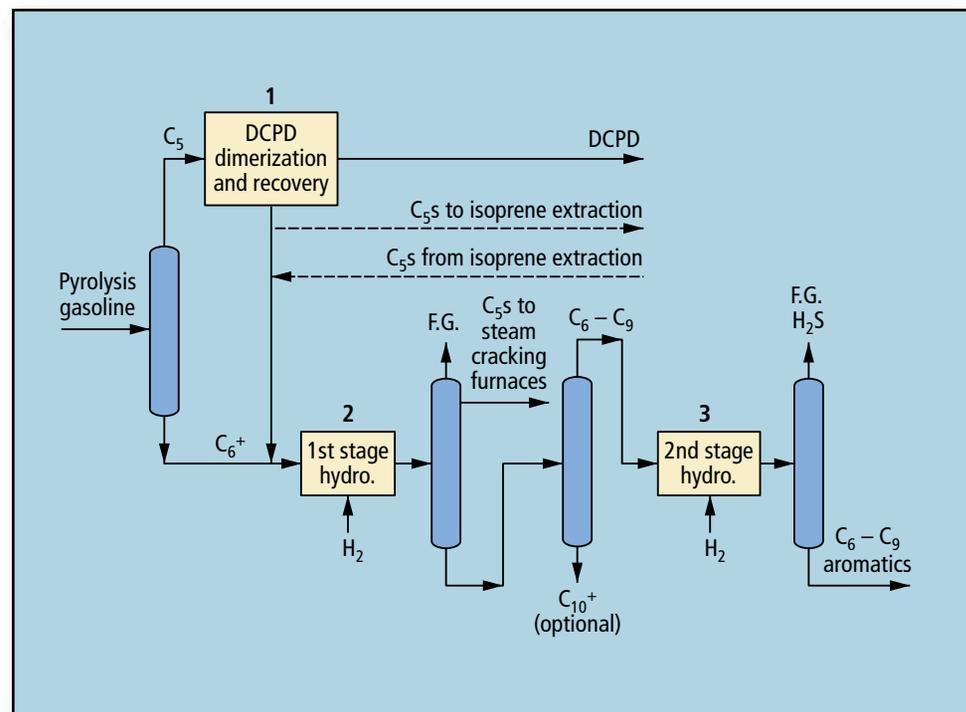
The C₅s are recycled to the steam cracker or an isomerization unit. Sulfur and nitrogen compounds are removed in the second stage (3) hydrogenation units. The BTX cut is ideal for processing in an aromatics complex.

Yields: For the new generation catalysts, recovery and product quality parameters are as follows:

C ₆ to C ₉ aromatics recovery, %	99.5
Benzene recovery, %	99.7
Diene value	0
Bromine Index, mg/100g	100
Sulfur, ppm	< 1
Thiophene, ppm	< 0.2
C ₆ cut Bromine Index, mg/100g	20
C ₆ cut acid wash color	1-

Economics: Based on a 1 million metric tpy naphtha steam cracker producing a 620,000 tpy pygas stream, ISBL Gulf Coast location in 2004:

Investment, US\$/ metric ton of feed	40
Utilities & catalysts, US\$/ metric ton	10



References: Debuisschert, Q., P. Travers and V. Coupard, "Optimizing Pyrolysis Gasoline Upgrading," *Hydrocarbon Engineering*, June 2002.

Commercial plants: Over 90 1st stage and 60 2nd stage pygas hydrogenation units have been licensed.

Licensors: Axens, Axens NA.

Styrene

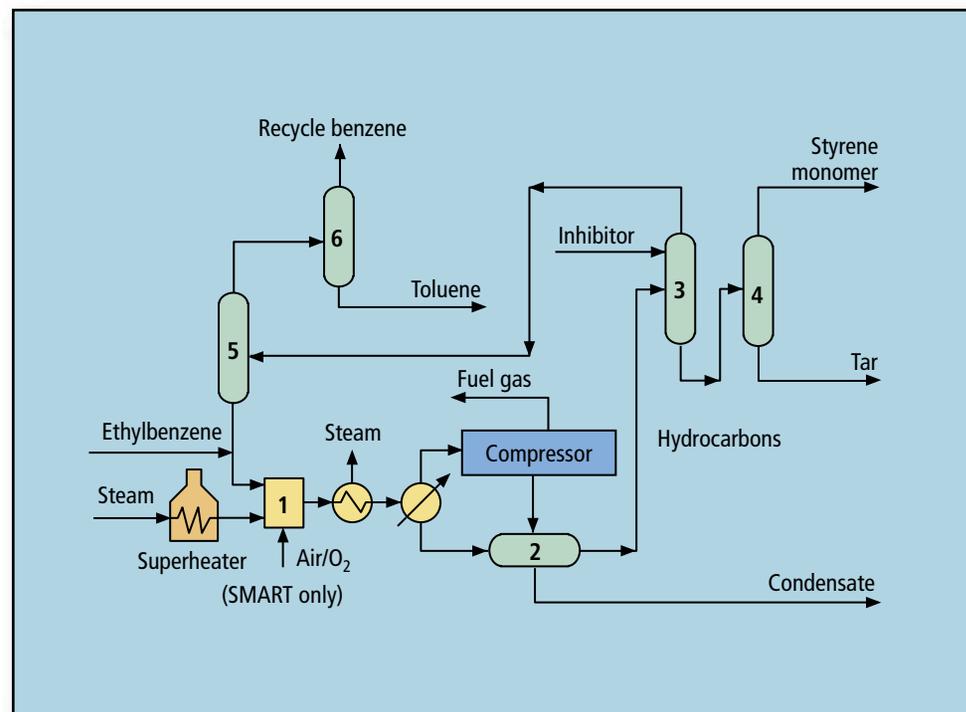
Application: To produce polymer-grade styrene monomer (SM) by dehydrogenating ethylbenzene (EB) to form styrene using the Lummus/UOP "Classic" styrene process for new plants and the Lummus/UOP SMART process for revamps involving plant capacity expansion.

Description: In the Classic SM process, EB is catalytically dehydrogenated to styrene in the presence of steam. The vapor phase reaction is carried out at high temperature under vacuum. The EB (fresh and recycle) is combined with superheated steam, and the mixture is dehydrogenated in a multistage reactor system (1). A heater reheats the process gas between stages. Reactor effluents are cooled to recover waste heat and condense the hydrocarbons and steam. Uncondensed offgas—containing mostly hydrogen—is compressed and is used as fuel. Condensed hydrocarbons from an oil/water separator (2) are sent to the distillation section. Process condensate is stripped to remove dissolved aromatics.

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

Typical SM product purity ranges from 99.85% to 99.95%. The process provides high-product yield due to a unique combination of catalyst and operating conditions used in the reactors and the use of a highly effective polymerization inhibitor in the fractionation columns.

The SMART SM process is the same as Classic SM except that oxidative reheat technology is used between the dehydrogenation stages of the multistage reactor system (1). Specially designed reactors are used to achieve the oxidation and dehydrogenation reactions. In oxidative reheat, oxygen is introduced to oxidize part of 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 about 80% EB conversion per pass, elimi-



nates the costly interstage reheater, and reduces superheated steam requirements. For existing SM producers, revamping to SMART SM may be the most cost-effective route to increased capacity.

Economics: (Classic) 500,000 mtpy, ISBL, US Gulf Coast:

Investment, US\$ million	78
Ethylbenzene, ton/ton SM	1.055
Utilities, US\$/mton SM	29

Commercial plants: Currently, 36 operating plants incorporate the Lummus/UOP Classic Styrene technology. Seven operating facilities

Styrene, *continued*

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 ideally suited for revamps.

Licensors: ABB Lummus Global and UOP LLC.

Styrene

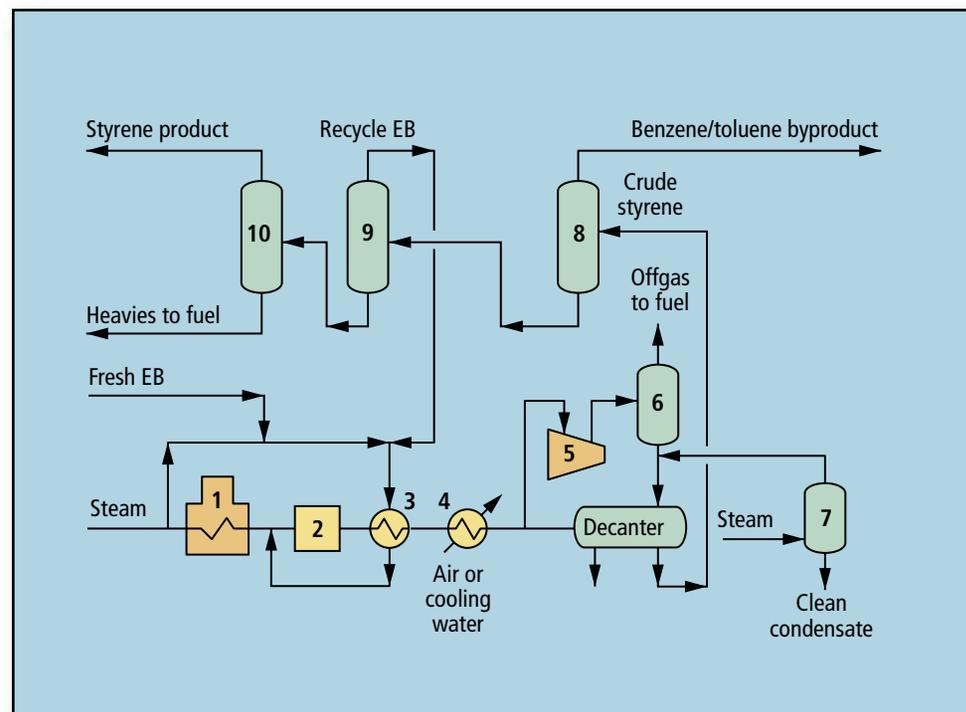
Application: Process to manufacture styrene monomer (SM) by dehydrogenating ethylbenzene (EB) to styrene. Feedstock EB is produced by alkylating benzene with ethylene using the Mobil/Badger EBMax process.

Description: EB is dehydrogenated to styrene over potassium promoted iron-oxide catalyst in the presence of steam. The endothermic reaction is done under vacuum conditions and high temperature. At 1.0 weight ratio of steam to EB feed and a moderate EB conversion, reaction selectivity to styrene is over 97%. Byproducts, benzene and toluene, are recovered via distillation with the benzene fraction being recycled to the EB unit.

Vaporized fresh and recycle EB are mixed with superheated steam (1) and fed to a multi-stage adiabatic reactor system (2). Between dehydrogenation stages, heat is added to drive the EB conversion to economic levels, typically between 60% and 75%. Heat can be added either indirectly using conventional means such as a steam heat exchanger or directly using a proprietary Direct Heating Technology developed by Shell Oil.

Reactor effluent is cooled in a series of exchangers (3) to recover waste heat and to condense (4) the hydrocarbons and steam. Uncondensed offgas—primarily hydrogen—is compressed (5) and then directed to an absorber system (6) for recovery of trace aromatics. Following aromatics recovery, the hydrogen-rich offgas is consumed as fuel by process heaters. Condensed hydrocarbons and crude styrene are sent to the distillation section, while process condensate is stripped (7) to remove dissolved aromatics and gases. The clean process condensate is returned as boiler feedwater to offsite steam boilers.

The distillation train first separates the benzene/toluene byproduct from main crude styrene stream (8). Unconverted EB is separated from styrene (9) and recycled to the reaction section. Various heat recovery schemes are used to conserve energy from the EB/SM column system. In the final purification step (10), trace C₉ components and heavies are separated from the finished SM. To minimize polymerization in distillation equipment, a dinitrophenolic type inhibitor is co-fed with the crude feed from the reaction section. Typical SM purity ranges between 99.90% and 99.95%.



Economics:

Ethylbenzene consumption, per ton of SM	1.052
Net energy input, kcal per ton of SM	1.25
Water, cooling, m ³ per ton of SM	150

Note: Raw material and utility requirements presented are representative; each plant is optimized based on specific raw material and utility costs.

Commercial plants: The technology has been selected for use in over 40 units having design capacities (single train) ranging from 320 to 850 Mmtpy. The aggregate capacity of these units exceeds 8 MMmtpy.

Licensor: Badger Licensing LLC.

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 heartcut 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 containing less than 50 ppm phenyl acetylene.

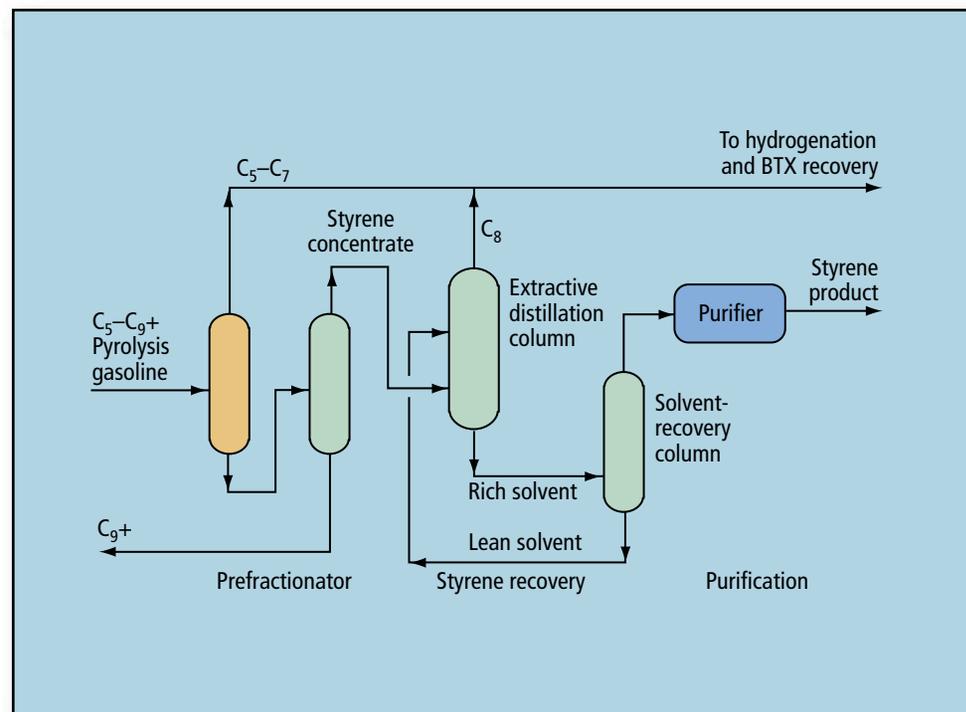
The extractive-distillation column overhead can be further processed to recover a high-quality mixed xylene stream. A typical world-scale cracker could produce approximately 25,000 tpy styrene and 75,000 tpy mixed xylenes from pyrolysis gasoline.

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 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 US GC capital cost, \$MM:	20
Styrene value in pygas, \$/t	250



Styrene product sales value, \$/t	700
Processing cost, \$/t	100
Gross margin, \$MM/yr	8.75
Pretax ROI, %	43

Commercial plants: One license has been placed.

Reference: "Generate more revenues from pygas processing," *Hydrocarbon Processing*, June 1997.

Licensor: GTC Technology.

Styrene acrylonitrile (SAN) copolymer

Application: To produce a wide range of styrene acrylonitrile (SAN) copolymer with excellent chemical resistance, heat resistance and suitable property for compounding with ABS via the continuous bulk polymerization process using Toyo Engineering Corp. (TEC)/Mitsui Chemicals Inc. technology.

Description: Styrene monomer, acrylonitrile, a small amount of solvent and additives are fed to the specially designed reactor (1) where the polymerization of the fed mixture is carried out. The polymerization temperature of the reactor is carefully controlled at a constant level to maintain the desired conversion rate. The heat of the polymerization is easily removed by a specially designed heat-transfer system. At the exit of the reactor, the polymerization is essentially complete.

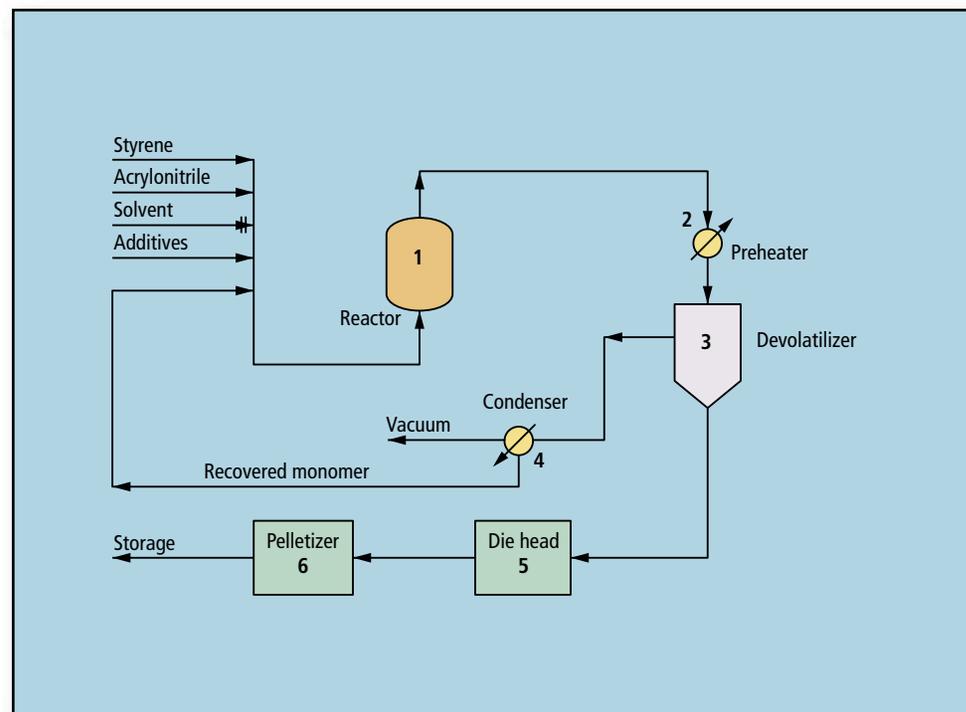
The mixture is preheated (2) and transferred to the devolatilizer (3). Volatile components are separated from the polymer solution by evaporation under vacuum. The residuals are condensed (4) and recycled to the process. The molten polymer is pumped through a die (5) and cut into pellets by a pelletizer (6).

Economics: Basis: 50,000 metric tpy SAN, US Gulf Coast:

Investment, million US\$	16
Raw materials consumption per one metric ton of SAN, kg	1,009
Utilities consumption per one metric ton of SAN, US\$	18

Installations: Seventeen plants in Japan, Korea, Taiwan, China and Thailand are in operation with a total capacity of 508,000 metric tpy.

Licensor: Toyo Engineering Corp. (TEC) / Mitsui Chemicals Inc.



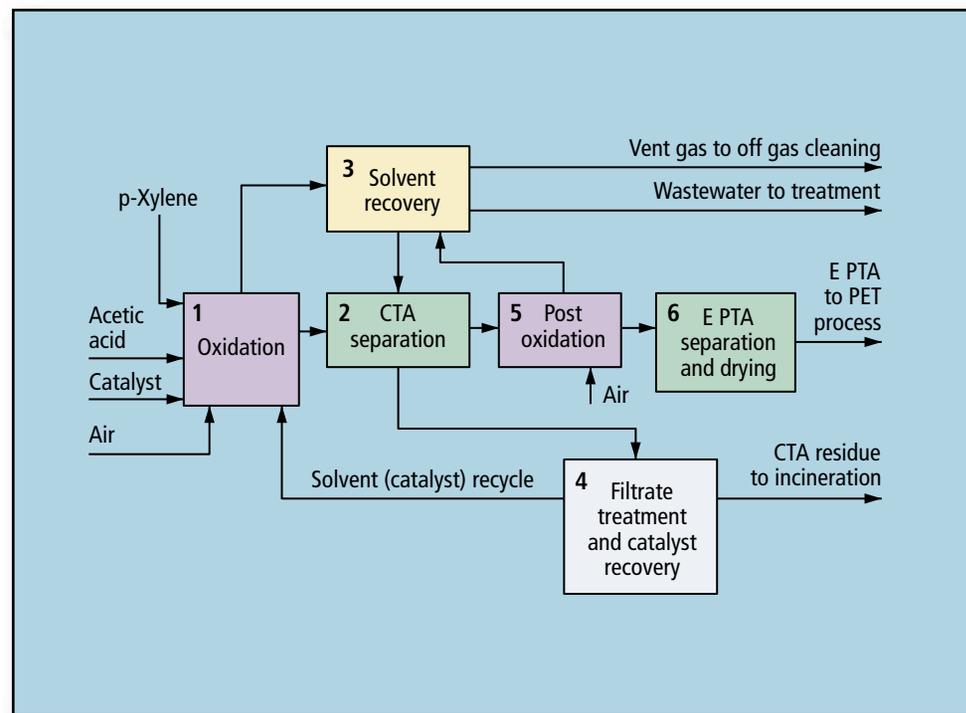
Terephthalic acid (E PTA)

Application: E PTA (Eastman polymer-grade terephthalic acid) is an excellent raw material for engineering plastics and packaging materials, bottles, other food containers including hot fill, as well as films. The process is proven to be suitable for the production of all kinds of polyester fibers and containers without limitation, at international first-grade quality.

Description: The general flow diagram to produce E PTA using Eastman Chemical's proprietary process comprises three different main sections—crude terephthalic acid (CTA), polymer-grade terephthalic acid (E PTA) and catalyst recovery.

Crude terephthalic acid (1,2,3): CTA is produced by the catalytic oxidation of p-xylene with air in the liquid phase using acetic acid as a solvent (1). The feed mix—p-xylene, solvent and catalyst—together with compressed air is continuously fed to the reactor, which is a bubble-column oxidizer. It operates at moderate temperature and offers an extremely high yield. The oxidizer product is known as crude terephthalic acid (CTA) due to the high level of impurities contained. Many impurities are fairly soluble in the solvent. In the CTA separation step (2), impurities can be effectively removed from the product by exchanging the reaction liquor with lean solvent 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 offgas is sent to a regenerative thermal oxidation unit for further cleaning.

Polymer-grade terephthalic acid (5,6): The crude acid is purified to obtain E PTA in a post-oxidation step, at elevated temperature conditions. The post oxidizers serve as reactors to increase conversion of the partially oxidized compounds to terephthalic acid. The level of 4-carboxy benzaldehyde (4-CBA) p-toluic acid (p-TA)—the main impurities in terephthalic acid—is significantly lowered. In a final step (6), E PTA



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 suspended solids are separated and removed as CTA residue, which can be burned in a fluidized-bed incinerator or, if desirable, used as land fill. The soluble impurities are removed from the filtrate within the filtrate treatment section, and the dissolved catalyst is recycled.

Economics: The advanced Eastman E PTA technology uses fewer processing steps. In combination with the outstanding mild-oxidation tech-

Terephthalic acid (E PTA), *continued*

nology, this technology leads to considerable capital cost savings and lower production cost than in other technologies.

Commercial plants: Commercial plants are operating in the US, Europe and Asia Pacific.

The latest plant with a capacity of 660,000 tpy for Zhejiang Hualian Sunshine Petro-Chemical Co. Ltd. in Shaoxing, China, is under construction and will be started up in April 2005, increasing the worldwide capacity to 2.1 million tpy.

Licensors: Lurgi AG.

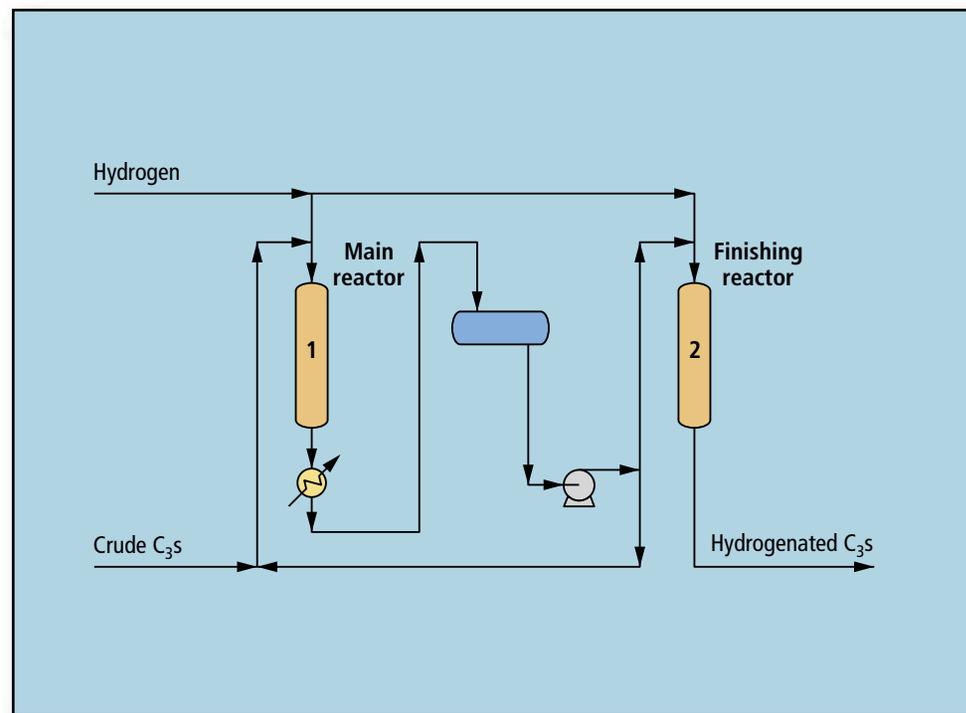
Upgrading steam cracker C₃ cuts

Application: To purify propylene-propane cuts from pyrolysis processes via selective catalytic hydrogenation of methylacetylene and propadiene impurities (MAPD). Steam cracker C₃ effluents typically contain over 90% propylene with propane and MAPD making up the balance. Although distillation can be used to remove MAPD, it is often not practical or economical for achieving a propylene product meeting the parts-per-million levels required by chemical and polymer-grade propylene specifications. Furthermore, distillation results in propylene losses. Selective hydrogenation is the route most commonly employed as it not only achieves the tight MAPD specifications, but it produces more propylene.

Description: The C₃ cut is joined by recycled C₃s and make-up hydrogen prior to entering the main reactor (1). There the MAPD is catalytically hydrogenated, forming propylene and traces of propane. A single reactor suffices for polymer-grade propylene (MAPD content <10 ppm) when a C₃ splitter is used. A finishing reactor (2) can be used to reduce MAPD content to five or even one ppm. A second reactor is advantageous when making chemical-grade propylene. With a typical specification of 95% propylene, 5% propane and <5 ppm MAPD, a costly C₃ splitter system is avoided.

Yields: The highly selective, active and stable catalyst, LD 273, provides the typical yields shown below compared to its predecessor, LD 265, which is used in most of the units worldwide:

	Feed	Product with LD-273, wt%	Δ Performance
Ethane	0.10	0.11	
Propane	3.28	4.21	
Propylene	94.03	95.55	+1
Propadiene	1.23	1 ppm	
Methylacetylene	1.33	< 1 ppm	
Cyclopropane	0.03	0.03	
C ₆	0	0.12	
Propylene yield		101.6	+1.1



Economics: Based on a 1-million tpy capacity steam cracker, ISBL Gulf Coast location in 2004:

Investment, US\$/metric ton of propylene	4.9
Utilities & catalysts, US\$/metric ton of propylene	0.24

Commercial plants: Over 100 C₃ hydrogenation units have been licensed.

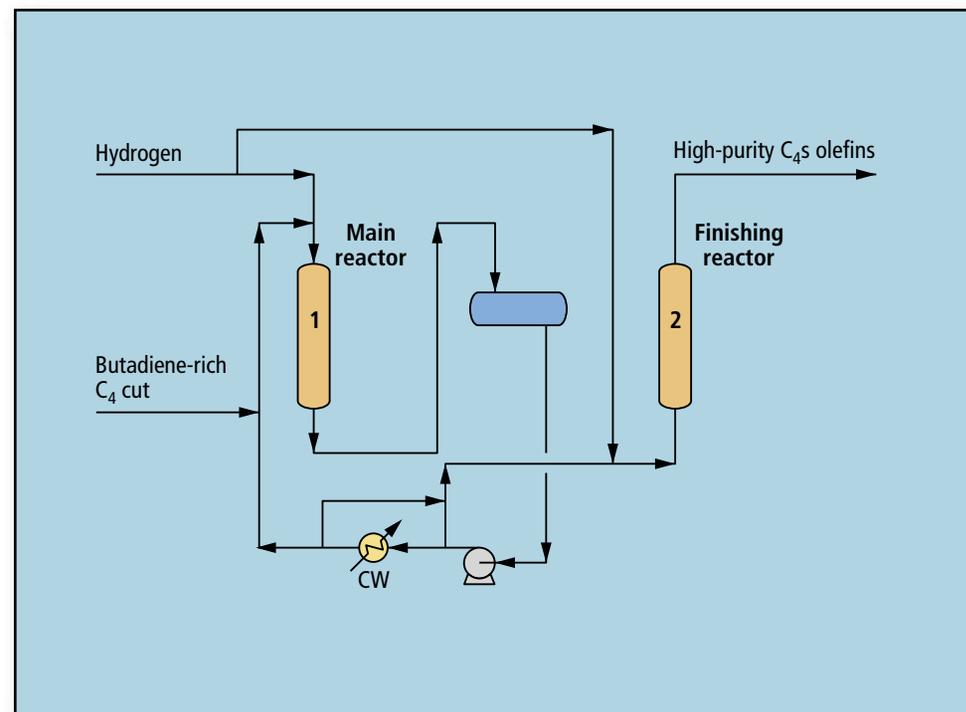
Licensors: Axens, Axens NA.

Upgrading steam cracker C₄ cuts

Application: Increase the value of steam cracker C₄ cuts via low-temperature selective hydrogenation and hydroisomerization catalysis. Several options exist: removal of ethyl and vinyl acetylenes to facilitate butadiene extraction processing downstream; conversion of 1, 3 butadiene to maximize 1-butene or 2-butene production; production of high-purity isobutylene from crude C₄ cuts; total C₄ cut hydrogenation; and total hydrogenation of combined C₃/C₄ and C₄C₅ cuts for recycle to cracking furnaces or LPG production.

Description: Each application uses a specific process, catalyst and operating conditions. The basic process for maximizing 1-butene consists of sending a combined butadiene-rich C₄ cut, recycled C₄s, make-up hydrogen to the main reactor (1) where acetylenes and 1, 3 butadiene (in the case of hydroisomerization to a specified product distribution) are hydrogenated. A finishing reactor (2) is used if required. Reactions take place in the liquid phase at relatively low temperatures to provide significant advantages in the area of heat removal, approach to equilibrium, catalyst life and reaction homogeneity. Information here is for the C₄ selective hydrogenation process employed to maximize 1-butene. Distillation is used to separate the products. The process is different in the case of high purity isobutylene production where a reactor and distillation column operate on the C₄ stream simultaneously.

Yields: In the example below, a highly selective, active and stable catalyst, LD 271, provides the typical yields shown below (50% of the 1, 3 butadiene converts to 1-butene):



Cis 2-butene	3.88	9.27
1, 3 Butadiene	48.58	1.3 ppm
1, 2 Butadiene	0.15	0
Vinylacetylene	0.61	0
Ethylacetylene	0.15	0.05

Economics: Based on a 160,000-tpy crude C₄ feed, ISBL Gulf Coast location in 2004:

Investment, US\$	3.1 million
Utilities & catalysts, Water, cooling, m ³ /h	500
Electrical power, kWh/h	250

	Feed	Product with LD-271, wt%
C ₃ s	0.03	0.03
Isobutane	0.62	0.63
n-Butane	3.42	5.71
1-Butene	12.93	37.22
Isobutene	24.51	24.44
Trans 2-butene	5.11	22.65

Upgrading steam cracker C₄ cuts, *continued*

Commercial plants: A total of over 50 C₄ hydrogenation units have been licensed for this process application.

Licensors: Axens, Axens NA.

Urea

Application: To produce urea from ammonia (NH_3) and carbon dioxide (CO_2) using the Stamicarbon CO_2 stripping Urea 2000plus Technology.

Description: Ammonia and CO_2 react at synthesis pressure of 140 bar to urea and carbamate (Fig. 1). The conversion of ammonia as well as CO_2 in the synthesis section is 80% resulting in an extreme low recycle flow of carbamate. Because of the high-ammonia efficiency, no pure ammonia is recycled in this process. The synthesis temperature of 185°C is low, and, consequently, corrosion in the plant is negligible.

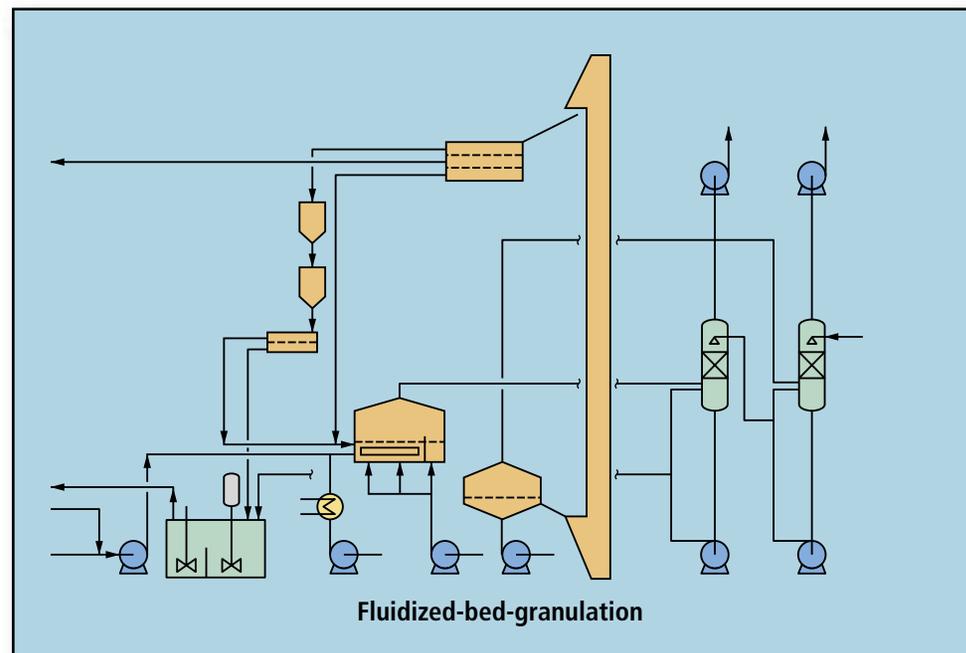
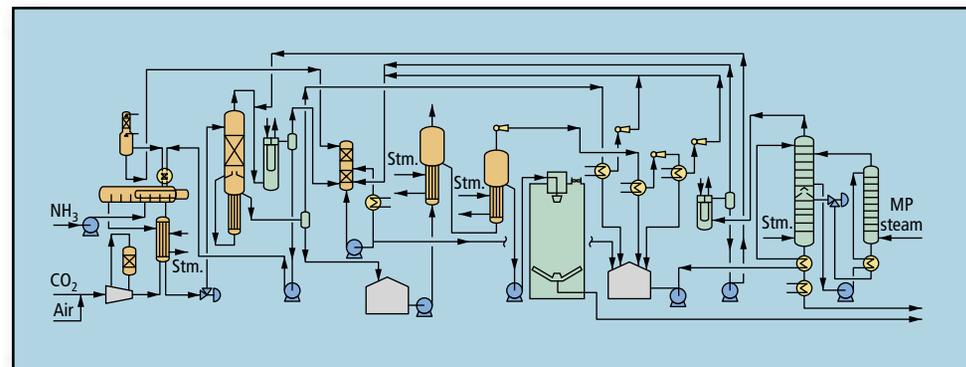
Because of the elevation difference within the synthesis section, internal synthesis recycle is based on gravity flow. **Result:** Electrical energy requirement is very low. Synthesis-gas condensation in the pool reactor generates steam, which is used in downstream sections within the plant. Process steam consumption is low.

Processing inerts are vented to the atmosphere after washing; thus, ammonia emissions from the plant are virtually zero.

Because of the high conversions in the synthesis, the recycle section of the plant is very small. An evaporation stage with vacuum condensation system produces urea melt with the required concentration either for the Stamicarbon fluidized-bed granulation or for prilling. Process water produced in the plant is treated in a desorbition/hydrolyzer section. This section produces an effluent, which is suitable for use as boiler feedwater.

Stamicarbon licenses several proprietary technologies:

- Urea 2000Plus Technology for capacities up to 5,000 metric tpd
- Stamicarbon fluidized bed urea granulation (Fig. 2)
- UAN technology
- Several revamp technologies
- Proprietary material Safurex.



Urea, *continued*

Economics: Depending on heat exchange options included within the design, the raw material and utility consumptions per metric ton of urea melt are:

Ammonia, 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 desorbition/hydrolyzes section.

Commercial plants: More than 200 plants based on Stamicarbon's CO₂ stripping technology are in operation. The largest single-line unit with Urea 2000plus technology produces more than 3,250 metric tpd.

Highlights in 2005 include:

- Three urea plants with Stamicarbon's new Granulation technology are under construction.
- One Urea 2000plus Technology plant with a complete synthesis in Safurex is under construction.
- More than six major capacity increase revamps are under construction.

Licensors: Stamicarbon BV.

Urea

Application: To produce urea from ammonia and carbon dioxide (CO₂) using the CO₂ stripping process.

Description: Ammonia and carbon dioxide react at 155 bar to synthesize urea and carbamate. The reactor conversion rate is very high under the N/C ratio of 3.7 with a temperature of 182–185°C. Unconverted materials in synthesis solution are efficiently separated by CO₂ stripping. The milder operating condition and using two-phase stainless steel prevent corrosion problems. Gas from the stripper is condensed in vertical submerged carbamate condenser. Using an HP Ejector for internal synthesis recycle, major synthesis equipment is located on the ground level.

The urea solution from synthesis section is sent to MP decomposer at 17 bar and LP decomposer at 2.5 bar for further purification. No pure ammonia recycle is required due to the high separation efficiency in the stripper.

The vacuum evaporator unit produces urea melt at the required concentration either for prilling or granulation.

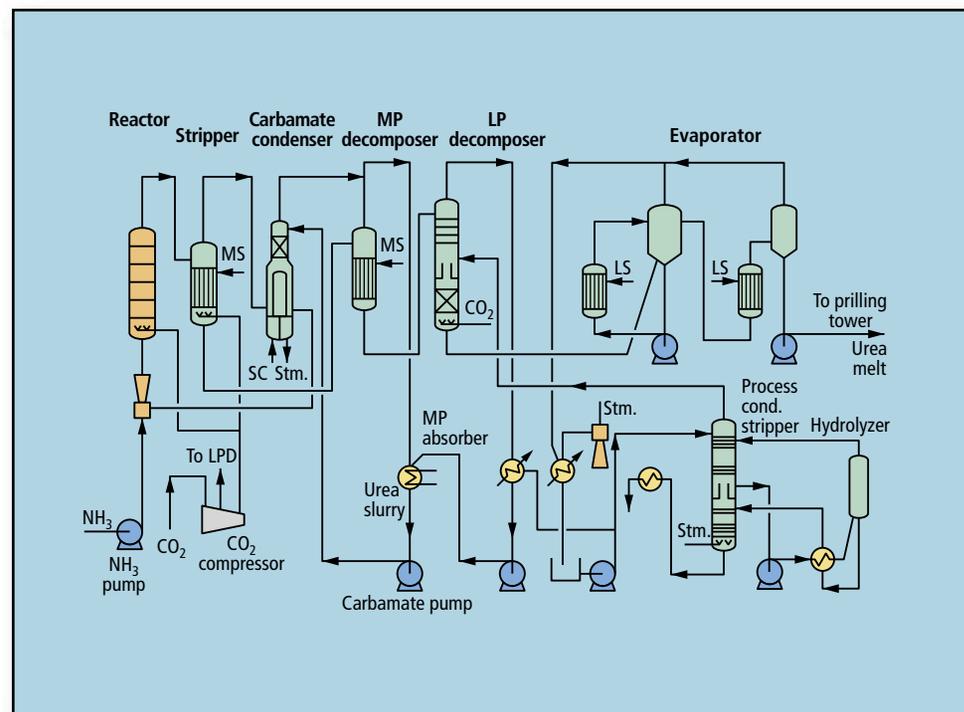
The vent scrubber and process condensate treatment unit treat all emission streams; thus, the plant is pollution free. Process condensate is hydrolyzed and reused as boiler feedwater.

Toyo Engineering Corp. (TEC) has a spout-fluid bed granulation technology to produce granular urea—typically 2–4 mm size. Due to proprietary granulator, electric power consumption is the lowest among granulation processes.

Economics: Raw materials and utilities consumptions per metric ton of prilled urea are:

Ammonia, kg	566
Carbon dioxide, kg	733
Steam, 110 bar, 510°C	690 ¹
Electric power, kWh	20
Water, cooling, m ³	75

¹ Includes steam for CO₂ compressor turbine and steam for process condensate treatment



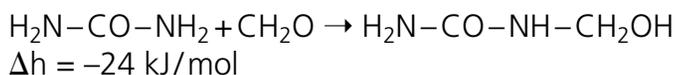
Commercial plants: More than 100 plants including urea granulation plants have been designed and constructed based on TEC technology.

Licensor: Toyo Engineering Corp. (TEC).

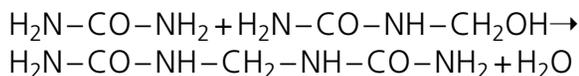
Urea-formaldehyde

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 are: Formaldehyde and urea are by polyaddition:



The hydroxymethyl compounds undergo further slow reaction by polycondensation:

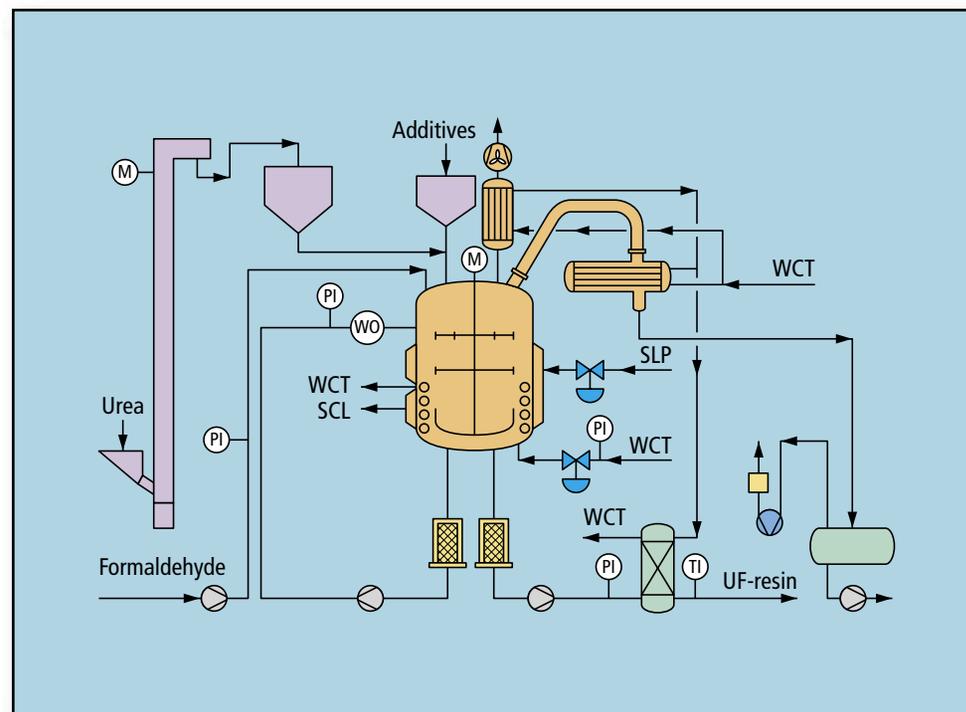


which is also responsible for the viscosity increase during the storage.

The formation of methylene bridges can 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.

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 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 the hot pressing process. The quality of the bonding complies with the requirements of DIN 68705, Part 2 respectively to DIN 68763–V20. For particle board, a perforate value according to DIN EN 120 of less 10 mg HCHO/100 g dry board will be maintained.



Licensor: Uhde Inventa-Fischer.

VCM by thermal cracking of EDC

Application: Vinnolit's medium-pressure EDC-cracker provides an energy efficient cracking technology operating at moderate cracking pressure, with the benefit of low byproduct formation and long operation cycles between cleaning intervals.

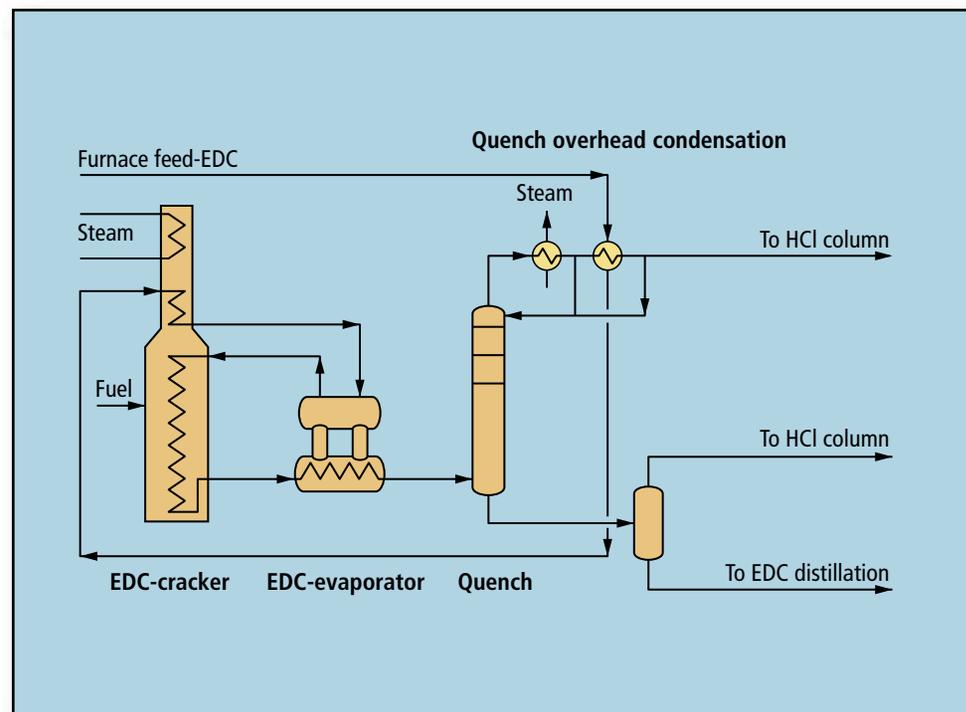
Description: In the cracking furnace, feed EDC (ethylene dichloride) from the EDC purification section or from the EDC storage facility is cracked to vinyl chloride and hydrogen chloride (HCl) at approximately 490°C and at 1.5 MPa g. Prior to cracking, the feed EDC is preheated in the quench overhead exchanger and in the radiation coils of the EDC-cracker. The hot reaction gases downstream of the EDC cracking furnace are cooled in the EDC-evaporator by vaporizing the feed EDC. Additional cooling of the reaction gas occurs in the quench tower. Fractions of the quench overhead stream are condensed in the steam generator, in the feed EDC preheater of the quench column prior to entering the HCl-column. The quench-bottom product is filtered and fed through a high-efficiency flash system to remove coke.

Process features and economics: Processing benefits of the VINNOLIT EDC cracking process consist of EDC cracking furnace and external EDC evaporation, and include:

Energy savings: More than 50% savings of electrical energy compared to low-pressure cracking furnace technology are available, because of 12.5 bar g condensation pressure in the HCl column, further reduced fuel consumption by using the heat of the cracking gas to heat and evaporate EDC nets savings of 500 kg 20 bar g steam/ton VCM. Furthermore, steam is generated via flue gas from the furnace. EDC is preheated on quench top prior to entering the furnace.

Operation: The continuous operation time is approximately two years without decoking. The high conversion rate is 55%, due to the vapor EDC-feed. No iron enters the radiant section.

As the coke carry-over with the product stream is avoided, the Vinnolit desuperheated quench system allows a long operation time of



the vinyl chloride monomer (VCM) distillation unit.

Low maintenance cost: The natural EDC circulation in EDC vaporizer minimizes maintenance costs (no pumps, no sealing problems and no plugging).

Commercial plants: The process is used in 19 plants with an annual production of around 3.8 million metric tons (mtons) of VCM. A single stream plant with an annual capacity of 400,000 mtons of VCM was commissioned in a record time of two months in September 2004. One VCM plant with an annual capacity of 300,000 mtons of VCM is under construction.

VCM by thermal cracking of EDC, *continued*

Licensors: Vinnolit.

Contractor: Uhde GmbH.

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 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.

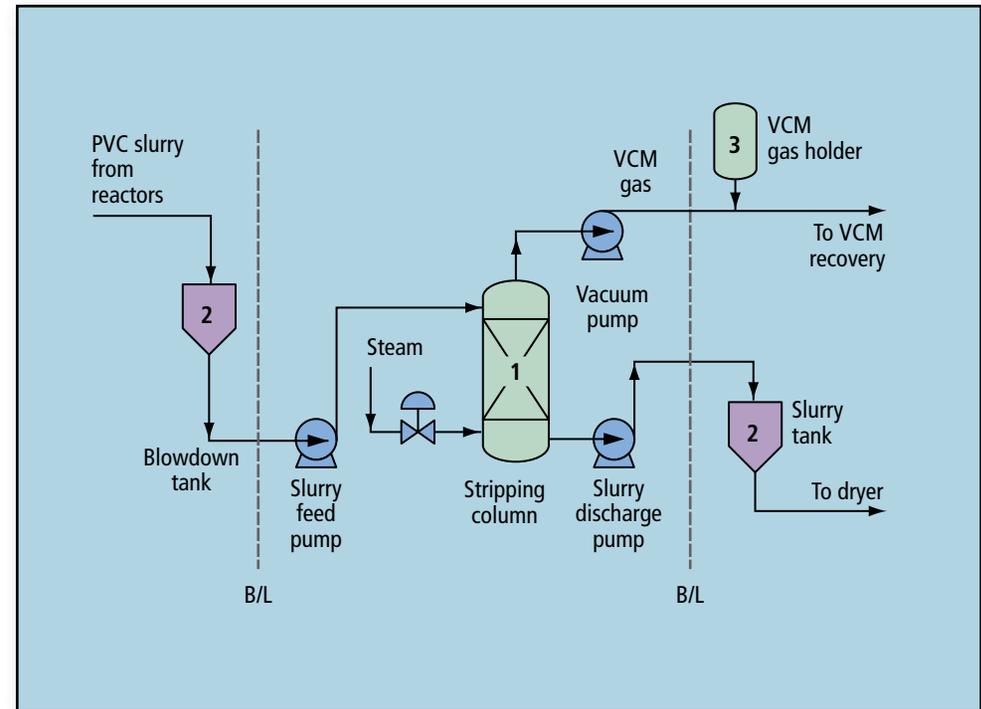
The process design is compact with a small area requirement and low investment cost. The size of the column is 2.5 t/h to 30 t/h.

Economics:

Steam

130 kg/t of PVC

Commercial plants: Chisso has licensed the technology to many PVC producers worldwide. More than 100 columns of the Chisso process are under operation or construction, and total capacity exceeds 5 million tpy of PVC.



Licensor: Chisso Corp.

Wet air oxidation (WAO), spent caustic

Application: To oxidize sodium sulfide (Na_2S) component in the caustic scrubber effluent of olefin plants with air using wet air oxidation (WAO) process developed by Nippon Petrochemicals Co., Ltd. (NPCC), the license being available from Toyo Engineering Corp. (TEC).

Description: Conventional wet oxidation processes adopt a plug-flow type of reactor system, which usually has problems such as:

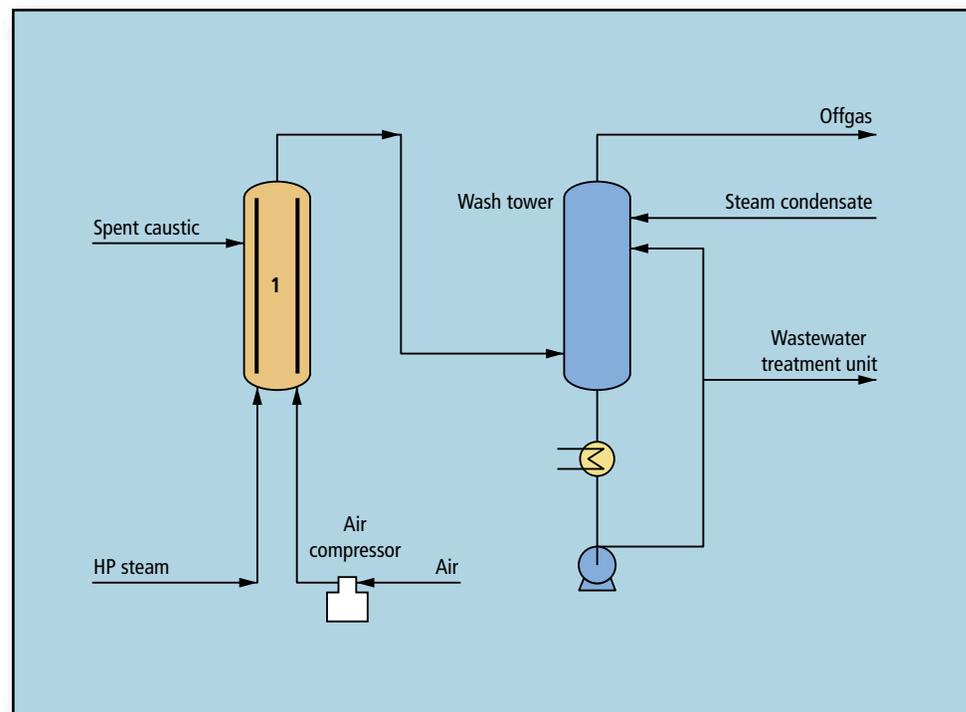
- Plug-flow reactors require higher reaction temperature for the oxidation reaction and need a feed preheater. Clogging problems in the outlets of the reactor and preheater often occur.
- High processing temperatures cause corrosion problems. High-grade construction materials such as nickel or nickel alloy are needed for the reactor.

NPCC process, conversely, uses a complete mixing type of reactor (1) and has several advantages, such as:

- Mild and uniform reactor conditions can be maintained by complete mixing with very fine bubbles generated by a special nozzle application.
- No preheater is required.
- A lower-grade construction material such as stainless steel is used for the reactor.
- Less clogging problems and easier operation are due to the simple flow scheme.

Economics: Typical performance data

Base	Spent caustic flowrate, tph	2.5
	Na_2S Inlet, wt%	2
	Outlet, wt ppm	less than 10
Utilities	Electric power, kWh/h	175
	Steam, HP kg/h	750
	Water, cooling, m^3/h	55
	Washwater, m^3/h	2



Commercial plants: Many olefins plants worldwide use this WAO process. Fourteen processing units have been designed by TEC since 1989.

Licensors: Nippon Petrochemicals Co., Ltd.

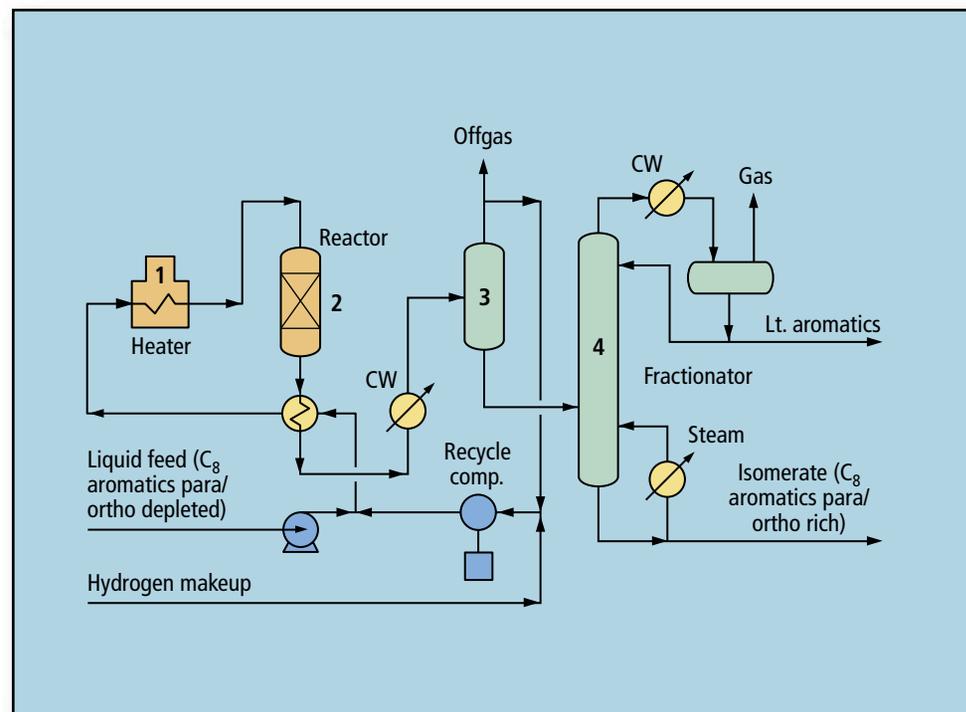
Xylene isomerization

Application: To selectively isomerize a paraxylene depleted- C_8 aromatics mixture to greater than equilibrium paraxylene concentration using ExxonMobil Chemical's XyMax and Advanced MHAI processes. Simultaneously, ethylbenzene (EB) and nonaromatics in the feed are converted to benzene and light paraffins, respectively. Conversion of EB is typically 60–80%.

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 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 Chemical. The first technology, 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, referred to as XyMax, further increases yield performance and debottleneck potential. This technology can operate at even higher EB conversion, with higher selectivity and significantly lower xylene loss.

Operating conditions: XyMax and AMHAI 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, these technologies can provide



significant savings in associated paraxylene recovery facilities. Both technologies offer 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 XyMax technology was brought onstream in 2000. Since then, two additional applications of the XyMax technology have been licensed. Including other ExxonMobil xylene isomerization technologies, there are a total of 22 units in operation.

Licensor: ExxonMobil Chemical Technology Licensing LLC (retrofit applications); Axens, Axens NA (grassroots applications).

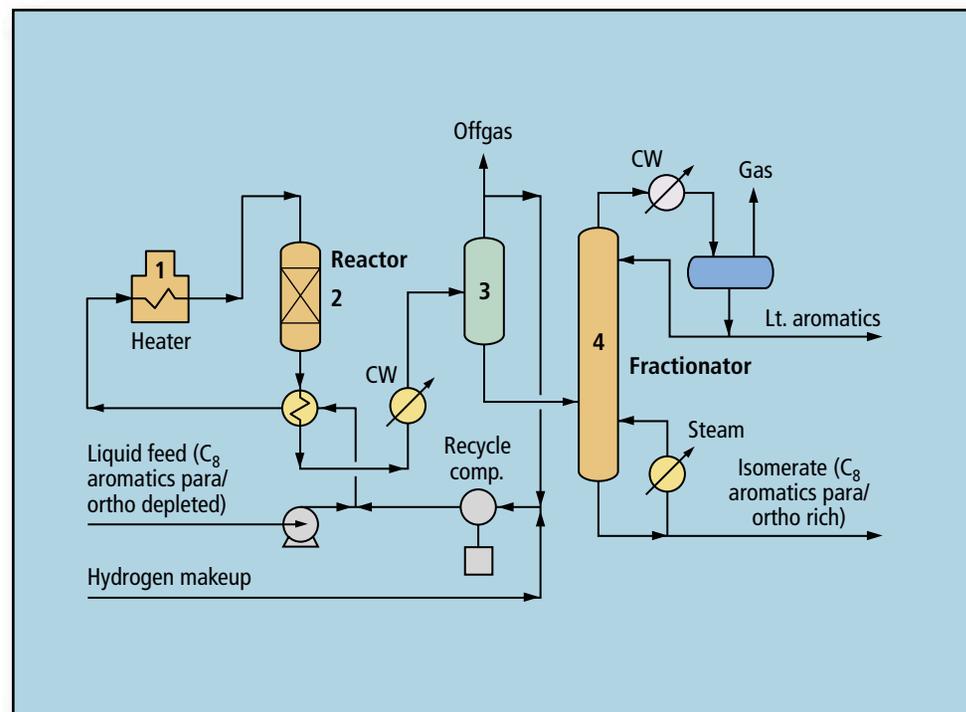
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Operating conditions: XyMax and AMHAI units operate with a high-space velocity and a low hydrogen-to-hydrocarbon ratio, which results in increased debottleneck potential and decreased utilities costs. By converting a high portion of EB in the feed, these technologies can provide significant savings in associated paraxylene recovery facilities.



Both technologies offer long operating cycles.

Commercial plants: The AMHAI process was first commercialized in 1999. Seven AMHAI units are currently in operation. The first commercial unit using XyMax technology was brought onstream in 2000. Since then, five additional (total of six) applications of the XyMax technology have been licensed. Including other ExxonMobil xylene isomerization technologies, there are a total of 19 units in operation.

Licensors: ExxonMobil Chemical (retrofit applications); Axens, Axens NA (grassroots applications).

Xylene isomerization

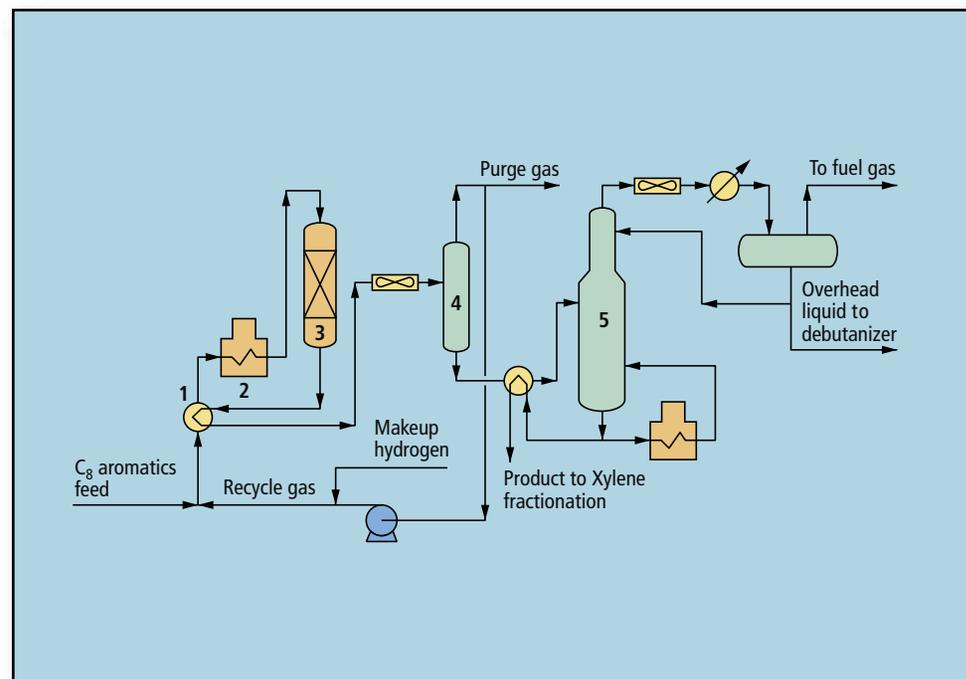
Application: The Isomar process isomerizes C_8 aromatics to mixed xylenes, to maximize the recovery of paraxylene in a UOP aromatics complex. Depending on the type of catalyst used, ethylbenzene (EB) is also converted into xylenes or benzene.

Description: The Isomar process re-establishes an equilibrium distribution of xylene isomers, essentially creating additional paraxylene from the remaining ortho- and meta-xylenes. The feed typically contains less than 1 wt% of paraxylene and is first combined with hydrogen-rich recycle gas and makeup gas. The combined feed is then preheated by an exchanger (1) with reactor effluent, heated in a fired heater (2) and raised to the reactor operating temperature. The hot feed vapor is then sent to the reactor (3), where it is passed radially through a fixed-bed catalyst.

The reactor effluent is cooled by exchanger with the combined feed and then sent to the product separator (4). Hydrogen-rich gas is taken off the top of the product separator and recycled back to the reactor. Liquid from the bottom of the products separator is charged to the deheptanizer column (5). The C_7^- overhead from the deheptanizer is cooled and separated into gas and liquid products. The gas is exported to the fuel gas system and the liquid is sent to a debutanizer column or a stripper. The C_8^+ fraction from the bottom of the deheptanizer is recycled back to a xylene column.

There are two broad categories of xylene isomerization catalysts: EB isomerization catalysts, which convert ethylbenzene into additional xylenes; and EB dealkylation catalysts, which convert ethylbenzene to valuable benzene coproduct. The selection of the isomerization catalyst depends on the configuration of the UOP aromatics complex, the composition of the feedstocks and the desired product slate.

Economics: A summary of the investment cost and the utility consumption for a typical Isomar unit (processing capacity of 1.84 million mtpy) is shown below. The estimated inside battery limits (ISBL) erected cost for the unit assumes construction on a US Gulf Coast site in 2003:



Investment, US\$ million	29
Utilities (per mt of feed)	
Electricity, kWh	3.2
Steam, mt	0.065
Water, cooling, m ³	3.6
Fuel, Gcal	0.096

Commercial plants: UOP has licensed more isomerization units than any other licensor in the world. The first Isomar unit went onstream in 1968. Since that time, UOP has licensed a total of 61 Isomar units.

Licensor: UOP LLC.

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