HYDROCARBON PROCESSING®

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Petrochemical Processes 2010

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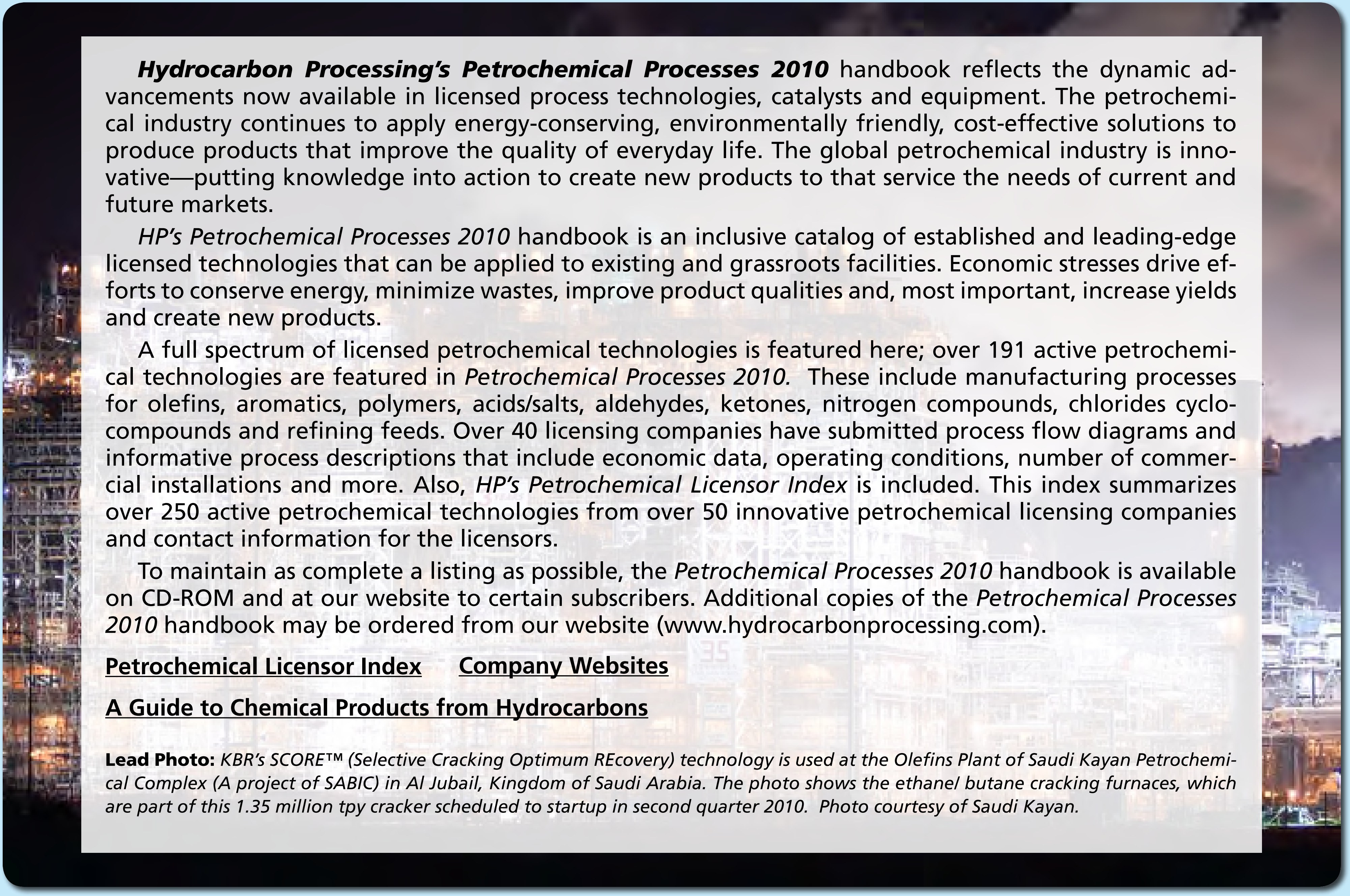
START



Hydrocarbon Processing's Petrochemical Processes 2010 handbook reflects 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 to that service the needs of current and future markets.

HP's Petrochemical Processes 2010 handbook is an inclusive catalog of established and leading-edge licensed technologies that can be applied to existing and grassroots facilities. Economic stresses drive efforts to conserve energy, minimize wastes, improve product qualities and, most important, increase yields and create new products.

A full spectrum of licensed petrochemical technologies is featured here; over 191 active petrochemical technologies are featured in *Petrochemical Processes 2010.* These include manufacturing processes for olefins, aromatics, polymers, acids/salts, aldehydes, ketones, nitrogen compounds, chlorides cyclo-compounds and refining feeds. Over 40 licensing companies have submitted process flow diagrams and informative process descriptions that include economic data, operating conditions, number of commercial installations and more. Also, *HP's Petrochemical Licensor Index* is included. This index summarizes over 250 active petrochemical technologies from over 50 innovative petrochemical licensing companies and contact information for the licensors.

To maintain as complete a listing as possible, the *Petrochemical Processes 2010* handbook is available on CD-ROM and at our website to certain subscribers. Additional copies of the *Petrochemical Processes 2010* handbook may be ordered from our website (www.hydrocarbonprocessing.com).

Petrochemical Licensor Index **Company Websites**

A Guide to Chemical Products from Hydrocarbons

Lead Photo: *KBR's SCORE™ (Selective Cracking Optimum REcovery) technology is used at the Olefins Plant of Saudi Kayan Petrochemical Complex (A project of SABIC) in Al Jubail, Kingdom of Saudi Arabia. The photo shows the ethane/ butane cracking furnaces, which are part of this 1.35 million tpy cracker scheduled to startup in second quarter 2010. Photo courtesy of Saudi Kayan.*

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Olefins-by dehydrogenation – *Uhde GmbH*
Olefins--catalytic – *The Shaw Group*
Paraxylene – *Axens*
Paraxylene – *Axens*
Paraxylene – *ExxonMobil Chemical Technology Licensing LLC*
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Axens

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Aromatics recovery
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BTX aromatics
BTX aromatics and LPG
Butene-1
Cyclohexane
Ethylene feed pretreatment-mercury, arsenic and lead removal
Hexene-1
Mixed xylenes
MTBE/ETBE and TAME/TAEE:Etherification technologies
Octenes
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Paraxylene
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Xylene isomerization

Badger Licensing LLC

Bisphenol-A

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Ethylbenzene

Styrene

Basell Polyolefins and LyondellBasell

Polyethylene, LDPE, tubular reactor

Borealis A/S

Polyethylene

Polypropylene

Casale SA

Ammonia

Methanol (2)

Urea

China Petrochemical Technology Co., Ltd.

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Petroleum coke, naphtha, gasoil and gas

Propylene and iso-olefin

Xylenes and benzene

Chiyoda

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Ethanolamines

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Methylamines

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Dow Chemical Co.

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Polyethylene, LDPE, autoclave reactor

ExxonMobil Chemical Technology Licensing LLC

Aromatics treatment

Mixed xylenes

Mixed xylenes

Paraxylene

Polyethylene-LDPE

Polypropylene

Xylene isomerization

GTC Technology

Aromatics, transalkylation
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BTX extraction
BTX recovery from FCC gasoline
Carboxylic acid
Dimethyl terephthlate
Isomerization
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Aniline
Ethylene, SUPERFLEX
n-Paraffins
Phenol
Propylene
Propylene, Advanced Catlytic Olefins

Linde AG

Alpha olefins
Ammonia
Ethylene

Lummus Novolen Technology GmbH

Polypropylene

Lummus Technology

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Cumene
Dimethyl carbonate
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CDTECH/Lummus Technology and Chemical Research & Licensing

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Lurgi

Lurgi GmbH, a company of the Air Liquide Group

Acrylic acid
Aromatics extractive distillation
Butadiene, 1,3
Melamine, low-pressure process
Methanol

LyondellBasell

Polyethylene, LL/MD/HDPE
Polypropylene, Metallocene upgrade
Polypropylene, Sheripol
Polypropylene, Spherizone
Polyethylene, HDPE

Mitsui Chemicals, Inc.

Polyethylene, HDPE

Polypropylene

NOVA Chemicals (International) S.A.

Polyethylene

Saipem

Butene-1, polymerization grade
Ethers
Isobutylene, high-purity
Iso-octene/Iso-octane
Urea

Scientific Design Company, Inc.

Ethanol-to-ethylene oxide/ethylene glycols
Ethylene oxide
Ethylene oxide/ethylene glycols

Shell Global Solutions International B.V.

Ethylene glycols (EG)
Ethylene glycol, mono (MEG)
Ethylene oxide

Stamicarbon B.V.

Urea, 2000Plus
Urea, AVANCORE process
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Technip

Ethylene
Ethylene
Ethylene

The Shaw Group

Ethylene

Ethylene recovery from refinery offgas with contaminant removal

High-olefins FCC and ethylene plant integration

Olefins—catalytic

Toyo Engineering Corp (TOYO)

Dimethyl ether (DME)
Methanol
Polystyrene, general purpose (GPPS)
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Uhde
ThyssenKrupp

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UOP LLC, A Honeywell Company

Alkylbenzene, linear
Aromatics extraction
Aromatics extractive distillation
BTX aromatics
BTX aromatics
Cumene
Ethylene
Mixed xylenes
Mixed xylenes
m-Xylene
Normal parafins, C_{10}-C_{13}
Paraxylene
Paraxylene
Paraxylene (PX-Plus XP Process)
Phenol
Propylene
Propylene
Propylene and ethylene
Xylene isomerization

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).

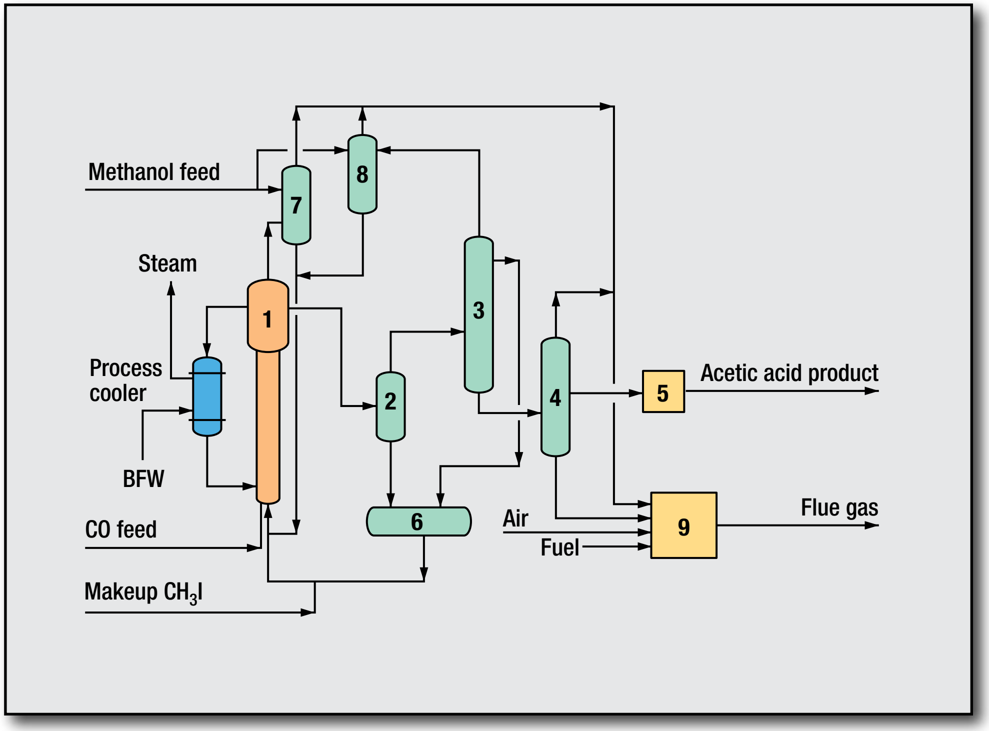
Carbon monoxide is compressed and sparged into the reactor riser. The reactor has no mechanical moving parts, and is free from leakage/maintenance problems. The ACETICA Catalyst is an immobilized Rh-complex catalyst on solid support, which offers higher activity and operates under less water conditions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

Feed and utility consumption:

Methanol, mt/mt	0.537
CO,mt/mt	0.50
Power (@CO Supply 0 K/G), kWh/mt	129
Water, cooling, m^3/mt	122
Steam @100 psig, mt/mt	1.6



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.

Licensor: Chiyoda Corp. - CONTACT

Acrylic acid

Application: Acrylic acid (AA) is used as feedstock for numerous applications. The Lurgi/Nippon Kayaku combined technology produces ester-grade acrylic acid (EAA). Main uses are adhesives, paints and coatings (acrylic esters).

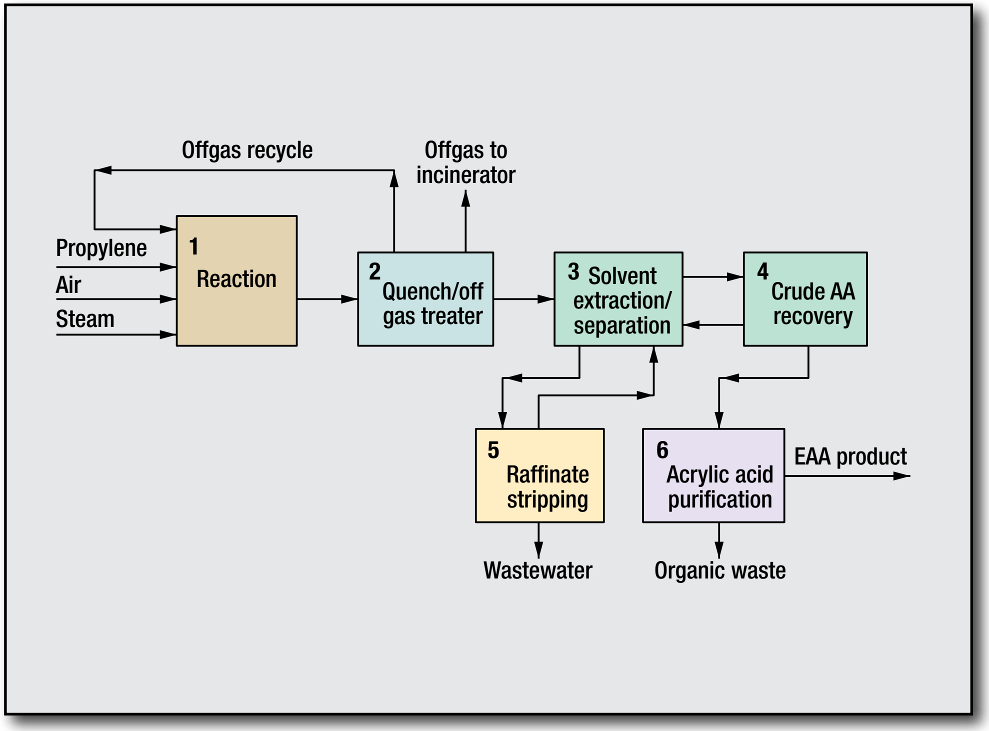
Description: The general flow diagram comprises six main sections: reaction, quench, solvent extraction, crude acrylic acid recovery, raffinate stripping and acrylic acid purification.

Reaction (1): Acrylic acid is produced by catalyzed oxidation of propylene in a two-stage tubular, fixed-bed reactor system. The reactors are cooled by circulating molten heat transfer salt. The heat of reaction is used to produce steam.

Quench (2): The AA is recovered from the reactor product gas in a quench tower. The AA solution is routed to an extractor (3). Uncondensed gases are sent to an offgas treater to recover the remaining AA. A side draw of the offgas is sent to incineration. Overhead gas is recycled to the first reactor.

Solvent extraction (3): Liquid-liquid extraction is used to separate water and AA. The top of the extractor is forwarded to a solvent separator. The extractor bottom is sent to the raffinate stripper (5) to recover solvents. Crude acrylic acid (CAA) is separated from the solvents by distillation. The overhead vapor is condensed in an internal thermoplate condenser. The two-phase condensate is separated. The organic phase is recycled. The aqueous phase is sent to the raffinate stripper (5). The column bottom, mostly AA and acetic acid, is routed to the CAA separator (4).

Crude AA recovery (4): In this section, two columns work together to separate solvent and acetic acid from the CAA. The CAA separator produces a concentrated AA bottoms stream. The overhead vapors are condensed in an internal thermoplate condenser and sent to the recovery column. The bottom stream is routed to the ester-grade acrylic acid (EAA) column (6). The recovery column separates solvent and acetic acid from AA. The overhead vapors from the recovery column are condensed by an internal thermoplate condenser and recycled. The bottom stream is returned to the CAA separator.



Raffinate stripping (5): The raffinate stripper recovers solvents from the wastewater streams. The overhead is recycled. Some of the bottom is recycled to the offgas treater; the remaining is removed as wastewater.

Acrylic acid purification (6): CAA is purified in the EAA column. The column base stream is sent to a dedimerizer, which maximizes AA recovery by converting AA dimer back to AA. The overhead EAA product is condensed in an internal thermoplate condenser.

Continued ▼

Acrylic Acid, *continued*

Economics: The Lurgi/Nippon Kayaku technology combines high-performance catalysts with highest acrylic acid yields and outstanding catalyst longevity with an optimized process. With low raw material and energy consumption, low environmental impact and high onstream time, this technology exhibits competitive production costs.

Commercial plants: One plant with a capacity of 140,000 metric tpy of EAA is under construction; startup is scheduled for 2011.

Licensor: Lurgi GmbH / Nippon Kayaku Co., Ltd. - CONTACT

Acrylonitrile

Application: The INEOS acrylonitrile technology, known as the SOHIO acrylonitrile process, is used in the manufacture of over 95% of the world's acrylonitrile. INEOS Technologies licenses the acrylonitrile process technology and manufactures and markets the catalyst that is used in the acrylonitrile process.

Description: The INEOS acrylonitrile technology uses its proven fluidized-bed reactor system. The feeds containing propylene, ammonia and air are introduced into the fluid-bed catalytic reactor, which operates at 5 psig–30 psig with a temperature range of 750°F–950°F (400°C–510°C). This exothermic reaction yields acrylonitrile, byproducts and valuable steam.

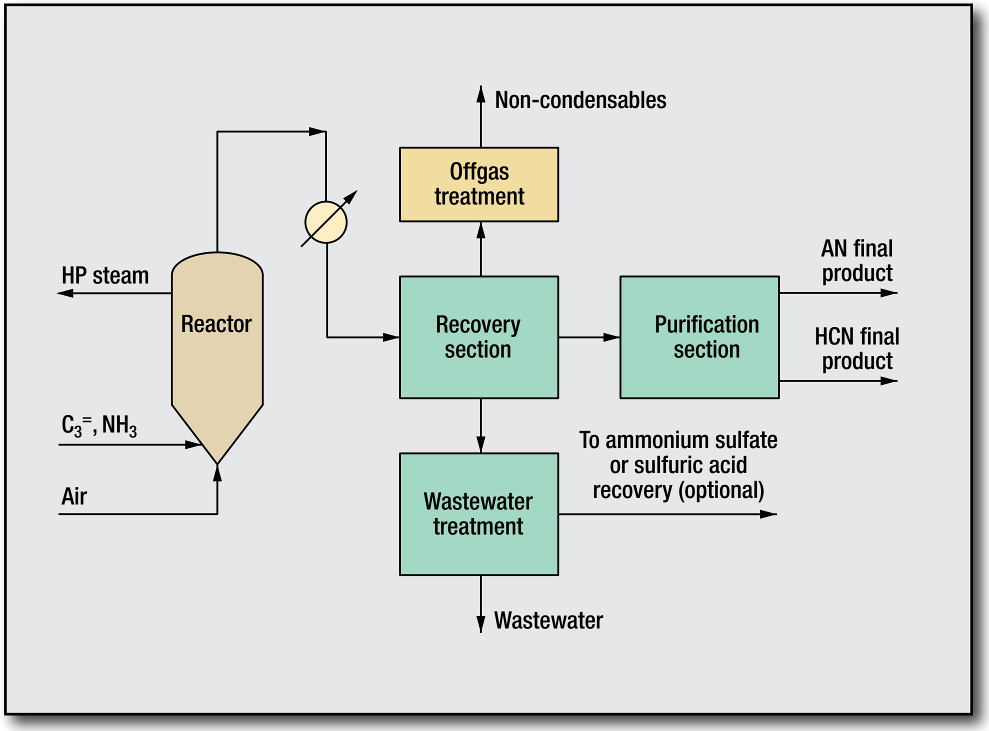
In the recovery section, the effluent vapor from the reactor is scrubbed to recover the organics. Non-condensables may be vented or incinerated depending on local regulations. In the purification section, hydrogen cyanide, water and impurities are separated from the crude acrylonitrile in a series of fractionation steps to produce acrylonitrile product that meets specification. Hydrogen cyanide (HCN) may be recovered as a byproduct or incinerated.

Basic chemistry

Propylene + Ammonia + Oxygen → Acrylonitrile + Water

Products and economics: Production includes acrylonitrile (main product) and byproducts. Hydrogen cyanide may be recovered as a byproduct of the process or incinerated. In addition, ammonium sulfate-rich streams may be processed to recover sulfuric acid or concentrated and purified for sale of ammonium sulfate crystals depending upon economic considerations. The INEOS acrylonitrile process offers robust, proven technology using high-yield catalysts resulting in low-cost operation. The process is also designed to provide high onstream factor.

Catalyst: The development and commercialization of the first fluid-bed catalyst system for the manufacture of acrylonitrile was complete in 1960. This catalytic ammoxidation process was truly revolutionary. Since the introduction of this technology, INEOS has developed and commercialized several improved catalyst formulations. These catalyst advancements have improved yields and efficiencies vs. each prior generation to continually lower the cost to manufacture acrylonitrile. INEOS continues to improve upon and benefit from this long and successful history of catalyst research and development. In fact, many of INEOS's licensees have been able to achieve increased plant capacity through a simple catalyst changeout, without the need for reactor or other hardware modifications. INEOS's catalyst system does not require changeout overtime, unless the licensee chooses to introduce one of INEOS's newer, more economically attractive catalyst systems.



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Acrylonitrile end uses: The primary use for acrylonitrile is in the manufacture of polyacrylonitrile (PAN) for acrylic fiber, which finds extensive uses in apparel, household furnishings, and industrial markets and applications, such as carbon fiber. Other end-use markets such as nitrile rubber, styrene-acrylonitrile (SAN) copolymer and acrylonitrile-butadiene-styrene (ABS) terpolymers have extensive commercial and industrial applications as tough, durable synthetic rubbers and engineering plastics. Acrylonitrile is also used to manufacture adipinitrile, which is the feedstock used to make Nylon 6,6.

Commercial plants: INEOS is the world's largest manufacturer and marketer of acrylonitrile. With four wholly-owned, world-scale acrylonitrile plants (in Lima, Ohio; Green Lake, Texas; Koeln, Germany; Teeside, UK), INEOS has extensive manufacturing expertise and commercial experience in the international marketplace. INEOS total acrylonitrile production capacity is approximately 1.3 million tpy. The SOHIO process was first licensed in 1960. Since then, through more than 45 years of licensing expertise and leadership, INEOS has licensed this technology into over 20 countries around the world.

Licensor: INEOS Technologies. From SOHIO to its successor companies, BP Chemicals, BP Amoco Chemical, Innovene and now INEOS benefit from the extensive acrylonitrile operating experience, and successful licensing and transfer of acrylonitrile technology. - CONTACT

Alkylbenzene, linear

Application: The UOP/CEPSA process uses a solid, heterogeneous catalyst to produce linear alkylbenzene (LAB) by alkylating benzene with linear olefins made by the UOP Pacol, DeFine and PEP processes.

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 PEP adsorber (5) where heavy aromatics are removed prior to being sent to a Detal reactor (6) where the olefins are alkylated with benzene. The reactor effluent is sent to a fractionation section (7, 8) 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 (9) separates the LAB product from the heavy alkylate bottoms stream.

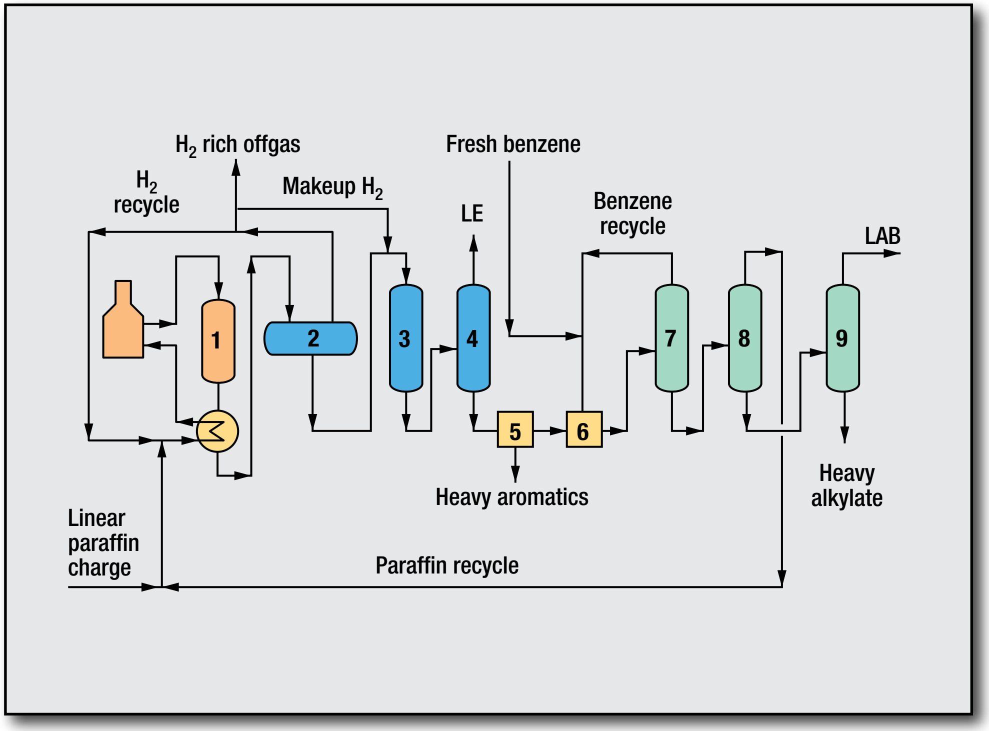
Feedstock is typically C_{10} to C_{13} normal paraffins of 98+% purity. LAB product has a typical Bromine Index of less than 10.

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: $1,400/tpy.

Commercial plants: Thirty-three UOP LAB complexes based on the Pacol and Define processes have been built. Eight of these plants use the Detal process.

Licensor: UOP LLC, A Honeywell Company - CONTACT



Alpha olefins

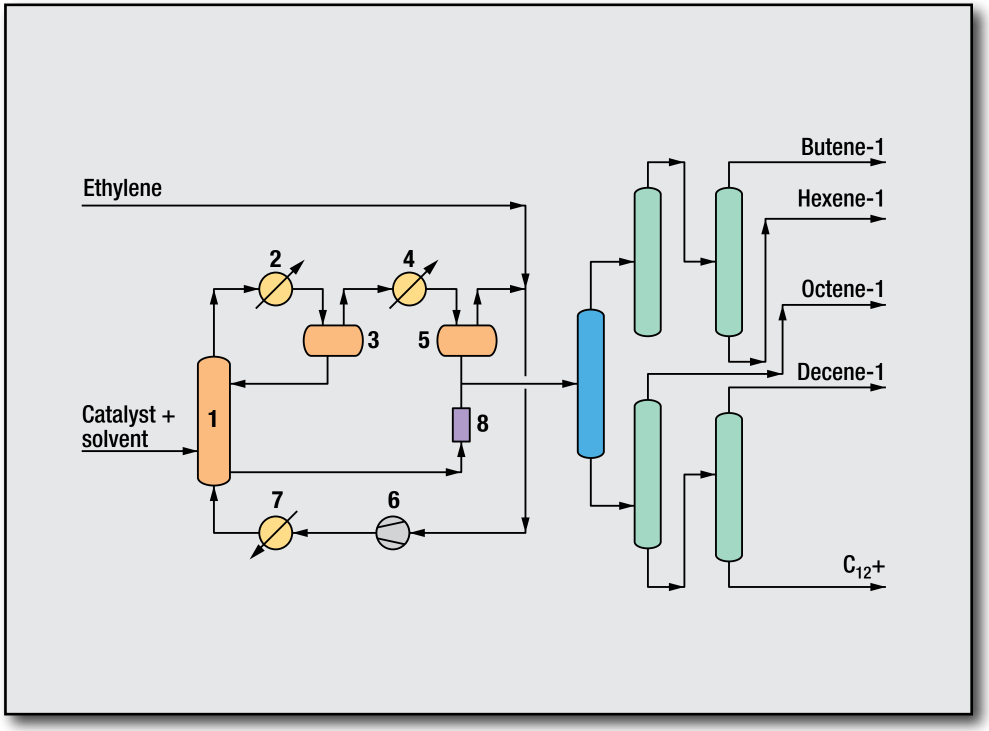
Application: The α-Sablin process produces α-olefins such as butene-1, hexane-1, octene-1 decene-1, etc. from ethylene in a homogenous catalytic reaction. The process is based on a highly active bifunctional catalyst system operating at mild reaction conditions with highest selectivities to α-olefins.

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 in operation at Jubail United in Al-Jubail, Saudi Arabia.

Licensor: The technology is jointly licensed by Linde AG and SABIC - CONTACT

Alpha olefins, linear

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

Description: Polymer-grade ethylene is oligomerized in a liquid-phase reactor (1) with a liquid homogeneous catalyst 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) in order to produce high-purity alpha olefins. Spent catalyst is treated to remove volatile hydrocarbons before safe disposal. 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.

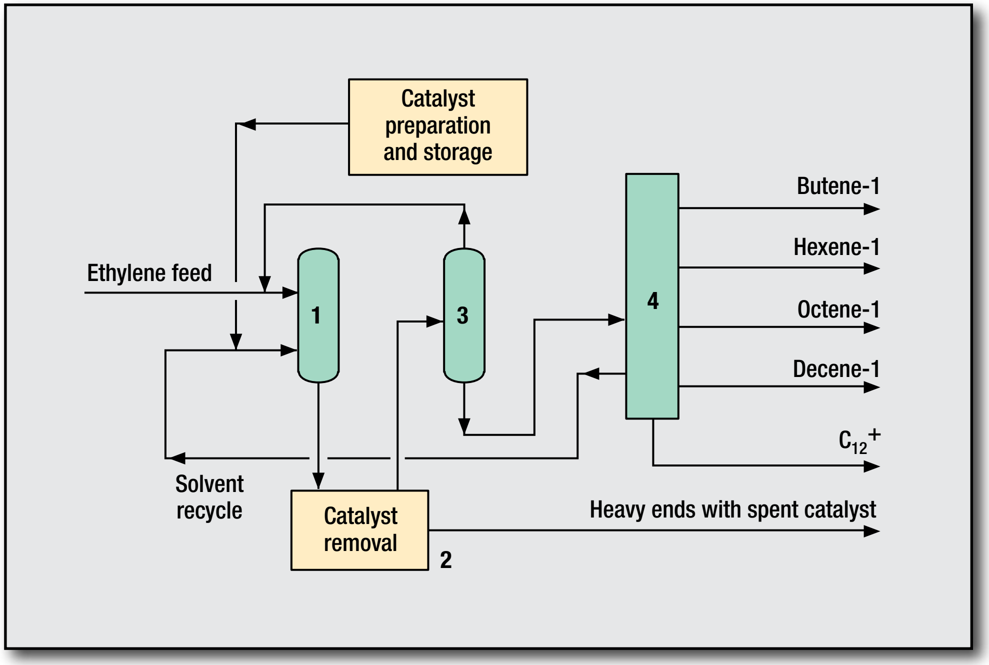
Yields: Yields are adjustable to meet market requirements and very little high boiling polymer is produced as illustrated:

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 2010 ISBL investment at a Gulf Coast location producing 65,000 tpy of C_4–C_{10} alpha-olefins is:

Investment, million US$	44



Raw material	
Ethylene, tons/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

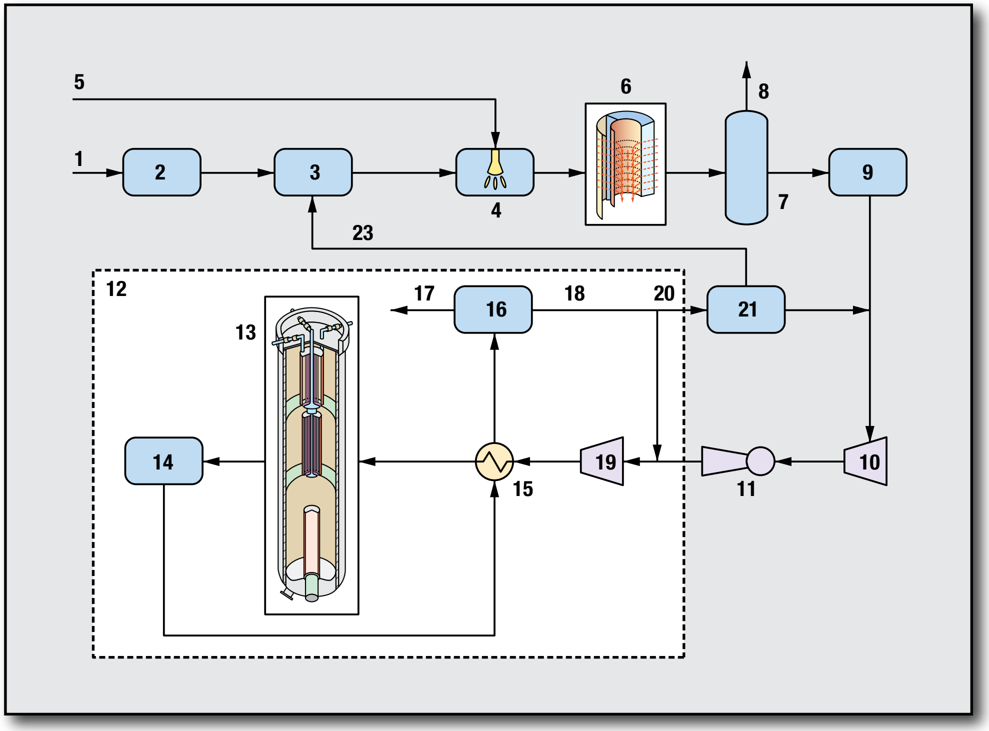
Commercial plants: The AlphaSelect process is strongly backed by extensive Axens industrial experience in homogeneous catalysis, in particular, the Alphabutol process for producing butene-1 for which 27 units have been licensed with a cumulated capacity of 570,000 tpy.

Licensor: Axens - CONTACT

Ammonia

Application: To produce anhydrous ammonia from natural gas. The process is based on applying Casale's highly efficient equipment, including:

- Casale high-efficiency design for the secondary reformer
- Casale axial-radial technology for shift conversion
- CASALE ejector ammonia wash system
- Casale axial-radial technology for the ammonia converter
- Casale advanced waste-heat boiler design in the synthesis loop.



Description: Natural gas (1) is first desulfurized (2) before entering a steam reformer (3) where methane and other hydrocarbons are reacted with steam to be partially converted to synthesis gas, i.e., hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2). The partially reformed gas enters the secondary reformer (4) where air (5) is injected, and the methane is finally converted to syngas. In this unit, Casale supplies its high-efficiency process burner, characterized by low ΔP and a short flame. The reformed gas is cooled by generating high-pressure (HP) steam, and then it enters the shift section (6), where CO reacts with steam to form hydrogen and CO_2. There are two shift converters, the high-temperature shift and low-temperature shift; both are designed according to the unique axial-radial Casale design for catalyst beds, ensuring a low ΔP, lower catalyst volume, longer catalyst life and less expensive pressure vessels.

The shifted gas is further cooled and then it enters the CO_2 removal section (7), where CO_2 is washed away (8). The washed gas, after preheating, enters the methanator reactor (9), where the remaining traces of carbon oxides are converted to methane.

The cleaned synthesis gas can enter the synthesis gas compressor (10), where it is compressed to synthesis pressure. Within the syngas compressor, the gas is dried by the ejector driven Casale liquid ammonia wash (11) to remove saturation water and possible traces of CO_2. This proprietary technology further increases the efficiency of the synthesis loop, by reducing the power requirements of the synthesis gas compressor and the energy duty in the synthesis loop refrigeration section.

The compressed syngas reaches the synthesis loop (12) where it is converted to ammonia in the Casale axial-radial converter (13), characterized by the highest conversion per pass and mechanical robustness. The gas is then cooled in the downstream waste-heat boiler (14), featuring the Casale water tubes design, where HP steam is generated. The gas is further cooled (15 and 16) to condense the product ammonia (17) that is then separated, while the unreacted gas (18) is circulated (19) back to the converter. The inerts (20), present in the synthesis gas, are purged from the loop via the Casale purge recovery unit (21), ensuring almost a complete recovery of the purged hydrogen (22) back to the

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synthesis loop (12), while the inerts are recycled as fuel (23) back to the primary reformer (3).

Economics: Thanks to the high efficiency of the process and equipment design, the total energy consumption (evaluated as feeds + fuel + steam import from package boiler and steam export to urea) is lower than 6.5 Gcal/metric ton of produced ammonia.

Commercial plants: One 2,050 metric tpd plant has been in operation since early 2008, and four more are under construction, 2,050 metric tpd each.

Licensor: Ammonia Casale SA, Switzerland - CONTACT

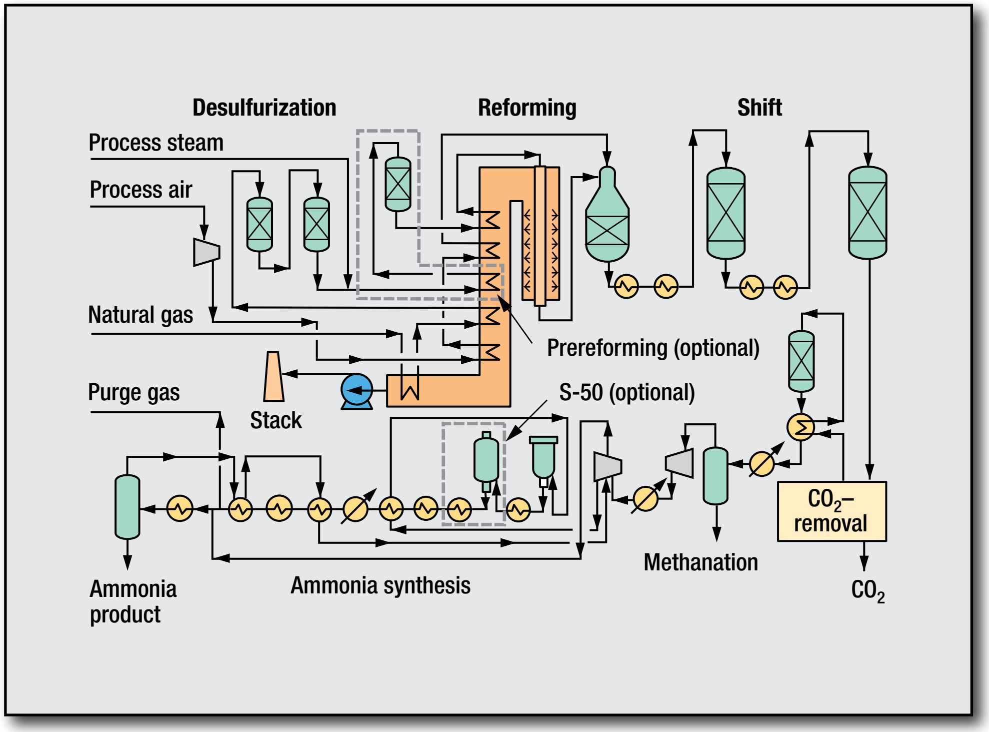
Ammonia

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 three-bed S-300 or the S-350 concept using an S-300 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.

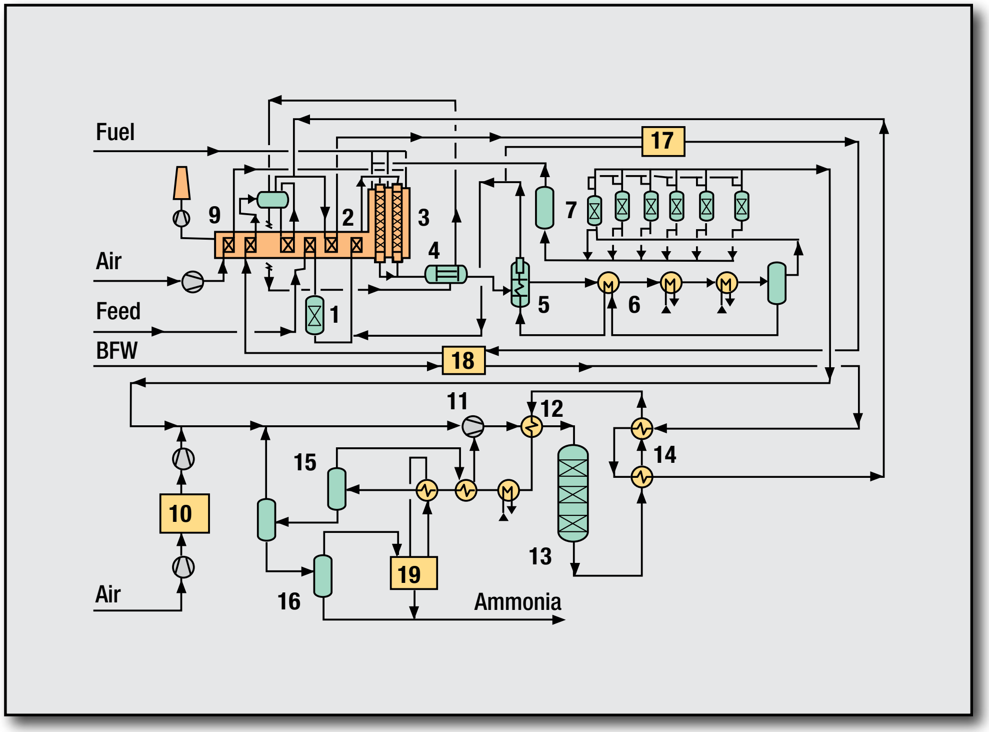


Commercial plants: More than 60 plants use the Topsøe process concept. Since 1990, 50% of the new ammonia production capacity has been based on the Topsøe technology. Capacities of the plants constructed within the last decade range from 650 metric tpd up to more than 2,000 metric tpd. Design of new plants with even higher capacities are available.

Licensor: Haldor Topsøe A/S - CONTACT

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.

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Commercial plants: The first complete LAC plant, for 1,350-metric tpd ammonia, has been built for GSFC in India. Two other LAC plants, for 230-metric tpd and 600-metric tpd ammonia, were commissioned in Australia. The latest LAC plant was erected in China and produces hydrogen, ammonia and CO_2 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.

Licensor: Linde AG - CONTACT

Ammonia

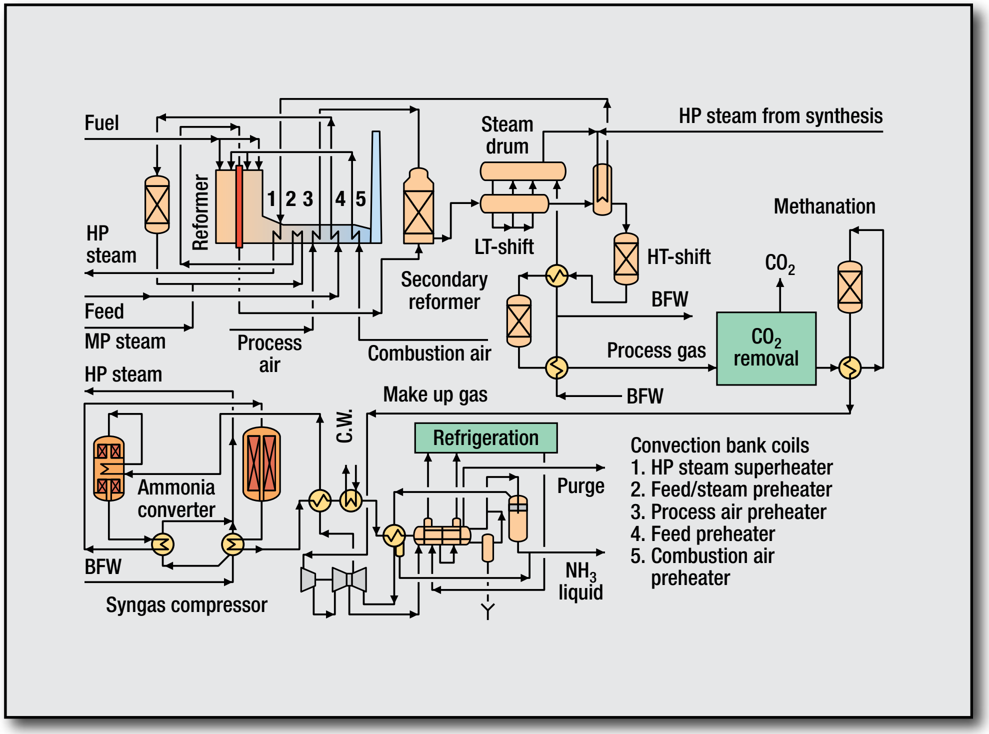
Application: To produce ammonia from natural gas, LNG, LPG or naphtha. Other hydrocarbons—coal, oil, residues or methanol purge gas—are possible feedstocks with an adapted front-end. The process uses conventional steam reforming synthesis gas generation (front-end) and an ammonia synthesis loop. It is 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 2,200 metric tons per day. 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 CO_2 in the HT and LT shift over standard catalysts. CO_2 is removed in a scrubbing unit, which is normally either the BASF-aMDEA or the UOP-Benfield process. Remaining carbon oxides 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 high-pressure 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.



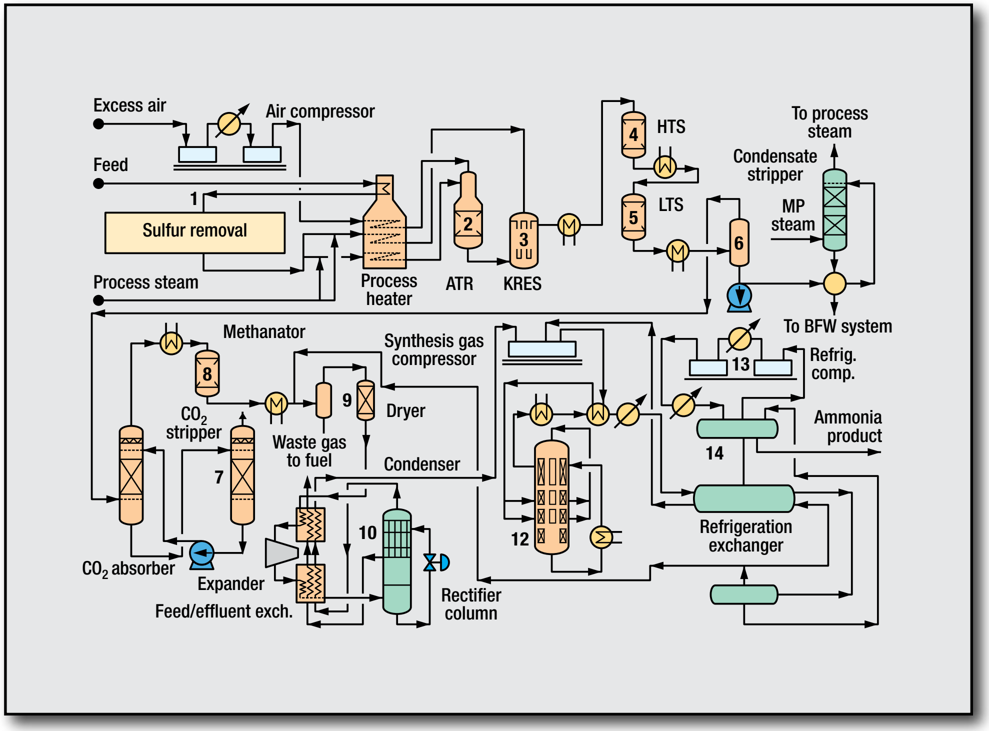
Liquid ammonia is separated by condensation from the synthesis loop and is either subcooled and routed to storage, or conveyed at moderate temperature to subsequent consumers.

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: Nine ammonia plants have been commissioned between 1998 and 2010, and six facilities are under engineering or construction with capacities ranging from 600 metric tpd up to 2,200 metric tpd, resp. 3,300 metric tpd for the Dual Pressure Ammonia Process.

Licensor: Uhde GmbH - CONTACT

Ammonia, KAAP*plus*



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

Description: The key steps in the KAAP*plus* 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 efficiently 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 it 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 is separated (6) and then routed to the gas purification section. CO_2 is removed from synthesis gas using a wet CO_2 scrubbing system such as hot potassium carbonate or MDEA (methyl diethanolamine) (7).

After CO_2 removal, final purification includes methanation (8), gas drying (9), and cryogenic purification (10). The resulting pure synthesis gas is compressed in a single-case 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 relatively 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 KAAP*plus* process is less than 25 MMBtu (LHV)/short-ton. Elimination of the primary reformer combined with low-pressure synthesis provides a capital cost savings of about 10% over conventional processes.

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Ammonia, KAAP*plus*, *continued*

Commercial plants: More than 200 large-scale, single-train ammonia plants of KBR design are onstream or have been contracted worldwide. The KAAP*plus* advanced ammonia technology provides a low-cost, low-energy design for ammonia plants, minimizes environmental impact, reduces maintenance and operating requirements and provides enhanced reliability. Three plants use KRES technology and 26 plants use Purifier technology. Six grassroots KAAP plants are in full operation and a seventh is under construction. Capacities range from 1,800 metric tpd to 2,000 metric tpd.

Licensor: Kellogg Brown & Root, LLC - CONTACT

Ammonia, KBR Purifier

Application: To produce ammonia from hydrocarbon feedstocks and air.

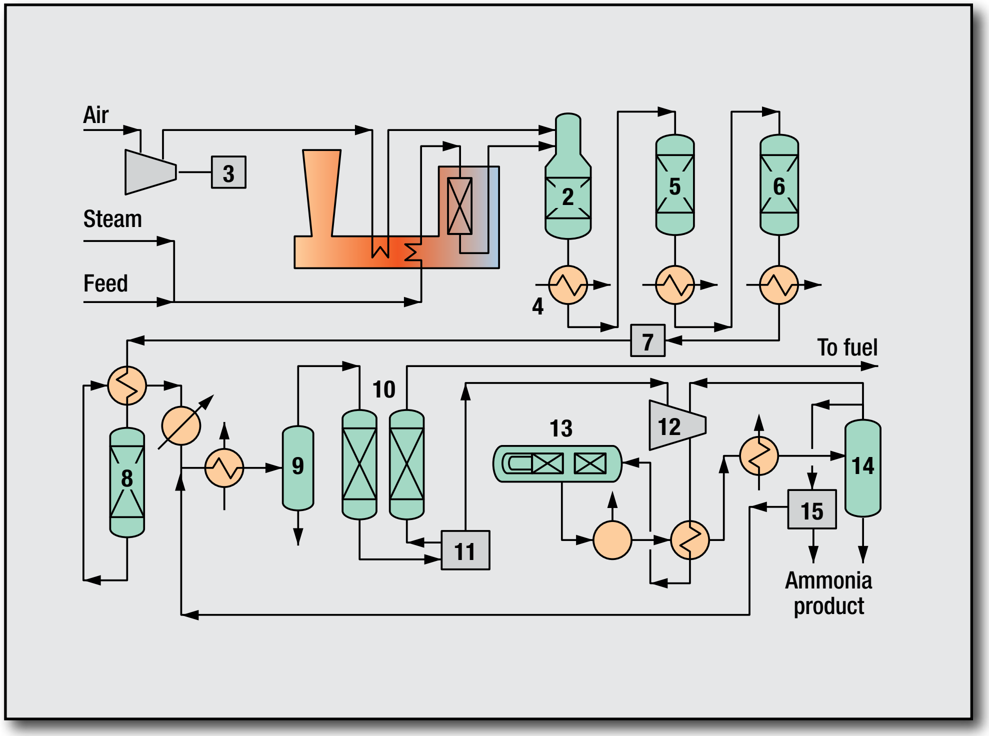
Description: The key features of the KBR Purifier process are mild primary reforming, secondary reforming with excess air, cryogenic purification of syngas, and synthesis of ammonia over magnetite catalyst in a horizontal converter.

Desulfurized feed is reacted with steam in the primary reformer (1) with an exit temperature of about 700°C. Primary reformer effluent is reacted with excess air in the secondary reformer (2) with an exit temperature of 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 Purifier*plus* ammonia process.

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 CO_2 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.

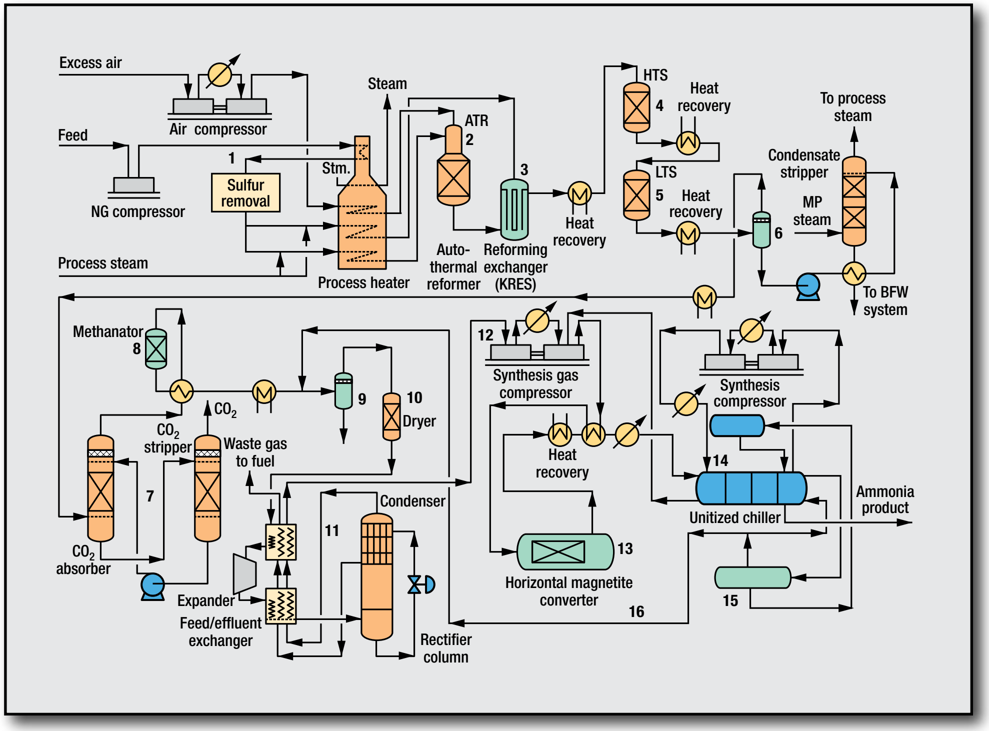
A small, low-speed expander provides the net refrigeration. The purified syngas is compressed in the syngas compressor (12), mixed with the loop-cycle stream and fed to the converter (13). Converter effluent is cooled and then chilled by ammonia refrigeration. Ammonia product is separated (14) from unreacted 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: More than 200 single-train plants of KBR design have been contracted worldwide. Nineteen of these plants use the KBR Purifier process, including a 2,200-metric tpd plant commissioned in 2006. Four large-capacity Purifier plants are currently in design or under construction. Three more plants are being converted from conventional technology to Purifier technology.

Licensor: Kellogg Brown & Root, LLC - CONTACT

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 a 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 is separated (6) and then routed to the gas purification section. CO_2 is removed from synthesis gas using a wet-CO_2 scrubbing system such as hot potassium carbonate or MDEA (methyl diethanolamine) (7).

Following CO_2 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 it 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)

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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: More than 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. Three plants use KRES technology and 26 plants use PURIFIER technology.

Licensor: Kellogg Brown & Root, LLC - CONTACT

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 metric tpd).

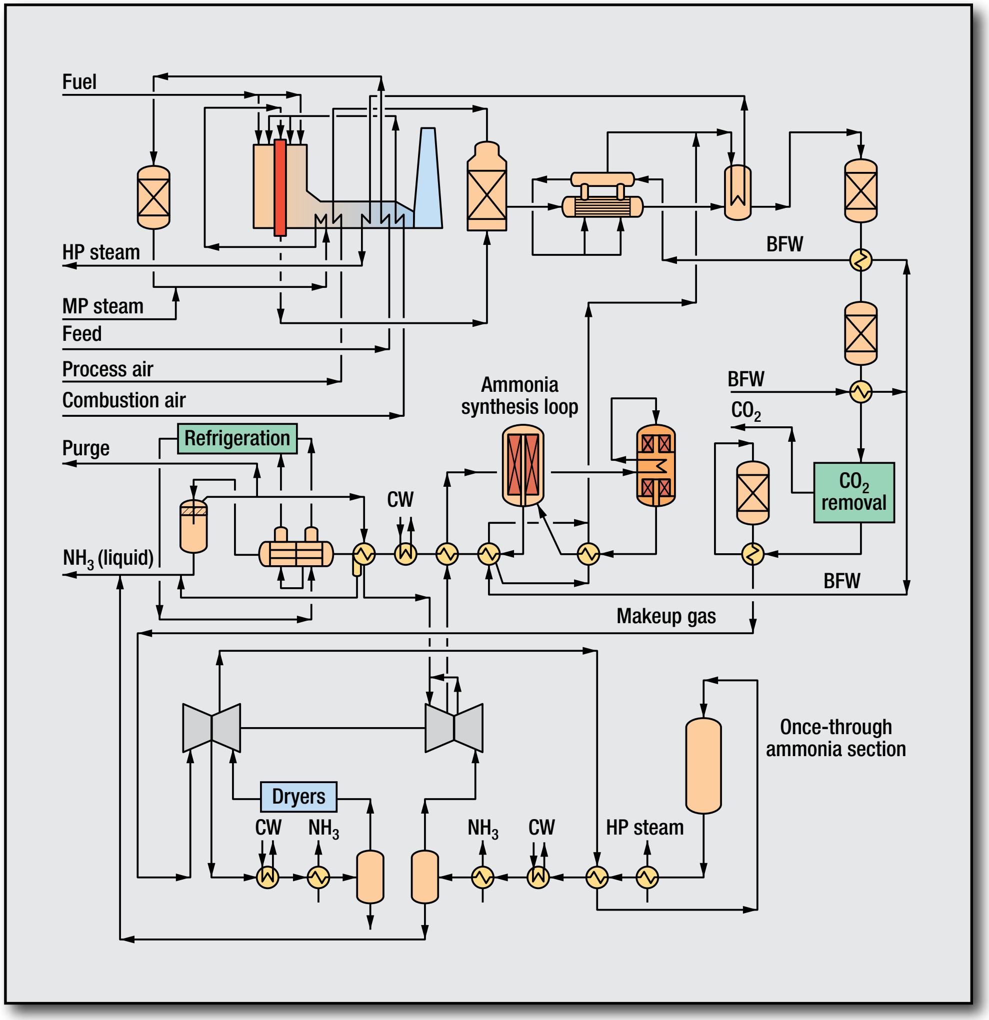
Description: The feedstock (e.g. natural gas) is desulfurized, mixed with steam and converted into synthesis gas over nickel catalyst at approximately 42 bar and 800–850°C in the primary reformer. The Uhde steam reformer is a top-fired reformer with tubes made of centrifugal micro-alloy steel and a proprietary "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 CO_2 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

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is achieved by combination of the chilled second casing of the syngas 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 is the SAFCO IV ammonia plant with 3,300 metric tpd in Al-Jubail, Saudi Arabia, in operation since 2006. A second plant is under construction.

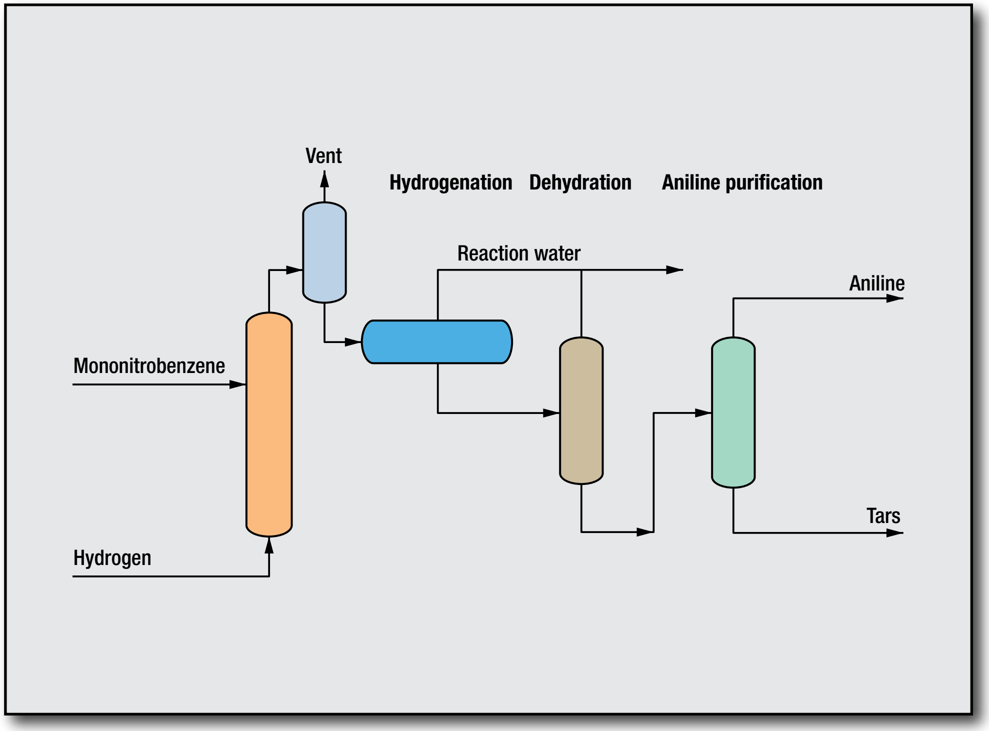
Licensor: Uhde GmbH - CONTACT

Aniline

Application: A process for the production of high-quality aniline from mononitrobenzene.

Description: Aniline is produced by the nitration of benzene with nitric acid to mononitrobenzene (MNB) which is subsequently hydrogenated to aniline. In the DuPont process, 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.



Product quality: The DuPont aniline process consistently produces a very high quality aniline product, suitable for all MDI production technologies, and other specialty chemical applications. The typical product quality is:

Aniline, wt%	99.95
MNB, ppmwt	0.1
Water, ppmwt	300
Color, APHA	30
Freeze point (dry basis), °C	–6.0

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 four new licenses have been awarded since 2004 with aniline capacities of up to 360,000 tpy in a single unit.

Licensor: Kellogg Brown & Root LLC - CONTACT

Aromatics extraction

Application: The UOP Sulfolane process recovers high-purity C_6–C_9 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.

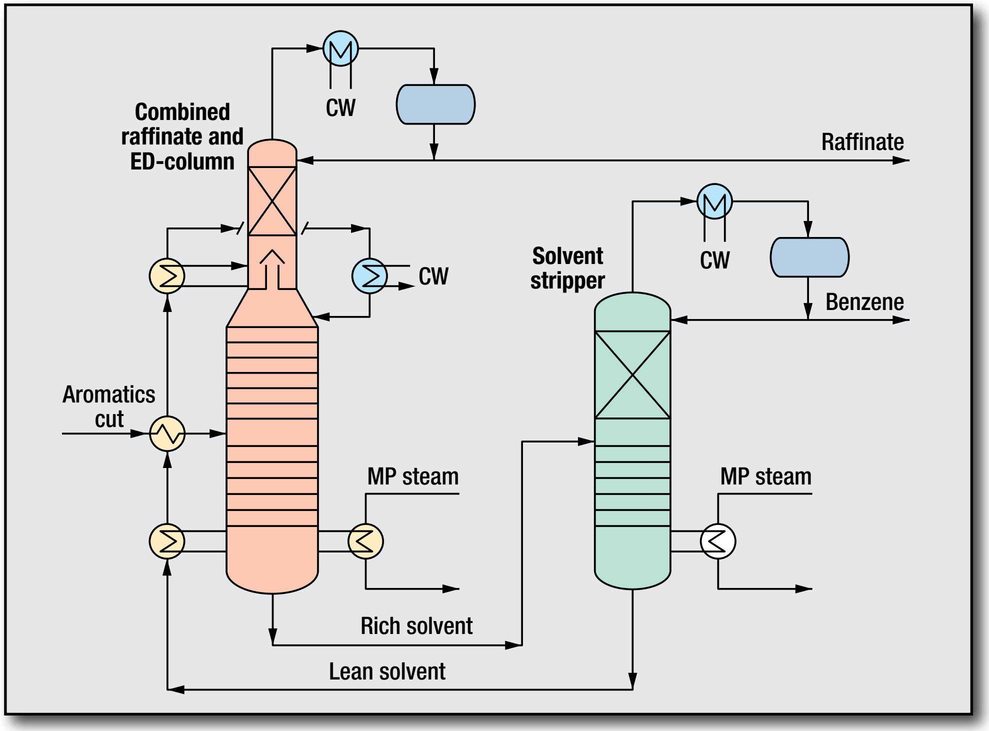
Estimated inside battery limits (ISBL) costs based on unit processing 460,000 metric tpy of BT reformate feedstock with 68 LV% aromatics (US Gulf Coast site in 2003).

Investment, US$ million	32
Utilities (per metric ton of feed)	
Electricity, kWh	4.4
Steam, metric ton	0.46
Water,cooling, m^3	14.4

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 139 Sulfolane units throughout the world.

Licensor: UOP LLC, A Honeywell Company - CONTACT

Aromatics extractive distillation



Application: The DISTAPEX process uses extractive distillation to recover individual aromatics from a heart-cut feedstock containing the desired aromatic compound.

Description: The feedstock enters the extractive distillation column in its middle section while the solvent, N-methylpyrrolidone (NMP), is fed on the top tray of its extractive distillation section. The NMP solvent allows the separation of aromatic and non-aromatic components by enhancing their relative volatilities.

The vapors rising from the extractive distillation section consisting of non-aromatic components still contain small quantities of solvent. These solvent traces are separated in the raffinate section located above the extractive distillation section. The purified non-aromatics are withdrawn as overhead product.

The rich solvent comprising the aromatic component is withdrawn at the bottom of the column and sent to the solvent stripper column, in which the contained components are stripped off under vacuum conditions. The aromatic stream is withdrawn as overhead product, while the stripped solvent is circulated back to the extractive distillation column.

An optimized heat integration results in a very low consumption of medium-pressure steam. In contrast to competing technologies, solidification of the solvent during maintenance works will not occur due to the low solidification point of NMP.

Ecology: Due to the unique properties of NMP, the process has an excellent ecological fingerprint.

Recovery rate: Typically more than 99.5% depending on the aromatic content in the feedstock.

Economics: The DISTAPEX process requires a minimum number of equipment items and is especially renowned for reliability and availability as well as low operating costs. Due to the low boiling point of the solvent only medium-pressure steam is required.

Utilities, e.g., per ton benzene

Steam, ton	0.7
Electricity, kWh	8
Water, cooling, m^3	19
Solvent loss, kg	0.01

Commercial plants: The DISTAPEX process is applied in more than 25 reference plants.

Licensor: Lurgi GmbH, a company of the Air Liquide Group - CONTACT

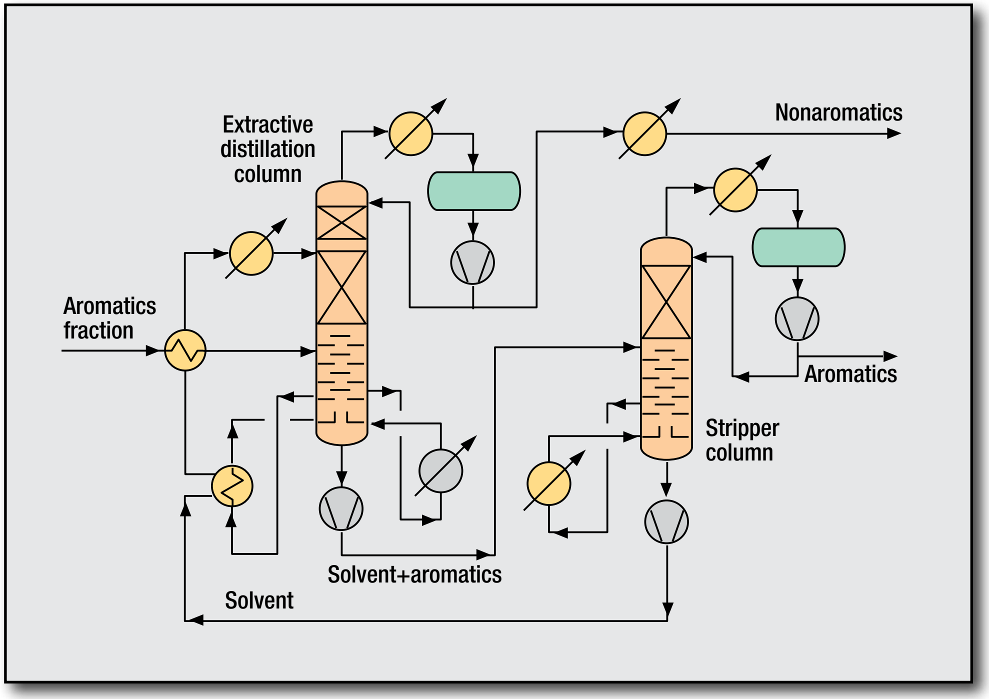
Aromatics extractive distillation

Application: Recovery of high-purity aromatics from reformate, 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**

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

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

Commercial plants: More than 55 Morphylane plants (total capacity of more than 6 MMtpy).

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.

Licensor: Uhde GmbH - CONTACT

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

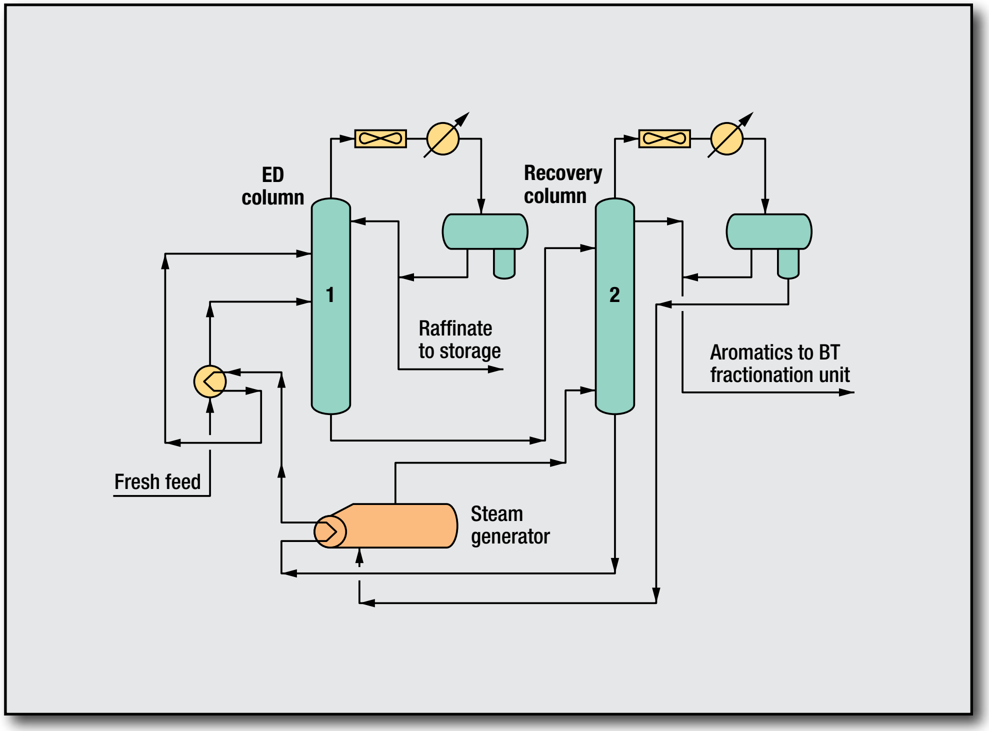
Aromatics extractive distillation

Application: The UOP Extractive Distillation (ED) Sulfolane process recovers high-purity aromatics from hydrocarbon mixtures by extractive distillation. Extractive Distillation is a lower cost, more suitable option for feeds rich in aromatics containing mostly benzene and/or toluene.

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 preheated 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. Nonaromatics 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 Sulfalane process minimizes concern about trace nitrogen contamination that occurs with nitrogen-based solvents. Estimated inside battery limits (ISBL) costs based on a unit processing 1.12 million metric tpy of BT reformate feedstock with 67 LV% aromatics (US Gulf Coast site in 2010).

Investment, US$ million	29
Utilities (per metric ton of feed)	
Electricity, kWh	5.6
Steam, metric ton	0.33
Water, cooling, m^3	4.2



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. As of 2010, UOP has licensed a total of 139 Sulfolane units throughout the world with 20 of these being ED Sulfolane units.

Licensor: UOP LLC, A Honeywell Company - CONTACT

Aromatics recovery

Application: Recovery via extraction of high-purity C_6–C_9 aromatics from pyrolysis gasoline, reformate, coke oven light oil and kerosine fractions.

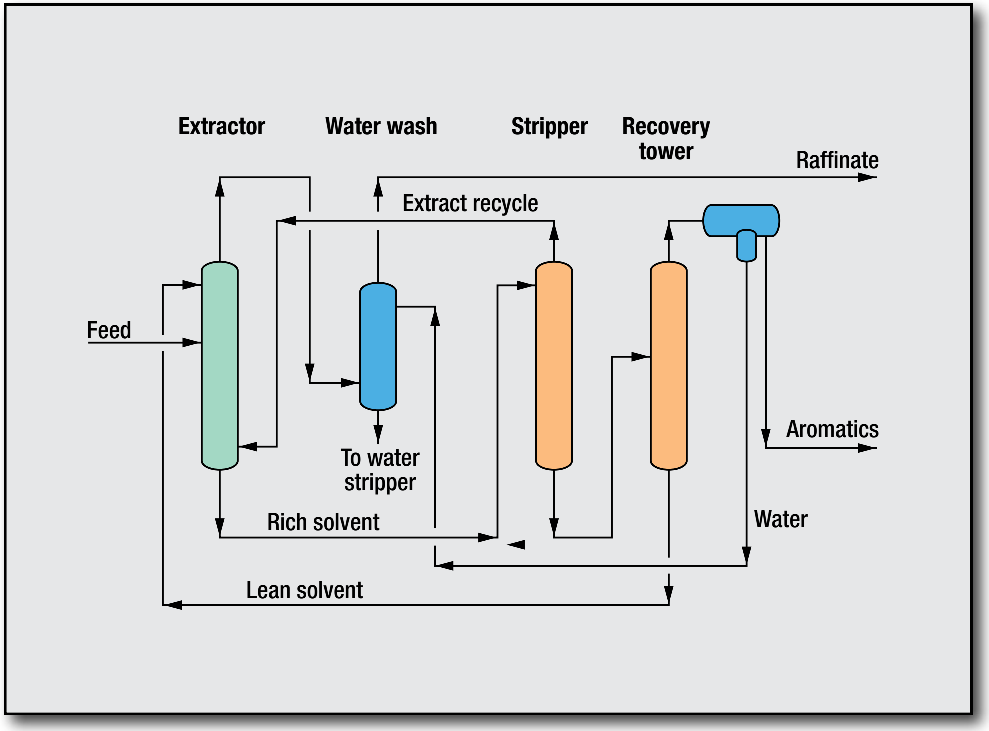
Description: Hydrocarbon feed is pumped to the liquid-liquid extraction column (1) where the aromatics are dissolved selectively in the sulfolane water-based solvent and separated from the insoluble non-aromatics (paraffins, olefins and naphthenes). The non-aromatic raffinate phase exits at the top of 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.

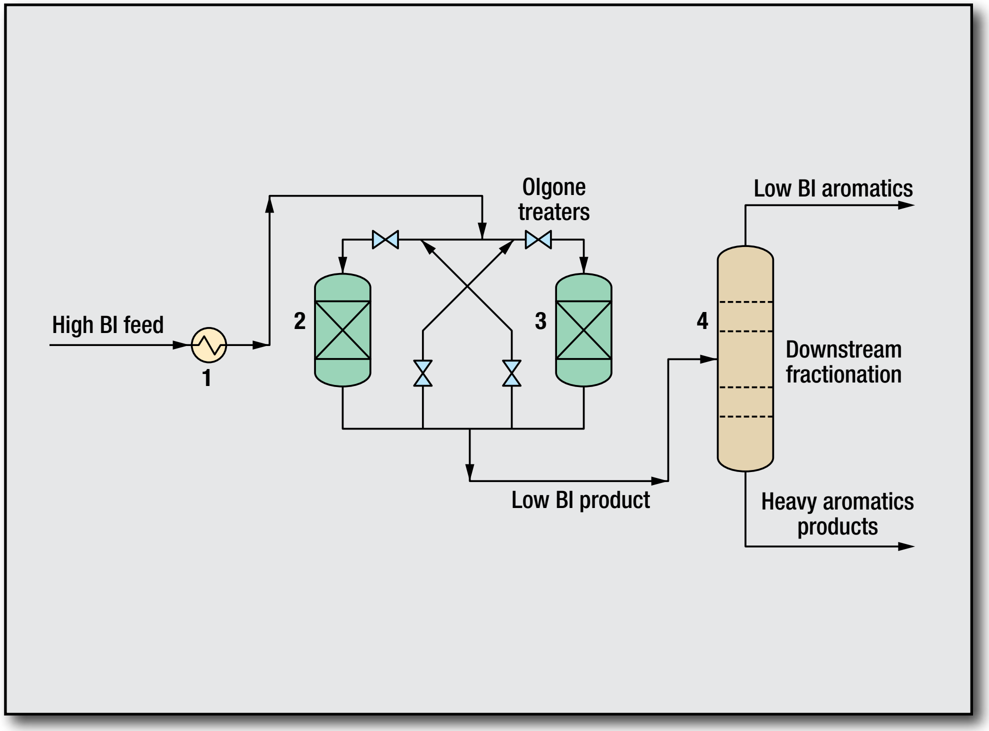
Yields: Overall aromatics' recoveries are > 99% while solvent losses are extremely small—less than 0.006 lb/bbl of feed.

Commercial plants: Over 20 licensed units are in operation.

Licensor: Axens - CONTACT



Aromatics treatment



Application: To reduce olefinic content in either a heavy reformate feed or an aromatic extract feed using ExxonMobil Chemical's Olgone process.

Description: Olgone is an alternative solution to clay treating that is used to reduce olefins content and thus, lower the Bromine Index (BI) of heavy reformate and aromatic extract streams. In this process, a stream of either mixed xylenes, benzene/toluene or a combination of each is preheated in a feed heater (1). The stream is then sent to a liquid-phase reactor (2) containing the ExxonMobil proprietary EM-1800 catalyst. Similar to a clay treater system, a typical Olgone treater system consists of two vessels with one in service and one in standby mode (3).

The primary reaction is the acid-catalyzed alkylation of an aromatic molecule with an olefin, resulting in the formation of a heavy aromatic compound. The heavy aromatic compound is then fractionated out of the low BI liquid product downstream of the Olgone reactor (4).

The catalyst used in the Olgone process exhibits a BI capacity typically six times greater than conventional clay.

Operating conditions: The Olgone process is essentially a drop-in replacement for clay treating. Olgone operates at temperatures and pressures similar to clay operations, sufficient to keep the feed in the liquid state. The catalyst offers long uninterrupted operating cycles and can be regenerated multiple times.

Economics: By virtue of the Olgone technology's very long cycles and reuse via regeneration, solid waste can be reduced by greater than 90% and clay waste can be reduced by 100% where Olgone is deployed in its catalyst-only configuration. The user enjoys both disposal cost reductions and tremendous environmental benefits. Operating costs are significantly lowered by less frequent unloading/reloading events, and downstream units are better protected from BI excursions due to the technology's enhanced capacity for olefins removal. Olgone also provides a potential debottleneck for units limited by short clay treater cycles.

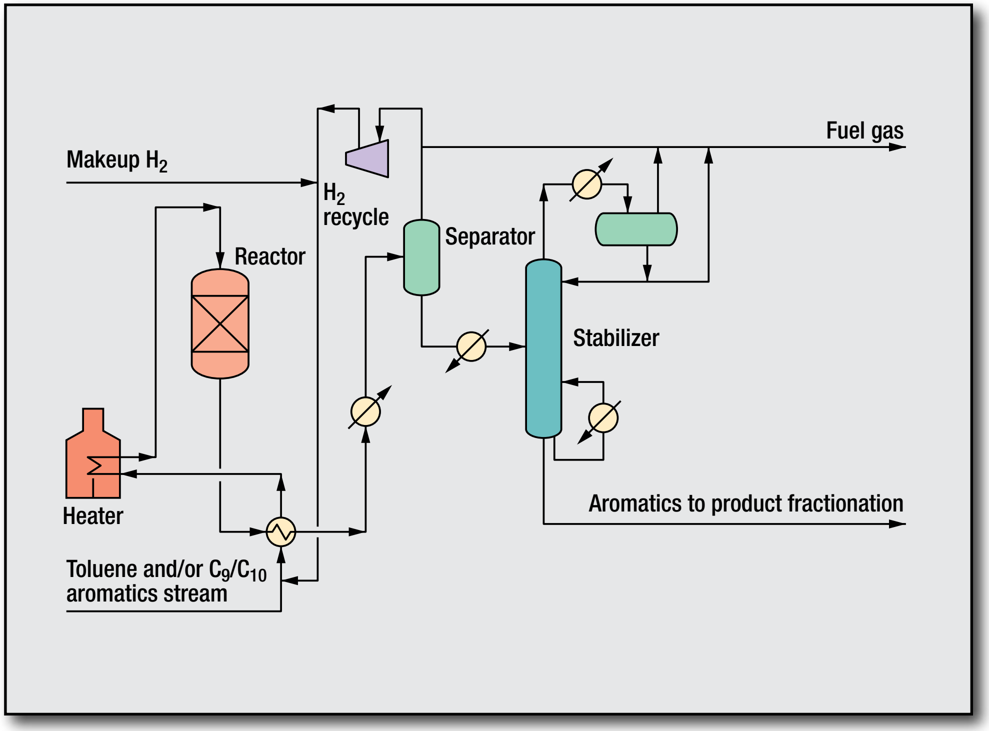
Commercial plants: The Olgone technology was first commercialized in 2003. There are currently eight Olgone units in operation.

Licensor: ExxonMobil Chemical Technology Licensing LLC (retrofit, grassroots applications) - CONTACT

Aromatics, Transalkylation

Application: GT-TransAlk process technology produces benzene and xylenes through transalkylation of the methyl groups from toluene and/or heavy aromatics streams. The technology features a proprietary zeolite catalyst and can accommodate varying ratios of feedstock, while maintaining high activity and selectivity.

Description: The C_9/C_{10} aromatics stream is mixed with toluene and hydrogen, vaporized and fed to the transalkylation reactor section. The reactor gaseous product is primarily unreacted hydrogen, which is recycled to the reactor. The liquid product stream is subsequently stabilized to remove light components. The resulting aromatics are routed to product fractionation to produce the final benzene and xylene products. The reactor is charged with a zeolite catalyst, which exhibits both long life and good flexibility to manage 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:

- 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
- Flexible to handle up to 90^+% C_9^+ components in feed with high conversion
- Catalyst is resistant to impurities common to this service
- Moderate operating parameters; catalyst can be used as a replacement to other transalkylation units, or in grass roots designs
- Decreased hydrogen consumption due to low cracking rates
- Significant decrease in energy consumption due to efficient heat integration scheme.

Economics:

Basis	1 million tpy (22,000 bpsd) feedrate
Erected cost	$18 million (ISBL, 2009 US Gulf Coast basis)

Commercial plants: Three commercial licences.

Licensor: GTC Technology - CONTACT

Aromatization

Application: GTC Technology, in alliance with our technology partner, offers commercially proven aromatization technology for gasoline octane improvement or aromatics production. The technology uses a proprietary catalyst in fixed-bed reactors with periodic catalyst regeneration.

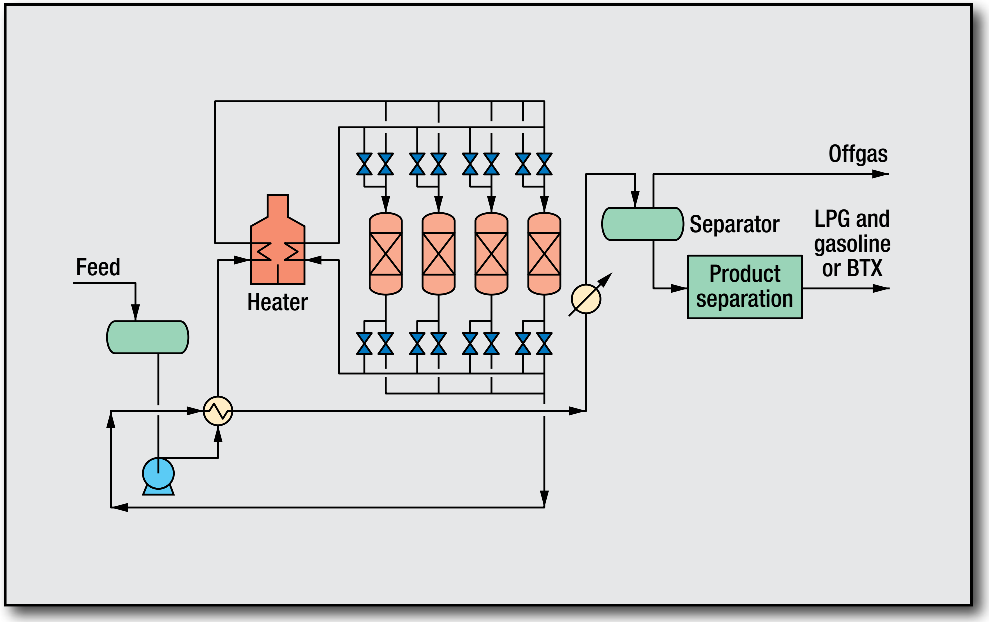
Description: The feed, either paraffinic or olefinic C_4–C_8 fraction, is heated through heat exchangers and a furnace to the desired temperature. The vaporized feed is fed to the top of the aromatization reactor. There are two reactors in series are in operation, and the other two reactors are in regeneration or standby. The effluent from the bottom of the second reactor is fed to the aromatization feed/effluent heat exchanger. After the feed/effluent heat exchanger, the reactor effluent is further cooled by air coolers and trim coolers with cooling water and chilled water. This cold effluent is then sent to the aromatization effluent separator (low pressure) where the rich net gas stream is separated from the aromatic-rich liquid.

The rich net gas (offgas) is further compressed in downstream separation to recover the valuable aromatic-rich liquid. The final product streams after downstream separation include C_2^- dry gas, LPG, and premium gasoline or benzene, toluene and xylene (BTX) products. The regeneration is a typical coke-burning step.

Process advantages:

Aromatization technology for octane improvement

- Upgrade low-octane gasoline to premium gasoline
- Overall product utilization (gasoline + LPG) is greater than 93%
- The upgraded RON 90 gasoline has low sulfur and olefins and is excellent gasoline blending stock



Aromatization technology for aromatics production

- Convert C_4–C_8 olefins into aromatics
- No hydrogen needed
- Complete integration with steam cracker possible with dry gas for hydrogen recovery; LPG and paraffins recycled to steam cracking
- Simple distillation is typically used to meet the aromatics specifications for paraxylene manufacture
- Feedstocks can be from FCC, steam cracking and coking.

Economics:

Basis	500,000 tpy (11,000 bpsd) feedrate
Erected cost	$49 million (ISBL, 2009 US Gulf Coast basis)

Commercial plants: One commercial license.

Licensor: GTC Technology - CONTACT

Benzene

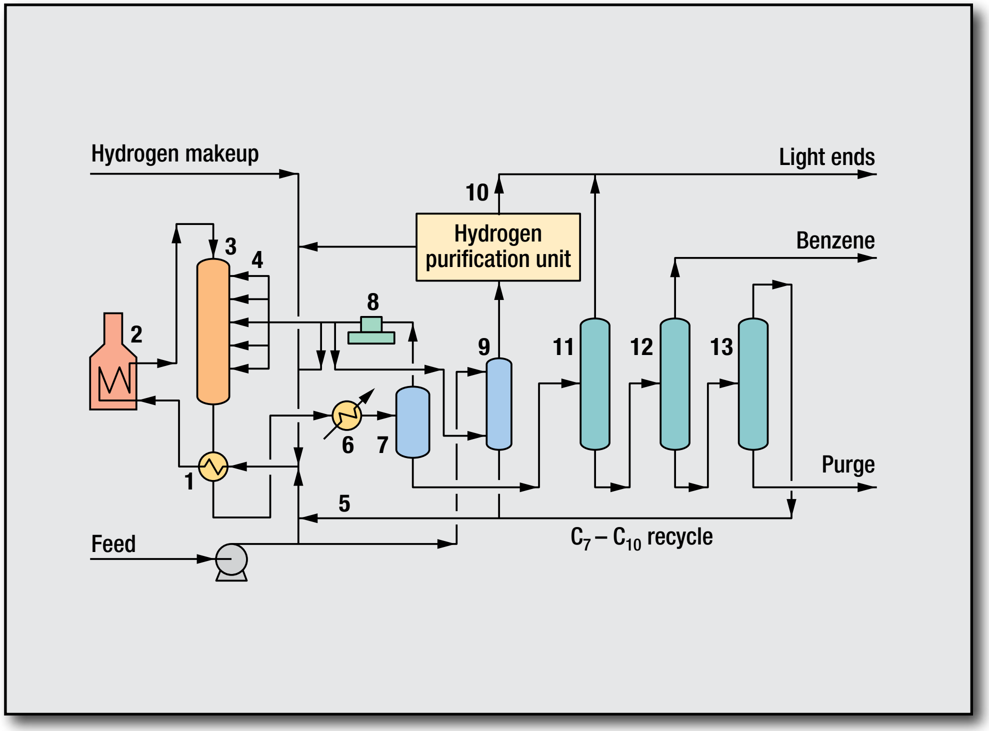
Application: Produce benzene via the hydrodealkylation of C_7–C_{11} aromatics.

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 counter currently with a feed side stream 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.

Commercial plants: Thirty-six plants have been licensed worldwide for processing a variety of feedstocks including toluene, mixed aromatics, reformate and pyrolysis gasoline.

Licensor: Axens - CONTACT

Benzene

Application: To produce high-purity benzene and heavier aromatics from toluene and heavier aromatics using the Detol process. The process has also been applied to pyrolysis gasoline (Pyrotol) and light coke-oven cases (Litol).

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).

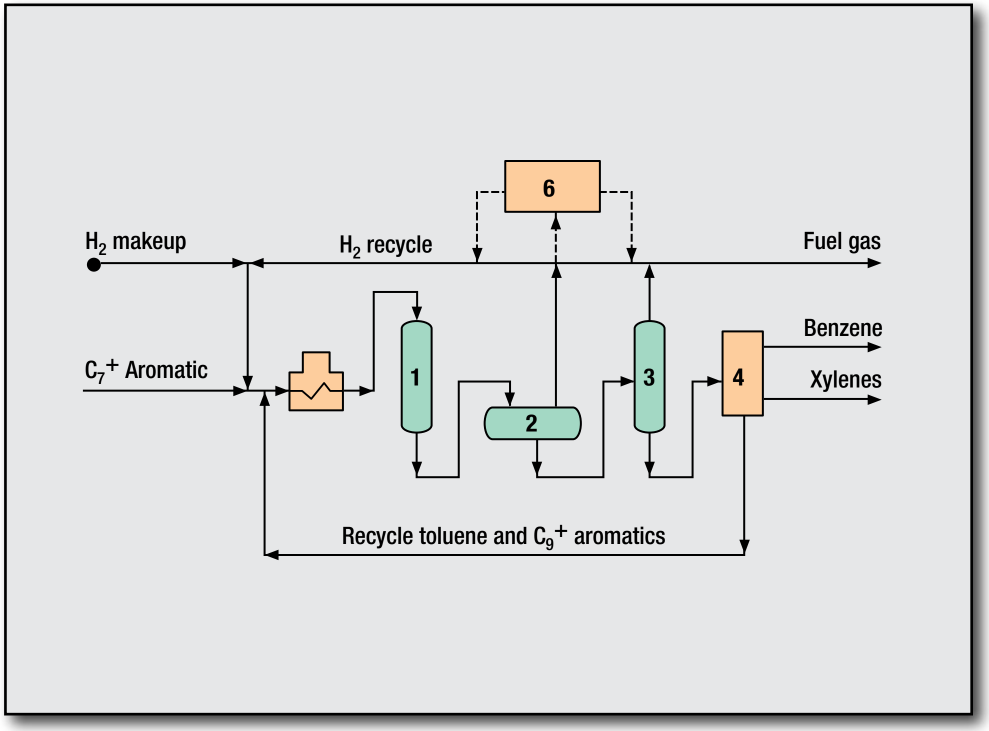
To meet acid wash color specifications, stabilizer bottoms are passed through a fixed-bed clay treater, then distilled (4) to produce the desired specification benzene. The cryogenic purification of recycle hydrogen to reduce the make-up hydrogen requirement is optional (6).

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:

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 Detol plants with capacities ranging from about 12 million gpy to 100 million gpy have been licensed. A total of 29 hydrodealkylation plants have been licensed.

Licensor: Lummus Technology - CONTACT

Benzene and toluene

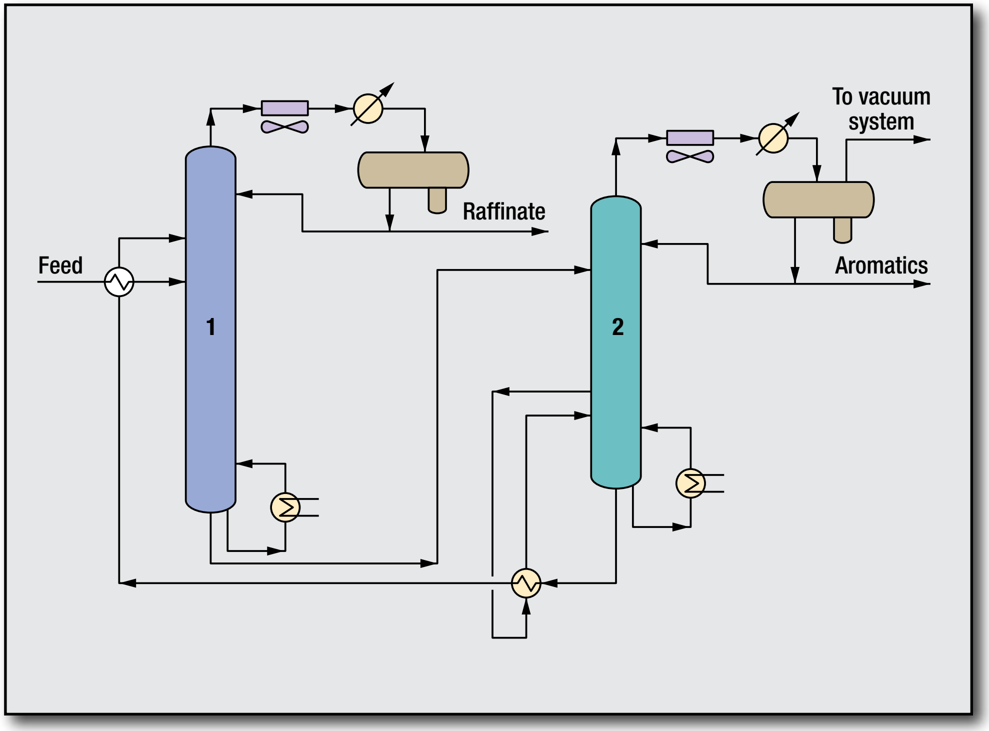
Application: The sulfolane extractive distillation (SED) process uses a complex solvent system composed of sulfolane (as the main solvent) and a co-solvent. The SED process can be used to recover high-purity benzene or benzene and toluene from hydrocarbon mixtures such as hydrogenated pyrolysis gasoline, reformate or coal tar oil.

Description: A typical SED unit mainly consists of an extractive distillation column and a solvent recovery column. The hydrocarbon feed is separated into non-aromatics and aromatics products through extractive distillation with the solvent. For the benzene-recovery case, benzene is directly produced from the SED unit. For the benzene and toluene recovery case, pure benzene and pure toluene are produced from the aromatics product of the SED unit through downstream fractionation.

The SED process uses sulfolane as the main selective solvent in which a co-solvent is added. The unique solvent system, accurate simulator, optimized process scheme, reliable and economical equipment design, advanced and reasonable control strategy ensure that the SED technology can provide these superior benefits:

- Good processing flexibility; able to handle feedstocks including hydrogenated pyrolysis gasoline, coal tar oil and reformate
- High product quality and high recovery
- Low capital investment and low operating costs—about 30% lower than sulfolane liquid-liquid aromatics extraction process
- Extra-low solvent consumption—about 70% lower than sulfolane liquid-liquid aromatics extraction process.

Commercial plants: The first SED commercial plant was put onstream in 2001. Since 2006, 11 SED units with a total capacity of 1.2 million metric tpy of benzene and 240,000 metric tpy of toluene have been commercialized by SINOPEC. All of these units have operated with good performance, including a 350,000-metric tpy SAE unit in SECCO, which can onstream in 2005.



Licensor: China Petrochemical Technology Co., Ltd. - CONTACT

Benzene saturation

Application: GT-BenZap is suggested for refineries limited by economies of scale required for benzene extraction or for units located in remote areas away from benzene consumers. When implementing GT-BenZap, GTC's experts simulate the existing process and provide custom integration with the refiner's existing units for effective benzene management.

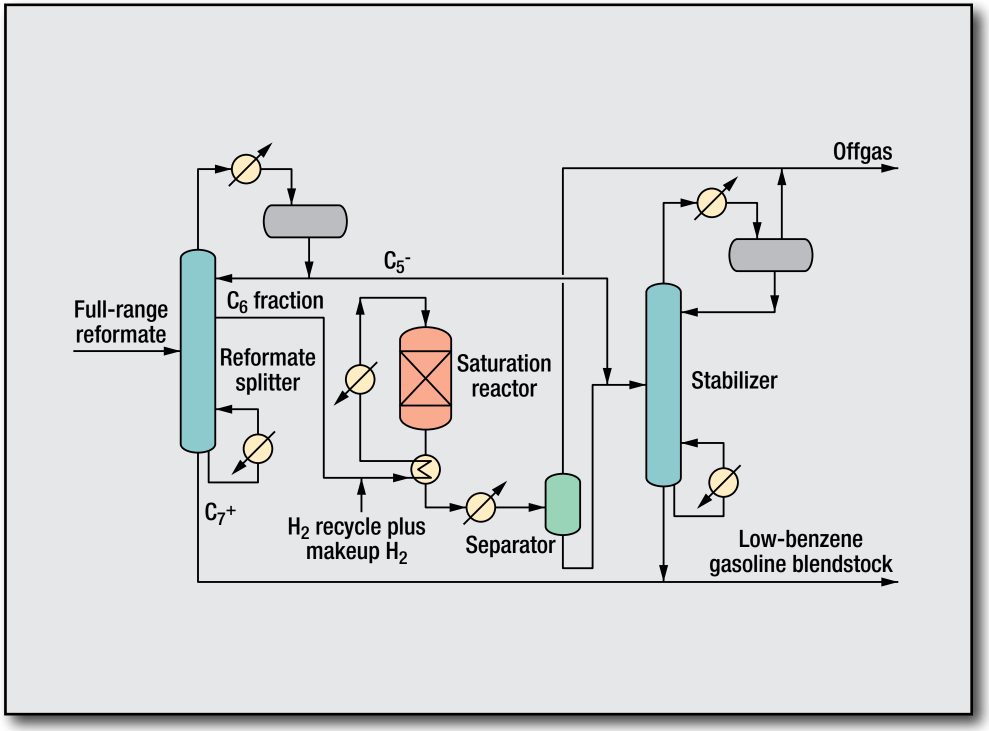
Description: GTC's GT-BenZap process features a reliable traditional design paired with a proven active hydrogenation catalyst. The process consists of hydrotreating a narrow-cut C_6 fraction, which is separated from the full-range reformate to saturate the benzene component into cyclohexane. The reformate is first fed to a reformate splitter, where the C_6 heart cut is separated as a side-draw fraction while the C_7^+ cut and the C_5^- light fraction are removed as bottom and top products of the column.

The C_6 olefins present in the C_6 cut are also hydrogenated to paraffins while the C_5^- olefins removed at the top of the splitter are not, thus preserving the octane number. The hydrogenated C_6 fraction from the reactor outlet is sent to a stabilizer column where the remaining hydrogen and lights are removed overhead. The C_5^- cut, produced from the splitter overhead, is recombined with the hydrogenated C_6 cut within the GT-BenZap process in a unique manner that reduces energy consumption and capital equipment cost.

The light reformate is mixed with the C_7^+ cut from the splitter column and together form the full-range reformate, which is low in benzene. GTC also offers a modular construction option and the possibility to reuse existing equipment.

Process advantages:

- Simple process to hydrogenate benzene and remove it from gasoline
- Reliable technology that uses an isolated hydrogenation reactor
- Reduces benzene in reformate streams by over 99.9%
- Minimal impact to hydrogen balance and octane loss



Economics:

Basis	15,000 bpsd C_6 cut stream
Erected cost	$12 million (ISBL, 2009 US Gulf Coast basis)

Commercial plants: Two licensed units

Licensor: GTC Technology - CONTACT

Benzene, Ethylbenzene dealkylation

Application: The DX process was developed to convert ethylbenzene (EB) contained in the C_8 aromatic feedstocks to high-purity benzene plus ethane, and upgrade the mixed xylenes to premium grade. The feedstocks can be either pygas C_8 or reformer C_8 streams. The technology features a proprietary catalyst with high activity, low ring loss and superior long catalyst cycle length. This technology is partnered with Toray Industries, Inc., of Japan.

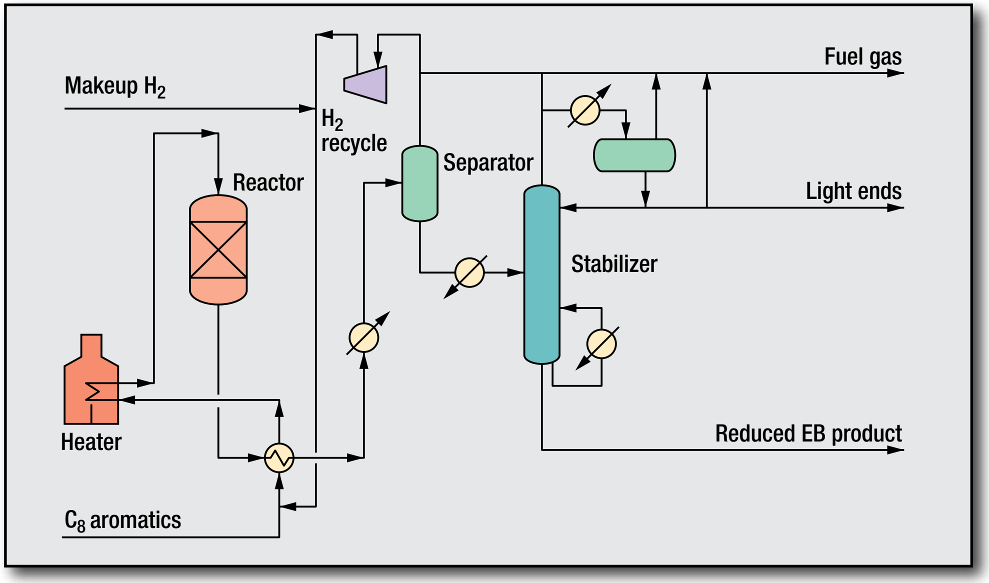
Description: The technology encompasses two main processing areas: reactor section and product distillation section. In this process, C_8 aromatics feed stream is first mixed with hydrogen. The mixed stream is then heated against reactor effluent and sent through a process furnace. The heated mixture is fed into the DX reaction unit, where EB is de-alkylated at very high conversion,k and xylenes are isomerized to equilibrium.

The reactor effluent is cooled, it flows to the separator, where the hydrogen-rich vapor phase is separated from the liquid stream. A small portion of the vapor phase is purged to control purity of the recycle hydrogen. The recycle hydrogen is then compressed, mixed with makeup hydrogen and returned to the reactor.

The liquid stream from the separator is pumped to the deheptanizer to remove light hydrocarbons. The liquid stream from the deheptanizer overhead contains benzene and toluene, and is sent to distillation section to produce high-purity benzene and toluene products. The liquid stream from the deheptanizer bottoms contains mixed xylenes and a small amount of C_9^+ aromatics. This liquid stream is sent to the paraxylene (PX) recovery section. The mixed xylenes stream is very low in EB due to high EB conversion in the DX reactor, which debottlenecks the PX recovery unit.

Process advantages:

- Simple, low-cost fixed-bed reactor design
- Flexible feedstocks and operation



- High EB conversion per pass can be nearly 100 wt%
- DX products are isomerized to equilibrium composition of xylene, which relaxes isomerization unit
- Low ring loss at very high EB conversion
- On-specification benzene with traditional distillation
- Extremely stable catalyst
- Low-hydrogen consumption
- Moderate operating parameters
- Efficient heat integration scheme reduces energy consumption
- Turnkey package for high-purity benzene, toluene and PX production available from licensor.

Economics:

Basis	100,000 tpy (2,200 bpsd) feedrate
Erected cost	$10 million (ISBL, 2009 US Gulf Coast basis)

Commercial plants: Commercialized technology available for license.

Licensor: GTC Technology - CONTACT

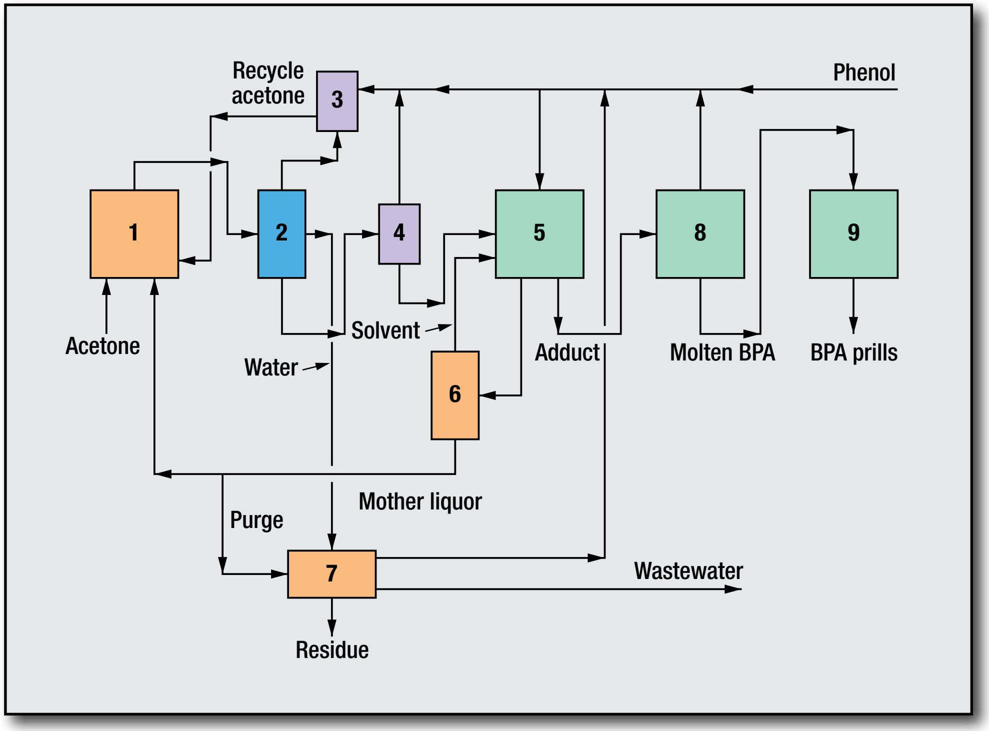
Bisphenol A

Application: The Badger BPA technology is used to produce high-purity bishenol 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 cracking and recovery system (7) along with the process water to recover phenol. The 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 Hexion Specialty Chemicals. Since that time, five other world-scale plants were licensed to the Asia-Pacific and Middle East markets.

Licensor: Badger Licensing LLC - CONTACT

BTX aromatics

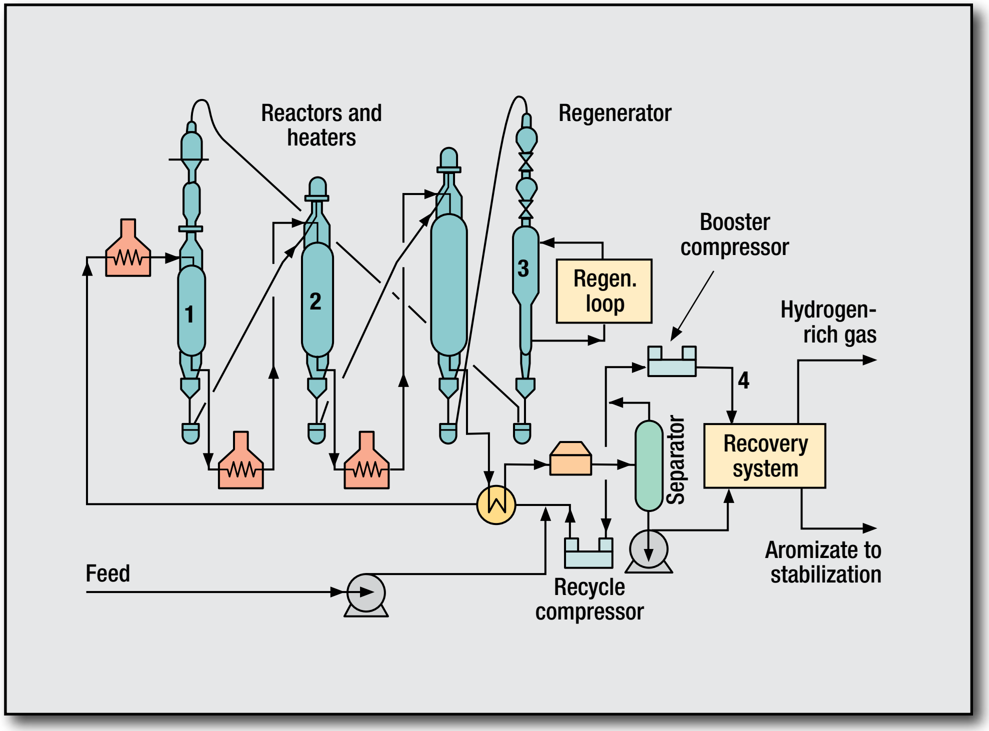
Application: To produce high yields of benzene, toluene, xylenes (BTX) and hydrogen from hydrotreated naphtha via the CCR Aromizing process coupled with RegenC continuous catalyst regeneration technology. Benzene and toluene cuts are fed directly to an aromatics extractive distillation unit. The xylenes fraction is obtained by fractionation. Depending on capacity and operation severity, implementation of an Arofining reactor aiming at the selective hydrogenation of diolefins and olefins can represent a valuable option to reduce clay usage.

Description: This process features moving bed reactors and a continuous catalyst regeneration system. 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 701 and 707) catalyst smoothly 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. The catalyst exiting the last reactor is lifted to the regeneration section with an inert gas lift system, thus isolating the process side from the regeneration section.

The coked catalyst is regenerated across the RegenC section (3). Coke burning and noble metal redispersion on the catalyst are managed under carefully controlled conditions. Catalyst chemical and mechanical properties are maintained on the long term. Regenerated catalyst is lifted back to the inlet of 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 distributed control system (DCS), requiring only a minimum of supervisory and maintenance efforts.



Commercial plants: Ninety-eight CCR reforming units have been licensed, including the gasoline-mode and BTX-mode operation targets.

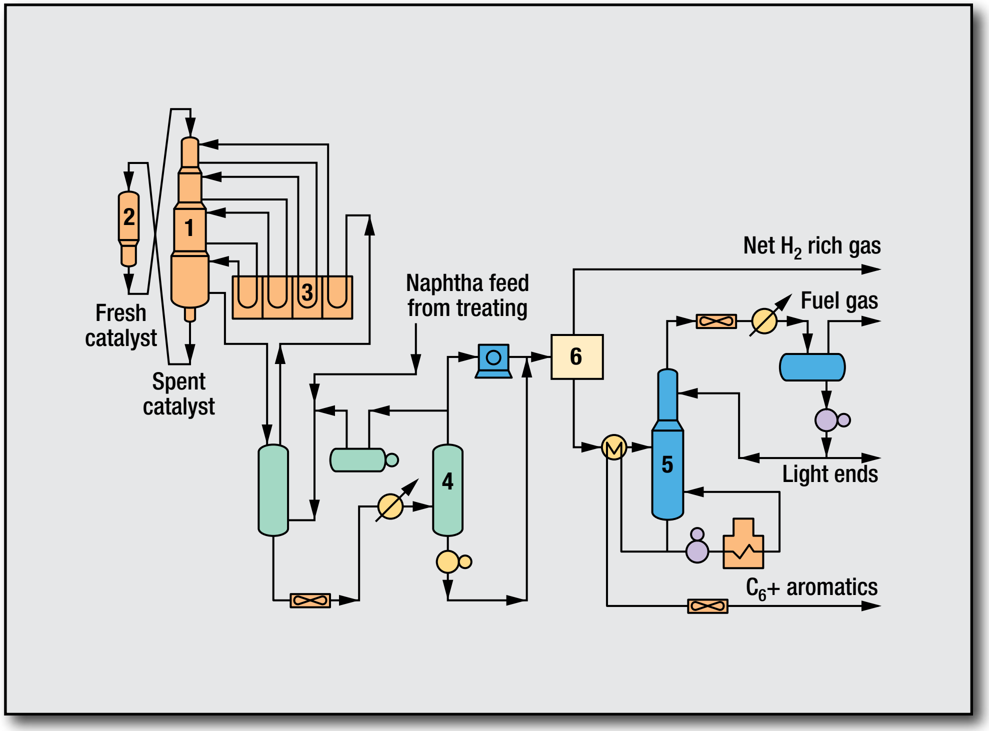
Licensor: Axens - CONTACT

BTX aromatics

Application: To produce reformate, 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-260 series catalyst maximizes aromatics yields.



Yields: Typical yields from lean Middle East naphtha:

H_2, wt%	3.8
C_5^+, wt%	87

Economics: Estimated ISBL investment per metric tpy of feed:

US$	50–65
Utilities per metric ton feedrate	
Electricity, kWh	100
Steam, HP, mt	0.13
Water, cooling m^3	5
Fuel, MMkcal	0.53

Commercial plants: There are 226 units in operation and 37 additional units in design and construction.

Licensor: UOP LLC, A Honeywell Company - CONTACT

BTX aromatics

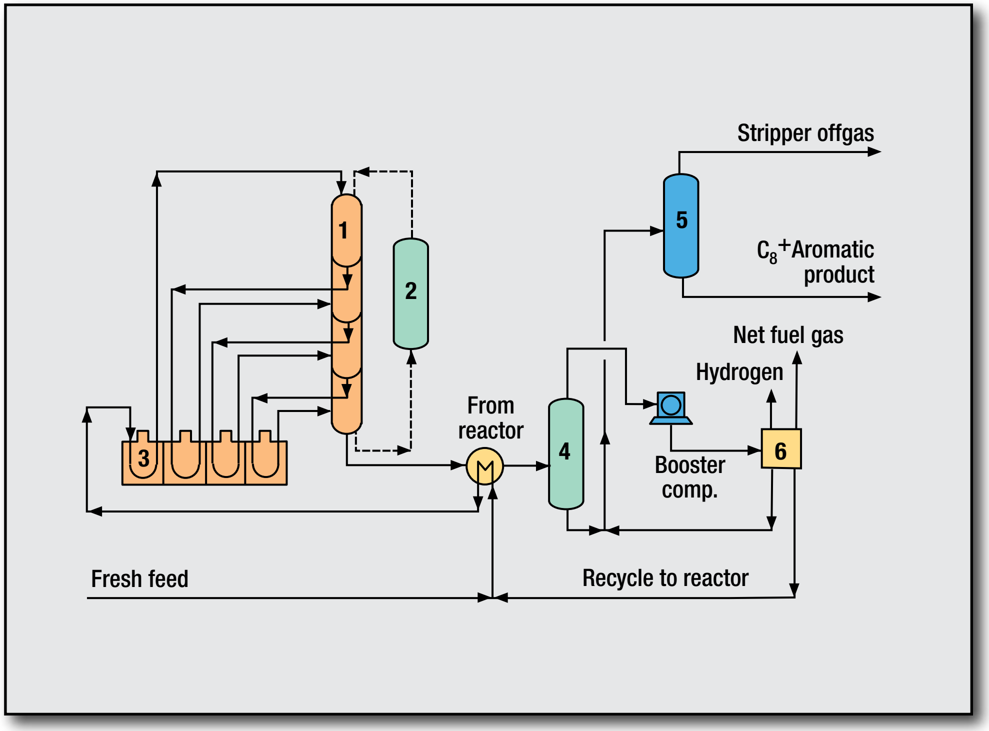
Application: To produce petrochemical-grade benzene, toluene and xylenes (BTX) via the aromatization of propane and butanes using the BP-UOP Cyclar process.

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 of feed	200–300
Typical utility requirements, unit per metric ton of feed	
Electricity, kWh	102
Steam, MP, metric ton	(0.5)
Water, cooling, metric ton	12
Fuel, MMkcal	1.3



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.

Licensor: UOP LLC, A Honeywell Company - CONTACT

BTX aromatics and LPG

Application: Advanced Pygas Upgrading (APU) is a catalytic process technology developed by SK Corp. and is exclusively offered by Axens to convert pyrolysis (ex steam cracking) gasoline to a superior steam-cracker feed (LPG), and benzene, toluene and xylene (BTX) aromatics.

Description: Cuts originating from second-stage pygas hydrogenation units are used as feedstocks. The principal catalytic reactions are:

- Conversion of non-aromatics (especially C_6 to C_{10} alkanes) into ethane and LPG.
- Conversion of C_9^+ aromatics into BTX, thereby increasing BTX yield.

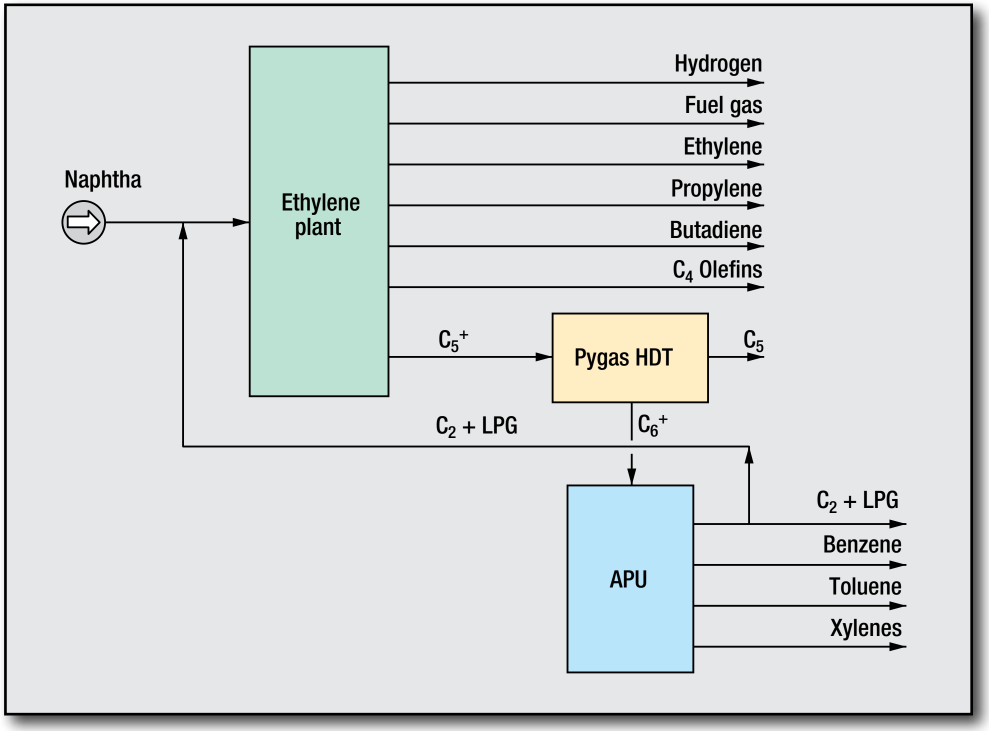
The reaction section product delivers after standard distillation high-purity individual BTX cuts, and there is no need for further extraction.

Typical yields:

	Feed, wt%	APU effluent, wt%
Hydrogen	1.0	–
Methane	–	0.7
Ethane	–	6.6
LPG	–	17.7
C_5+ non aro.	19.2	1.4
Benzene	42.3	44.4
Toluene	16.5	22.5
EB	5.9	0.5
Xylene	4.0	5.2
C_9+ Aro.	12.1	1.0

The BTX product quality after simple distillation is:

Typical APU BTX product quality	
Benzene	99.9%
Toluene	99.75%
Xylenes	Isomer grade



In some locations, ethane and LPG are the desired products; they provide valuable cracking furnace feedstocks. Typical olefin yields based on the original pygas feed are:

Typical APU olefins yields	
Ethylene	12.5%
Propylene	3.2%

Economics: APU technology is the ideal choice for:

- Complementing or debottlenecking existing extraction units for the production of high-purity aromatics (routing of excess pygas to the APU)
- Converting low-value pygas, especially the C_9+ fraction often sent to fuel oil, into BTX, ethane, propane and butanes

Continued ▼

BTX aromatics and LPG, *continued*

- Increasing ethylene and propylene production by recycling the C_2–C_4 paraffins to the cracking furnaces
- Displaying a significant net value addition per ton of pygas processed (over $250/ton based on 2007 European prices).

Reference: Debuisschert, Q., "New high value chain for Pygas Upgrading," ARTC 2008, May 24–25, 2008, Kuala Lumpur.

Commercial plants: Two APU units have been licensed by Axens and SK Corp.

Licensor: Axens - CONTACT - and SK Corp.

BTX extraction

Application: GT-BTX is an aromatics recovery technology that uses extractive distillation (ED) to purify benzene, toluene and xylene (BTX) from refinery or petrochemical aromatic streams such as catalytic reformate, pyrolysis gasoline (Pygas) or coke oven light oil (COLO).

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. The non-aromatic hydrocarbons exit the top of the column and pass through a condenser. A portion of the overhead stream is returned to the top of the column as reflux to wash out any entrained solvent. The balance of the overhead stream is the raffinate product, which does not require further treatment.

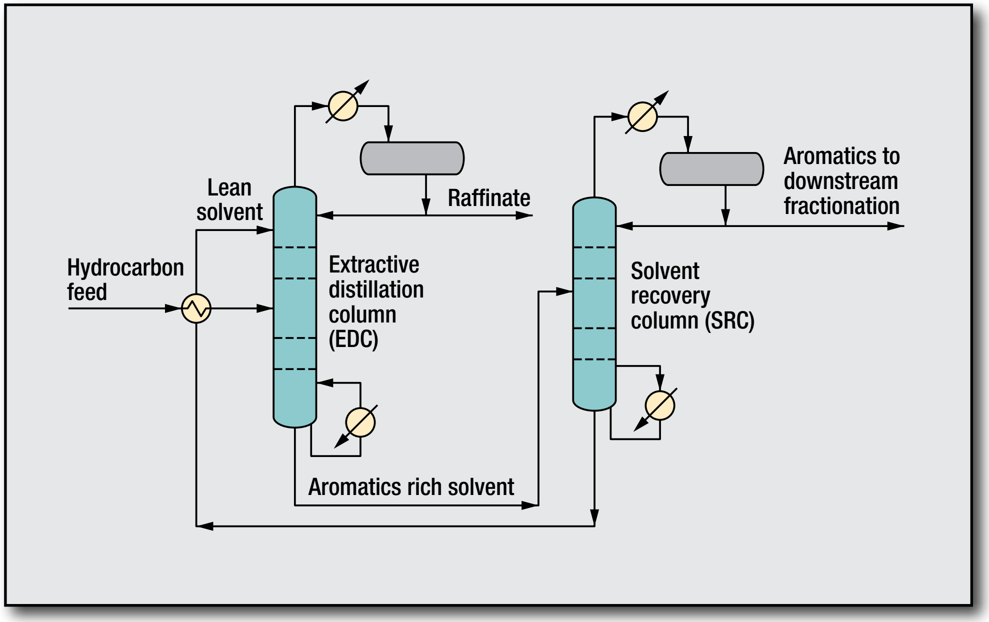
Rich solvent from the bottom of the EDC is routed to the solvent-recovery column (SRC), where the aromatics are stripped overhead. Stripping steam from a closed-loop water circuit facilitates hydrocarbon stripping. The SRC is operated under a vacuum to reduce the boiling point at the base of the column.

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.

The SRC overhead mixed aromatics product is routed to the purification section, where it is fractionated to produce chemical-grade benzene, toluene and xylenes.

Process advantages:

- Lower capital cost compared to conventional liquid-liquid extraction or other extractive distillation systems
- Energy integration options to further reduce operating costs
- Higher product purity and aromatic recovery



- Recovers aromatics from full-range BTX feedstock
- Distillation-based operation provides better control and simplified operation
- Proprietary formulation of commercially available solvent exhibits high selectivity and capacity
- Low solvent circulation rates
- Insignificant fouling due to elimination of liquid-liquid contactors
- Fewer hydrocarbon emission sources for environmental benefits

Economics:

Basis	12,000 bpsd reformate or pygas
Erected cost	$15 million (ISBL, 2009 US Gulf Coast)

Commercial plants: Twenty-five commercial licenses of new and revamp units.

Licensor: GTC Technology - CONTACT

BTX recovery from FCC gasoline

Application: GT-BTX PluS is a variation of GT-BTX that uses extractive distillation technology for simultaneous recovery of benzene, toluene and xylene (BTX) and thiophenic sulfur species from refinery or petrochemical aromatic-containing streams. The technology helps produce low-sulfur gasoline meeting the 10 ppm limit of sulfur without changes in octane value.

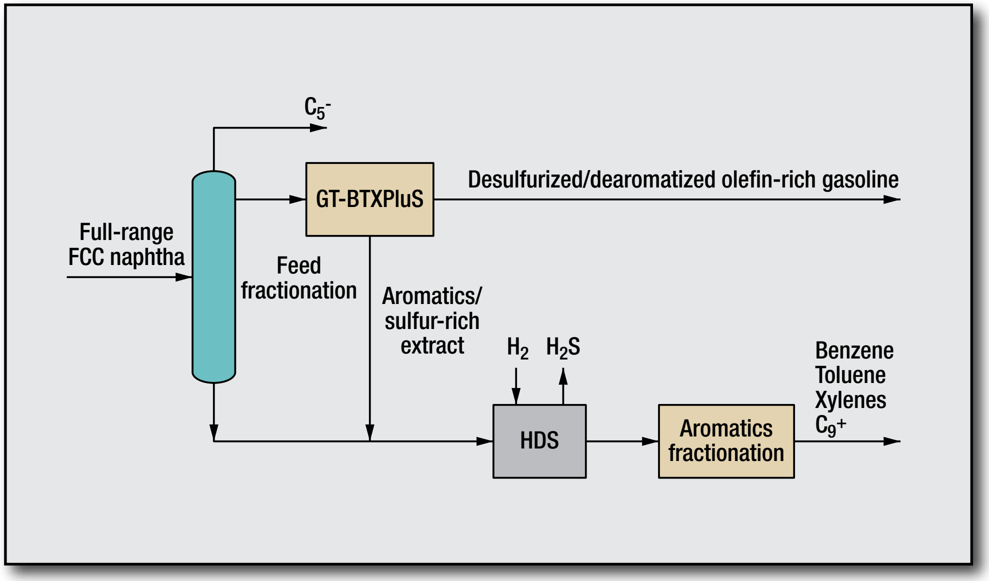
Description: The optimum feed is the mid-fraction of FCC gasoline from 70°C–150°C. This material is fed to the GT-BTX PluS unit, which extracts the sulfur and aromatics from the hydrocarbon stream. The sulfur-plus aromatic components are processed in a conventional hydrotreater to convert the sulfur into hydrogen sulfide (H_2S). Because the portion of gasoline being hydrotreated is reduced in volume and free of olefins, hydrogen consumption and operating costs are greatly reduced.

The stream from the feed fractionation unit is fed to the extractive distillation column (EDC). In a vapor-liquid operation, the solvent extracts the sulfur compounds into the bottoms of the column along with the aromatic components, while rejecting the olefins and non-aromatics into the overhead as raffinate. Nearly all of the non-aromatics, including olefins, are effectively separated into the raffinate stream. The raffinate stream can be optionally caustic washed before routing to the gasoline pool or to other units such as aromatization, olefins to diesel, or olefin alkylation to fully utilize this olefin-rich stream.

Rich solvent, containing aromatics and sulfur compounds, is routed to the solvent recovery column (SRC) where the hydrocarbons and sulfur species are separated, and lean solvent is recovered in column bottoms. The SRC overhead is hydrotreated by conventional means and either used as desulfurized gasoline or directed to an aromatics plant. Lean solvent from the SRC bottoms is recycled back to the EDC.

Process advantages:

- Eliminates FCC gasoline sulfur species to meet a pool gasoline target of 10 ppm sulfur.



- Rejects olefins from being hydrotreated in the hydrodesulfurization (HDS) unit to prevent loss of octane rating and to reduce hydrogen consumption.
- Fewer components (only the heavy-most fraction and the aromatic concentrate from the ED unit) sent to hydrodesulfurization, resulting in a smaller HDS unit and less yield loss.
- Purified benzene and other aromatics can be produced from the aromatic-rich extract stream after hydrotreating.
- Olefin-rich raffinate stream can be directed to other process units for product upgrade.

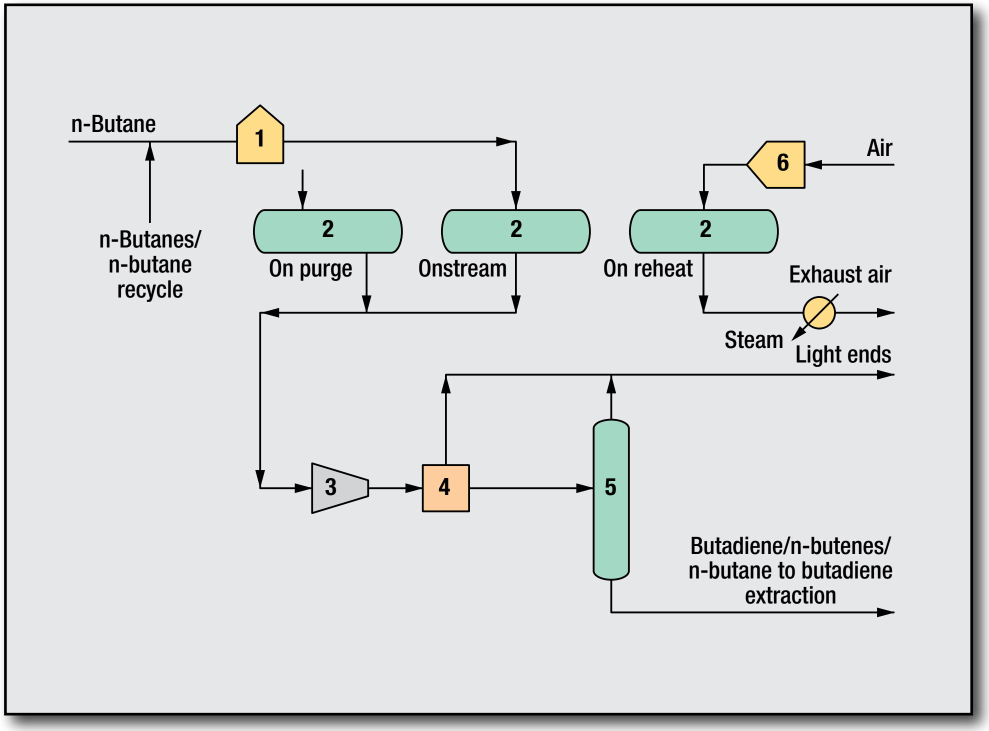
Economics:

Basis	1 million tpy (22,000 bpsd) feedrate
Erected cost	$30 million (ISBL including fractionation and HDT, 2009 US Gulf Coast basis)

Commercial plants: One licensed unit.

Licensor: GTC Technology - CONTACT

Butadiene from n-butane



Application: Technology for dehydrogenation of n-butane to make butadiene. The CATADIENE process uses specially formulated proprietary catalyst from Süd-Chemie.

Description: The CATADIENE 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 the regeneration air system operate in a continuous manner.

Fresh n-butane feed is combined with recycle feed from a butadiene extraction unit. The total feed is then vaporized and raised to reaction temperature in a charge heater (1) and fed to the reactors (2). Reaction takes place at vacuum conditions to maximize n-butane conversion and butadiene selectivity. The reactor effluent gas is quenched with circulating oil, compressed (3) and sent to the recovery section (4), where inert gases, hydrogen and light hydrocarbons are separated from the compressed reactor effluent. Condensed liquid from the recovery section is sent to a depropanizer (5), where propane and lighter components are separated from the C_4s. The bottoms stream, containing butadiene, n-butenes and n-butane, is sent to an OSBL butadiene extraction unit, which recovers butadiene product and recycles n-butenes and n-butane back to the CATADIENE 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 (6) 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.

The low operating pressure and temperature of CATADIENE reactors, along with the robust Süd-Chemie catalyst, allow the CATADIENE technology to process n-butane feedstock with stable operation and without fouling of process equipment. The simple reactor construction, with its simple internals, results in very high on stream factors for the CATADIENE technology.

Butadiene yield: The consumption of n-butane (100%) is 1.67 metric ton (mt) per mt of butadiene product.

Commercial plants: The CATADIENE process has been licensed for 18 plants. Of these, three are currently in operation, producing 270,000 mtpy of butadiene.

Licensor: Lummus Technology - CONTACT

1,3 Butadiene (Extraction from mixed C_4)

Application: To produce high-purity butadiene (BD) from a mixed C_4 stream, typically a byproduct stream from an ethylene plant using liquid feeds (liquids cracker). The BASF process uses n-methylpyrrolidone (NMP) as the solvent.

Description: The mixed C_4 feed stream is fed into the main washer, the first extractive distillation column (1), which produces an overhead butanes/butenes stream (raffinate-1) that is essentially free of butadiene and acetylenes.

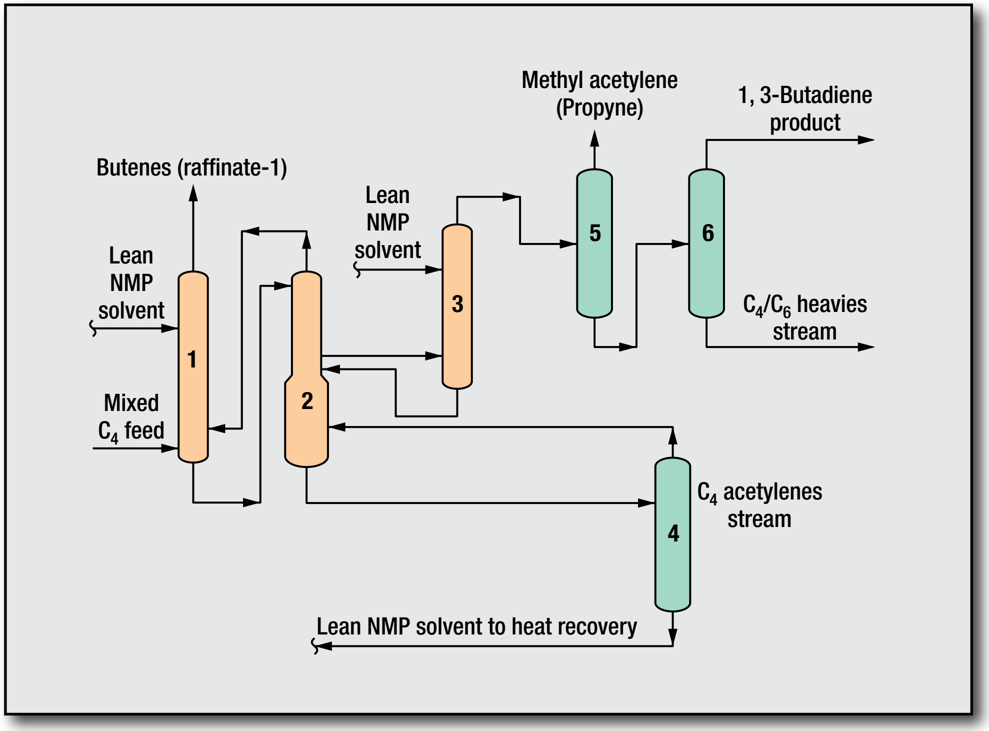
The bottoms stream from this column is stripped free of butenes in the top half of the rectifier (2). A side stream containing butadiene and a small amount of acetylenic compounds (C_3 and C_4-acetylenes) is withdrawn from the rectifier and fed into the after-washer, the second extractive distillation column (3). In recent designs, the rectifier (2) and after-washer are combined using a divided wall column.

The C_4 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 after-washer 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, C_4 acetylenes and C_5 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 fed to the bottom of the rectifier.



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 C_4 acetylenes, are purged to disposal.

In the propyne column (5), the propyne (C_3 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 C_5 hydrocarbons as bottoms.

Yield: Typically, more than 98% of the 1,3-butadiene contained in the mixed C_4 feed is recovered as product.

Continued ▼

1,3 Butadiene, *continued*

Economics: **Typical utilities,** per ton BD

Steam, ton	1.8
Water, cooling, m^3	150
Electricity, kWh	150

Commercial plants: Currently, 32 plants are in operation using the BASF butadiene extraction process. Twelve additional projects are in the design or construction phase.

Licensor: BASF/Lummus Technology - CONTACT

1,3 Butadiene

Application: 1,3 Butadiene is recovered from a crude C_4 stream from olefins plants by extractive distillation. N-methylpyrrolidone (NMP) as the selective solvent substantially improves the volatilities of the components. Different process configurations are available.

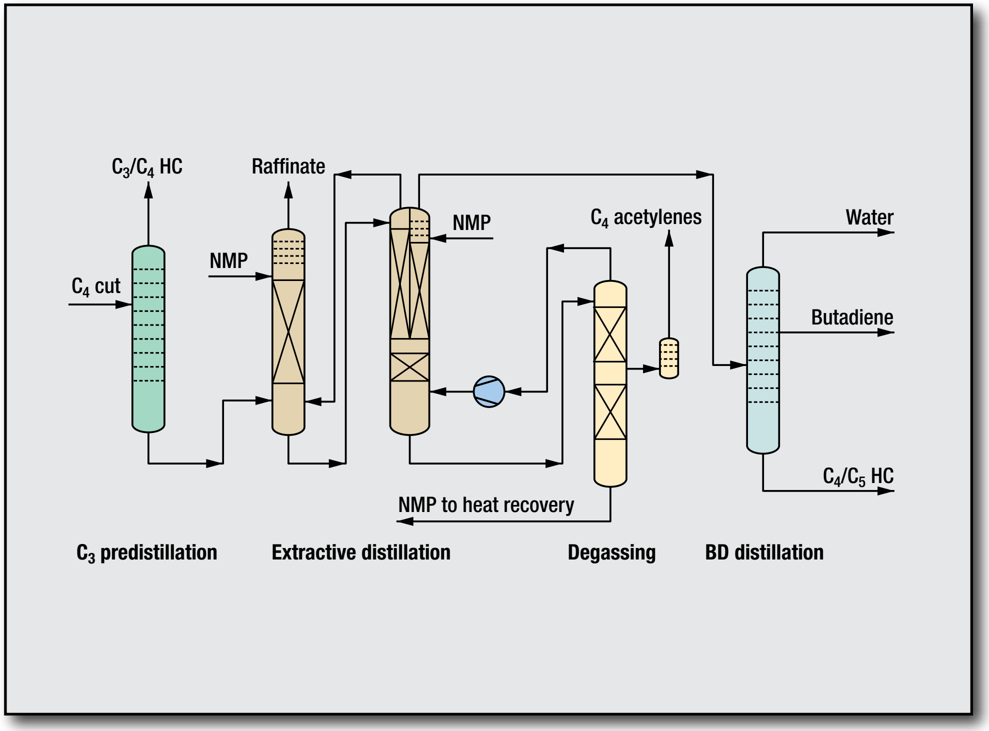
Description: The C_4 cut enters the pre-distillation tower, in which methyl acetylene, propadiene and other light components are separated as gaseous overhead product. Its bottom product enters the bottom section of the main washer column while NMP solvent enters at the column top. Overhead product C_4 raffinate consisting of butanes and butenes is drawn off. The loaded solvent is sent to the rectifier, which comprises a vertical plate in its upper section. In its first compartment, the less soluble butenes are stripped and fed back into the main washer. In its second compartment, the C_4 acetylenes are separated from crude butadiene (BD) due to their higher solubility in NMP.

The solvent from the rectifier bottoms is sent to the degassing tower, where it is completely stripped from hydrocarbons. The stripped hydrocarbons are fed back to the rectifier bottoms via a recycle gas compressor. The side stream of the degassing tower containing diluted C_4 acetylenes is fed into a scrubber to recover NMP solvent. After further dilution with raffinate or other suitable materials, the C_4 acetylene stream is discharged to battery limits for further processing.

The crude butadiene withdrawn as overhead product from the rectifier is sent to the butadiene column. In its top section, mainly water and some remaining light components are separated, while heavy ends are drawn off as bottom product. The butadiene product is withdrawn as liquid side product.

Ecology: Due to the excellent properties of NMP the process has a better ecological fingerprint than competing BD extraction technologies.

Recovery rate: Typically more than 98% of 1,3-butadiene.



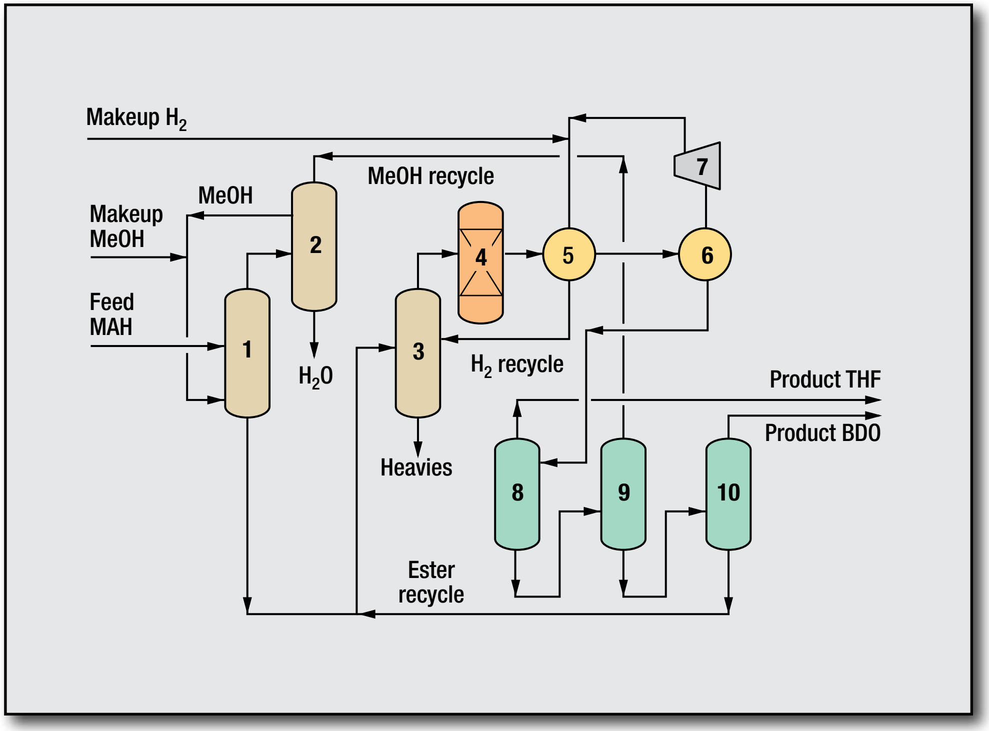
Economics: The BASF process requires less equipment items than other BD extraction technologies and is especially renowned for reliability and availability as well as low operating costs.

Utilities, per ton BD	
Steam, tons	1.7
Electricity, kWh	150
Water, cooling, m^3	150

Commercial plants: Thirty-two units using the BASF process are in operation.

Licensor: BASF SE/ Lurgi GmbH, a company of the Air Liquide Group - CONTACT

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 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 butyralactone (GBL) are recycled to the vaporizer (3) to maximize process efficiency.

The process can be adapted to produce up to 100% of co-product THF and/or to extract the GBL as a co-product if required.

Economics: per ton of BDO equivalent:

Maleic anhydride	1.125
Hydrogen	0.115
Methanol	0.02
Electric power, kWh	160
Steam, ton	3.6
Water, cooling, m^3	320

Commercial plants: Since 1989, 11 plants have been licensed with a total capacity of 600,000 tpy.

Licensor: Davy Process Technology, UK - CONTACT

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 a liquid-phase reactor (1) with a homogeneous liquid system that has high activity and selectivity.

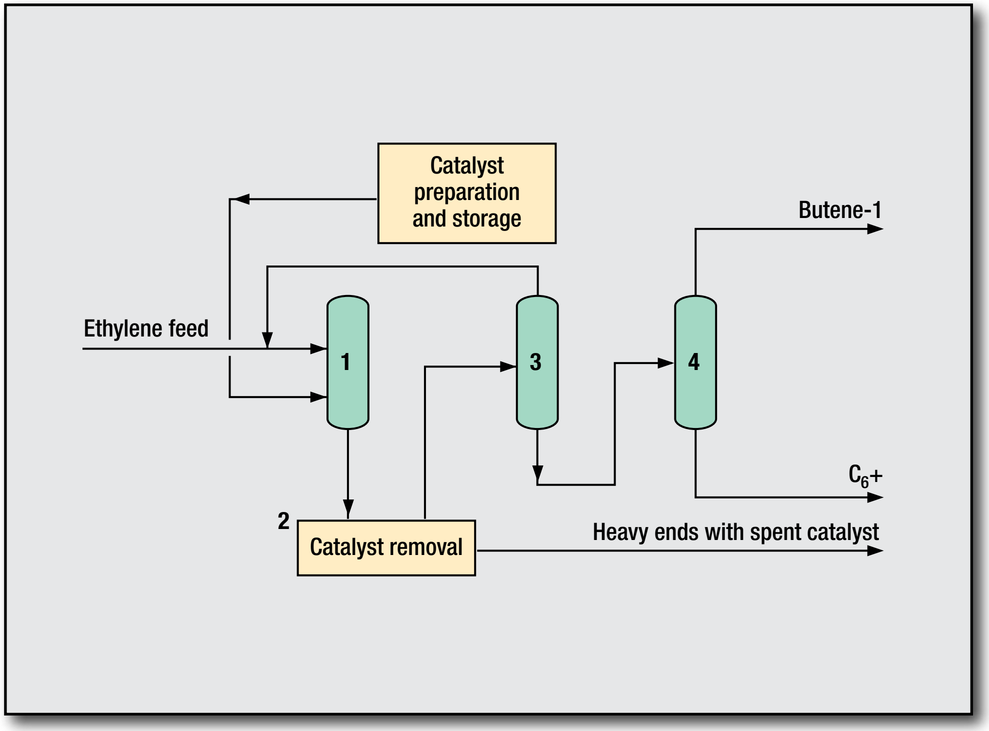
Liquid effluent and spent catalyst are then separated (2); the liquid is distilled (3) for recycling of unreacted ethylene to the reactor, and fractionated (4) in order to produce high-purity butene-1. Spent catalyst is treated to remove volatile hydrocarbons before safe disposal.

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_4s (butenes + butanes)	< 0.3 wt%
Ethane	< 0.15 wt%
Ethylene	< 0.05 wt%
C_6 olefins	< 100 ppmw
Ethers (as DME)	< 2 ppmw
Sulfur, chlorine	< 1 ppmw
Dienes, acetylenes	< 5 ppmw each
CO, CO_2, O_2, H_2O, MeOH	< 5 ppmw each

Economics: Case for a 2010 ISBL investment at a Gulf Coast location for producing 20,000 tpy of butene-1 is:



Investment, million US$	10
Raw material	
Ethylene, tons/ton of butene-1	1.1
Byproducts, C_6 + tons/ton of butene-1	0.08
Typical operating cost, US$/ton of butene-1	38

Commercial plants: Twenty-seven Alphabutol units have been licensed producing 570,000 tpy. Eighteen units are in operation.

Licensor: Axens - CONTACT

Butene-1

Application: To produce high-purity butene-1 from a mixed C_4 stream using Lummus' comonomer production technology (CPT). The feedstock can contain any amount of butene-1, butene-2 and butane.

Description: The CPT process for butene-1 production has two main steps: butene isomerization and butene distillation. While the following description uses raffinate-2 feed, steam-cracker raw C_4s or raffinate-1 can be used with additional steps for butadiene hydrogenation or isobutene removal before the CPT unit.

In the butene isomerization section (1), raffinate-2 feed from OSBL is mixed with butene recycle from the butene distillation section and is vaporized, preheated and fed to the butene isomerization reactor, where butene-2 is isomerized to butene-1 over a fixed bed of proprietary isomerization catalyst. Reactor effluent is cooled and condensed and flows to the butene distillation section (2) where it is separated into butene-1 product and recycle butene-2 in a butene fractionator. Butene-1 is separated overhead and recycle butene-2 is produced from the bottom. The column uses a heat-pump system to efficiently separate butene-1 from butene-2 and butane, with no external heat input. A portion of the bottoms is purged to remove butane before it is recycled to the isomerization reactor.

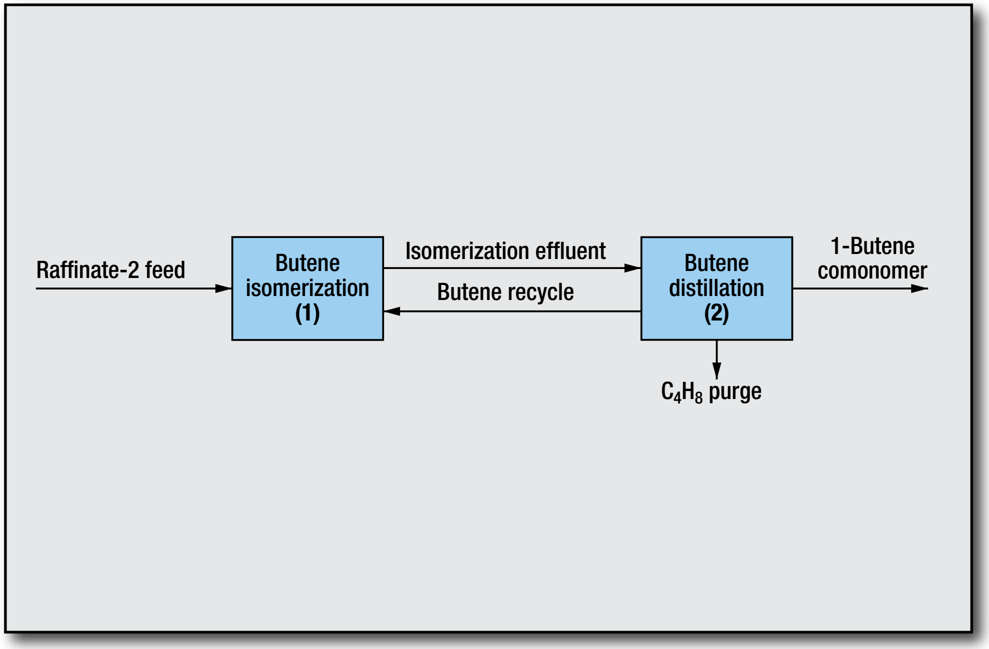
Yields and product quality:

Typical yields

metric ton butene-1/metric ton n-butenes	0.75–0.9, depending on feed quality

Typical product quality

Butene-1	99 wt %	min
Other butenes + butanes	1 wt %	max
Butadiene and Propadiene	200 ppm wt	max



Economics:

Typical utilities, per metric ton butene-1 (80% butenes in feed)

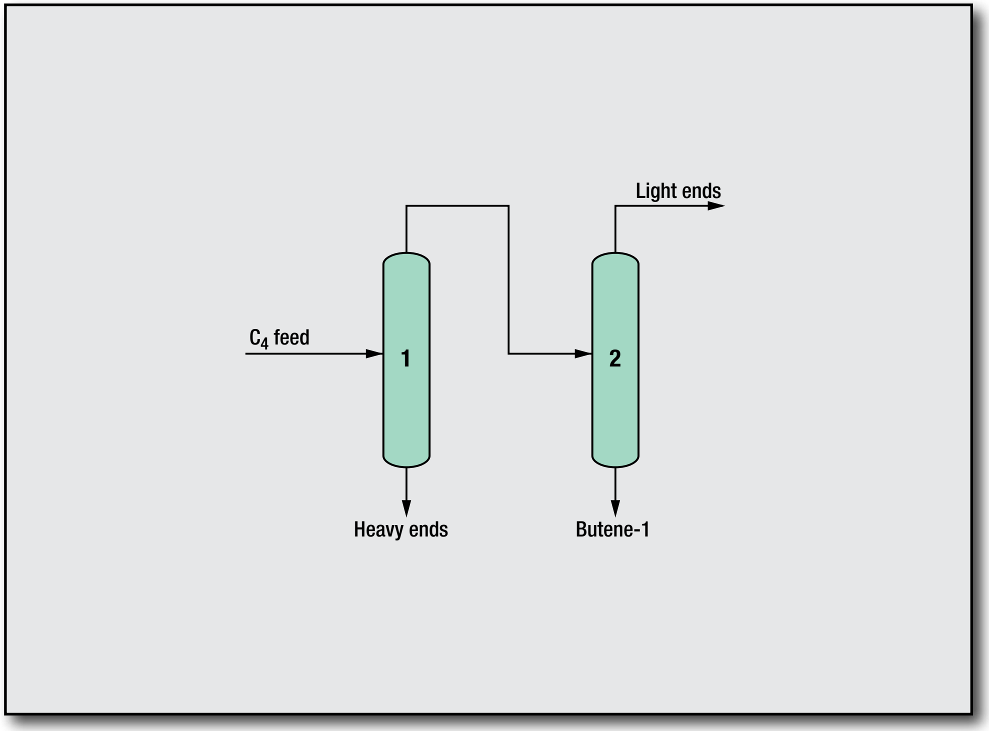
Steam + fuel, MMKcal	1.3
Water, cooling (10°C rise), m^3	190
Electricity, MWh	1.0

Commercial plants: The process has been demonstrated in a semi-commercial unit in Tianjin, China. The first CPT facility for butene-1 production is expected to start up in 2011 and will produce 40,000 metric tpy.

Reference: Gartside, R. J., M. I. Greene and H. Kaleem, "Maximize butene-1 yields," *Hydrocarbon Processing*, April 2006, pp. 57–61.

Licensor: Lummus Technology - CONTACT

Butene-1, polymerization grade



Application: The Snamprogetti Butene-1 Technology allows extracting a C_4 cut as a very high-purity butene-1 stream that is suitable as a comonomer for polyethylene production.

Feed: Olefinic C_4 streams from steam cracker or fluid catalytic cracking (FCC) units can be used as feedstock for the recovery of butene-1.

Description: The Snamprogetti technology for butene-1 is based on proprietary binary interaction parameters that are specifically optimized after experimental work to minimize investment cost and utilities consumption. The plant is a super-fractionation unit composed of two fractionation towers provided with traditional trays.

Depending on the C_4 feed composition, Saipem offers different possible processing schemes. In a typical configuration, the C_4 feed is sent to the first column (1) where the heavy hydrocarbons (mainly n-butane and butene-2) are removed as the bottom stream. In the second column, (2) the butene-1 is recovered at the bottom and the light ends (mainly isobutane) are removed as overhead stream.

This plant covers a wide range of product specifications including the more challenging level of butene-1 purities (99.3 wt%–99.6 wt%).

Utilities:

Steam, ton/ton butene-1	4
Water, cooling, m³/ton butene-1	110
Power, kWh/ton butene-1	43

Installations: Four units have been licensed by Saipem.

Licensor: Saipem - CONTACT

Butenes (extraction from mixed butanes/butenes)

Application: The BASF process uses n-methylpyrrolidone (NMP) as solvent to produce a high-purity butenes stream from a mixture of butanes and butenes. The feedstock is typically the raffinate byproduct of a butadiene extraction process or an "onpurpose" butene process.

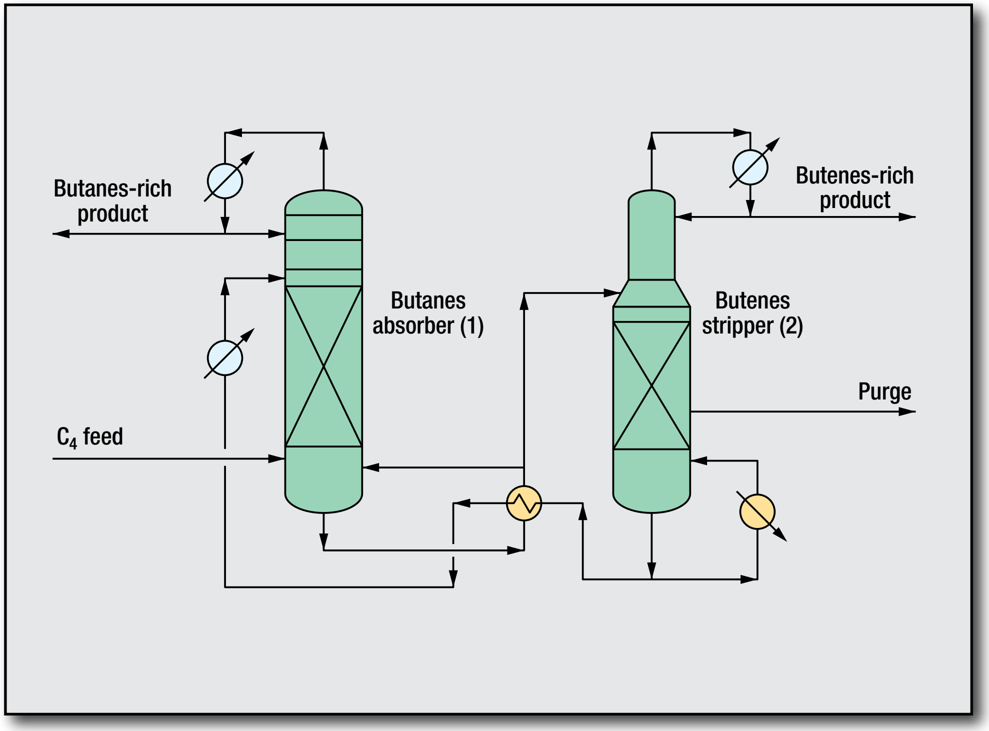
Description: The C_4 feed, containing a mixture of butanes and butenes, is fed to the butenes absorber column (1), which produces an overhead butanes stream containing only a few percent butenes. The bottoms stream from this column contains butenes absorbed in the solvent. The butenes are stripped from the solvent in the butenes stripper (2). The overhead of the butenes stripper is a butenes stream that contains a few percent butanes.

The vapor overheads of both the absorber and stripper are condensed with cooling water, generating the respective butanes and butenes products. Each column has a small reflux flow that washes the overhead product to minimize solvent losses.

The bottoms of the stripper is lean solvent, which is cooled against process streams and then cooling water before being sent to the butenes absorber. The butenes stripper is reboiled using medium pressure steam.

Yields and product quality: Typical product qualities are 5% butanes in the butenes product and 5% butenes in the butanes product. Higher quality products can be achieved if required. C_4 losses are essentially zero.

Economics: Typically, this technology is used to improve the economics of associated upstream or downstream units. Therefore, overall economics are determined on a case-by-case basis depending on the other units associated with this process.



Typical raw material and utilities, per metric ton of butenes

MP Steam, metric ton	3
Power, kWh	50

Commercial plants: Currently, more than 30 plants are in operation using NMP solvent for separation of 1,3 butadiene from mixed C_4s. While no commercial plants are currently operating for the separation of butanes and butenes using NMP as solvent, a mini-plant and a pilot plant have been operating for more than one year demonstrating this separation.

Licensor: BASF/Lummus Technology - CONTACT

Butyraldehyde, n and i

Application: To produce normal and iso-butyraldehyde from propylene and synthesis gas (CO + H_2) using the LP Oxo SELECTOR Technology, utilizing a low-pressure, rhodium-catalyzed oxo process.

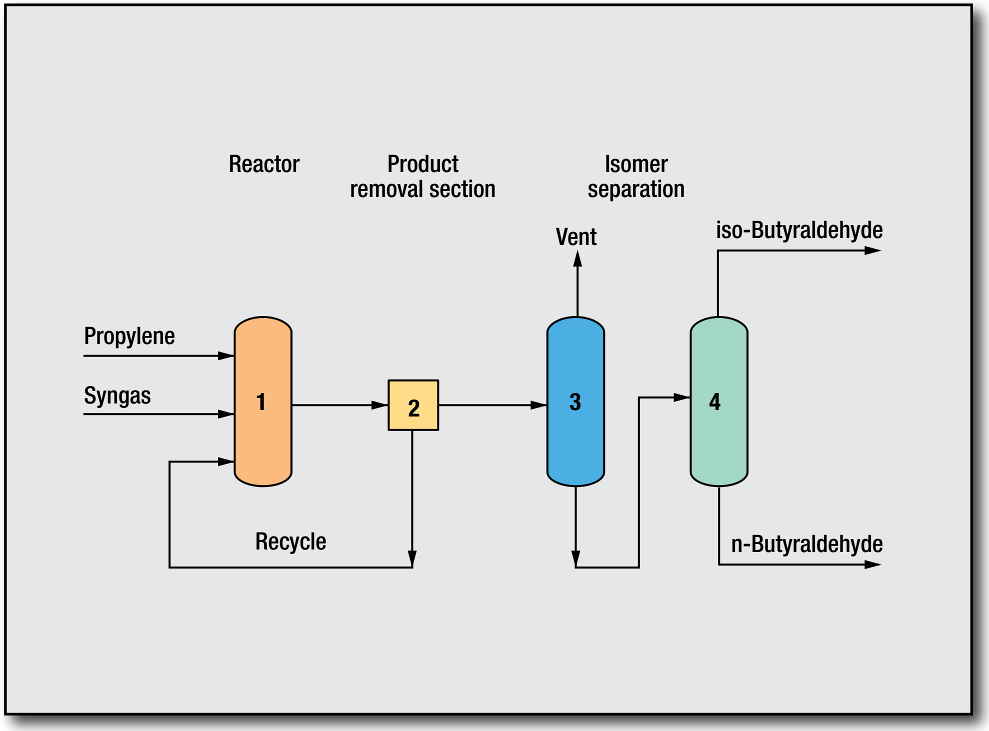
Description: The process reacts propylene with a 1:1 syngas at low pressure (< 20/kg/cm²g) in the presence of a rhodium catalyst complexed with a ligand (1). Depending on the desired selectivity, the hydroformylation reaction produces normal and iso–butyraldehyde ratios, which can be varied from 2:1 to 30:1 with typical n/i ratios of 10:1 or 30:1. The butyraldehyde product is removed from the catalyst solution (2) and purified by distillation (3). N-butyraldehyde is separated from the iso (4).

The LP Oxo SELECTOR Technology is characterized by its simple flowsheet, low operating pressure and long catalyst life. This results in low capital and maintenance expenses and product cost, and high plant availability. Mild reaction conditions minimize byproduct formation, which 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 LP Oxo Technology has been licensed to produce valeraldehyde (for the production of 2-propylheptanol) from a mixed butene feedstock, and another version to produce higher alcohols (up to C_{15}) from Fischer Tropsch produced olefins.

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

Feedstocks	
Propylene, kg (contained in chemical grade)	600
Synthesis gas (CO + H_2), Nm^3	639
Utilities	
Steam, kg	1,100
Water, cooling (assuming 10°C ΔT), m^3	95
Power, kW	35



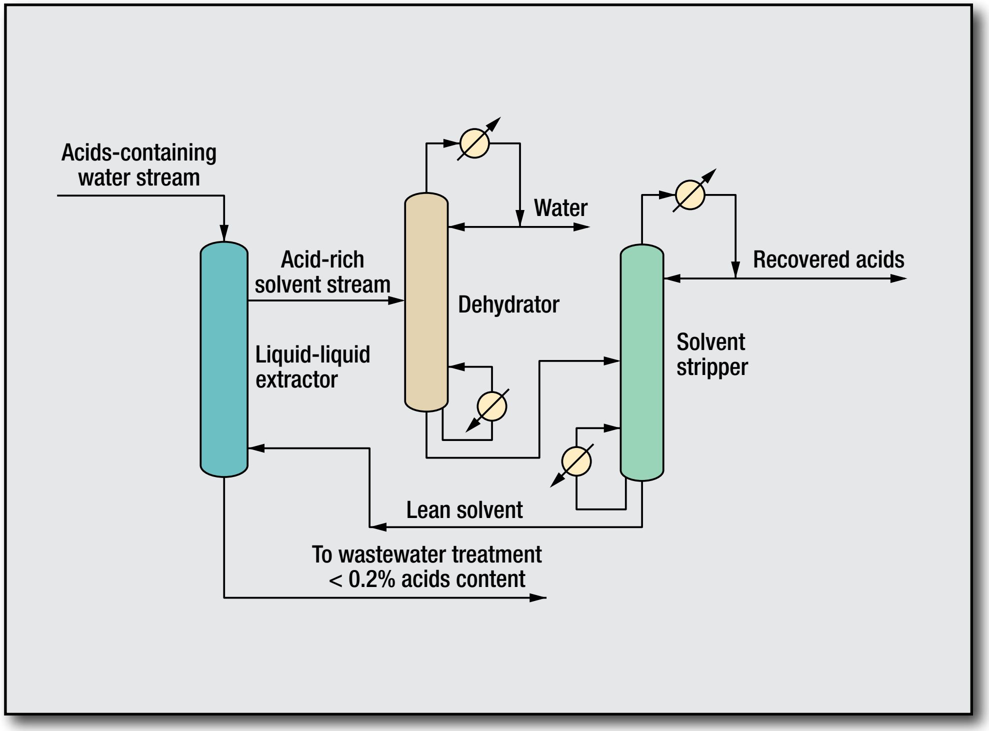
Commercial plants: The LP Oxo Technology has been licensed to over 30 plants worldwide and is now used to produce more than 85% of the world's licensed butyraldehyde capacity. Plants range in size from 30,000 tpy to 350,000 tpy of butyraldehyde. The technology is also practiced by Union Carbide Corp., a wholly owned subsidiary of The Dow Chemical Co., at its Texas City, Texas, and Hahnville, Louisiana, plants.

Licensees: Twenty-six worldwide since 1978.

Licensor: Davy Process Technology Ltd., UK, and Dow Global Technologies Inc., a subsidiary of The Dow Chemical Co., US - CONTACT

Carboxylic acid

Application: GT-CAR is GTC's carboxylic acid recovery technology that combines liquid-liquid extraction technology with distillation to recover and concentrate carboxylic acids from wastewater. The GT-CAR process is economical for any aqueous stream generated in the production of dimethyl terephthalate (DMT), purified terephthalic acid (PTA), pulp/paper, furfural and other processes.



Description: An acid-containing aqueous stream is fed to an extraction column, which operates using a proprietary, high-boiling point solvent, which is selective to carboxylic acids. The acid-rich solvent stream is carried overhead from the extraction column for regeneration. In the two-stage regeneration step, surplus water is removed (dehydration), and the acids are recovered by acid stripping. The solvent is routed back to the extraction column for reuse. Final processing of the concentrated acids is determined on a plant-by-plant basis. The treated wastewater stream, containing acid levels on the order of < 2,000 ppm, exits the system to the plant's wastewater treatment area.

Advantages:

- Up to 98% of the acids can be recovered
- Acid concentrations as low as 0.5%+ can be economically recovered
- Low capital investment results in typical ROI up to 40%
- Modular systems approach means minimal disruption of plant operation and shorter project schedule
- Use of high-boiling solvent yields high-acetic recovery and substantial energy savings
- Solvent is easily separated from water, giving a solvent-free (< 20 ppm) wastewater exit stream
- Acetic acid product purity allows for recycle or resale
- High acid recovery provides environmental benefits, unloading the biological treatment system.

Commercial plants: Two licensed units.

Licensor: GTC Technology - CONTACT

Chlor-alkali

Application: BICHLOR electrolysers are used to produce chlorine, sodium hydroxide (or potassium hydroxide) and hydrogen by the electrolysis of sodium chloride (or potassium chloride) solutions. BICHLOR electrolysers are state-of-the art, having zero electrode gap and separate anode and cathode compartments ensuring the highest product quality at the lowest electrical energy usage.

Basic electrolyser chemistry:

Key features:

Low power consumption:

- Zero Gap electrode configuration
- Uniform current and electrolyte distribution
- Sub structure designed to reduce electrical resistance
- Use of low resistance high performance membranes

Low maintenance costs:

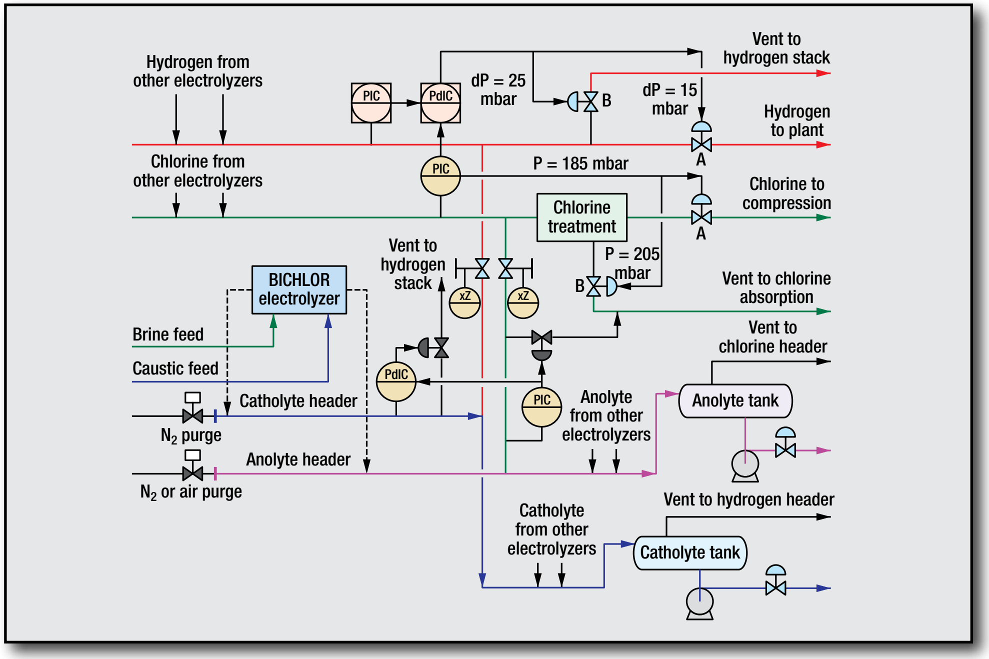
- Modular technology minimises down time and personnel
- Long life electrode coatings
- Electrodes can be re-coated "IN PAN"

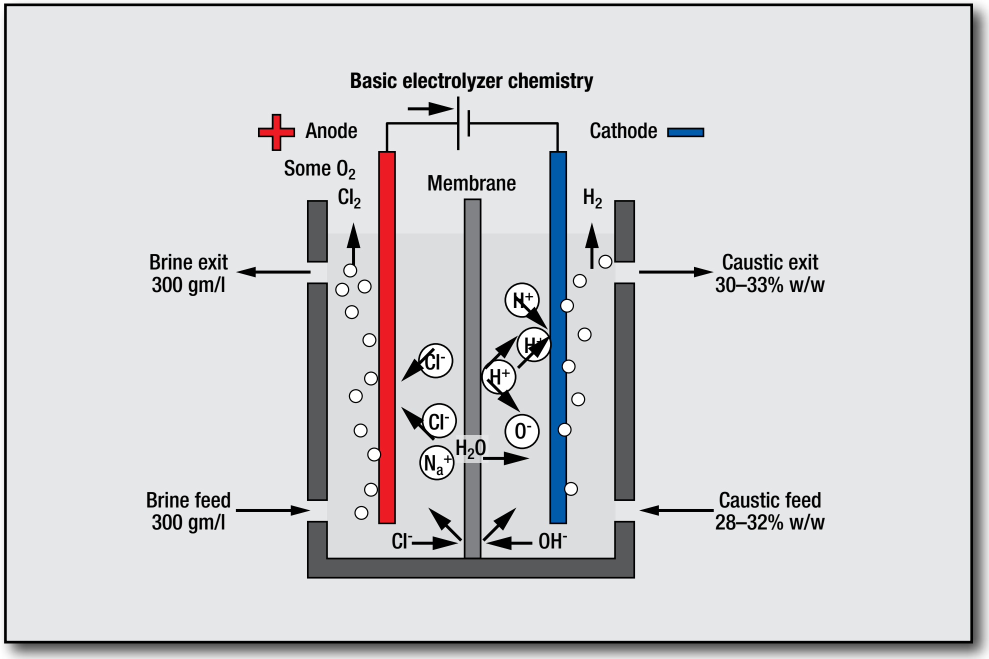
BICHLOR operating data:

Max Modules per electrolyser	186
Current density	2–8 kA/m^2
Power consumption	< 2,100 kWh/metric ton of caustic soda (as 100%)
Operating pressure,	–15 mbarg to 400 mbarg
Max capacity per electrolyser	35,000 metric tpy of chlorine

Commercial plants: Since 2003, over 30 plants licensed worldwide ranging from 5,000 metric ton to 440,000 metric ton.

Licensor: INEOS Technologies - CONTACT





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.

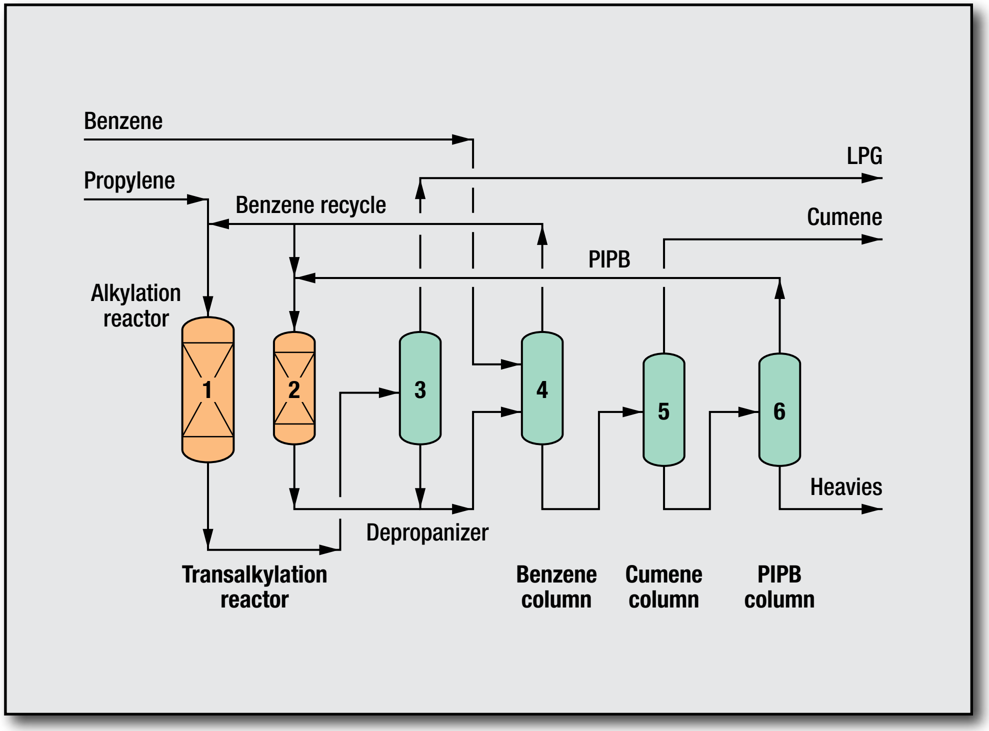
Process features: The process allows a substantial increase in capacity for existing SPA, $AlCl_3$ or other zeolite cumene plants while improving product purity, feedstock consumption and utility consumption. The new catalyst is environmentally inert, does not produce byproduct oligomers or coke and can operate at extremely low benzene to propylene ratios.

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

Economics:

Utility requirements, per ton of cumene product:

Heat, MMkcal (import)	0.32
Steam, ton (export)	(0.40)



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 18 operating plants with a combined capacity of nearly 7 million metric tpy. In addition, five grassroots plants and one SPA revamp are in the design phase.

Licensor: Badger Licensing LLC - CONTACT

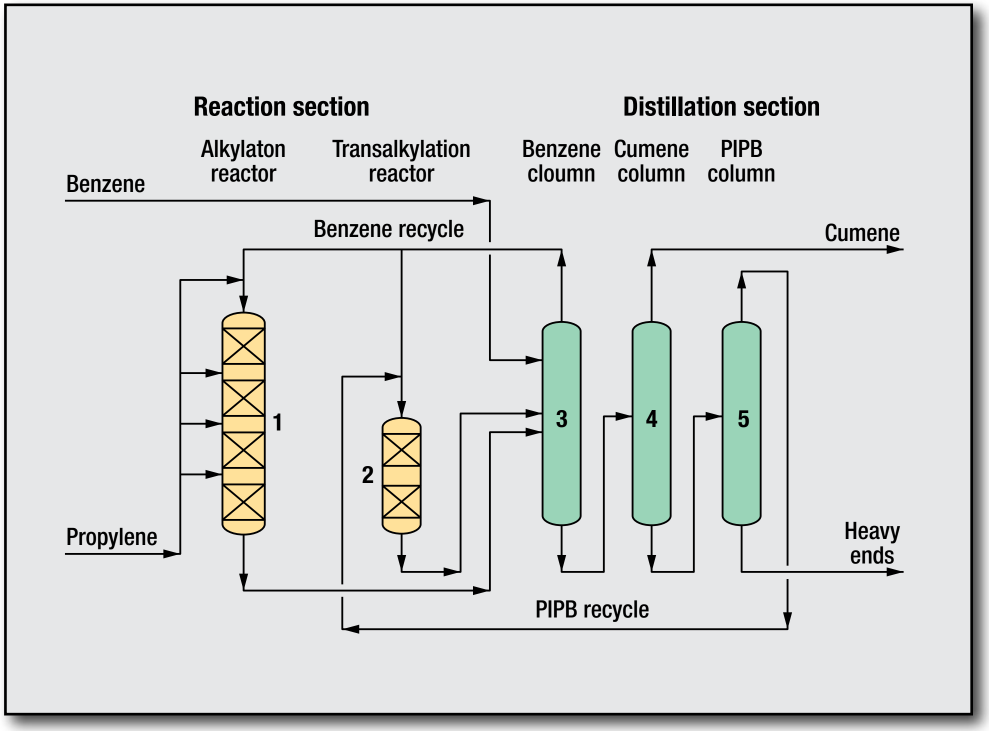
Cumene

Application: The Polimeri/Lummus process is used to produce high-purity cumene from propylene and benzene using a proprietary zeolite catalyst provided by Polimeri Europa. The process can handle a variety of propylene feedstocks, ranging from polymer grade to refinery grade.

Description: Alkylation and transalkylation reactions take place in the liquid phase in fixed-bed reactors. Propylene is completely reacted with benzene in the alkylator (1), producing an effluent of unconverted benzene, cumene and PIPB (diisopropylbenzene and small amounts of polyisopropylbenzenes). The specially formulated zeolite catalyst allows production of high-purity cumene while operating at reactor temperatures high enough for the reaction heat to be recovered as useful steam. PIPB is converted to cumene by reaction with benzene in the transalkylator (2). The process operates with relatively small amounts of excess benzene in the reactors.

Alkylator and transalkylator effluent is processed in the benzene column (3) to recover unreacted benzene, which is recycled to the reactors. On-specification cumene product is produced as the overhead of the cumene column (4). The PIPB column (5) recovers polyalkylate material for feed to the transalkylator and rejects a very small amount of heavy, non-transalkylatable byproduct. The PIPB column can also reject cymenes when the benzene feedstock contains an excessive amount of toluene. Propane contained in the propylene feedstock can be recovered as a byproduct, as can non-aromatic components in the benzene feedstock.

The PBE-1 zeolite catalyst has a unique morphology in terms of its small and uniform crystal size and the number and distribution of the Bronsted and Lewis acid sites, leading to high activity and selectivity to cumene in both the alkylation and transalkylation reactions. The catalyst is very stable because it tolerates water and oxygenates and does not require drying of the fresh benzene feed. Run lengths are long due to the catalyst's tolerance to trace poisons normally present in benzene and propylene feedstocks, and the extremely low rate of coke formation in the catalyst as a result of its unique extrazeolite pore size distribution. Regeneration is simple and inexpensive.



Equipment is constructed of carbon steel, thereby reducing investment.

Yields and product quality: Cumene produced by the process can have a purity greater than 99.95%. The consumption of propylene (100%) is typically 0.351 metric ton per metric ton of cumene product. The consumption of benzene (100%) is typically 0.652 metric ton per metric ton of cumene product.

Continued ▼

Economics:

Typical utilities, per metric ton of cumene

High-pressure steam, metric ton	0.9
Low pressure steam export, metric ton	(1.0)
Power, kWh	10

Commercial plants: The process is used in Polimeri Europa's 400,000 metric tpy cumene plant at Porto Torres, Sardinia.

Licensor: Lummus Technology - CONTACT

Cumene

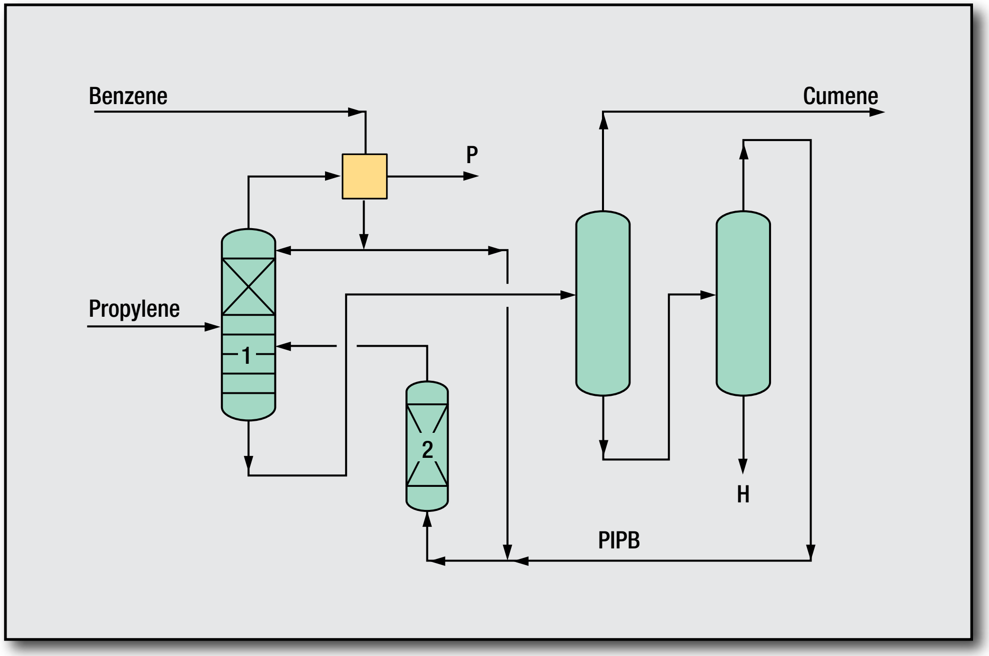
Application: Advanced technology to produce high-purity cumene from propylene and benzene using patented catalytic distillation (CD) technology. The CD Cumene process uses a specially formulated zeolite alkylation catalyst packaged in a proprietary CD structure and another specially formulated zeolite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



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

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

Licensor: CDTECH, a partnership between Lummus Technology and Chemical Research & Licensing - CONTACT

Cumene

Application: The Q-Max process produces high-quality cumene (isopropylbenzene) by alkylating benzene with propylene (typically refinery, chemical or polymer grade) using zeolitic catalyst technology.

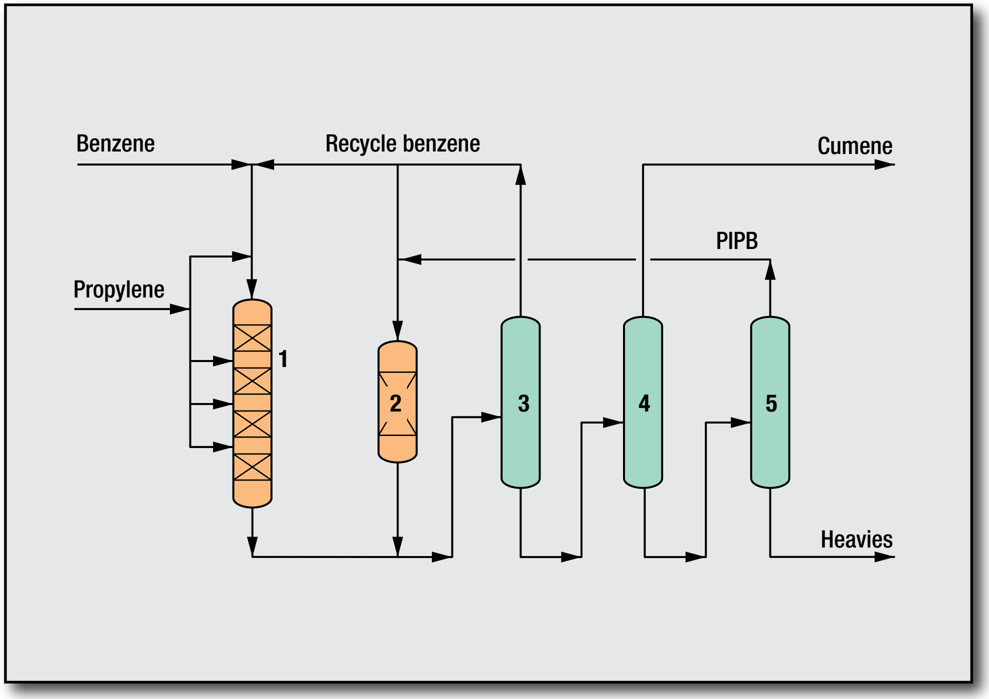
Description: Benzene is alkylated to cumene over a zeolite catalyst in a fixed-bed, liquid-phase reactor. Fresh benzene is combined with recycle benzene and fed to the alkylation reactor (1). The benzene feed flows in series through the beds, while fresh propylene feed is distributed equally between 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, unreacted benzene is recovered from the overhead of the benzene column (3) and cumene product is taken as overhead from the cumene column (4). Poly-isopropylbenzene (PIPB) is recovered in the overhead of the PIPB column (5) and recycled to the transalkylation reactor (2) 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 PIPB column (5) and is typically blended to fuel oil. A depropanizer column is required to recover propane when refinery or chemical-grade propylene feed is used. 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 five years and longer. The catalyst is fully regenerable for an ultimate catalyst life of 10 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 (270,000 tpy of cumene) 65



Raw materials & utilities, per metric ton of cumene

Propylene, tons	0.35
Benzene, tons	0.66
Electricity, kW	13
Steam, tons (import)	0.8
Water, cooling, m^3	0.6

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

Commercial plants: Fourteen Q-Max units have been licensed with a total cumene capacity of 4.1 million tpy.

Licensor: UOP LLC, A Honeywell Company - CONTACT

Cyclohexane

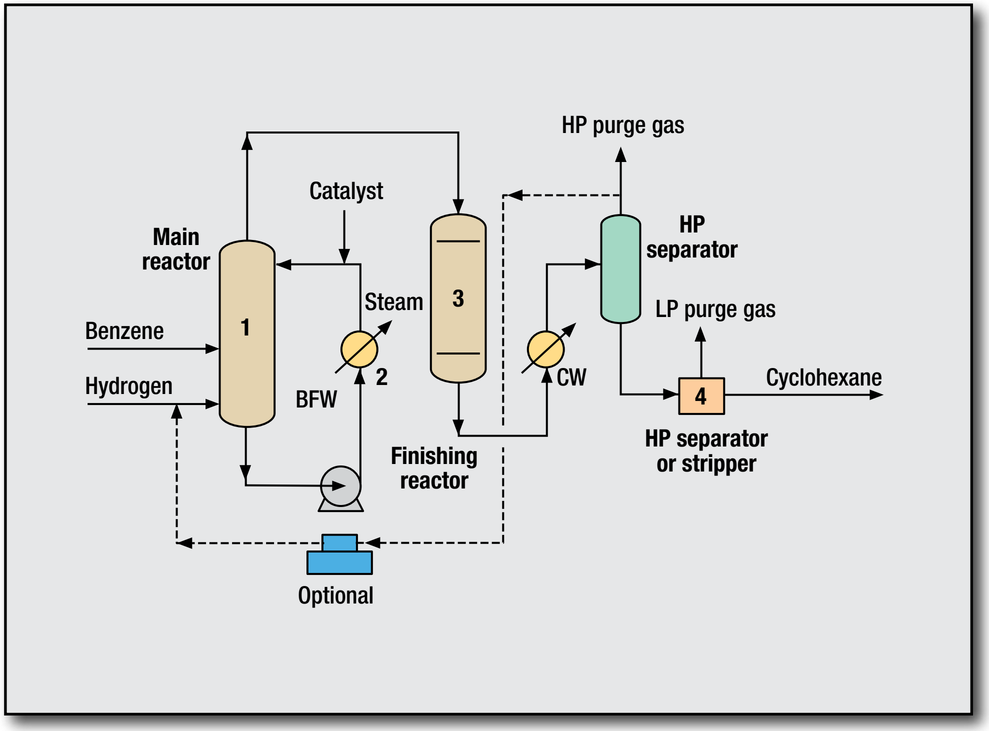
Application: Produce high-purity cyclohexane by liquid-phase catalytic hydrogenation of benzene.

Description: The main reactor (1) converts essentially all of 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 using 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 purity of the hydrogen makeup gas, the stabilization section includes either an LP separator (4) or a small stabilizer to remove 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 as 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 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. If the catalyst is deactivated by feed quality upsets, then fresh catalyst can be injected without a shutdown.



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

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

Licensor: Axens - CONTACT

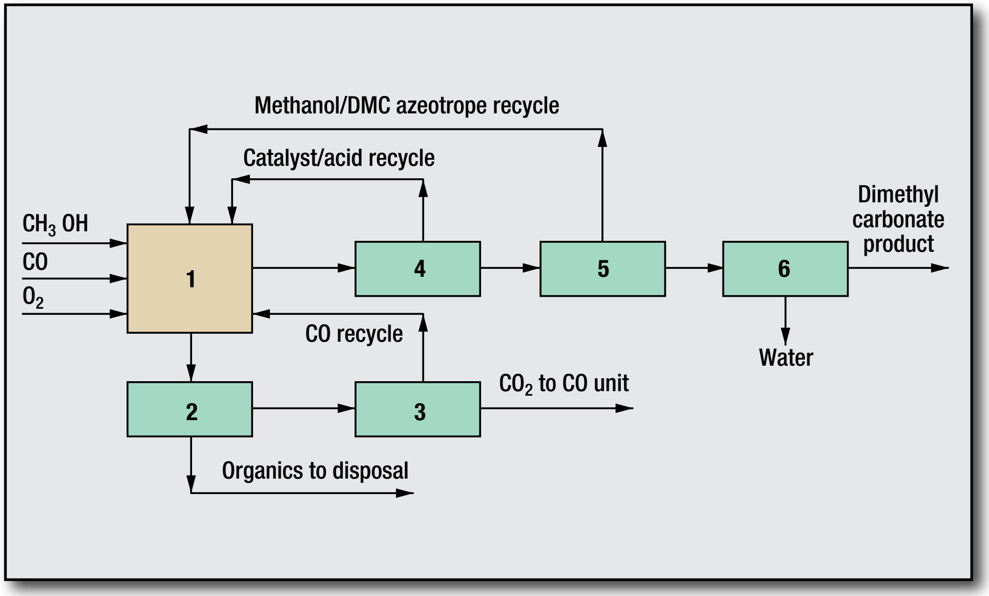
Dimethyl carbonate

Application: The Polimeri/Lummus process is a non-phosgene route using CO, CH_3OH (methanol) and O_2 to produce dimethyl carbonate (DMC). DMC is a nontoxic intermediate used in the production of polycarbonates, lubricants, solvents, etc., and is also used directly as a solvent or a gasoline/diesel fuel additive. This environmentally safe process can be applied to large capacity plants.

Description: Methanol, CO and O_2 react in the presence of a copper-containing catalyst to yield DMC and water (1). The main byproduct is CO_2, with minor amounts of organics like dimethyl ether and methyl chloride. A small quantity of HCl is fed to the reactor to maintain catalyst activity. Unreacted gases, saturated with organics, are fed to the organics removal section (2). The clean gases, composed of CO, CO_2 and inerts, are subsequently fed to the CO recovery unit (3) from where CO is recycled back to the reaction section and CO_2 is sent to an OSBL CO generation unit. This CO can be sent back to the DMC process.

The reaction section effluent, containing unreacted methanol, DMC, water, and traces of catalyst and HCl, is sent to the acid recovery section (4) where catalyst and HCl are separated and recycled back to the reaction section. The remaining effluent is fed to the azeotropic distillation section (5). Methanol is recycled back to the reaction section as a methanol/DMC azeotrope, while DMC with water is fed to the final purification section (6) to obtain DMC product.

Since Lummus also offers the Polimeri/Lummus diphenyl carbonate (DPC) process, there are opportunities for energy integration as well.



Typical yields and product quality:

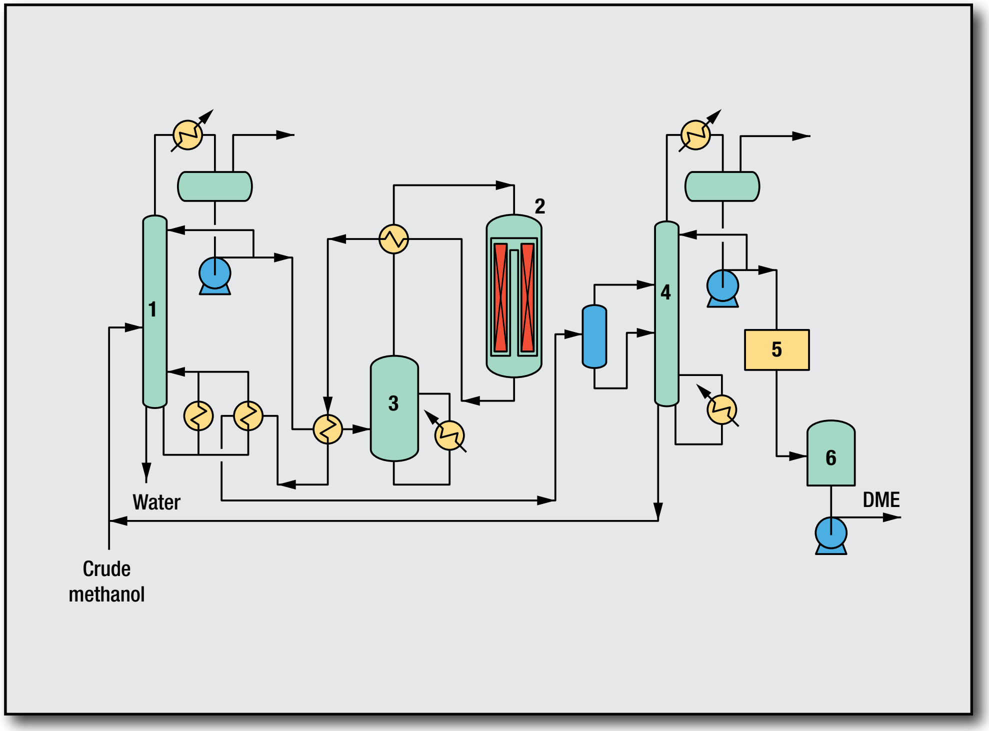
	metric ton/metric ton DMC product
Feeds	
Methanol, 100% basis	0.77
CO, 100% basis	0.52
O_2, 100% basis	0.30
Main Products	
Dimethyl carbonate	1.00
CO_2 to CO unit	0.30

Typical DMC product quality	
Purity	99.9 wt% min.
Color APHA	5 max.
Acidity (as H_2CO_3)	50 ppm wt max.
Chlorine (organics cmpd)	20 ppm wt max.
Methanol	50 ppm wt max.
Water	50 ppm wt max.

Commercial plants: The process has been commercialized in four different plants of various sizes. The largest plant has a DMC capacity of 50,000 metric tpy.

Licensor: Lummus Technology - CONTACT

Di methyl ether (DME)



Application: To produce dimethyl ether (DME) from methanol using Toyo Engineering Corp.'s (TOYO's) DME synthesis technology based on a 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 MPaG–2 MPaG. The inlet temperature is 220°C–275°C, and the outlet temperature is 300°C–375°C. This process is a one-pass conversion from methanol to DME. DME reactor yields are 70%–80%. 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 bulk 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 of methanol per ton of DME.

Commercial plants: Four DME Plants, under license by TOYO, have been commissioned and are under commercial operation. A 10,000-tpy world's first fuel-use DME production plant started operation in 2003. A second 110,000-tpy facility started up in 2006; a third 210,000-tpy unit came onstream in 2007 and a fourth 140,000-tpy unit was commissioned in 2008.

Licensor: Toyo Engineering Corp. (TOYO) - CONTACT

Dimethyl terephthalate

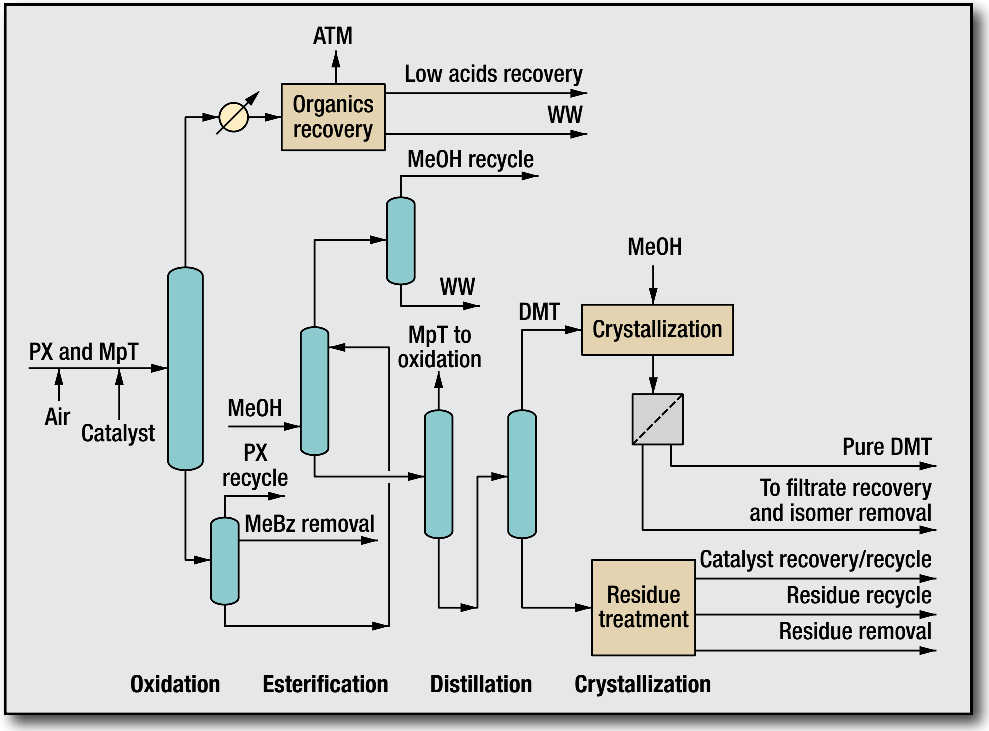
Application: GTC's GT-DMT technology is a series of process enhancements for dimethyl terephthalate (DMT) production. This technology addresses oxidation, distillation, esterification, crystallization and wastewater treatment resulting in lower energy consumption, increased capacity and yield improvements.

Description: The common method for the production of DMT from p-xylene and methanol consists of four major steps: oxidation, esterification, distillation and crystallization. A mixture of paraxylene (PX) and PT-ester is oxidized with air in the presence of a heavy metal catalyst. All useful organics are recovered from the offgas and recycled to the system. The acid mixture resulting from the oxidation is esterified with methanol to produce a mixture of esters. The crude ester mixture is distilled to remove all the heavy boilers and residue produced; the lighter esters are recycled to the oxidation section. The raw DMT is then sent to the crystallization section for removal of DMT isomers and aromatic aldehydes. This purification produces DMT that meets world-market specifications and is preferred in some polyester applications. Byproducts are recovered for sale or burned for fuel value, and usable intermediate materials are recycled.

The GTC process improvements enhance the traditional process in each of the four sections through changes in process configurations and operating conditions, alteration of separation schemes, revision of recovery arrangements, increase in the value of byproducts, and reduction in the overall recycles in the plant. The upgrade options may be implemented individually, combined, or through a series of revamps over a period of time.

Process advantages:

- Improved process yields (PX and methanol)
- Higher specific throughput
- Lower energy consumption/ton of DMT produced



- Flexible application for revamp projects
- Accumulated technical expertise available through engineering packages and follow-up services.

Oxidation Section

- Improved oxidation reduces side reactions and more effectively uses reaction volume, resulting in lower p-xylene consumption.
- New and more efficient scheme for the catalyst recovery in the plant helps reduce residue formation.
- Improved recovery of PX and removal of methyl benzoate: Product is upgraded to food or perfume grade.
- Carboxylic acid recovery: Recovery of formic and acetic acid as byproducts, upgrading value and reducing load in biotreatment unit.

Continued ▼

Dimethyl terephthlate, *continued*

Crystallization

- Typical double-crystallization scheme is simplified to increase throughputs and minimize equipment.
- New single-stage crystallization offers a low-cost alternative in revamps.
- Improved methanol recovery and handling system reduces plant losses.
- Improved isomer removal system helps reduce DMT losses.

Distillation section

- Improved distillation scheme increases purity of DMT to crystallization and reduces plant recycles.
- Improved residue treatment can increase the yields of the plant by recovering valuable materials.

Esterification

- Improved reactor design gives higher throughputs and improved methanol usage.

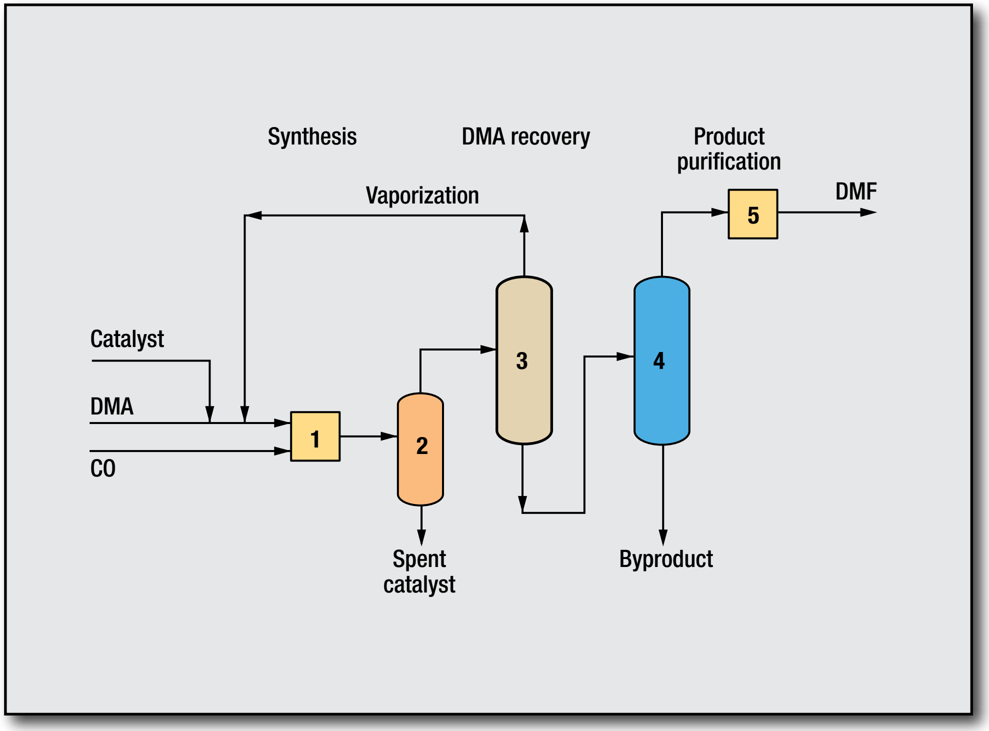
Commercial plants: Five licensed units.

Licensor: GTC Technology - CONTACT

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, ton	0.63
Carbon monoxide, ton	0.41
Steam, ton	1.3
Water, cooling, m^3	100
Electricity, kWh	10

Commercial plants: Fourteen plants in nine countries use this process with a production capacity exceeding 100,000 metric tpy. Most recent start-up (2010) was a 60,000-metric tpy plant in Saudi Arabia.

Licensor: Davy Process Technology, UK - CONTACT

Diphenyl carbonate

Application: The Polimeri/Lummus process is a phosgene-free route for the production of diphenyl carbonate (DPC)—a polycarbonate intermediate—from dimethyl carbonate (DMC) and phenol. The Polimeri/Lummus DPC process has no environmental or corrosion problems, and the byproduct methanol can be recycled back to the DMC process.

Description: DMC and phenol are reacted to produce DPC and methanol. DPC is produced in two steps: phenol and DMC react to form phenylmethyl carbonate (PMC), followed by PMC disproportionation to DPC.

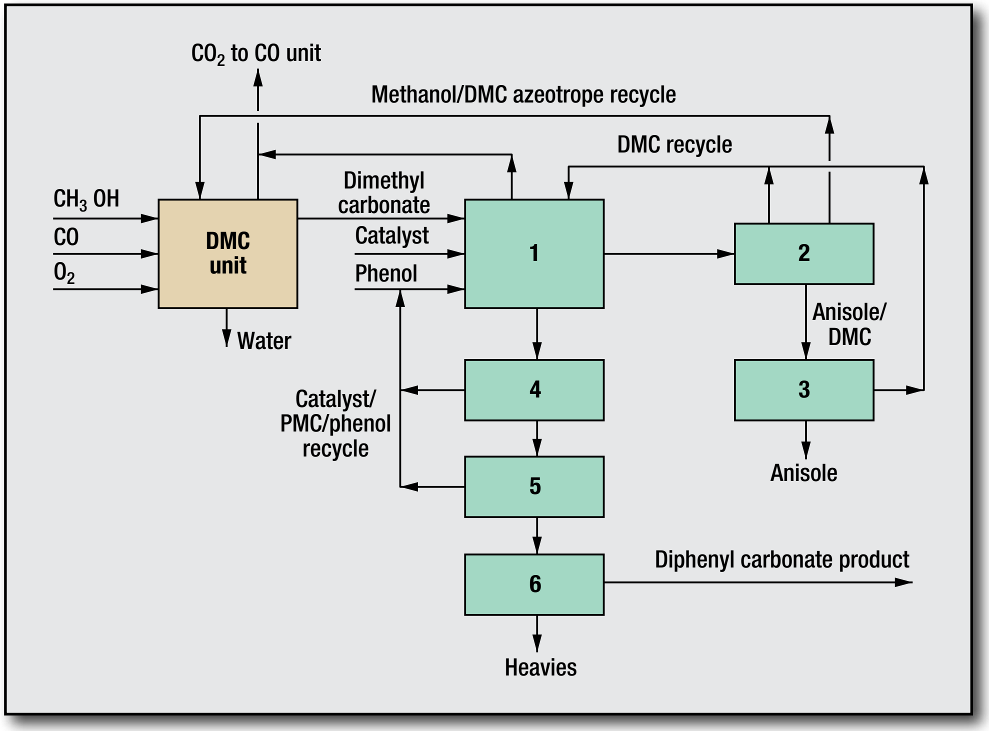
Phenol, DMC and catalyst are fed to the PMC reaction section (1) where a small amount of anisole and CO_2 are also produced. A "light" stream, containing mainly methanol, DMC and anisole, is fed to the azeotropic distillation section (2), from which a methanol-DMC azeotrope is recycled back to the DMC unit, some DMC is recycled to the PMC reaction section, and an anisole/DMC mixture is sent to the anisole recovery section (3).

A "heavy" stream, containing mainly PMC and phenol, is fed to the DPC reaction section (4) where disproportionation to DPC occurs. Unreacted phenol is recycled to the PMC section, while the balance is sent to the catalyst recovery area (5) from where recovered catalyst is also sent back to the PMC section. DPC is then purified (6) of any residual heavies.

Since Lummus also offers the Polimeri/Lummus DMC process, there are opportunities for energy integration between the DMC and DPC units.

Yields and product quality: Typical Integrated DMC/DPC unit overall material balance

Feeds	metric ton/metric ton DPC Product
Methanol, 100% basis	0.03
CO, 100% basis	0.22
O_2, 100% basis	0.13
Phenol	0.88



Main products	
Diphenyl carbonate	1.00
CO_2 to CO unit	0.13
Anisole (Methoxybenzene)	0.01

Typical DPC product quality	
Purity	99.6 wt% min.
Color APHA	20 max.
Ti	0.1 ppm wt max.
Fe	0.1 ppm wt max.

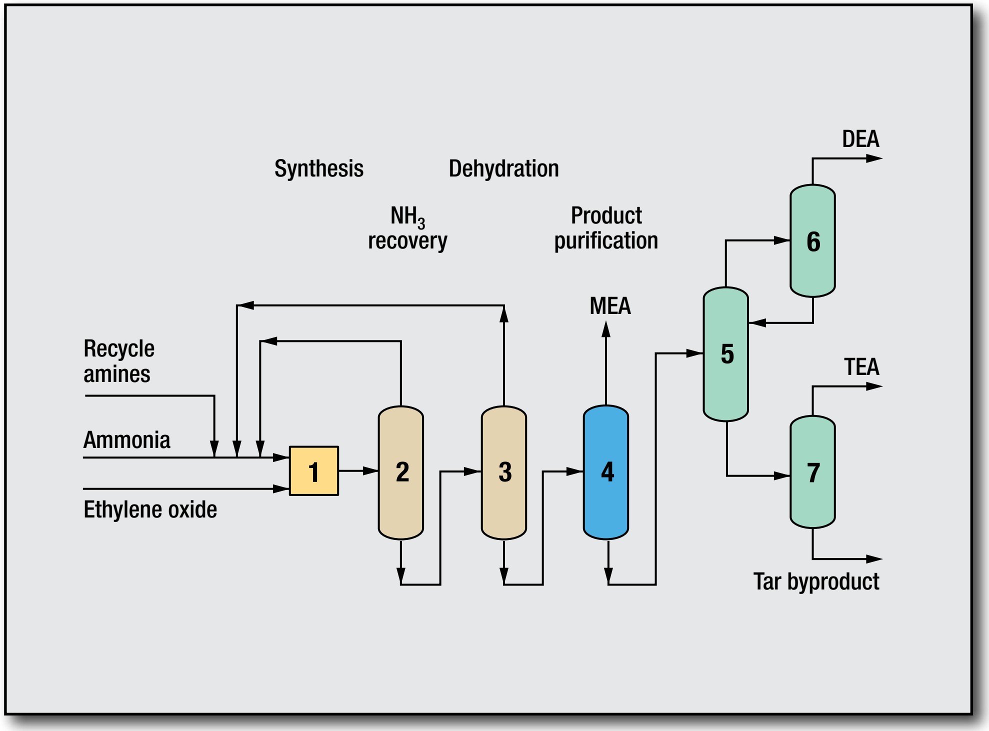
Commercial plants: The process has been commercialized in four different plants of various sizes. The largest plant capacity project using Polimeri/Lummus DPC technology has 115,000 metric tpy of DPC capacity.

Licensor: Lummus Technology - CONTACT

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, ton	0.82
Ammonia, ton	0.19
Steam, ton	5
Water, cooling , m^3	300
Electricity, kWh	30

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

Licensor: Davy Process Technology, UK - CONTACT

Ethanol-to-ethylene oxide/ ethylene glycols

Application: To produce ethylene oxide (EO) and ethylene glycols (EGs) from ethanol by dehydration to ethylene and 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 significant utilities savings as well as the recovery of bleed streams as high-grade product, which would otherwise be recovered as a lesser grade product. The integrated plant recovers all MEG as fiber-grade quality 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: A heated mixture of ethanol vapor and steam is fed to an adiabatic dehydration reactor (1). The steam provides heat for the endothermic reaction and pushes the reaction to 99^+% conversion of ethanol with 99^+% selectivity to ethylene. Recovered H_2O is stripped of light ends (2) and recycled as process steam. Product ethylene is compressed and put through a water wash (3) before passing to the ethylene oxide reactor section.

Ethylene and oxygen, in a dilute gas mixture of mainly methane or nitrogen, along with carbon dioxide (CO_2) and argon, are fed to a tubular catalytic reactor (4). The reaction heat is removed by generating steam on the shell side of the reactor while the reaction temperature is controlled by adjusting the pressure of the steam. The EO produced is removed from the excess gas by scrubbing with water (5) after heat exchange with the reactor feed gas.

Byproduct CO_2 is removed from the scrubbed gas (6, 7) before the recovered reaction gas is recompressed and returned to the reactor

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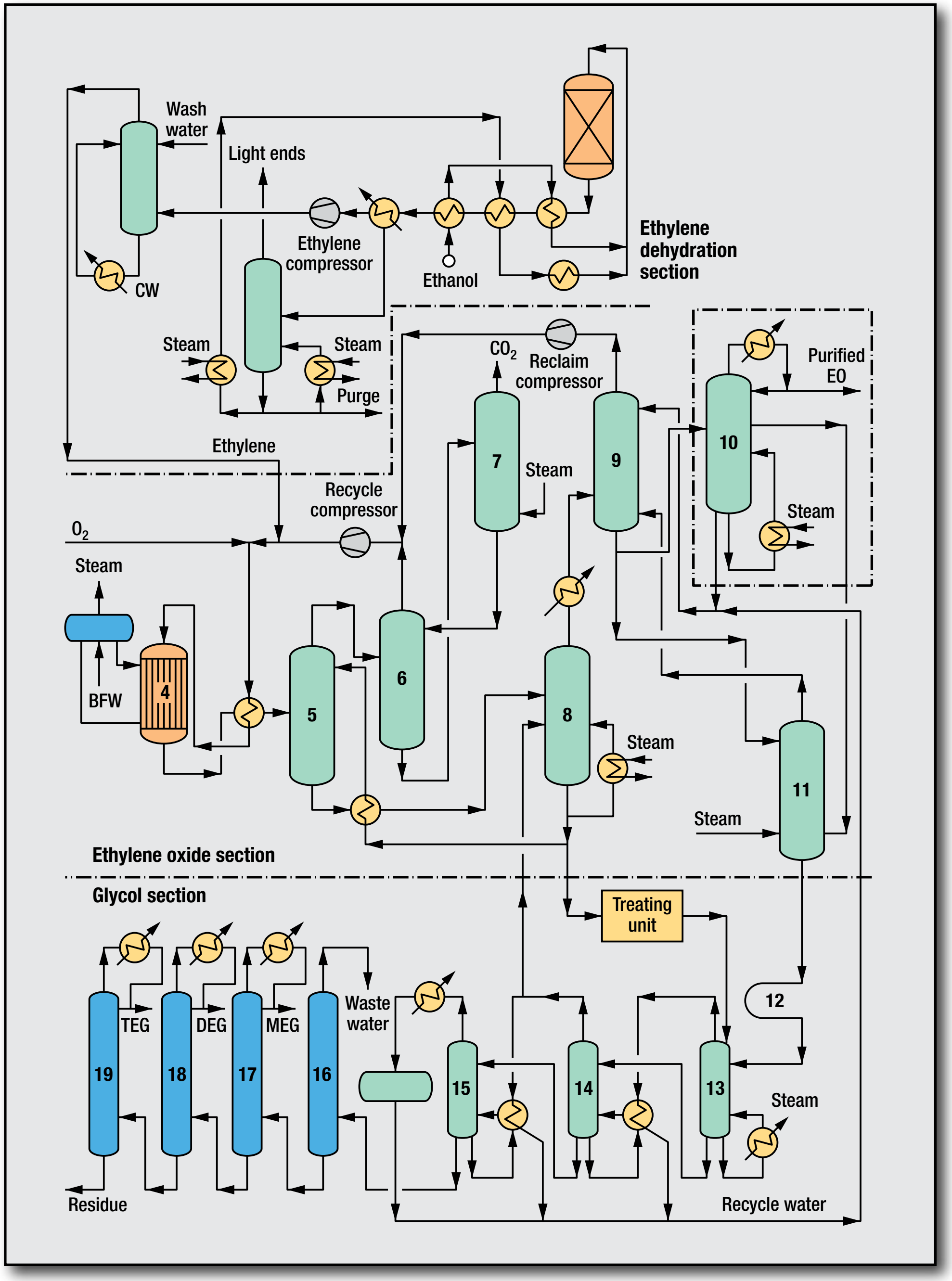


loop, along with the fresh ethylene and oxygen, which are controlled to achieve the desired concentrations in the EO reactor inlet gas.

The EO is steam stripped (8) from the scrubbing solution and recovered as a concentrated water solution (9) that is suitable as feed to a glycol plant (11) or to an EO purification system (10). The stripped water is cooled and returned to the scrubbing column.

The glycol plant feed, along with any high-aldehyde EO bleeds from the EO purification section, are sent to the glycol reactor (12). A multi-effect evaporator train (13, 14, 15) is used to remove the bulk of the water from the glycols. The glycols are then dried (16) and sent to the glycol distillation train (17, 18, 19) where the MEG, DEG and TEG products are recovered and purified.

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

Yield: The ethanol-to-glycols yield is 0.95 kg of total glycols per kg of ethanol (190 proof; 95 wt% ethanol). The ethanol yield for EO production is 0.68 kg of EO per kg of ethanol.

Commercial plants: Over 100 ethylene-to-EO/EG plants using SD technology have been built. One SD ethanol-to-EO/EG plant has been in operation for over 20 years with 2 expansions to the original plant, bringing the capacity to 124,400 metric tpy of EO/144,700 metric tpy of MEG. Five more plants with a total capacity of 294,600 metric tpy of EO are currently in design/construction, with one plant due for commissioning in October 2010.

Licensor: Scientific Design Co., Inc. - CONTACT

Ethers

Application: The Snamprogetti Etherification Technology allows producing high-octane oxygenates compounds such as methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), tert-amyl ethyl ether (TAEE) and etherified light cracked naphtha (ELCN).

Feed: C_4 streams from steam cracker, fluid catalytic cracking unit (FCCU) and isobutane dehydrogenation units, with isobutene contents ranging from 15 wt% to 50 wt%, C_5 and light cracked naphtha (LCN – FCC light gasoline 35°C–100°C) from FCC units.

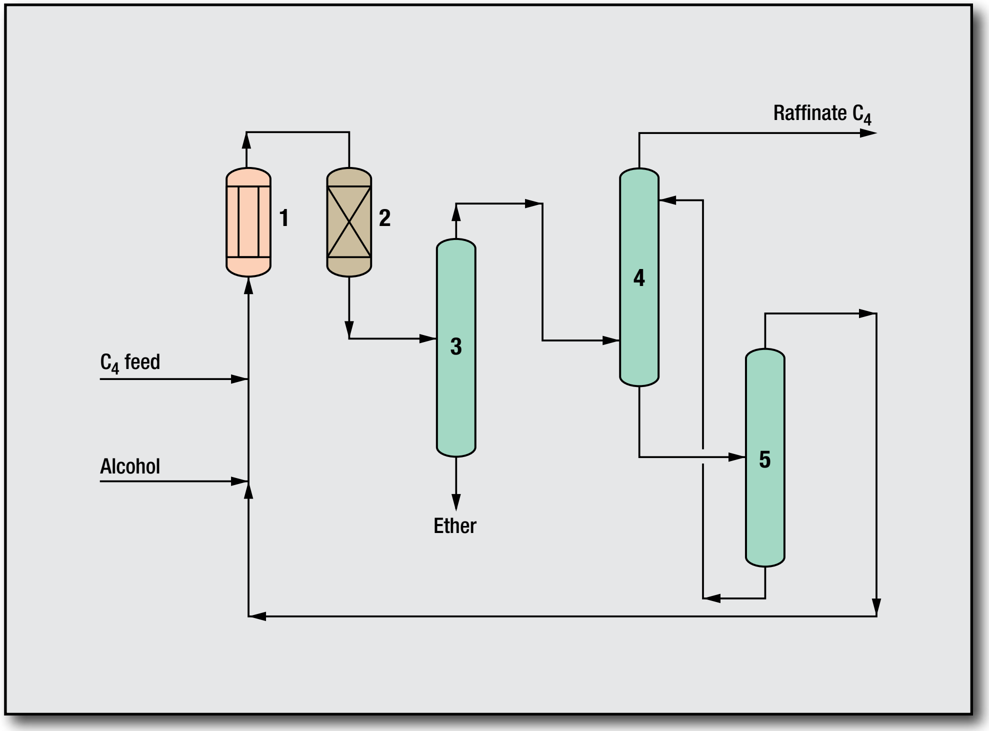
Description: A typical MTBE/ETBE unit using FCC cut is based on a single-stage scheme, with a tubular (1) and an adiabatic (2) reactor. The front-end reactor uses the proprietary water-cooled tubular reactor (WCTR). The WCTR is a very flexible reactor and can treat all C_4 cuts on a once-through basis.

It is the optimal solution for the etherification reaction since it enables an optimal temperature profile with the best compromise between kinetics and thermodynamics.

The reactor effluent is sent to the first column (3) where the product is recovered as a bottom stream while the residual C_4s are sent to the washing column (4) to separate the alcohol. The water/alcohol leaving the column is sent to the alcohol-recovery column (5), to recycle both alcohol and water.

This scheme will provide a total isobutene conversion up to 95%. With the double stage scheme, it is possible to reach more than 99%.

The industrial experience has proven that this plant with WCTR can be easily switched from ETBE to MTBE production, and vice versa, without stopping the plant and any reduction of feed rates. Process schemes are similar for production of heavier ethers starting from C_5 or LCN streams.



Utilities: (Referred to as C_4 feedstock with 20 wt% of isobutylene)

Steam, ton/ton ether	0.8 ÷ 0.9
Water, cooling, m³/ton of ether	53 ÷ 62
Power, kWh/ton of ether	8.4 ÷ 9.2

Commercial plants: Over 30 units including MTBE, ETBE, TAME and TAEE, have been licensed by Saipem.

Licensor: Saipem - CONTACT

Ethers—ETBE

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

Feeds: C_4 cuts from steam cracker and FCC units with isobutene contents ranging from 12% to 30%.

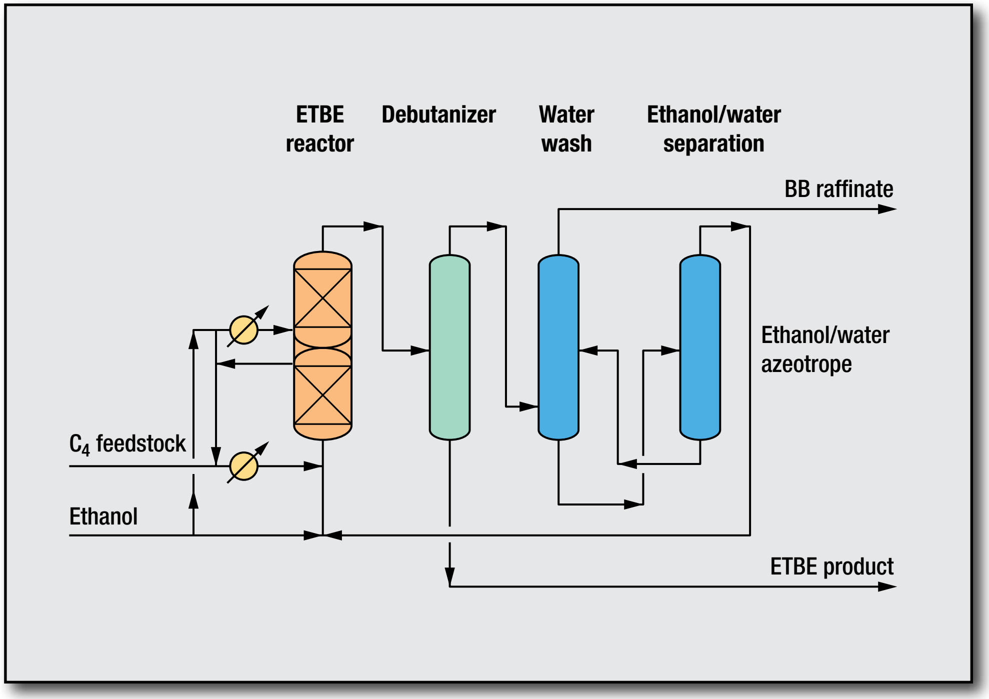
Products: ETBE and other tertiary alkyl ethers are primarily used in gasoline blending as an octane enhancer to improve hydrocarbon combustion efficiency. Moreover, blending of ETBE to the gasoline pool will lower vapor pressure (Rvp).

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 C_4 cuts that contain isobutene concentrations of about 25%.

ETBE is recovered as the bottoms product of the distillation unit. The ethanol-rich C_4 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 C_4 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: (C_4 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.

Licensor: Uhde GmbH - CONTACT

Ethers—MTBE

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

Feeds: C_4-cuts from steam cracker and FCC units with isobutene contents range from 12% to 30%.

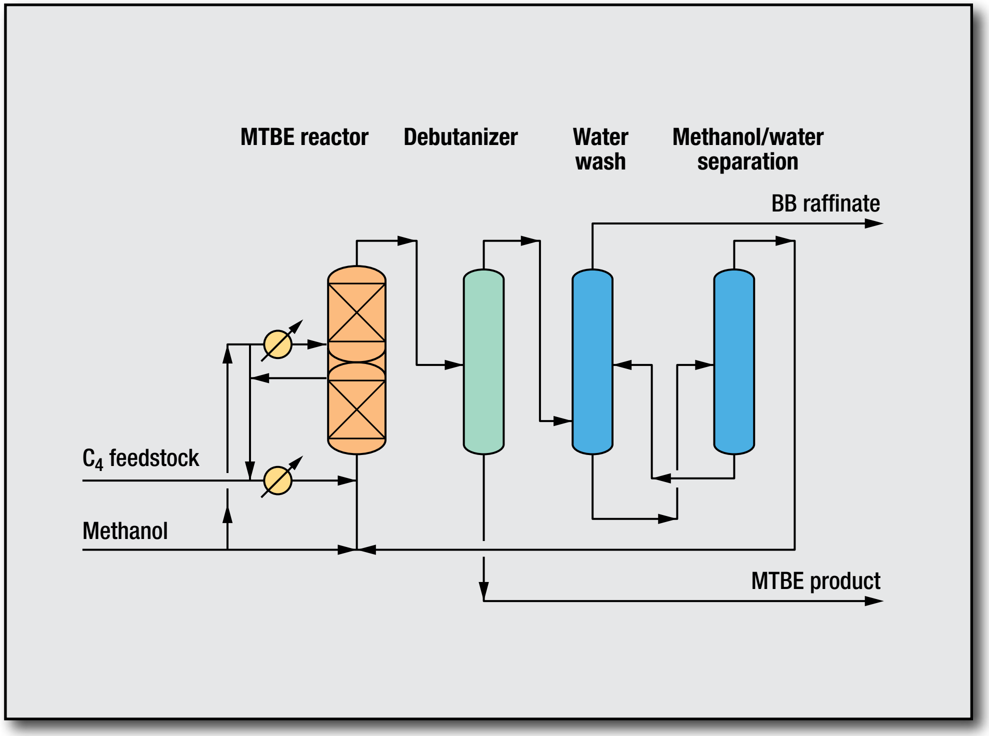
Products: MTBE and other tertiary alkyl ethers are primarily used in gasoline blending as an octane enhancer to improve hydrocarbon combustion efficiency.

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 C_4 cuts that contain isobutene concentrations of 25%.

MTBE is recovered as the bottoms product of the distillation unit. The methanol-rich C_4 distillate is sent to the methanol-recovery section. Water is used to extract excess methanol and recycle it back to process. The isobutene-depleted C_4 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 C_4 cut containing 22% isobutene, the isobutene conversion may exceed 98% at a selectivity for MTBE of 99.5%.

Utility requirements, (C_4 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

Continued ▼

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.

Licensor: Uhde GmbH - CONTACT

Ethyl acetate

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

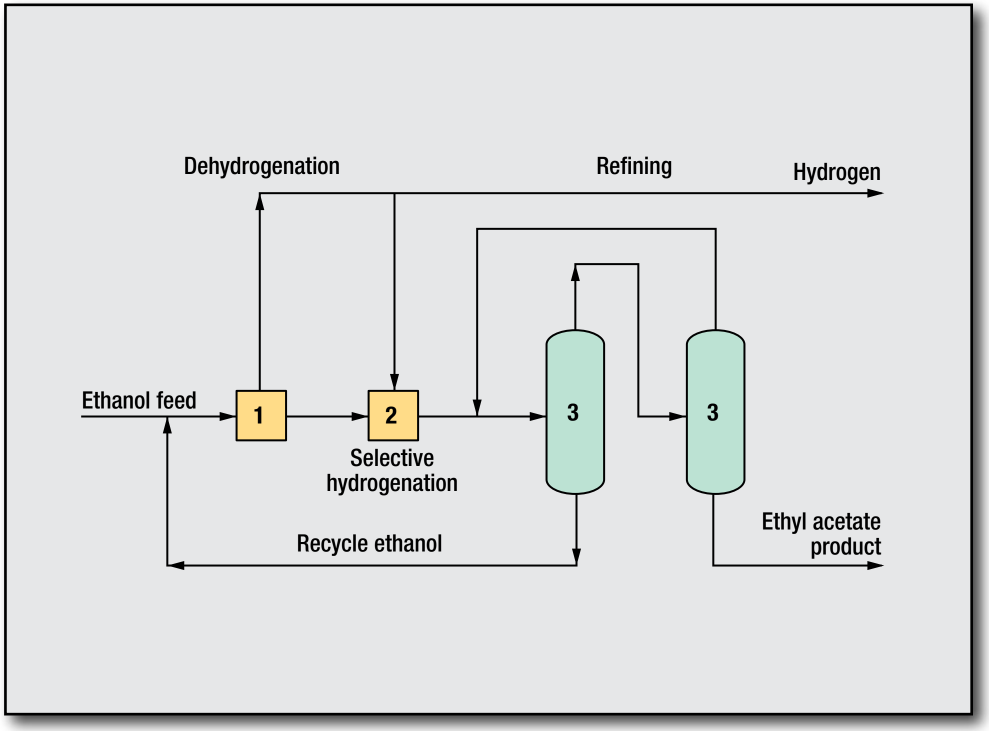
Description: Ethanol is heated and passed through a catalytic dehydrogenation reactor (1) where part of the ethanol is dehydrogenated to form ethyl acetate and hydrogen. The product is cooled in an integrated heat-exchanger system; hydrogen is separated from the crude product. The hydrogen is mainly exported. Crude product is passed through a second catalytic reactor (2) to allow "polishing" and remove minor by-products 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. There are two additional commercial plants (50,000 tpy and 100,000 tpy) in China using fermentation ethanol.

Licensees: Three since 1998.

Licensor: Davy Process Technology, UK - CONTACT

Ethylbenzene

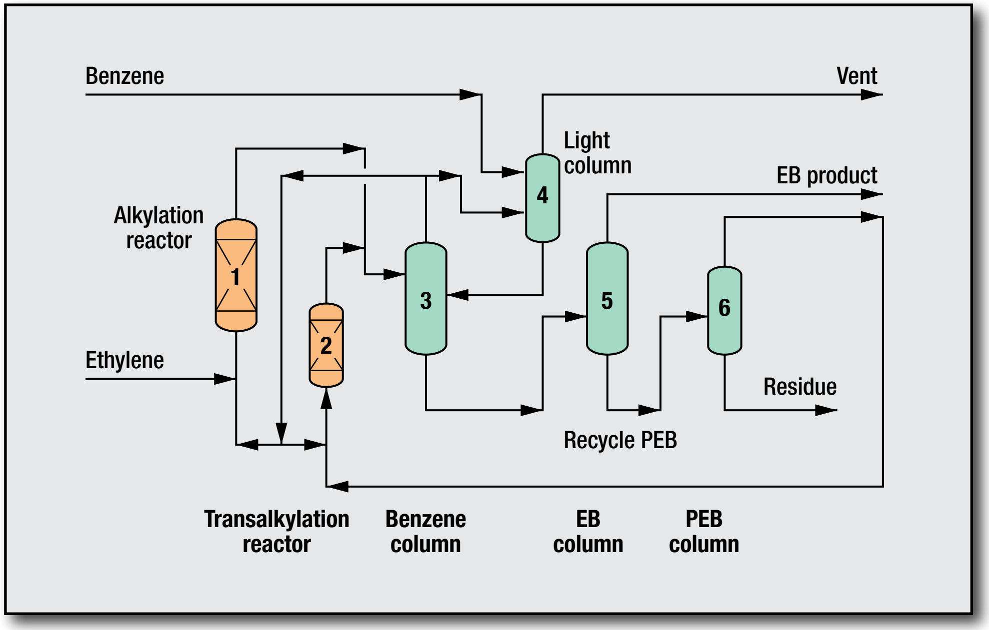
Application: To produce ethylbenzene (EB) from benzene and a polymer-grade ethylene or an ethylene/ethane feedstock using the Badger EBMax* process and proprietary ExxonMobil alkylation and transalkylation catalysts. The technology can be applied in the design of grassroots units, upgrading of existing 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. In the transalkylation reactor (2), polyethylbenzenes are converted to EB by reaction with benzene over ExxonMobil's transalkylation catalyst.

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 polyethylbenzenes are recovered as a distillate, and heavy 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.

*EBMax is a service mark of ExxonMobil Chemical Technology Licensing.



Product quality: The EB product contains less than 100 ppm of C_8 plus C_9 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: Badger has granted 47 zeolite technology EB licenses, totaling 22 million metric tpy of production capacity. The licensed capacity for the EBMax technology exceeds 17 million metric tpy.

Licensor: Badger Licensing LLC - CONTACT

Ethylbenzene

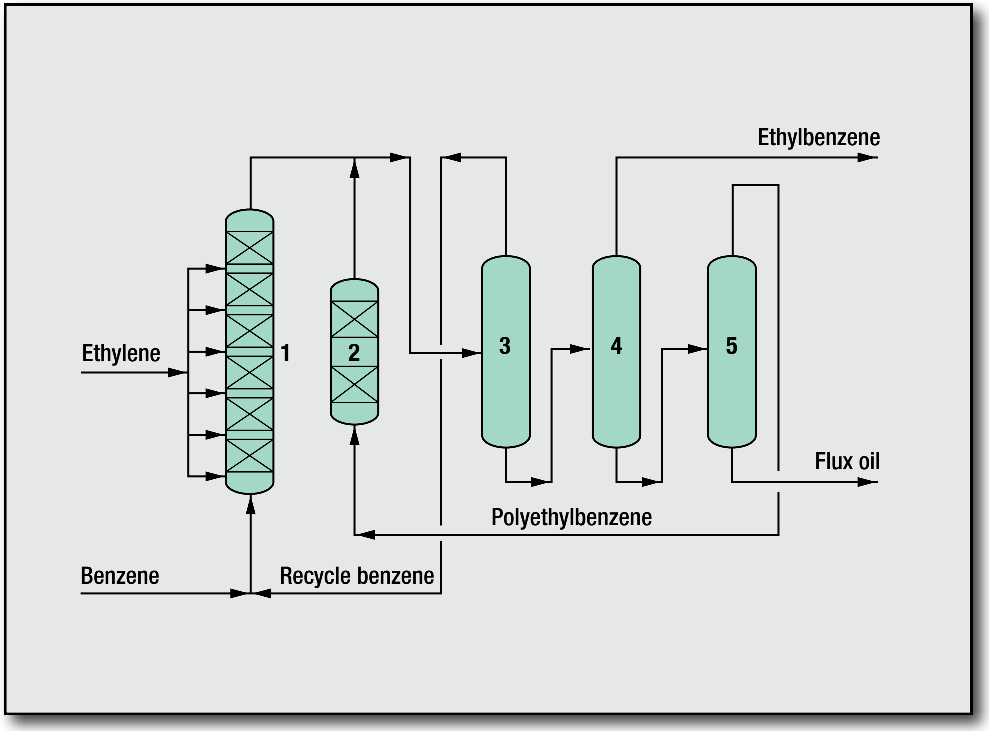
Application: State-of-the-art technology to produce high-purity ethylbenzene (EB) by liquid-phase alkylation of benzene with ethylene. The Lummus/UOP EBOne process uses specially formulated, proprietary zeolite catalyst from UOP. The process can handle a range of ethylene feed compositions ranging from chemical grade (70% ethylene/30% ethane) to polymer grade (100%).

Description: Benzene and ethylene are reacted 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 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 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 2–7 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 more than 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.

Typical raw material and utilities, per metric ton of EB	
Ethylene, mtons	0.265
Benzene, mtons	0.738
Net utilities, US$ (steam export)	–2

Commercial plants: EBOne technology has been selected for more than 35 projects worldwide, of which 22 plants are currently operating. Unit capacities range from 65,000 metric tpy to 1,250,000 metric tpy. Ethylene feedstock purity ranges from 80% to 100%. Ten additional units are either in design or under construction.

Licensor: Lummus Technology and UOP LLC - CONTACT

Ethylbenzene

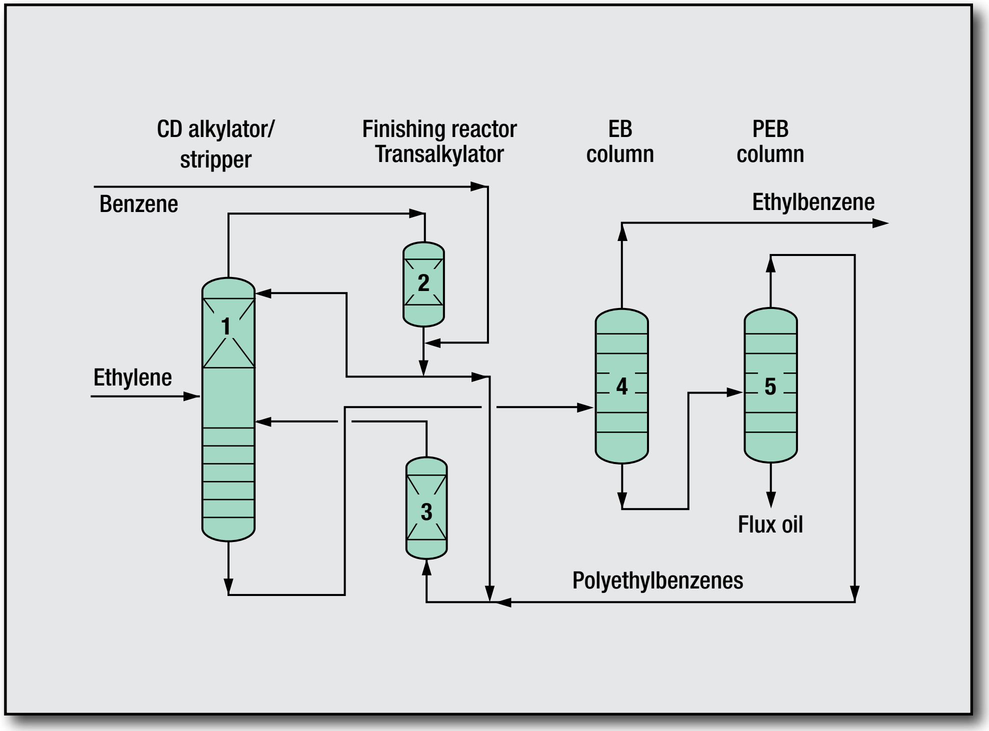
Application: Advanced technology to produce high-purity ethylbenzene (EB) by alkylating benzene with ethylene using patented catalytic distillation (CD) technology. The CDTECH EB process uses a specially formulated zeolite alkylation catalyst packaged in a proprietary CD structure. The process is able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

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 catlayst 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 up 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.

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



Ethylene, kg	265
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: Four commercial plants are in operation with capacities from 140,000 to 850,000 metric tpy. They process ethylene feedstocks with purities ranging from 35% ethylene to polymer-grade ethylene.

Licensor: CDTECH, a partnership between Lummus Technology and Chemical Research & Licensing - CONTACT.

Ethylene

Application: The CBL cracking technology is a steam cracking technology developed by SINOPEC. The steam-cracking furnace for ethylene production can be designed with this technology. This technology provides processing flexibility for ethylene cracking operations and can handle feedstocks from ethane to heavy vacuum gasoil (HVGO).

Description: The CBL technology is a state-of-the-art technology with low-investment cost of building new furnaces or revamping old furnaces. CBL furnace is applicable to many feedstocks such as ethane, light hydrocarbons, natural gas liquids (NGLs), naphtha, light gasoline oil and HVGO. Different feedstocks can be cracked in the same furnace with varying operating condition; two feedstocks (for example, naphtha and ethane) can also be cracked by different coils in one furnace. For heavy feedstocks in particular, the CBL technology shows special advantages—long run lengths (50 days to 70 days) and high ethylene/propylene yields.

For liquid and gas feedstocks, the characteristics of CBL technology are:

Liquid feed:

- **Coil configurations.** Two-pass, high-selectivity coil configurations (2-1, 2/1-1, 4-1, etc.) are possible furnace designs. The first pass has a small diameter with a large specific surface area, which leads to a quick temperature increase. The second pass has a large diameter, which leads to a lower pressure drop and lower hydrocarbon partial pressure. Appropriate coils are chosen based on different feeds and capacity requirements. The coil configuration of this technology combines the features of higher temperature, shorter residence time and lower hydrocarbon partial pressure and leads to the advantages of high cracking selectivity, long run length and larger capacity of a single coil.
- **Transfer line exchanger (TLE).** First stage or second stage options available.
- **Dilution steam Injection.** First stage (light feed) or second stage (heavy feed). By using this technique, coke formation from heavy oil in convection section coils can be minimized.
- **Heat supply.** Using a combination heat supply from hearth and sidewall allows temperature distribution of the hearth, and the heat transfer of the coil is uniform.
- **High thermal efficiency.** Up to 93%–94%
- Variable frequency speed control driving motor can be adopted for induced draft fan.

Gas feed:

- For gas feed, the four-pass coil configuration (2-1-1-1) with residence time between 0.4 to 0.8 second is adopted. Linear or U type TLE is directly coupled with the outlet tube of one group of 2-1-1-1 coils. The TLE can be one stage, two stages or three stages. For ethane- cracking furnace, the running cycle is longer than 100 days.

Commercial plants: CBL technology was first commercialized in 1984, with a total of 44 units, including recently built units and revamps. Total processing capacity of more than 3.56 million metric tpy has been licensed.

Licensor: China Petrochemical Technology Co., Ltd. - CONTACT

Ethylene

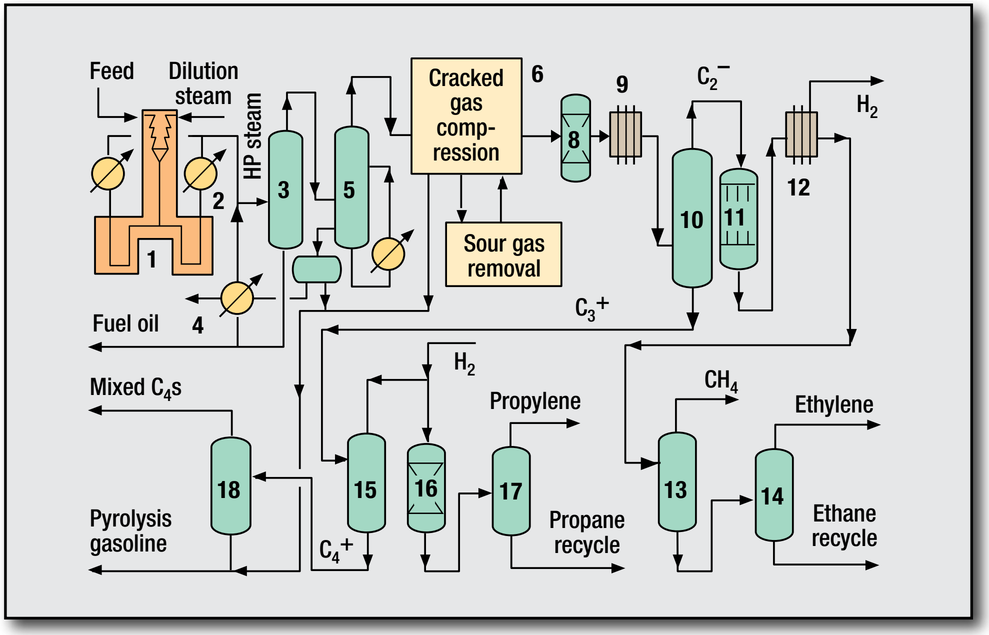
Application: To produce polymer-grade ethylene and propylene by thermal cracking of hydrocarbon fractions—from ethane through naphtha up to hydrocracker residue. Byproducts are a butadiene-rich C_4 stream, a C_6–C_8 gasoline stream rich in aromatics and fuel oil.

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 fractionatior (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 are 800 (1,100) US$/ton installed ethylene capacity.

Commercial plants: Over 20 million tons of ethylene are produced in more than 50 plants worldwide. Many plants have been expanded in capacity up to 50% and more.

Recent awards for world-scale ethylene plants include Borouge 2 and 3 (1.5 million metric tpy each) in Abu Dhabi.

Licensor: Linde AG - CONTACT

Ethylene

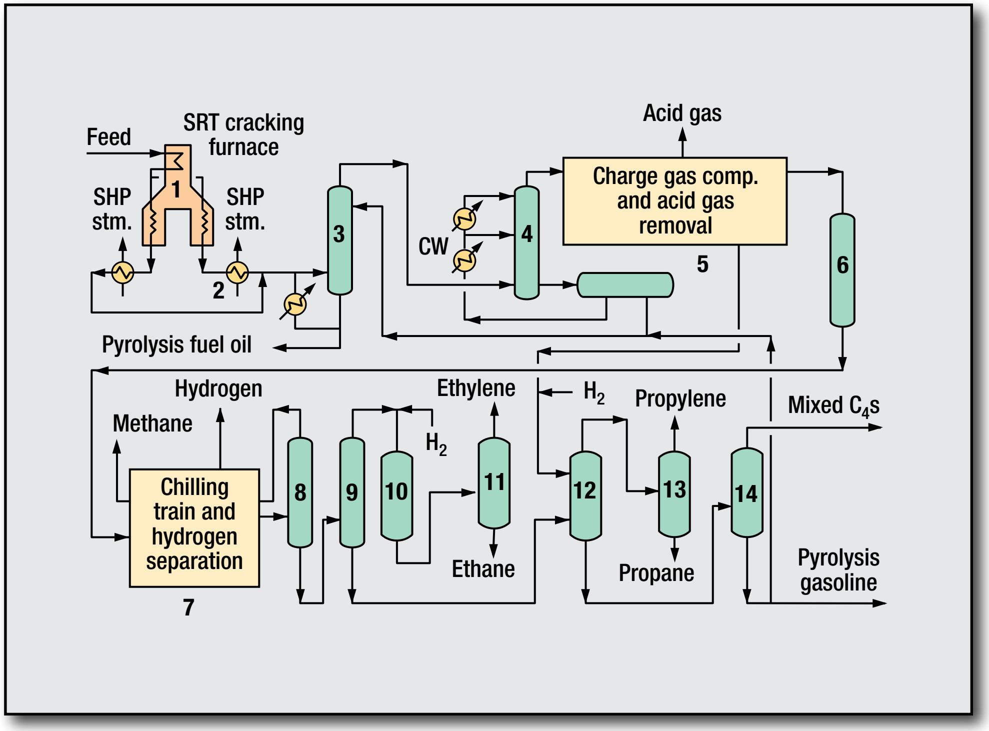
Application: To produce polymer-grade ethylene (99.95 vol%). Major byproducts are propylene (chemical or polymer-grade), a butadiene-rich C_4 stream, C_6 to C_8 aromatics-rich pyrolysis gasoline and high-purity hydrogen.

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 VII.

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 C_4 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 C_2 through C_4 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%.

Continued ▼

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

Licensor: Lummus Technology - CONTACT

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 a high-purity hydrogen by steam pyrolysis of hydrocarbons ranging from ethane to vacuum gasoils (VGOs). Progressive separation applied for concept in the fields either front-end or back-end hydrogenation is used in steam cracking.

Description: For either gaseous (ethane/propane) or liquid (C_4/naphtha/gasoil) feeds, this technology is based on Technip's proprietary pyrolysis furnaces and progressive separation. This allows processing of olefins at low energy consumption with a particularly low environmental impact. The progressive separation concept is applied for either front-end hydrogenation or back-end hydrogenation.

- The front-end hydrogenation corresponds to a front-end deethanizer for an ethane cracker or a front-end depropanizer for the heavier feedstocks both are placed at the third-stage discharge of the cracked-gas compressor.
- The back-end hydrogenation corresponds to a front end; the tower is placed at fifth-stage discharge.

Hydrocarbon feedstocks are preheated (also to recover heat) and then cracked by combining with steam in a tubular pyrolysis furnace 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 GK6 type (for liquid cracking). The GK6 type design can be oriented to a high olefins yield with very flexible propylene/ethylene ratios, or to a high BTX production. 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 (TLEs) or selective line exchangers (SLEs), generating high-pressure steam. In liquid crackers, cracked gas flows to a primary fractionator, after direct quench with oil, where fuel oil is separated from gasoline and lighter components, and then sent to a quench water tower for water recovery (to be used as dilution steam) and heavy gasoline production (end-point control). In a gas cracker, cracked gas flows to a quench water tower for water recovery and removal of tars. A caustic scrubber placed at the third-stage discharge of the cracked-gas compressor removes acid gases. The compressed gas at 450 psig is dried and then chilled.

For an ethane cracker, a single demethanizing stripping system operating at medium pressure is implemented; the overhead is recycled back to the cracked gas compressor.

For a liquid cracker, a double demethanizing stripping system operating at medium pressure and reboiled by cracked gas, minimizes the refrigeration required (heat integration) as well as the investment for

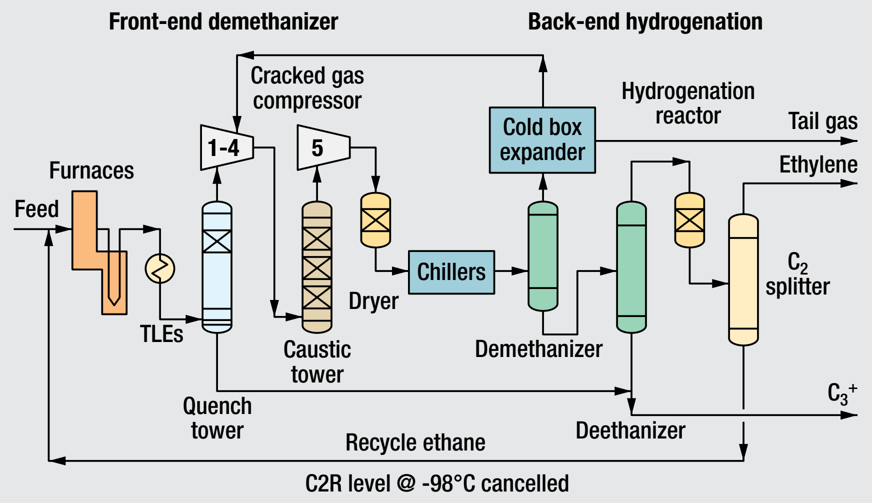


Fig. 1. Progressive separation applied in Back-end hydrogenation for an ethane cracker.

Continued ▼

separating methane (top) and C_2^+ cut (bottoms). A dual column concept (absorber concept: Technip's patent) is applied between the secondary demethanizer overheads, and the chilled cracked gas minimizes ethylene losses with a low-energy requirement. The high-purity hydrogen is produced in a cold box.

The bottoms from the demethanizers are sent to the C_2 cut treatment for ethylene purification.

The C_2 splitter is operating as a heat pump. The tower can be arranged as open heat pump integrated with the ethylene refrigerant when the front-end hydrogenation system or closed heat pump operating with the propylene refrigerant for the back-end hydrogenation scheme.

The residual ethane from the C_2 splitter is recycled for further cracking.

Polymer-grade propylene is separated from propane in a C_3 splitter. The residual propane is either recycled for further cracking or exported. C_4s and light gasoline are separated in a debutanizer.

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/absorber towers (single specification) instead of distillation towers (antagonistic top and bottom specifications).

Economics: Ultimate range of ethylene yields vary from 83% (ethane) to around 25% (VGOs), 35% for intermediate full-range naphtha. These correspond to the respective total olefins yields (ethylene and propylene) from 84% (ethane) to 38% (VGOs), and 49% for intermediate full-range naphtha. The specific energy consumption range is 3,100 kcal/kg ethylene (ethane) to 5,500 kcal/kg ethylene (GO) and 4,700 Kcal/Kg ethylene for an intermediate full-range naphtha.

Commercial plants: Since 2001, six grassroots ethylene plants have been awarded to Technip, out of which four have a capacity of over 1 million tpy of ethylene. In the same period, 148 furnaces using Technip's proprietary coils technology have been awarded to Technip as new furnaces or upgrading of existing facilities. More than 20 ethylene plants based on Technip's technology are in operation worldwide. The progressive separation is also applied for plant expansions over the nominal capacity, with up to an 80% capacity increase.

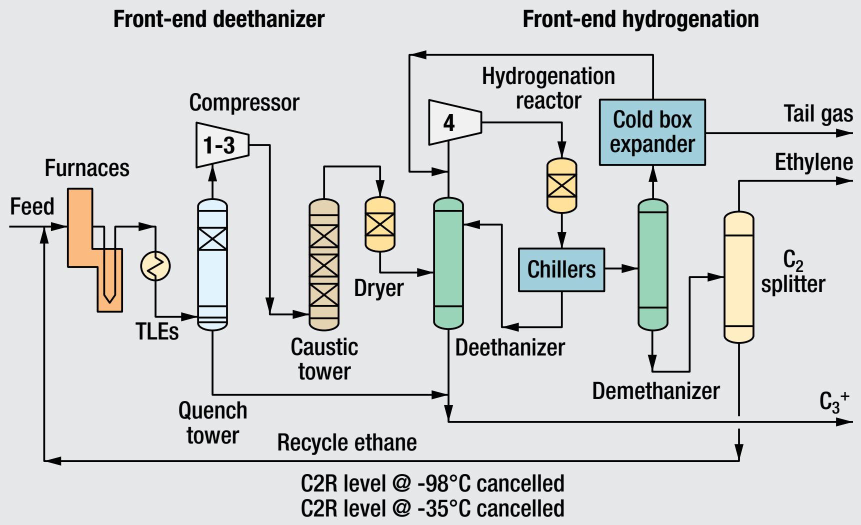


Fig. 1. Progressive separation applied in Front-end hydrogenation for an ethane cracker.

Licensor: Technip - CONTACT

Ethylene

Application: Thermal cracking of a wide range of feedstocks into light olefins (mainly ethylene and propylene) and aromatics using proprietary cracking coils.

Feedstocks: Ethane, propane through liquid feeds up to heavy gasoil or up to 600°C EP.

Products: Cracked gas rich in Ethylene, propylene, butadiene and BTX (benzene, toluene and xylene).

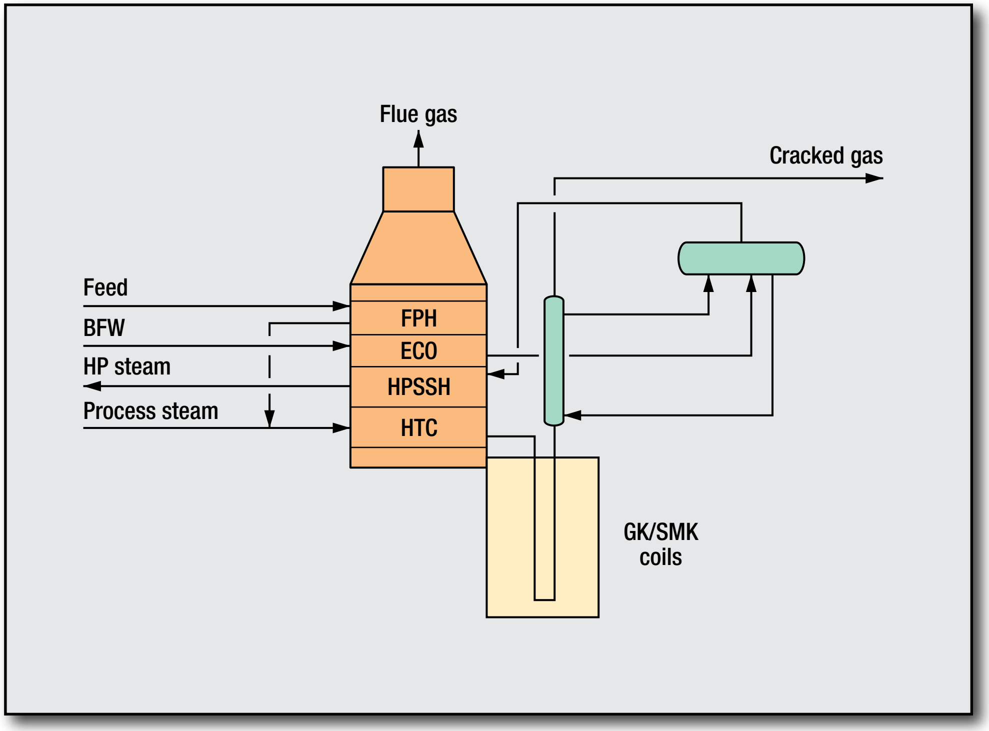
Description: Thermal cracking occurs in the presence of steam at high temperature in cracking coils located centrally in the firebox. Coil outlet temperature varies from 800°C up to 880°C depending on feed quality and cracking severity. The recent proprietary coils are GK6 and SMK coils used, respectively, for liquid and gas cracking. They feature high selectivity to ethylene, propylene, together with low coking rates (longer run length). Technip has also developed recently new patents (GK7 and Swirl Flow Tubes) to enhance both capacity and run length at lower investment cost.

Cracked gases from the furnaces coils pass through a transfer line exchanger (TLE) system, where heat is recovered to generate high-pressure steam. The primary TLEs are special S&T or linear types that ensure low to very low fouling rates and, thus, extending run lengths. Heat from the flue gases is recovered in the convection section to preheat feed and process steam, and to superheat the generated VHP.

The technology is also applied to retrofit furnaces. The furnaces performances are optimized by using Technip's proprietary software SPYRO. Depending on the regulations various, options of NO_x abatement are incorporated.

Performance data:

Ethane conversion, %	65–75
Naphtha cracking severity	0.4–0.75
Overall thermal efficiency %	92–95
Coil residence time, sec	
GK6	0.15–0.25
SMK	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 550 cracking furnaces since mid-1960s have been implemented using Technip's technology. Since 2000, the SMK technology has been applied in 77 furnaces, and GK6 technology in 71 furnaces.

Licensor: Technip - CONTACT

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.

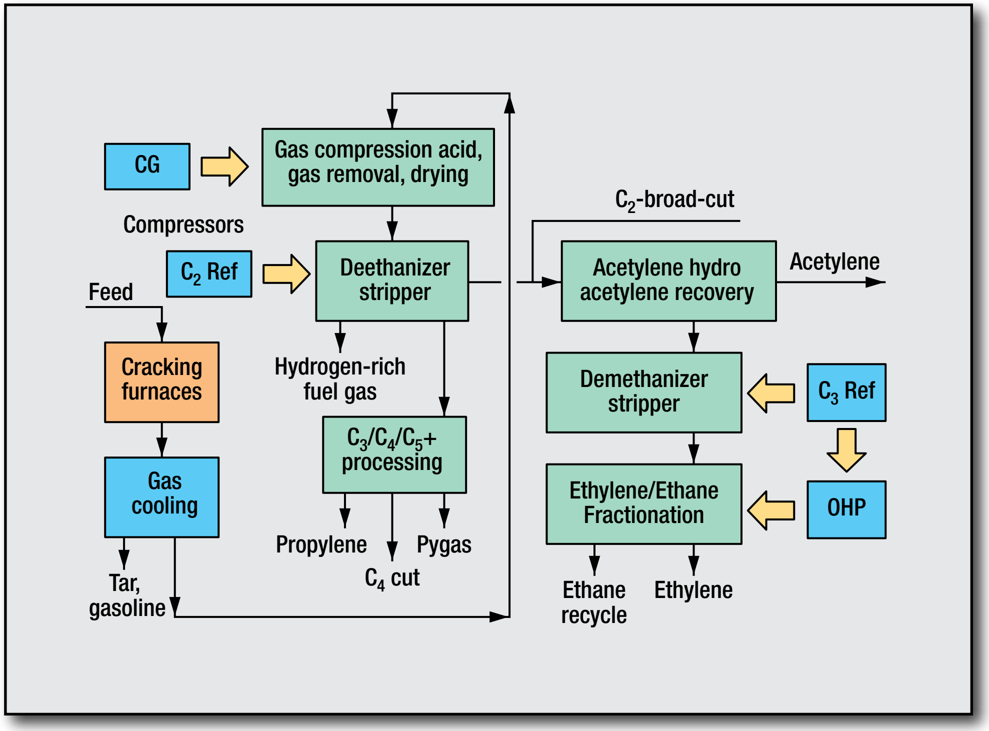
A multistage compressor, driven by a steam turbine, compresses the cooled gas. LP and HP condensates are stripped in two separate strippers where medium gasoline is produced and part of the C_3^+ cut is recovered respectively. A caustic scrubber removes acid gases.

Compressed gas at 450 psig is dried and then chilled. A multistream 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 - CONTACT

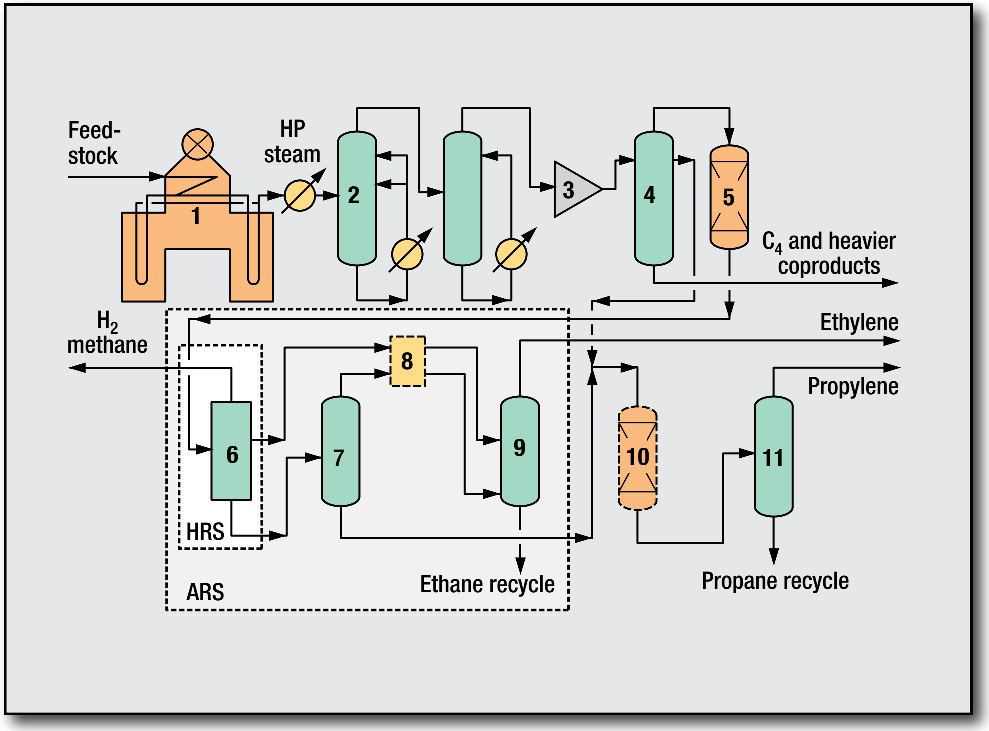
Ethylene

Application: To produce polymer-grade ethylene and propylene by thermally cracking hydrocarbon feedstocks (ethane through hydro-cracked residue). Shaw's key process technologies are:

1. Ultra-selective cracking (USC) furnaces—Selective pyrolysis with proprietary quench exchanger systems
2. Ripple tray and vapor flute—High capacity with fouling minimization for quench oil and quench water towers
3. Advanced recovery system with heat-integrated rectifier (ARS/HRS)—Energy efficient cold fractionation.

Description: The following description and diagram are given for liquid feedstock steam cracking. Fresh liquid feed as well as recovered ethane and propane are sent to USC furnaces (1). Contaminant removal may be installed on the fresh feed if required. A portion of the cracking heat may be supplied by gas turbine exhaust as preheated combustion air. Pyrolysis occurs at temperatures and residence time requirements specific to the feedstock and product requirements. The USC technology utilizes a number of radiant coil designs for the cracking furnaces to reduce residence time and coil pressure drop and to maximize ethylene yield.

Rapid quenching preserves olefin yields and the heat of quenching is used to generate high-pressure steam. Lower temperature heat is recovered for the production of dilution steam. Pyrolysis fuel oil and gasoline byproducts are recovered in the quench oil and quench water systems (2). Cracked gas (C_4 and lighter) is compressed (3), scrubbed with caustic to remove acid gases and dried prior to fractionation. C_3 and lighter components are separated from the C_4 and heavier components in the low fouling front-end dual pressure depropanizer (4). Overhead vapor of the high-pressure depropanizer is hydrogenated to remove acetylene, methyl acetylene and propadiene (5) and then routed to the HRS and demethanizer systems (6). The demethanization system includes a turbo-expander for energy efficiency and greater hydrogen recovery. Alternatively, the acetylene can be extracted as a high-purity product (8).



The ARS minimizes refrigeration energy by using distributed distillation and simultaneous heat and mass transfer in the HRS system.

Two C_2 streams of varying composition are produced within the ARS/HRS. The heavier C_2/C_3 stream is deethanized (7) and the C_2 overhead stream is fed directly to a low-pressure ethylene-ethane fractionator (9), which is integrated with the C_2 refrigeration system (9). Polymer-grade ethylene product is taken from the overhead from the ethylene-ethane fractionator.

C_3s from the dual pressure depropanizer system are combined and may require further hydrogenation to remove methyl acetylene and propadiene (10). Either polymer-grade or chemical-grade propylene can be produced overhead from a propylene-propane fractionator. The propyl-

Continued ▼

ene-propane fractionator can either be a high-pressure system that is condensed by cooling water or a low-pressure system that utilizes a heat pump (11).

C_4 and heavier byproducts are further separated in a sequence of distillation steps. Ethane and propane are typically recycled to pyrolysis. Refrigeration is typically supplied by a cascade ethylene/propylene refrigeration system.

Advantages of ARS technology are:

1. Reduced chilling train refrigeration requirements due to chilling/pre-fractionation in the HRS system.
2. Reduced methane content in feed to the demethanizer, which reduces the demethanizer condenser duty and refrigeration loads.
3. The dual feed ethylene fractionator (lower reflux ratio) reduces refrigeration loads and energy consumption.
4. Reduced refrigeration demand via the use of an integrated heat pump on the ethylene-ethane fractionator.

Economics: Once-through pyrolysis yields range from 57 wt% (ethane, high conversion) to 28 wt% (heavy hydrogenated gasoils) ethylene. Ultimate yields for ethylene of 85% from ethane feedstock and 32% from liquid feedstock are achieved. The ethylene plants with USC furnaces and an ARS/HRS recovery section are known for high reliability, low energy consumption, short startup time and environmental compliance.

Commercial plants: Shaw has designed and/or built 120 ethylene units. Expansion techniques based on ARS/HRS technology have increased original capacities by more than 100 percent. Shaw ethylene plants are now commonly integrated with refinery related processes such as FCC offgas recovery.

Licensor: The Shaw Group - CONTACT

Ethylene

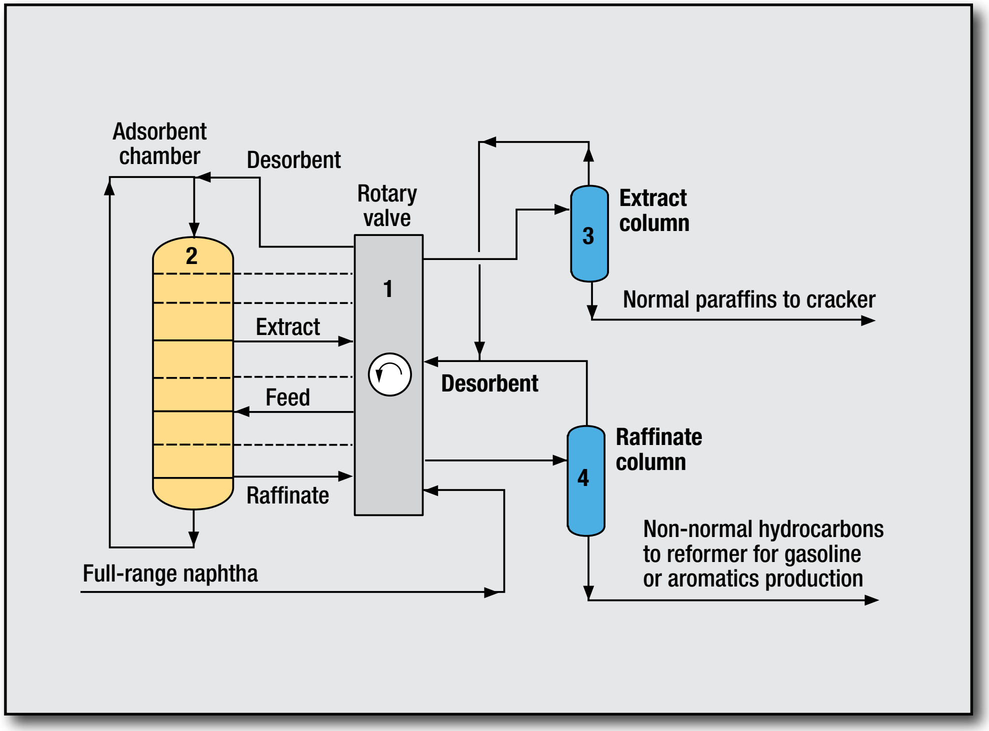
Application: The MaxEne process increases the ethylene yield from naphtha crackers by raising the concentration of normal paraffins (n-paraffins) in the naphtha-cracker feed. The MaxEne process is the newest application of UOP's Sorbex technology. The process uses adsorptive separation to separate C_5–C_{11}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

Yields: Ethylene yields from a naphtha cracker can be increased by over 30% using MaxEne extract as feedstock and the MaxEne raffinate can provide a 6% increase in octane-barrels from a refiner's catalytic naphtha reforming unit.



Economics: Capital costs and economics depend on feed composition as well as the desired increase in ethylene and propylene production in the steam cracker.

Commercial status: UOP's Sorbex technology is widely used in refining and petrochemical plants. The first commercial MaxEne unit is being installed in China.

Licensor: UOP LLC, A Honeywell Company - CONTACT

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 hydrogenation catalysts and, if present in the steam-cracker feed, are distributed in the C_2–C_5 + cuts. A condensate containing mercury may have negative added-value as a gas field product.

Description: Two RAM processes are available. In the presence of metallic mercury, a RAM I adsorber will be effective. In the presence of organo metallic mercury and/or arsenic and/or lead, a two-stage process (called RAM II) will effectively purify the stream, whatever its endpoint.

The RAM II process configuration is as follows: Feed is mixed with H_2 make-up and heated up in (1) to a 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	2,000	< 1*
Arsenic, ppb	100	< 1*

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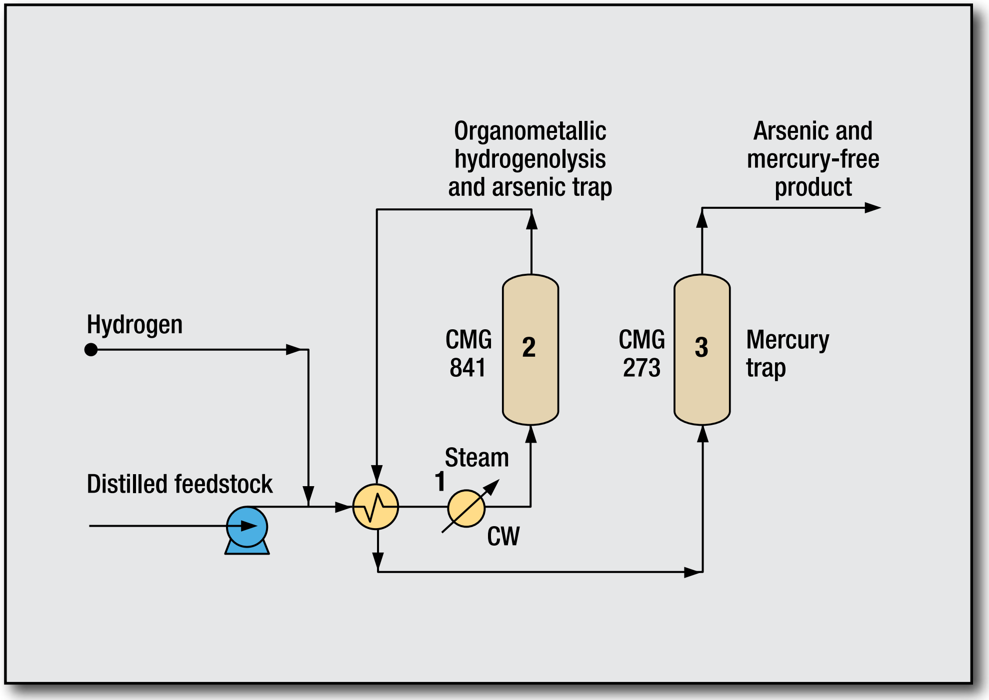
*3 ppb is the threshold limit of the analytical procedure commonly used. With provisions for eliminating solid matter, water and free oxygen and using a more sensitive method, levels of less than one ppb can be achieved.



Economics: The ISBL 2010 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

	Clear, oxygen-free condensate	Aerated condensate with particulate matter
Investment, US$/bpd	150	200
Utilities, US$/bpd	0.08	0.23
Catalyst cost, US$/bpd	0.03	0.03

Commercial plants: Fifteen RAM units have been licensed worldwide.

Reference: Debuisschert, Q., "Mercury Removal Technology," Axens seminar, Pattaya, 2009

Licensor: Axens - CONTACT

Ethylene glycols (EG)

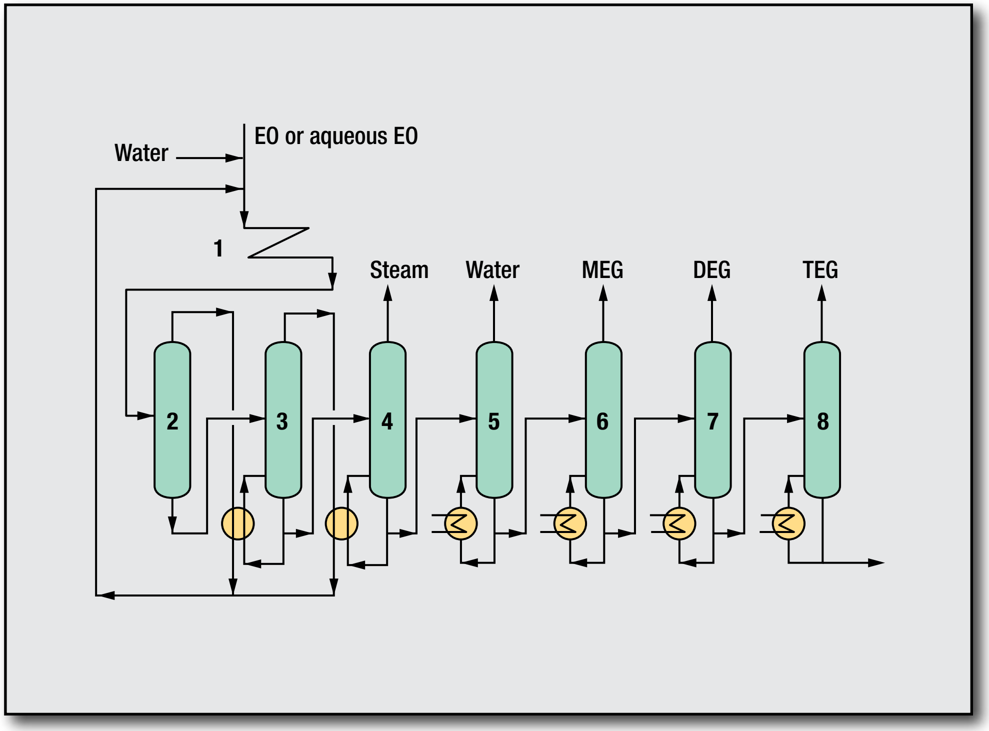
Application: To produce ethylene glycols (MEG, DEG and TEG) from ethylene oxide (EO).

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

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



Commercial plants: Since 1958, about 70 Shell-designed EG plants have been commissioned or are under construction.

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

Licensor: Shell Global Solutions International B.V. - CONTACT

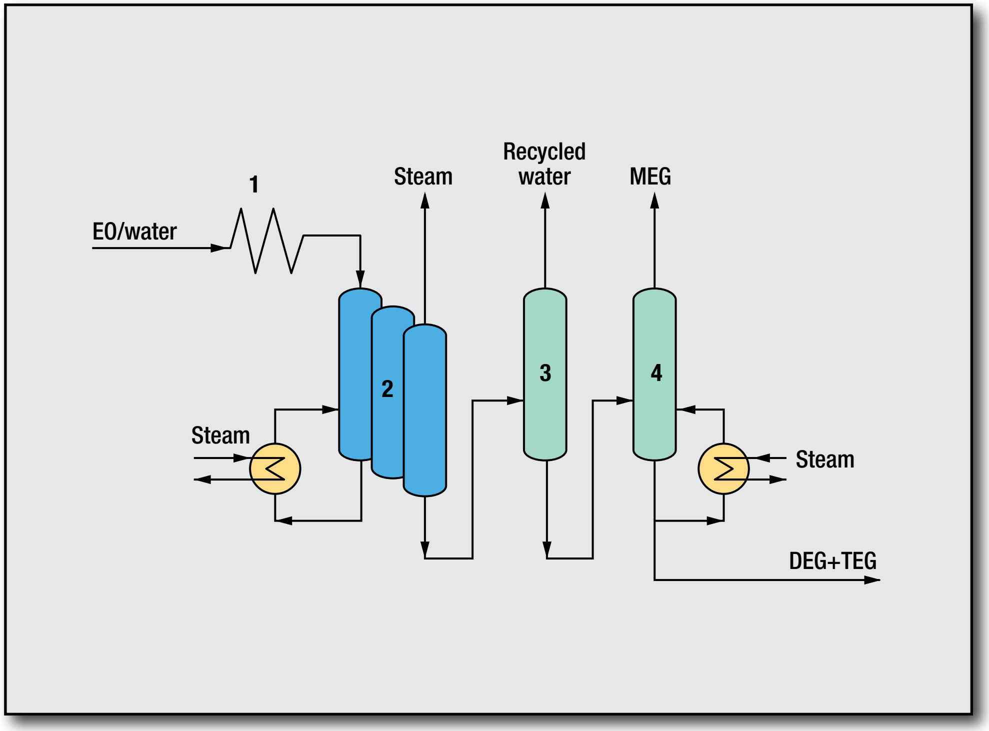
Ethylene glycol

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. High-purity DEG is typically recovered via the addition of a single fractionation column. 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.

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

Ethylene glycol, mono (MEG)

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

Description: EO in an aqueous solution is reacted with CO_2 in the presence of a homogeneous catalyst to form ethylene carbonate (1). The ethylene carbonate subsequently is reacted with water to form MEG and CO_2 (3). The net consumption of CO_2 in the process is nil since all of the CO_2 converted to ethylene carbonate is released again in the ethylene carbonate hydrolysis reaction. Unconverted CO_2 from the ethylene carbonate reaction is recovered (2) and recycled, together with CO_2 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.

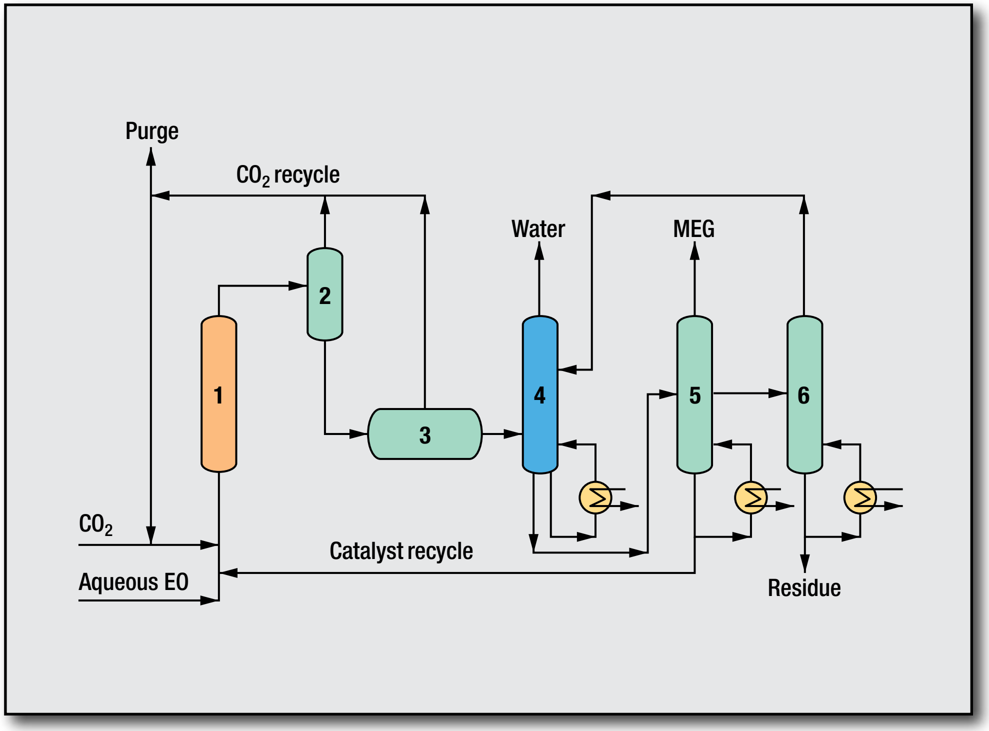
The process has a MEG yield of $99\%^{+}$. Compared to the thermal glycol process, steam consumption and wastewater production are relatively low, the latter because no contaminated process steam is generated.

MEG quality and the 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.

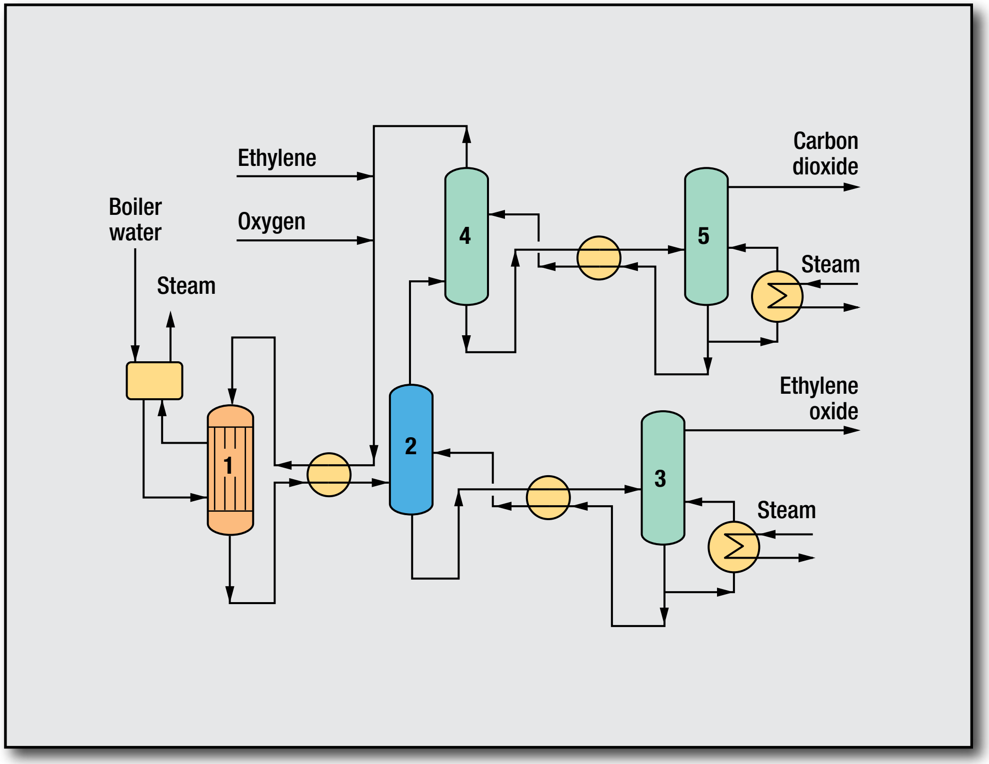
Commercial plants: Three commercial plants are currently in operation, the largest having a MEG capacity of 750,000 tpy. Two other process licenses have been also awarded.

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

Licensor: Shell Global Solutions International B.V. - CONTACT



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. Some impurities are removed by stripping and is then immediately reabsorbed in water (3), thus minimizing the handling of concentrated EO. The cycle gas exiting the absorber is fed to the CO_2 removal section (4,5) where CO_2, which is co-produced in the EO reactor, is removed via activated, hot potassium carbonate treatment. The CO_2 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 reabsorbed 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. - CONTACT

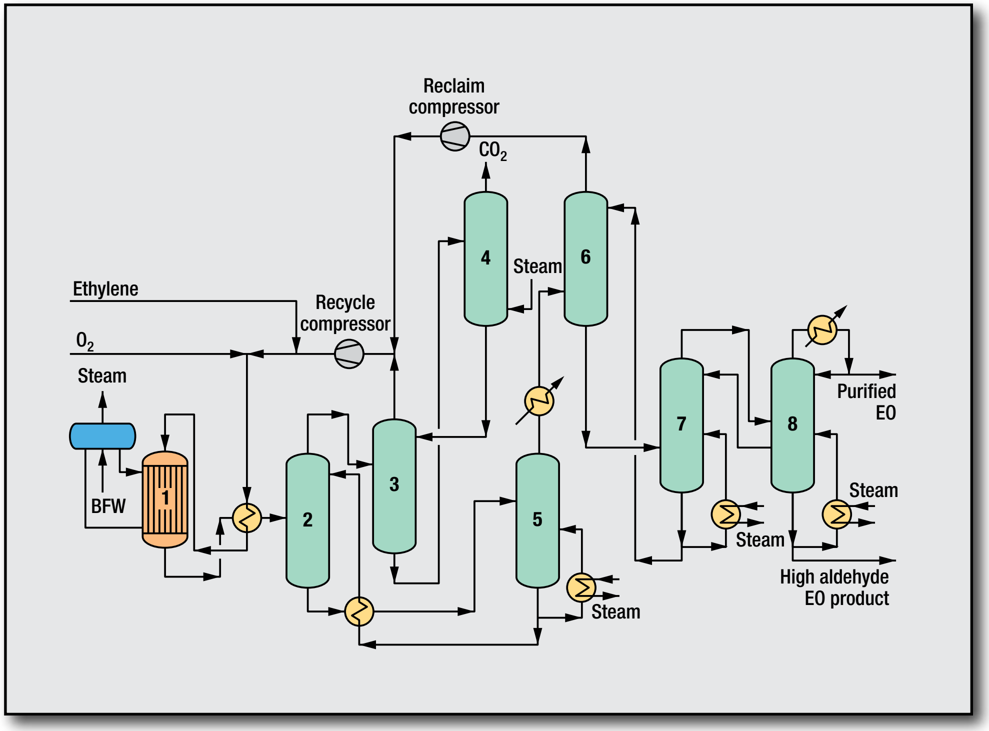
Ethylene oxide

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.



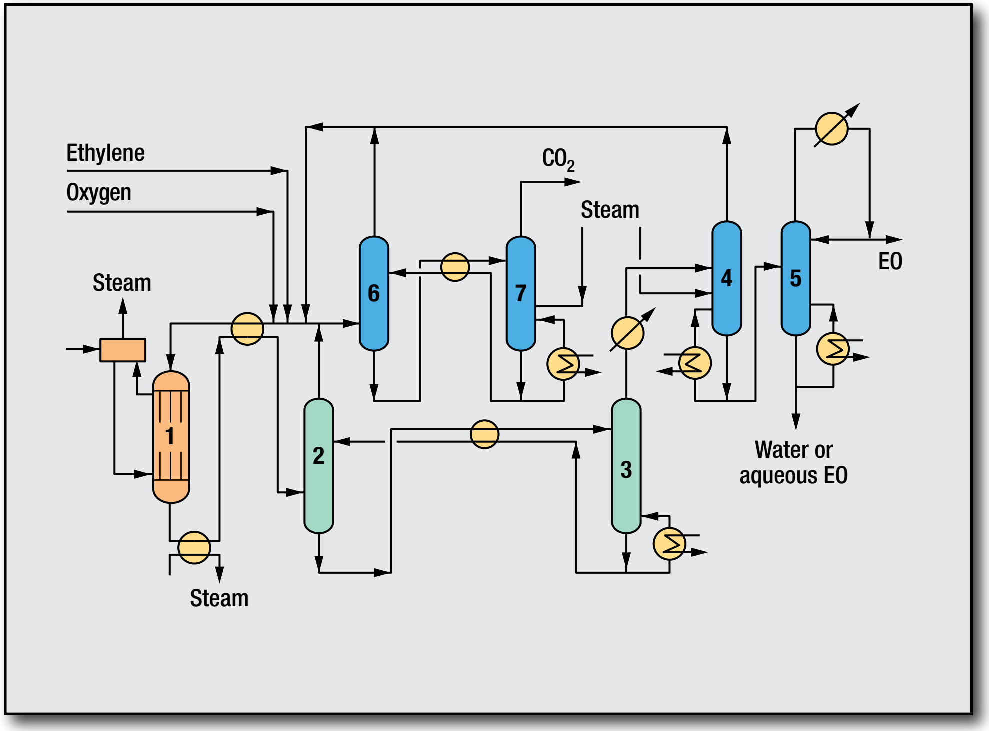
Product quality: The EO product meets the low aldehyde specification of 10 ppm maximum, which is required for EO derivatives production.

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: Over 50 purified EO licenses have been awarded to SD. This represents a total design capacity of about 4 million metric tons of purified EO with the largest plant exceeding 200,000 metric tpy.

Licensor: Scientific Design Company, Inc. - CONTACT

Ethylene oxide (EO)



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 reactors 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 CO_2, a byproduct of the EO reaction that has various commercial applications.

Most EO plants are integrated with (mono) ethylene glycol, (M)EG production facilities. In such an integrated EO/(M)EG facility, the steam system can be optimized to fully exploit the benefits of high-selectivity EO 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 CRI EO catalyst at a molar EO catalyst selectivity of 91%–92% with fresh catalyst and 89–90% as an average over three years of 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 times between catalyst changes.

Commercial plants: Since 1958, more than 70 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.

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.

Licensor: Shell Global Solutions International B.V. - CONTACT

Ethylene oxide/Ethylene glycols

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

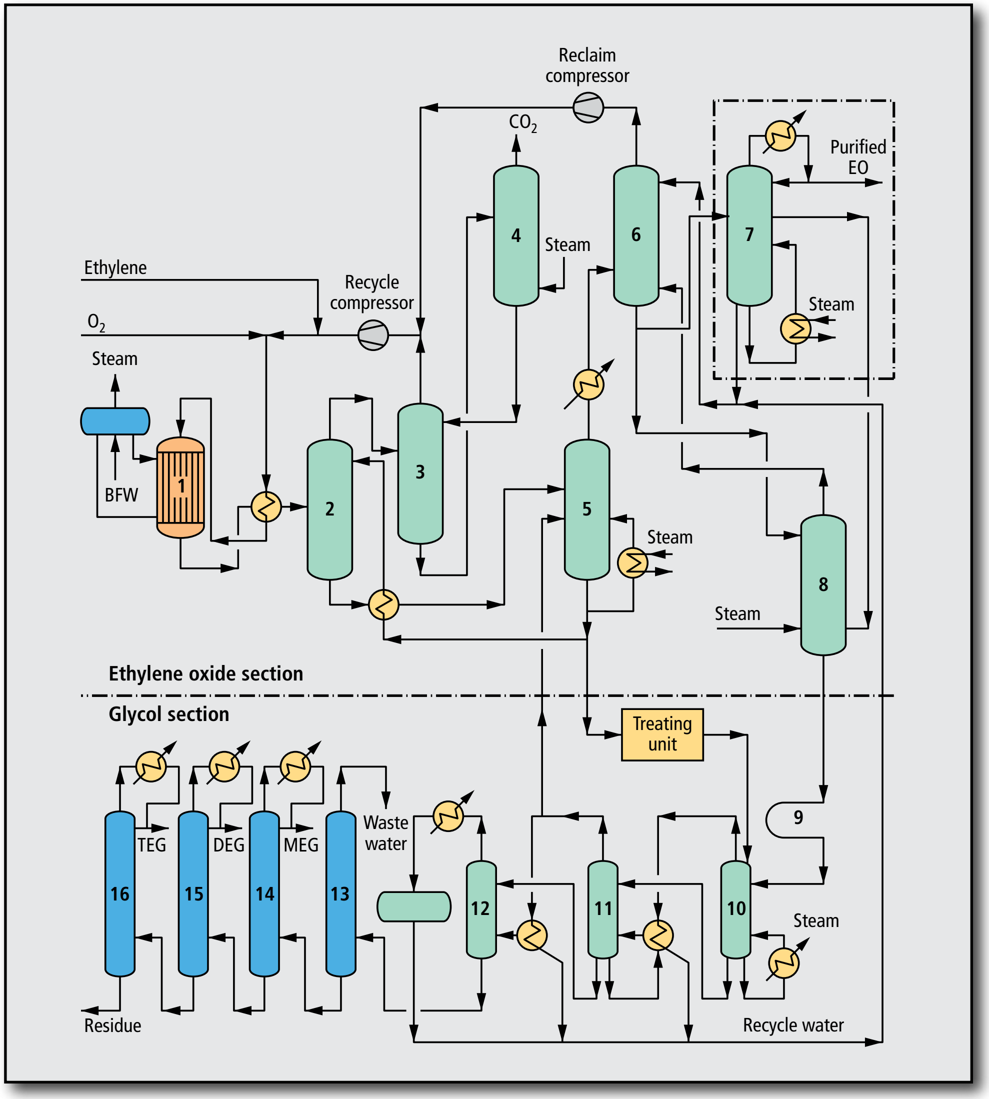
Modern EO/EG plants are highly integrated units where EO produced in the EO reaction system can be recovered as glycols (MEG, DEG and TEG) with a co-product of purified EO, if desired. Process integration allows for a significant utilities savings as well as the recovery of all bleed streams as high-grade 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 (CO_2) 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) 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.



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

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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 100 EO/EG plants using the SD technology have been built. Among the four world's largest capacity MEG plants, three were engineered by SD at 700,000 metric tpy MEG each. Two of these plants were commissioned in 2009, with the third scheduled for startup in the fall of 2010.

Licensor: Scientific Design Company, Inc. - CONTACT

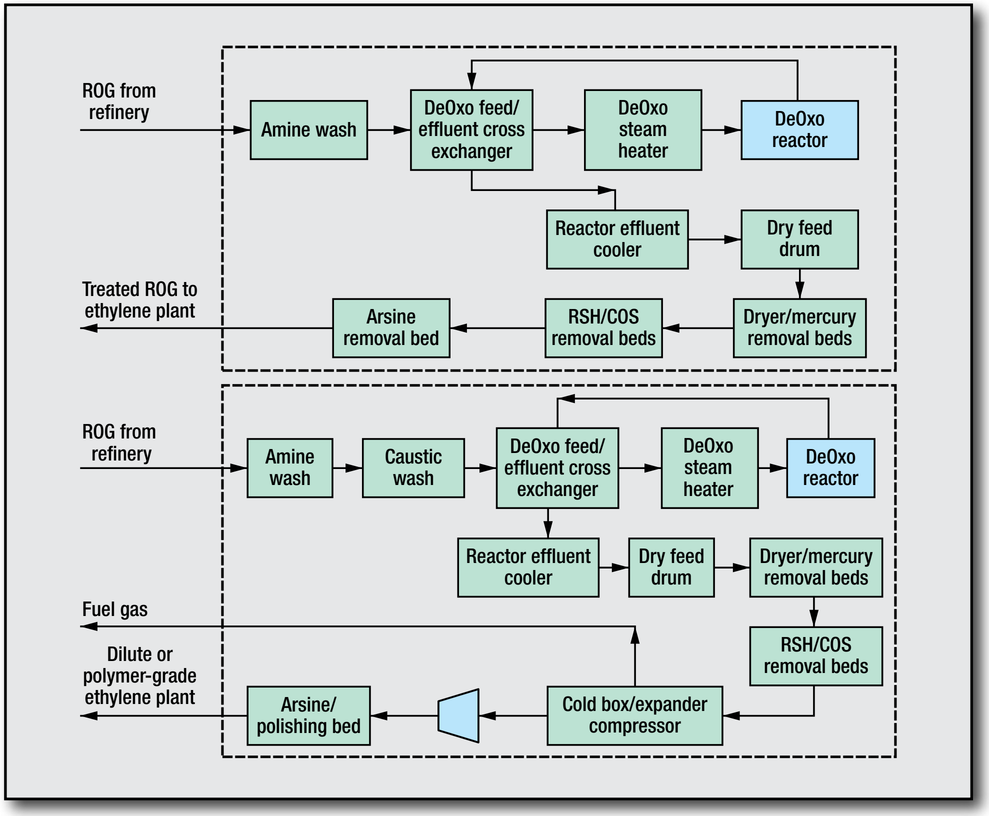
Ethylene recovery from refinery offgas with contaminant removal

Application: Shaw's Refinery Offgas (ROG) technology is used to purify fluid catalytic cracker (FCC) unit offgas. Normally, this contaminated gas is combined with the refinery fuel gas system. The ROG technology allows valuable ethylene and propylene to be recovered and sold primarily as polymer-grade product. However, FCC offgas often contains many light components and contaminants, making the contained ethylene unsalable as either a dilutant or polymer-grade product. An ROG unit can be designed to provide various levels of purification. At a minimum, the ROG unit provides a level of purity that allows the stream to be further processed in an ethylene plant recovery section.

Description: The ROG unit is broken down into sections including feed contaminant removal, ethylene recovery and propylene recovery. Feed contaminants including acid gases, oxygen, NO_x, arsine, mercury, ammonia, nitrites, COS, acetylenes and water must be removed. It is critical that the designer of the unit be experienced with feedstock pretreatment since many of the trace components in the offgas can have an impact on the ultimate product purity, catalyst performance and operational safety.

The ROG unit can include an ethylene recovery section that produces either dilutant or polymer-grade ethylene. Otherwise, the purified offgas stream is directed into the ethylene plant for further purification and recovery. Depending on the capacity constraints of the ethylene plant or the offgas quantity of methane, nitrogen and hydrogen, the ROG unit may include a cold box, followed by a demethanizer, a deethanizer and for polymer-grade ethylene, a C_2 splitter as well.

The ROG unit can be designed to remove contaminants including acid gases, COS, RSH, NO_2, NH_3, HCN, H_2O, AsH_3 and Hg. The difficult contaminants to remove are oxygen and NO_x, which are typically removed by hydrogenation to H_2O and NH_3. Commercially available hydrogenation catalysts generally cause significant loss of the ethylene to ethane.



BASF and Shaw worked together to develop a reactor design based on the BASF copper-based catalyst PuriStar(R) R3-81, which is capable of essentially complete hydrogenation of the oxygen and NO_x with minimal ethylene loss. The R3-81 catalyst is also more resistant to poisons and offers more operational stability than previous catalyst technologies. Elimination of oxygen and NO_x is necessary for the safe operation of the subsequent processing steps of the ethylene plant. Oxygen and NO_x can promote the formation of potentially explosive deposits or plug the cold box.

Continued ▼

Ethylene recovery, *continued*

Economics: ROG streams from FCC units, deep catalytic cracking (DCC) units, catalytic pyrolysis process (CPP) units and coker units are normally used as fuel gas in refineries. However, these streams contain significant amounts of olefins (ethylene and propylene), which can be economically recovered. In fact, many such streams can be recovered with project payout times of less than one year.

Commercial plants: The R3-81 catalyst has been in commercial operation at several refineries since 2005. There have been eight ROG units placed in operation since 1997. Five of those units utilize the R3-81 catalyst. There are seven more units planning start-ups in the next two years.

Licensor: The Shaw Group - CONTACT

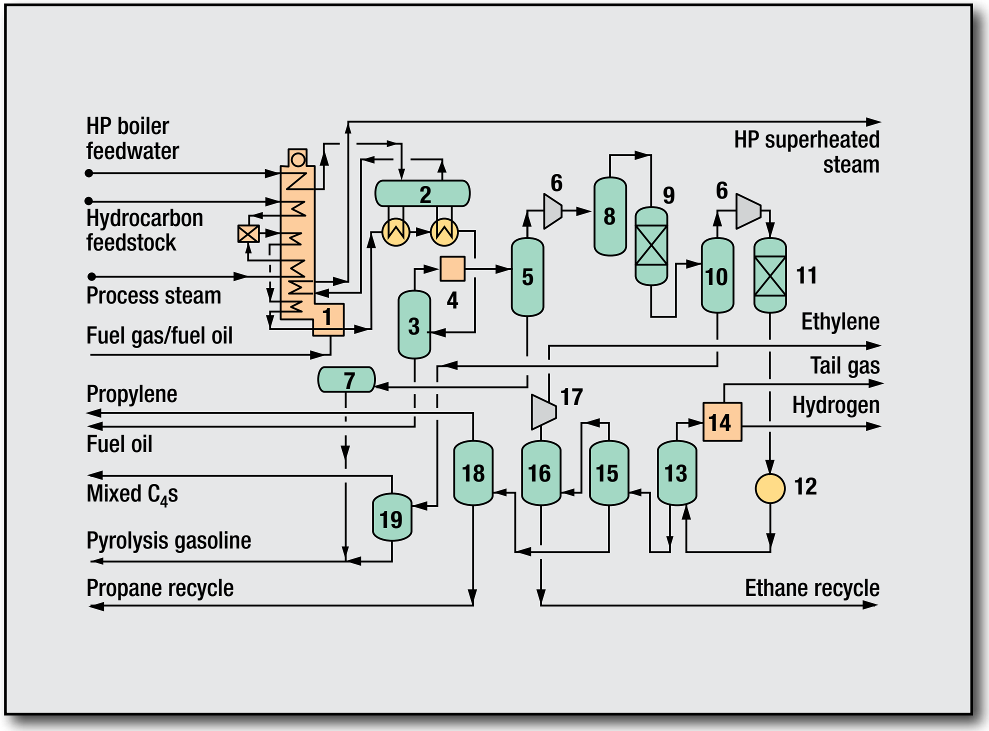
Ethylene, SUPERFLEX

Application: Advanced steam-cracking and cryogenic recovery process to produce polymer-grade ethylene and propylene, butadiene-rich mixed C_4s, aromatic-rich pyrolysis gasoline, hydrogen and fuel streams. Cracking feedstocks range from ethane through vacuum gasoils.

Description: The proprietary Selective Cracking Optimum REcovery (SCORE) olefins process combines the technologies, know-how and expertise of a major engineer designer, Kellogg Brown & Root (KBR) and one of the world's largest ethylene producers, ExxonMobil Chemical Co. KBR is the only licensor with a long-term, worldwide licensing agreement with such an ethylene producer. Through the efforts of both companies, the result is an innovative and differentiated technology backed by extensive ethylene operating experience to further improve operability and reliability, and reduce production costs.

The SCORE pyrolysis furnace features a single straight radiant-tube design with feed entering the bottom and cracked gas leaving the top of the furnace. This results in the lowest practical reaction time (~0.1 seconds) in the industry and low operating pressures. At these conditions, olefins yields are the highest that can be commercially attained. For today's large-scale ethylene plants, this yield advantage translates to over $30 million per year additional gross revenues. Additional features such as hybrid cracking, online decoking and ultra low-NO_x burners all combine to make the SCORE furnace safe, flexible, cost-effective and environmentally friendly. An optimized KBR design can eliminate an incremental furnace, thereby saving up to $30 million in capital costs.

The recovery section is based on a front-end acetylene reactor design pioneered by KBR. This feature, combined with integration of fractionators with the major compressors leads to a design with a lower equipment count and capital cost. Such integration also leads to a plant that is easy to operate with lower maintenance, yet highly competitive with regard to energy due to low-pressure operation. Because of these features and the higher olefins selectivity from cracking operations leading to lower overall plant throughput, recovery section capital cost is reduced significantly by tens of millions of dollars.



The pyrolysis furnace (1) cracks the feed hydrocarbon in the presence of dilution steam into large amounts of ethylene, propylene and byproducts. The furnace effluent is cooled by generating steam (2) and quenched further (3–5) to remove heavy gasoline (7), fuel oil and dilution steam. The cooled process gas is compressed (6), caustic-washed (8) and dried (9). The first fractionator is typically a deethanizer for light-gas feeds or a depropanizer for heavier feeds. Both schemes were pioneered by KBR and share common attributes leading to low cost and energy. The example which follows is for a depropanizer-first scheme. The depropanizer (10) is heat pumped by the last stage of the cracked-gas compressor (6). The acetylene in the depropanizer overhead is hydroge-

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nated in an acetylene reactor (11), and the C_3 and lighter stream is sent to the demethanizer system (12–14) to separate methane and lighter fraction from the mixed C_2/C_3 stream. The demethanizer (13) bottoms C_2/C_3 stream is sent to the deethanizer (15), which is integrated with the heat-pumped C_2 splitter (16) and C_2 refrigeration compressor (17) in a patented design to save both energy and capital. The C_2 splitter is operated at low pressure to produce ethylene product and ethane recycle. The deethanizer bottoms (mixed C_3 stream) flows to the C_3 splitter (18) where propylene is recovered and propane recycled. The depropanizer bottoms product (C_4^+ stream) flows to the debutanizer (19) for recovery of the mixed C_4 product and aromatic-rich pyrolysis gasoline.

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

Energy: Overall specific energy per ton of ethylene range from 3,000 kcal/kg to 6,000 kcal/kg, depending on feed type and battery limit conditions.

Commercial plants: KBR has been involved in over 150 ethylene projects worldwide with single-train ethylene capacities up to 1.35 million tpy, including 22 new grassroots ethylene plants since 1990. Single-cell SCORE furnaces, up to nearly 200,000 tpy of ethylene from liquid feed have also been commercialized.

Licensor: Kellogg Brown & Root LLC - CONTACT

Formaldehyde

Application: Formaldehyde as a liquid solution of 37 wt%–55 wt% is primarily used in the production of synthetic resins in the wood industry and as feedstock for a wide variety of industrially important chemical compounds.

Description: Formaldehyde solutions are produced by the oxidation of methanol with 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:

$$CH_3OH \rightarrow CH_2O + H_2 \ \Delta h = 84 \text{ kJ/mol}$$

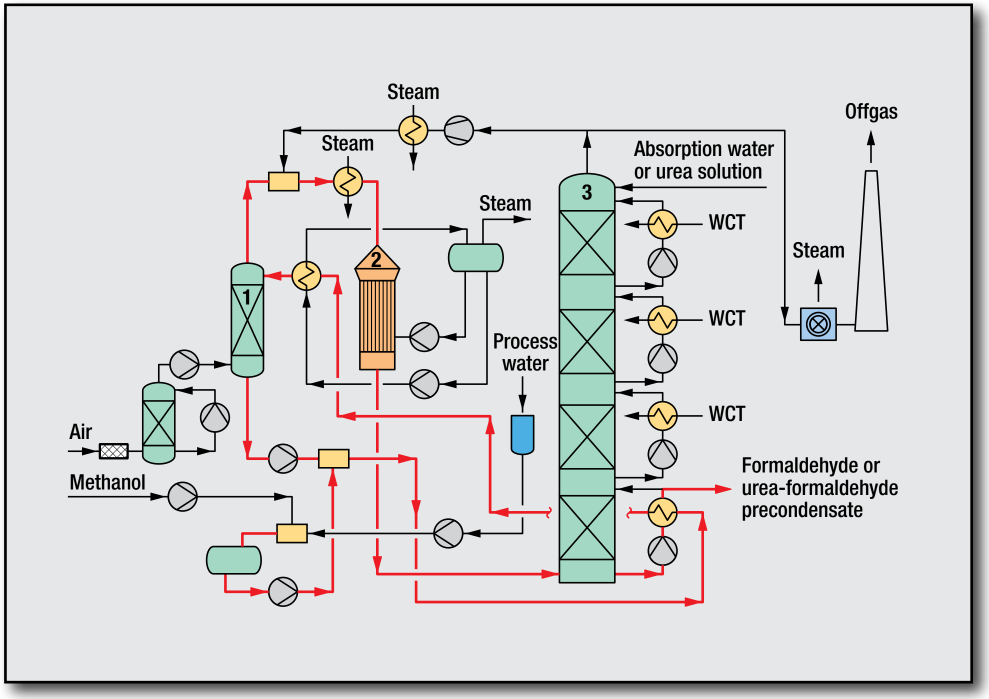
$$CH_3OH + ½ O_2 \rightarrow CH_2O + H_2O \ \Delta H = –159 \text{ kJ/mol}$$

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 unconverted 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 four-stage absorption tower (3), where absorption of formaldehyde occurs in counter-flow to an 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 2,000 kJ/m^3, 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.

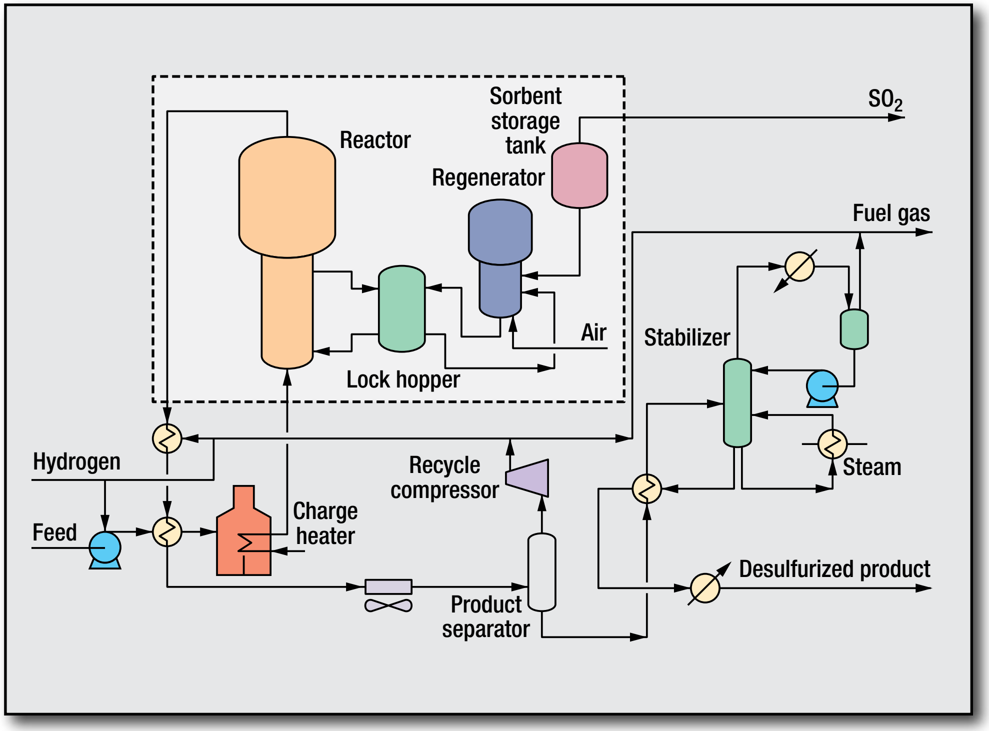
Economics: Due to the waste-gas recycling system, the methanol content in the formaldehyde solution can be reduced to less than 1 wt% and formic acid to less than 90 ppm.

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 - CONTACT

Gasoline, high-quality



Application: S Zorb sulfur removal technology (S Zorb SRT) was originally developed and commercialized by Phillips Petroleum Co. (now ConocoPhillips Co.) SINOPEC purchased the ownership of the S Zorb sulfur removal suite of technologies in July 2007.

Description: S Zorb SRT is designed to remove sulfur from full-range naphtha, from as high as 2,000 μg/g feed sulfur, to as low as < 10 μg/g product sulfur, in a one-step process with high liquid yield and high octane number retention. S Zorb SRT is different from what is commonly known as the hydrodesulfurization (HDS) technologies. What distinguishes S ZorbT SRT from the HDS processes includes:

- High octane number retention (especially for reducing > 1,000 μg/g feed sulfur to < 10 μg/g product sulfur in one step)
- Better selectivity and more reactive toward all sulfur-containing species for S Zorb sorbent
- Low net hydrogen consumption, low hydrogen feed purity needed; reformer hydrogen is an acceptable hydrogen source
- Low energy consumption, no pre-splitting of fluid catalytic cracker (FCC) feed stream, full-range naphtha is applicable
- High liquid yield, over 99.7 volume % in most cases
- Renewable sorbent with sustained stable activity to allow synchronization of maintenance schedule with the FCC unit.

Commercial plants: S Zorb SRT has been successfully commercialized in six units. Thirteen units will be commercially operating by the end of 2010.

Licensor: China Petrochemical Technology Co., Ltd. - CONTACT

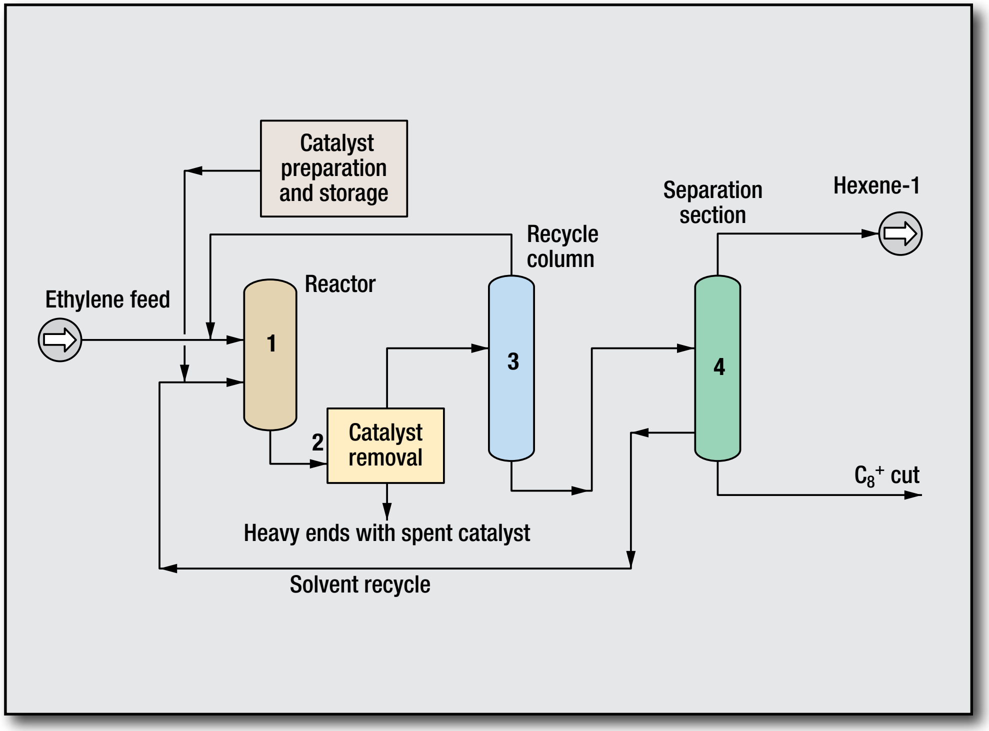
Hexene-1

Application: To produce high-purity hexene-1 that is suitable for copolymers in LLDPE production via the new AlphaHexol process developed by IFP and based on selective ethylene homogeneous trimerization.

Description: Polymer-grade ethylene is oligomerized in a liquid-phase reactor (1) with a liquid homogeneous catalyst system that has 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 and fractionated (4) to produce high-purity hexene-1. Spent catalyst is treated to remove volatile hydrocarbons before safe disposal.

The process is simple; it operates in liquid phase at mild operating temperature and pressure, and only carbon steel equipment is required. The technology has several advantages over other hexene-1 production or supply sources: ethylene feed efficient use, uniformly high-quality product, low impurities and low capital costs.



Yields: LLDPE copolymer grade hexene-1 is produced with a purity exceeding 99 wt%. Typical product specification is:

• Internal olefins	< 0.5
• n-Hexane	< 0.2
• Carbon less than C_6s	< 0.25
• Carbon more than C_6s	< 0.25

Commercial plants: The AlphaHexol process is strongly backed by extensive Axens industrial experience in homogeneous catalysis, in particular, the Alphabutol process for producing butene-1 for which 27 units have been licensed with a cumulated capacity of 570,000 tpy.

Licensor: Axens - CONTACT

Hexene-1

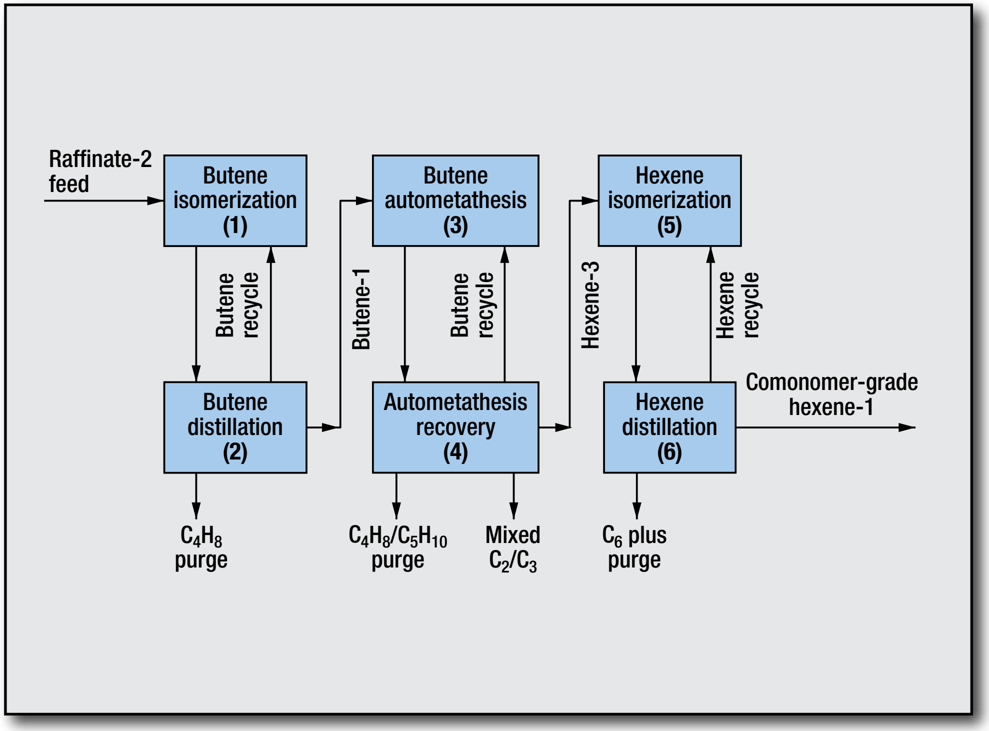
Application: To produce high-purity hexene-1 from a mixed C_4 stream using Lummus' comonomer production technology (CPT). The feedstock can contain any amount of butene-1, butene-2 and butane.

Description: While the following description uses raffinate-2 feed, steam-cracker raw C_4s or raffinate-1 can be used with additional steps for butadiene hydrogenation or isobutene removal before the CPT unit.

In the butene isomerization section (1), raffinate-2 feed from OSBL, mixed with butene recycle from the butene distillation section, is vaporized, preheated and fed to the butene isomerization reactor where butene-2 is isomerized to butene-1 over a fixed bed of proprietary isomerization catalyst. Reactor effluent is cooled and flows to the butene distillation section (2) where it is separated in a butene fractionator into butene-1 for feed to metathesis and recycle butene-2.

The butene-1 is mixed with butene recycle from the autometathesis recovery section and is vaporized, preheated and fed to the autometathesis reactor (3) where butene-1 reacts with itself to form hexene-3 and ethylene over a fixed bed of proprietary metathesis catalyst. Some propylene and pentene are also formed from the reaction of butene-2 in the butene-1 feed. Reactor effluent is cooled and flows to the autometathesis recovery section (4), where two fractionation columns separate it into a hexene-3 product that flows to the hexene isomerization unit (5), an ethylene/propylene mix, and butene-1 that is recycled to the butene autometathesis section. A purge of butenes/C_5s is sent to battery limits.

Hexene-3 from the autometathesis unit is mixed with hexene recycle from the hexene distillation section and is vaporized, preheated and fed to the hexene isomerization reactor where hexene-3 is isomerized to hexene-1 and hexene-2 over a fixed bed of proprietary isomerization catalyst. Reactor effluent is cooled and flows to the hexene distillation section (6) where fractionators separate it into hexene-1 product, recycle hexene-2/hexene-3, and a purge to remove any heavies present in the hexene-3 feed.



Yields and product quality:

Typical yields

	metric ton/metric ton hexene-1	
Feed		
n-Butenes (100% basis)	1.61	
Main products		
Hexene-1	1.00	
Ethylene	0.30	
Propylene	0.11	
C_5^+	0.20	
Typical product quality		
1-hexene	99 wt%	min
Other C_6 olefins	1 wt%	max

Continued ▼

Hexene-1, *continued*

Economics:

Typical utilities, per metric ton hexene-1 (80% butenes in feed)

Steam + fuel, MMKcal	5.3
Water, cooling (10°C rise), m^3	1400
Electricity, MWh	0.2
Refrigeration (–25°C) MMKcal	0.2

Commercial plants: The hexene-1 process has been demonstrated in a semi-commercial unit in Tianjin, China. The unit produced commercially accepted hexene-1 comonomer suitable for high-grade LLDPE used in film production. A CPT facility for butene-1 production is expected to start up in 2011.

Licensor: Lummus Technology - CONTACT

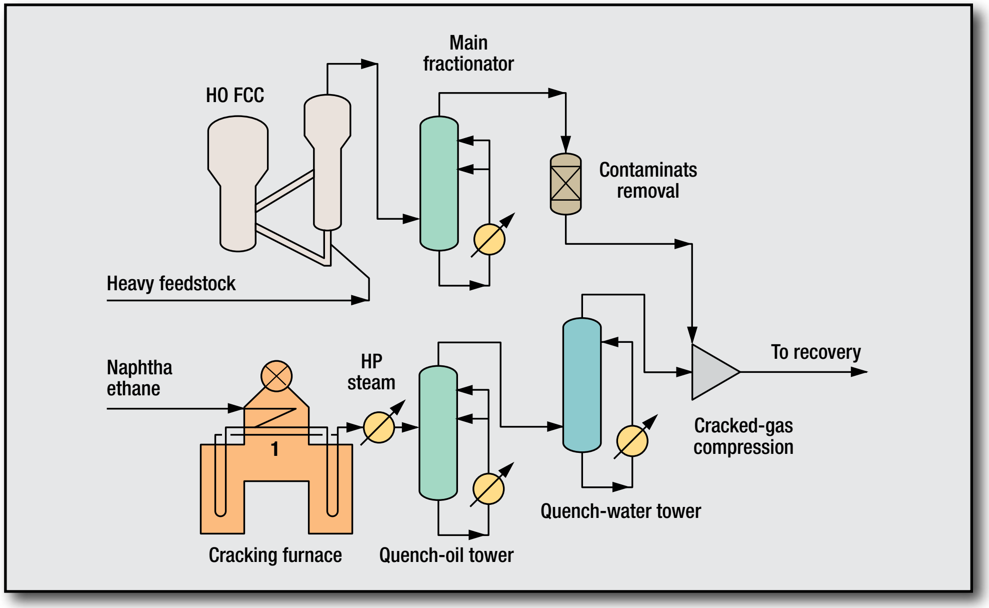
High-olefins FCC and ethylene plant integration

Application: To convert a wide range of hydrocarbon feedstocks, from ethane to vacuum gasoils (VGOs), into high-value light olefins. High olefins fluid catalytic cracking (HO FCC) processes, such as catalytic pyrolysis process (CPP) and deep catalytic cracking (DCC) are technologies that produce higher yields of ethylene and propylene than fluidized catalytic cracking (FCC). Both steam cracking and HO FCC reactor systems can be operated separately but are designed with a shared recovery system to reduce capital cost.

Description: HO FCC technologies are fluidized cracking processes that convert heavy feedstocks, including vacuum and atmospheric gasoils, to gasoline, diesel and light olefins. The HO FCC reactor systems produce 15 wt%–25 wt% propylene or 10 wt%–20 wt% ethylene. Steam cracking is commonly used on feedstocks from ethane to light GOs. The higher cracking temperatures of pyrolysis will result in higher ethylene yield than the HO FCC processes. Heavy GO feedstocks would foul the cracking furnace too quickly to be economical. To process both heavy GOs and light feeds, both fluidized catalytic cracking and steam cracking reactor systems are applied.

The HO FCC unit effluent must first be processed in an FCC style main fractionator. The main fractionator must remove catalyst fines from the heavy-oil product. The main fractionator also produces a light cycle oil and an overhead gas that is primarily light hydrocarbons and gasoline. The overhead of the main fractionator can be further processed via a wet-gas compressor. The gas is then stripped with the gasoline absorbed via a lean-oil absorber, followed by amine treatment and finally a caustic wash. The combined effluents are sent to compression and into a series of contaminant removal beds and hydrogenation steps.

The heavy GO feedstocks always include contaminants that foul subsequent purification processes like the driers and hydrogenation reactors. Therefore, the HO FCC effluent needs to be processed through contaminant removal beds prior to entering the ethylene recovery unit. If both steam cracking and the HO FCC reactor are processing contaminated feeds, the caustic system, oxygen and NO_x hydrogenation, mercaptan, mercury, COS and arsine removal beds can also be shared, as shown in the figure.



This integrated technology is suitable for revamps of ethylene plants, as well as grassroots applications. The figure shows a maximum integration scenario for an HO FCC and steam cracking. The level of integration is a function of contaminant levels, HO FCC effluent gas composition and other capital reduction considerations.

Commercial plants: Currently, one integrated DCC and ethane cracker is in operation in Rabigh, Saudi Arabia. A CPP unit has recently started up this year in Shenyang, China. There are three DCC units currently in design, with planned startup dates in 2011.

Licensor: The Shaw Group - CONTACT

Isobutylene

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

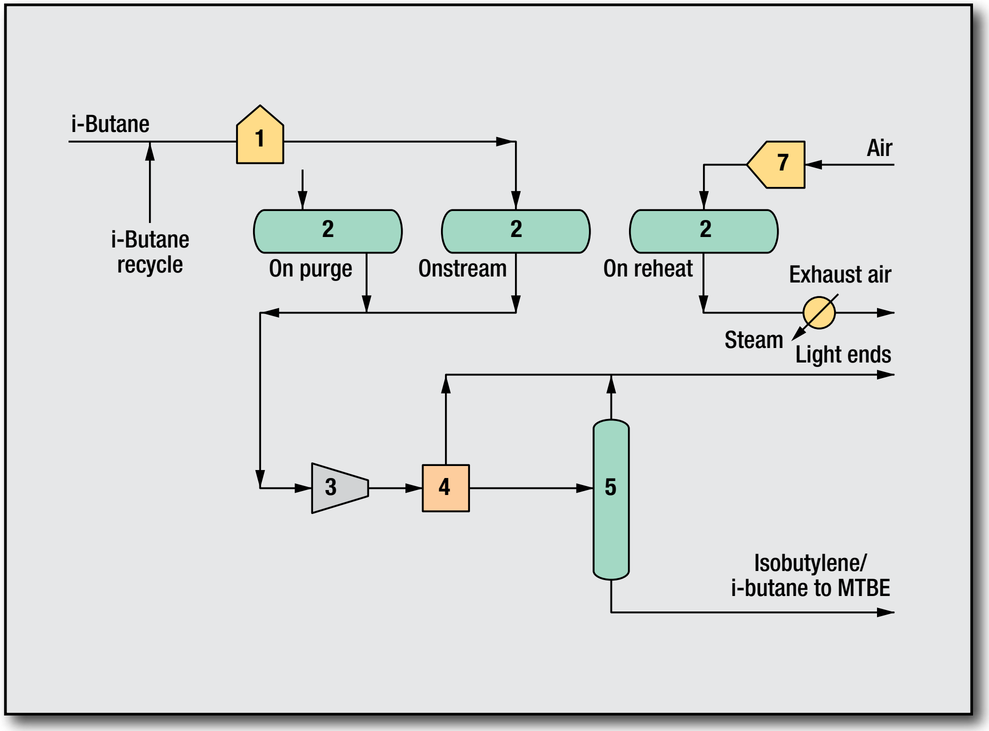
Description: The CATOFIN reaction system consists of parallel fixed-bed reactors and a regeneration air system. The reactors are cycled through a sequence consisting of reaction, regeneration and evacuation/purge steps. Multiple reactors are used so that the reactor feed/product system and regeneration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

Fresh isobutane feed is combined with recycle feed from the downstream unit, 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. Condensed liquid from the recovery section is sent to a depropanizer (5), where the remaining propane and lighter components are separated from the C_4s.The bottoms stream containing isobutane, isobutylene, and other C_4s is sent to the downstream unit (usually an MTBE unit). The unconverted isobutane is recycled back from the downstream MTBE unit to the CATOFIN 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.

The low operating pressure and temperature of CATOFIN reactors, along with the robust Süd-Chemie catalyst, allows the CATOFIN technology to process isobutane feedstock without fouling of process equipment. The simple reactor construction, with its simple internals, results in a very high on-stream factor.



Yields and product quality: Isobutylene produced by the CATOFIN process is typically used for the production of MTBE. The consumption of isobutane (100%) is 1.14 metric ton (mt) per mt of isobutylene 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 designed to date are for 650,000 mtpy propylene and 452,000 mtpy isobutylene) minimizes the investment cost/mt of product.

Continued ▼

Raw material and utilities, per metric ton of isobutylene

Isobutane, metric ton	1.14
Power, kWh	39
Fuel, MWh	0.49

Commercial plants: Currently eight CATOFIN dehydrogenation plants are on stream producing over 1.8 million metric tpy of isobutylene and 1.16 million metric tpy of propylene.

Licensor: Lummus Technology - CONTACT

Isobutylene, high-purity

Application: The Snamprogetti Cracking Technology allows producing high-purity isobutylene, which can be used as monomer for elastomers (polyisobutylene, butyl rubber) and/or as an intermediate for the production of chemicals—MMA, tertiary-butyl phenols, tertiary-butyl amines, etc.

Feed: Methyl tertiary butyl ether (MTBE) can be used as feedstock in the plant. In the case of high level of impurities, a purification section can be added before the reactor.

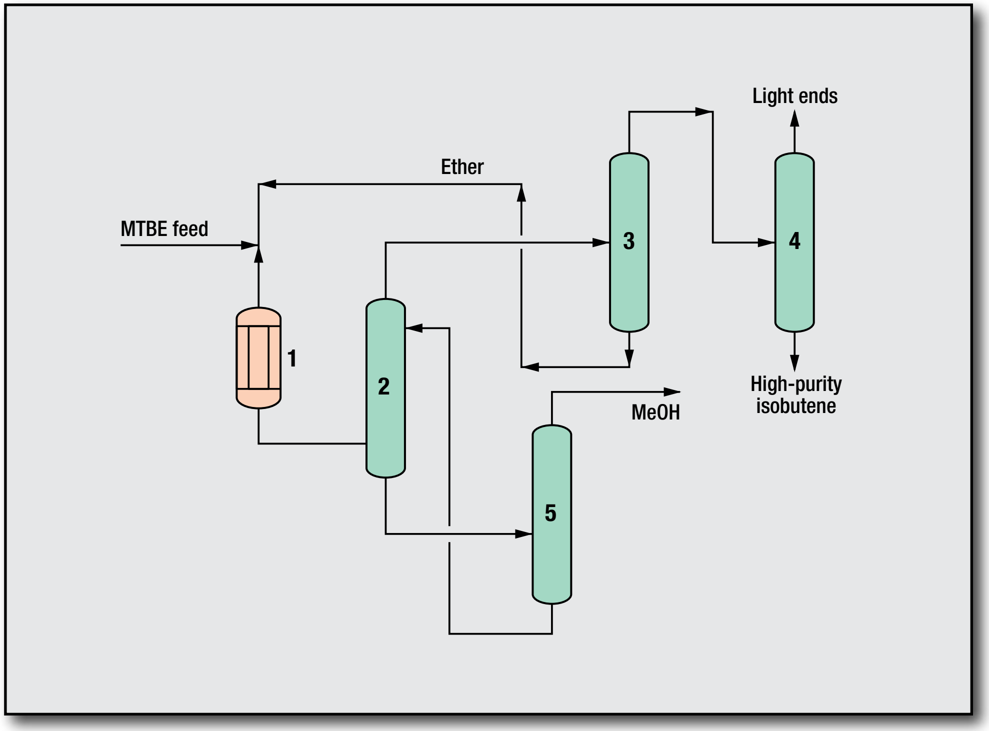
Description: The MTBE cracking technology is based on proprietary catalyst and reactor that carry out the reaction with excellent flexibility and mild conditions as well as without corrosion and environmental problems. With Snamprogetti consolidated technology, it is possible to reach the desired isobutylene purity and production with only one tubular reactor (1) filled with a proprietary catalyst characterized for the right balance between acidity and activity.

The reaction effluent, mainly consisting of isobutylene, methanol and unconverted MTBE, is sent to a counter-current washing tower (2) to separate out methanol, and then to two fractionation towers to separate isobutylene from unconverted MTBE, which is recycled to the reactor (3) and from light compounds (4). The produced isobutylene has a product purity of 99.9^{+} wt%.

The methanol/water solution leaving the washing tower is fed to the alcohol recovery section (5), where high-quality methanol is recovered.

Utilities:

Steam, ton/ton isobutylene	5
Water, cooling, m^3/ton isobutylene	186
Power, kWh/ton isobutylene	17.4



Commercial plants: Six units have been licensed by Saipem.

Licensor: Saipem - CONTACT

Isomerization

Application: Convert iso-olefins to normal olefins.

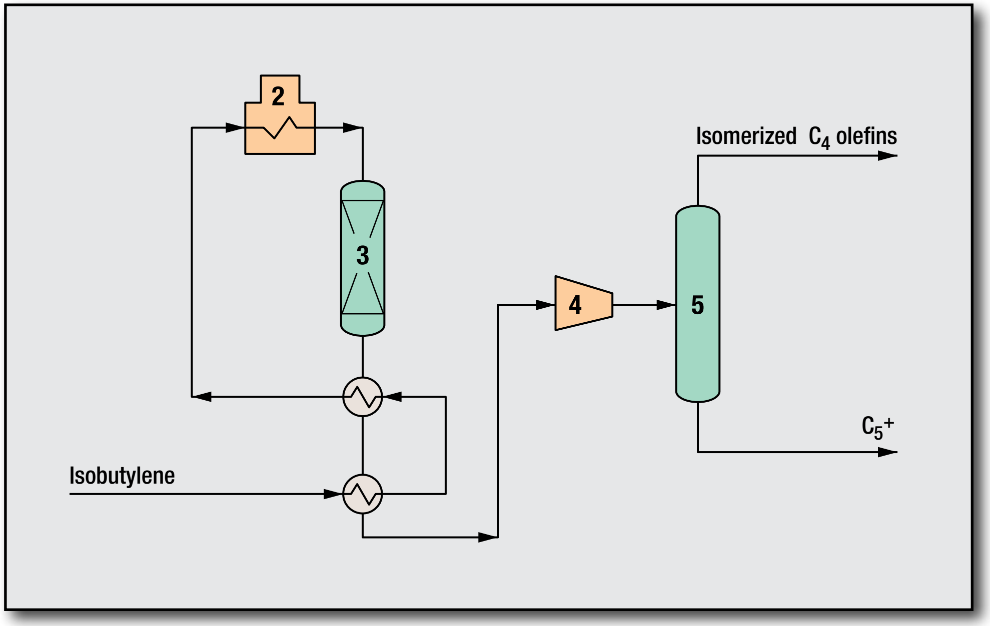
Description:

C_4 olefin skeletal isomerization (CD*Isis*)

A zeolite-based catalyst especially developed for this process provides near equilibrium conversion of isobutylene to normal butenes at high selectivity and long process cycle times. A simple process scheme and moderate process conditions result in low capital and operating costs. Hydrocarbon feed containing isobutylene, such as C_4 raffinate or FCC C_4s, can be processed without steam or other diluents, nor the addition of catalyst activation agents to promote the reaction. Near-equilibrium conversion of the contained isobutylene per pass is achieved at greater than 85% selectivity to isobutylene. At the end of the process cycle, the catalyst bed is regenerated by oxidizing the coke with an air/nitrogen mixture. The butene isomerate is suitable for making various petrochemical such as propylene via Olefin Conversion Technology.

Economics: The CD*Isis* isomerization process offers the advantages of low capital investment and operating costs coupled with a high yield of isobutylene. Also, the small quantity of heavy byproducts formed can easily be blended into the gasoline pool. Capital costs (equipment, labor and detailed engineering) for three different plant sizes are:

Total installed cost:	**Feedrate, Mbpd**	**ISBL cost, $MM**
	10	8
	15	11
	30	30



Utility costs: per barrel of feed (assuming an electric-motor-driven compressor) are:

Power, kWh	3.2
Fuel gas, MMBtu	0.44
Steam, MP, MMBtu	0.002
Water, cooling, MMBtu	0.051
Nitrogen, scf	57–250

Commercial plants: Three plants are in operation. Three licensed units are in various stages of design.

Licensor: CDTECH - CONTACT

Isomerization

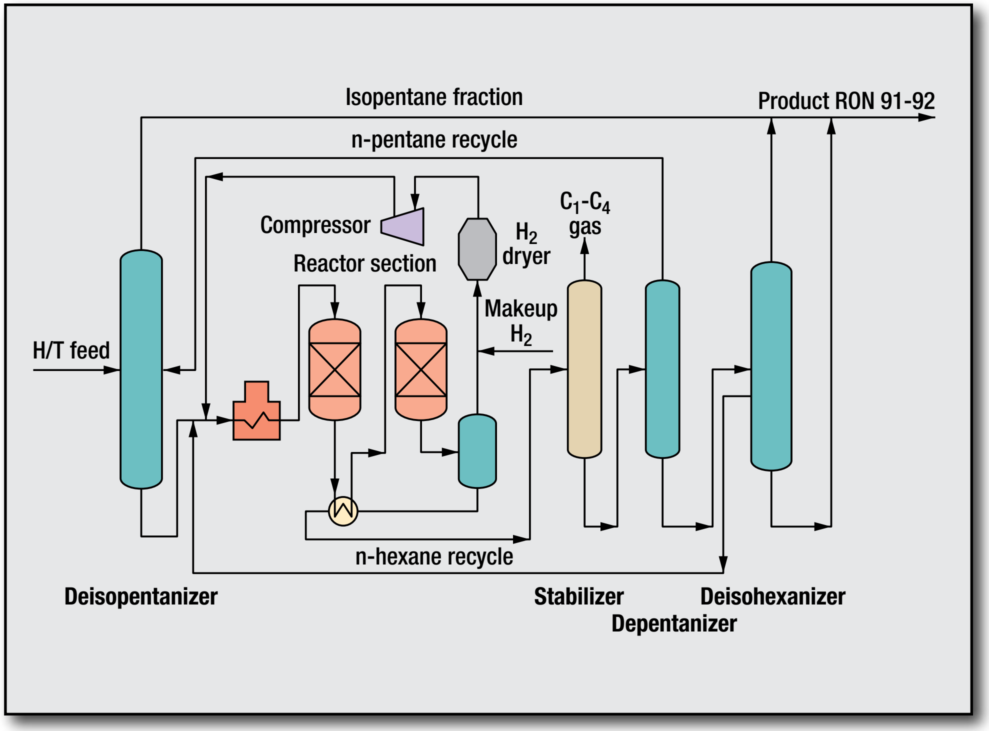
Application: Isomalk-2 is a broad-range isomerization technology developed by NPP Neftehim, which has been commercially proven in various regions of the world. Isomalk-2 is a competitive alternative to the three most commonly used light gasoline isomerization processes: zeolite, chlorinated alumina and sulfated oxide catalysts.

Description: Isomalk-2 offers refiners cost-effective isomerization options that have consistently demonstrated reliable performance with all standard process configurations, including once-through isomerization, once-through with pre-fractionation, recycle of low-octane pentanes and hexanes, and benzene reduction

Each scheme generates different yield and octane results. The examples given below are for a light straight-run (LSR) process stream, but could also be applied to a reformate stream or some LSR/reformate combinations. In a once-through isomerization process scheme, the LSR is mixed with the hydrogen makeup gas; the mixture is then heated and enters a first reactor where benzene saturation and partial isomerization take place.

The gas-product mixture exits the first reactor, is cooled and fed to a second reactor to complete the isomerization reaction at chemical equilibrium. The product mixture from the second reactor is cooled and fed to a gas separator, where the mixture is separated from the excess hydrogen gas. Excess hydrogen is combined with makeup hydrogen and fed through the recycle dryers for blending with feed. There is no hydrocarbon feed drying step required.

Saturated isomerate from the separator is heated and fed to the stabilizer. The stabilizer's overhead vapors are cooled and fed to a reflux drum. Liquid hydrocarbons from the reflux drum are returned to the stabilizer as reflux; while uncondensed light hydrocarbons are separated and sent to the offgas system. The bottom product or isomerate is cooled and sent to gasoline blending.



In an isomerization process scheme with recycle of low-octane hexanes, the isomerate is produced and then fed to a fractionation column(s). Overhead and bottoms isomerate streams are cooled and sent to gasoline blending. A low-octane C_6 isomerate stream is recycled back to the isomerization unit.

Prefractionation with low-octane recycle can utilize all of the above methods: prefractionation, isomerization and postfractionation. The prefractionation step consists of de-isopentanization of the feed and/or C_7^+ separation. The post fractionation step consists of separating the high octane portion of the C_5–C_6 isomerate and recycling the low-octane C_5 and C_6 isomerate stream.

Continued ▼

Isomerization, *continued*

Process advantages:

- Process capability to produce 82–93 RON gasoline
- Regenerable catalyst with superior tolerance to process impurities and water
- No chloride addition or alkaline wastes
- Operating temperature range of 120°C–180°C
- Mass yield > 98%, volume yield up to 100%
- Up to 5–6 year cycles between regenerations
- Service life 10–12 years
- Reduced hydrogen consumption vs. chloride systems.

Commercial plants: Commercialized technology available for license.

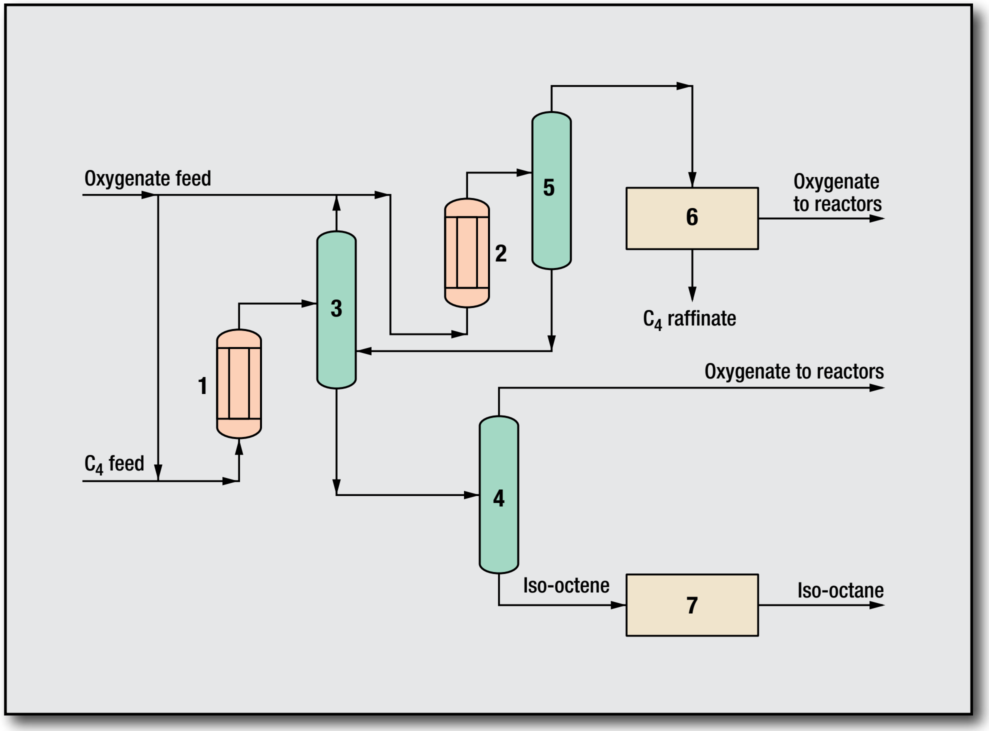
Licensor: GTC Technology - CONTACT

Iso-octene/Iso-octane

Application: The Snamprogetti Dimerization/Hydrogenation Technology is used to produce Iso-octene/Iso-octane—high-octane compounds (rich in C_8) for gasoline blending.

Feed: C_4 streams from steam cracker, fluid catalytic cracking (FCC) and isobutane dehydrogenation units with isobutene contents ranging from 15 wt% to 50 wt%.

Products: Iso-octene and Iso-octane streams contain at least 85 wt% of C_8s with less than 5,000 ppm of oligomers higher than C_{12}s.



Description: Depending on conversion and investment requirements, various options are available to reach isobutene conversion ranging from 85 wt% to 99 wt%.

Oxygenates such as methanol, methyl tertiary butyl ether (MTBE) and/or tert-butyl alcohol (TBA) are used as "selectivator" to improve selectivity of the dimerization reaction while avoiding formation of heavier oligomers.

A high conversion level of isobutene (99%) can be reached with a double-stage configuration where, in both stages, water-cooled tubular reactors (WCTR), (1, 2), are used for the isobutene dimerization to maintain optimal temperature control inside the catalytic bed.

The reactors effluents are sent to two fractionation columns (3, 5) to separate residual C_4 from the mixture oxygenate-dimers. At the end, the oxygenates are recovered from raffinate C_4 (6) and from dimers (4) and then recycled to reactors.

The Iso-octene product, collected as bottoms of column (4), can be sent to storage or fed to the hydrogenation unit (7) to produce the saturate hydrocarbon stream Iso-octane.

Due to a joint development agreement between Saipem and Catalytic Distillation Technologies (CDTech) for the isobutene dimerization (Dimer8 process), the plant configuration can be optionally modified with the introduction of a catalytic distillation (CD column), to have an alternative scheme particularly suitable for revamping refinery MTBE units.

Utilities: (Referred to a feedstock from isobutane dehydrogenation at 50 wt% isobutylene conc.)

Steam, ton/ton Iso-octene	1
Water, cooling, m³/ton Iso-octene	65
Power, kWh/ton Iso-octene	15

Commercial plants: Five industrial tests have been carried out with different feedstocks, and two units have been licensed by Saipem.

Licensor: Saipem - CONTACT

Maleic anhydride

Application: INEOS is the recognized world leader in fluid-bed reactor technology for maleic anhydride production, which it licenses through INEOS Technologies. In addition to technology licensing, INEOS Technologies manufactures and markets the catalyst that is used in both the fixed-bed and fluid-bed reactor maleic anhydride processes.

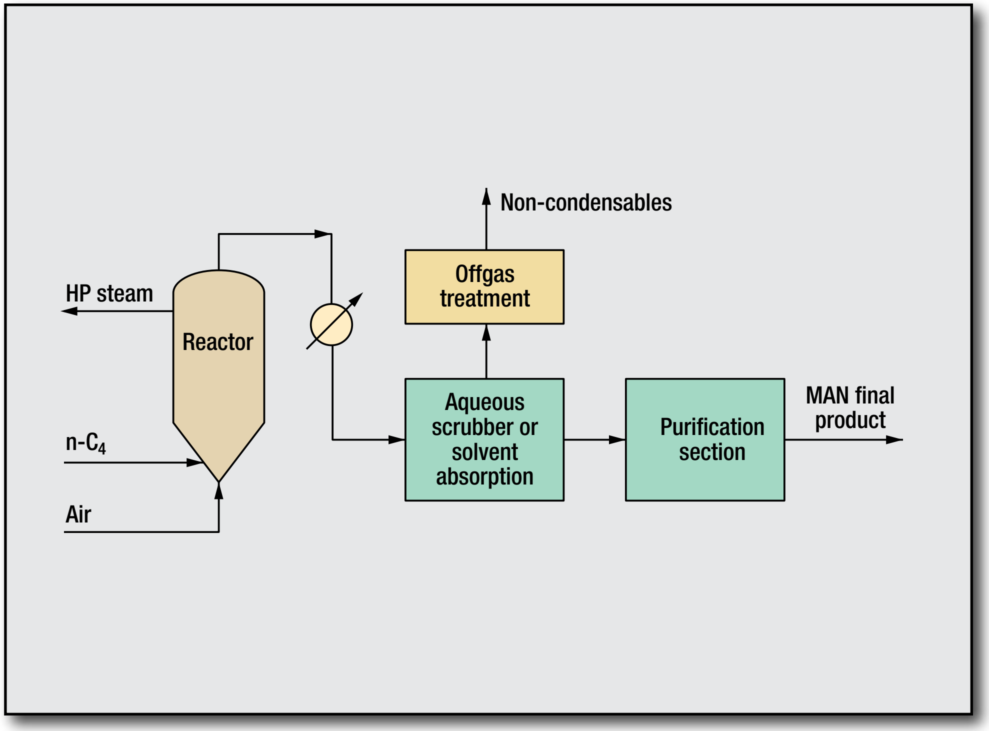
Description: INEOS' maleic anhydride technology uses its proven fluidized-bed reactor system. The feeds, containing n-butane and air, are introduced into the fluid-bed catalytic reactor, which operates at 5 psig to 50 psig with a temperature range of 730°F–860°F (390°C–460°C). This exothermic reaction yields maleic anhydride and valuable high-pressure (HP) steam. The energy-efficient process does not require using molten-salt heat transfer.

The reactor effluent may be either aqueous scrubbed or absorbed by an inorganic solvent. Through either process, essentially 100% recovery of maleic anhydride is achieved. Non-condensables may be vented or incinerated depending on local regulations. Water, light ends and high-boiling impurities are separated in a series of drying, dehydration and fractionation steps to produce maleic anhydride product.

Basic chemistry

n-Butane + Oxygen →Maleic Anhydride + Water

Products and economics: Products include maleic anhydride and HP steam. Instead of exporting steam, a turbo generator can be used to generate electricity. INEOS has applied more than 40 years of experience as an operator and licensor of fluid-bed technology to the INEOS maleic anhydride technology delivering high yields and efficiency with low investment and operating costs, maximum safety and flexibility, exceptional process reliability with less shutdowns and environmentally acceptable effluents. INEOS has also drawn on its many decades of experience in oxidation catalysis in both the fluid-bed and fixed-bed forms to deliver catalysts that meet the needs of the maleic anhydride market.



Catalyst: INEOS developed and commercialized its first fixed-bed catalyst system for the manufacture of maleic anhydride in the 1970s and fluid-bed catalyst system in the 1980s. Since the introduction of this technology, INEOS has also developed and commercialized three generations of improved catalysts. Catalyst improvements have increased yields and efficiencies vs. prior generations to lower manufacturing costs for maleic anhydride. INEOS continues to improve upon and benefit from its long and successful history of catalyst research and development. INEOS' fluid-bed catalyst system does not require change out or regeneration over time, unless the licensee chooses to introduce one of INEOS's newer, more economically attractive catalyst systems. Fixed-bed catalysts provide high yield, low pressure drop and long-term stability.

Continued ▼

Maleic anhydride, *continued*

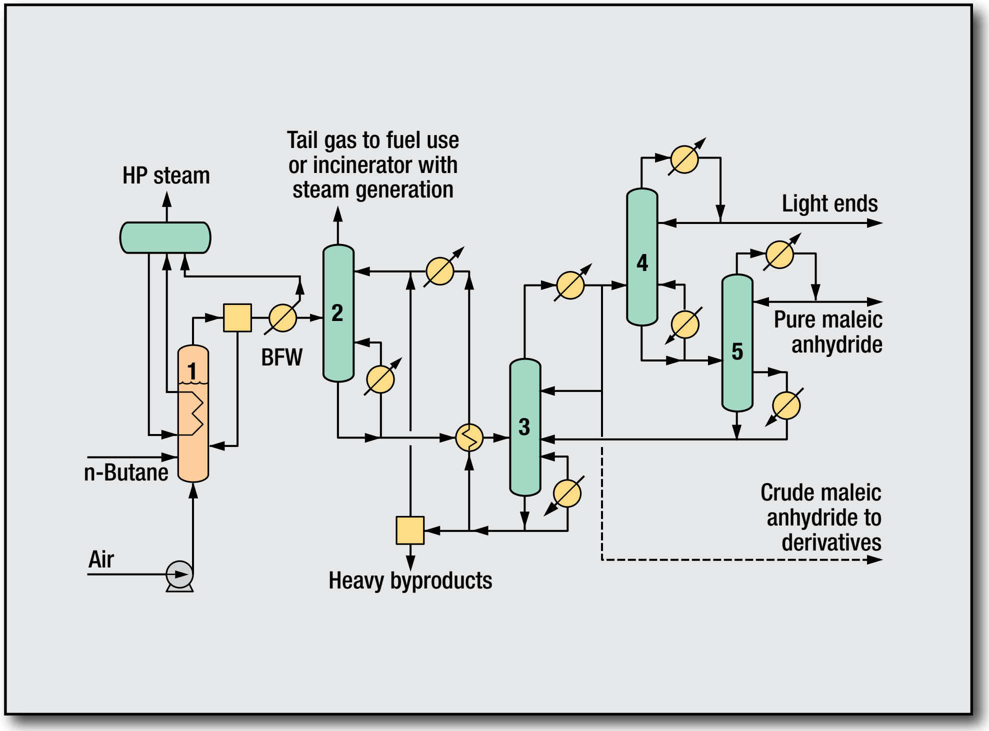
Maleic anhydride end uses: With three active sites (two carboxyl groups and one double bond), maleic anhydride is a preferred joining and cross-linking agent. Maleic anhydride is used as an additive in multiple applications, but also as an intermediate to several downstream products, the largest of which is unsaturated polyester resins (UPR) that is used in glass-fiber reinforced products (marine, automotive and construction applications) and castings and coatings (cultured marble and onyx manufacture). Another major use of maleic anhydride is as a feed to produce butanediol (BDO), which is used as an intermediate to tetrahydrofuran (THF) for spandex and solvents applications, polybutylene terephthalate (PBT) for engineered plastics and gamma-butyrolactone (GBL) for pharmaceutical and solvent applications.

Maleic anhydride is an important intermediate in the fine chemical industry, particularly in the manufacture of agricultural chemicals and lubricating oil additives. It is also a component of several copolymers in the engineering polymers sector as well as a raw material in the production of artificial sweeteners.

Commercial plants: Since the 1980s, INEOS's maleic anhydride fluid-bed reactor and catalyst technologies have been applied in plants ranging from 15,000 tpy to greater than 80,000 tpy; the technology has been demonstrated as safe, stable with efficient operating performance. The above-referenced 80,000-tpy plant is a single-reactor system and represents the largest single-train reactor assembly in the world for maleic anhydride production. In addition, INEOS has installed its fixed-bed maleic anhydride catalyst into commercial plants globally, providing long-life and excellent chemical and mechanical stability.

Licensor: INEOS Technologies. From SOHIO to its successor companies, BP Chemicals, BP Amoco Chemical, Innovene and now INEOS have delivered a successful licensing and technology transfer program with catalyst supply, training, plant start-up support and on-going technical assistance. - CONTACT

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 metric tpy. The largest commercial installation is Lonza's 55,000-metric tpy plant in Ravenna, Italy. Second generation process optimizations and catalyst have elevated the plant performances since 1998.

Licensor: Lummus Technology/Polynt - CONTACT

Melamine, low-pressure process

Application: The low-pressure melamine process is used to produce melamine powder from urea.

Description: The melamine process is a catalytic vapor-phase process operated at pressures below 10 bar.

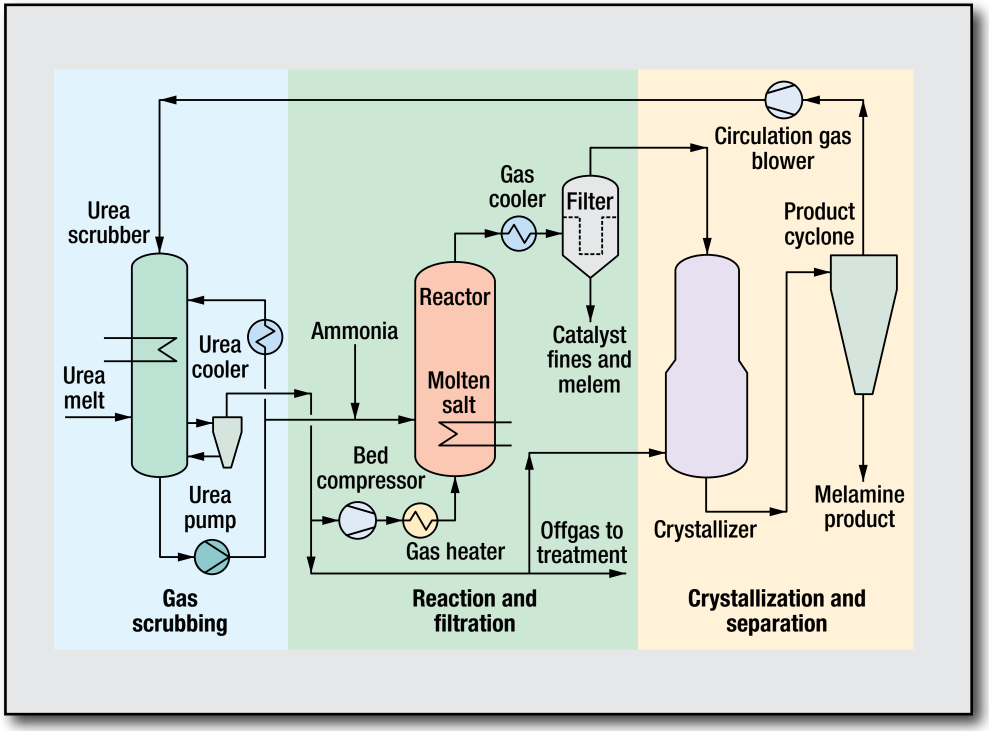
Urea melt is fed into the reactor and is atomized by spray nozzles with the aid of high-pressure ammonia. The reactor is a fluidized bed gas reactor using silica/aluminium oxide as catalyst. The reaction offgas, an ammonia and carbon dioxide mixture, is preheated and is used as fluidizing gas. Conversion of urea to melamine is an endothermic reaction; the necessary heat is supplied via heated molten salt circulated through internal heating coils.

The fluidizing gas leaves the reactor together with gaseous melamine and the byproducts ammonia, carbon dioxide, isocyanic acid and traces of melem. The gas also contains entrained catalyst fines. Melem is separated by desublimation and is removed together with the catalyst fines in a gas filter.

The filtered gas is further cooled in the crystallizer to the desublimation temperature of the melamine product. Cooling is performed using the offgas from the urea scrubber. The melamine forms fine crystals, which are recovered from the process gas in the product-cyclone. Leaving the product-cyclone, the cooled melamine is stored and can be used without further treatment. It has a minimum purity of 99.8%.

The process gas leaving the product-cyclone is fed to the urea scrubber, which is cooled with molten urea. The clean gas leaving the urea scrubber is partially used in the reactor as fluidizing gas and is partially recycled to the crystallizer as quenching gas. The surplus is fed to an offgas treatment unit for further recycling to the urea plant.

This outstanding straight-forward low-pressure process without any water quench, features low corrosion tendency, absence of complicated rotating equipment and need for a drying unit. All factors result in very low capital investment and operating costs.



Economics: Consumption per metric ton of melamine:

Urea melt, tons	3.15, net value 1.5 tons
Ammonia, tons	0.18
Catalyst, kg	3
HP Steam, tons	0.2
Electrical power, kWh	1,030
Natural gas, GJ	13 (approximately 384 Nm³)
Water, cooling, tons	26 t

No quench water required (no wastewater)

Continued ▼

Melamine, low-pressure process, *continued*

Commercial plants: A total capacity of 299,000 metric tpy has been licensed since 1993 within 17 plants. The latest plant, with a capacity of 50,000 metric tpy, was commissioned in October 2009 at the Sichuan Golden Elephant Chemical Industrial zone, Meishan, Sichuan, China. Recently, the list of references has been extended by a 50,000 metric tpy melamine plant to be started up in Russia in 2011.

Licensor: Edgein S&T Co. Ltd./Lurgi GmbH, a company of the Air Liquide Group - CONTACT

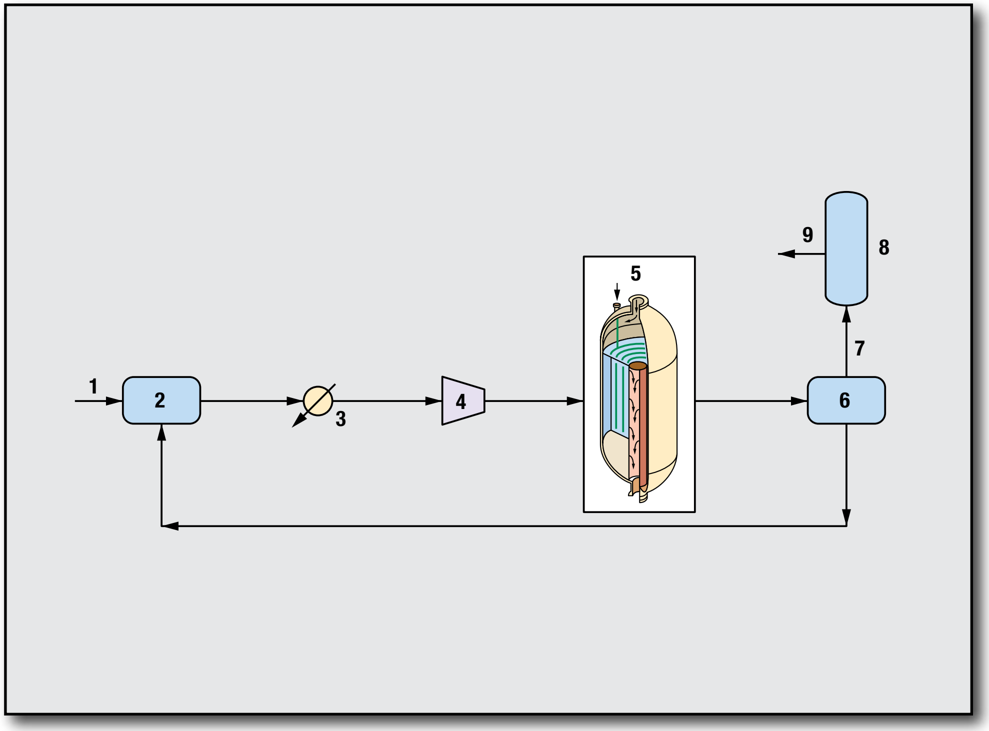
Methanol

Application: To produce methanol from natural gas. The process is based on Casale highly efficient equipment including: The Casale plate cooled technology for the methanol converter.

Description: The natural gas (1) is first desulfurized before entering a primary reformer (2), where it is reformed, reacting with steam to generate synthesis gas, i.e., hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2). The reformed gas is cooled (3) by generating high-pressure (HP) steam, which provides heat for the methanol distillation columns (8). The cooled gas enters the synthesis gas compressor (4), where it is compressed to synthesis pressure.

The compressed syngas reaches the synthesis loop where it is converted to methanol in the Casale plate-cooled converter (5), characterized by the highest conversion per pass and mechanical robustness. The heat of reaction is used to generate directly medium-pressure steam. The gas is cooled (6), and raw methanol (7) is condensed and separated, while the unreacted syngas is circulated back to the converter.

The raw methanol (7) is sent to the distillation section (8), comprising two or three columns, where byproducts and contained water are separated out to obtain the desired purity for the methanol product (9). The inerts contained in the synthesis gas are purged from the loop (10) and recycled as fuel to the primary reformer (2).



Economics: Thanks to the high efficiency of the process and equipment design, the total energy consumptions (evaluated as feeds + fuel + steam import from package boiler and steam export to urea) is about 7 Gcal/metric ton of produced methanol.

Licensor: Methanol Casale SA, Switzerland - CONTACT

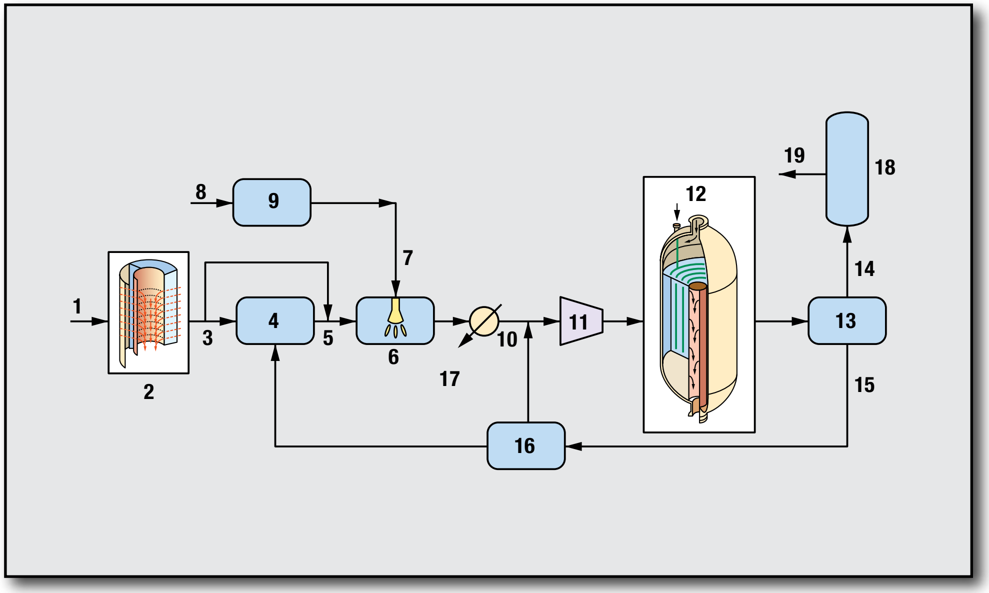
Methanol

Application: To produce methanol from natural gas. The process is based on Casale's highly efficient equipment, including its:

- Casale axial-radial pre-reformer
- Casale high efficiency design for the auto-thermal reformer (ATR)
- Casale plate-cooled technology for the methanol converter.

Description: The natural gas (1) is first desulfurized before entering a prereformer (2) where methane and other hydrocarbons are reacted with steam to be partially converted into synthesis gas, i.e., hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2). The pre-reformer is designed according to the axial-radial technology for catalyst beds from Casale. The partially reformed gas is split (3) in two streams, one entering a primary reformer (4), where the reforming process is further advanced. The second stream joins the first (5) at the primary reformer (4) exit, and the streams enter the ATR (6) where oxygen (7), from air (8) in the air separation unit (9) is injected, and the methane is finally converted into syngas. In this unit, Casale supplies its high-efficiency process burner, characterized by low ΔP, a short flame and high reliability. The reformed gas is cooled (10) by generating high-pressure (HP) steam, which provides heat to the methanol distillation columns (18). The cool reformed gas enters the synthesis gas compressor (11), where it is compressed up to the synthesis pressure.

The compressed syngas reaches the synthesis loop where it is converted into methanol via the Casale plate-cooled converter (12), characterized by the highest conversion per pass and mechanical robustness. The heat of reaction is used to generate directly medium-pressure steam. The gas is cooled (13), and the raw methanol is condensed and separated (14), while the unreacted syngas is circulated back to the converter. The inerts (15) contained in the synthesis gas are purged from the loop, and the hydrogen contained is recovered in a hydrogen recovery unit (HRU) (16) and recycled to the synthesis loop. The remaining inerts (17) are sent to the primary reformer (4) as a fuel.



The raw methanol (14) is sent to the distillation section (18), comprising three columns, where byproduct and contained water are separated out to obtain the desired product purity (19).

Economics: Thanks to the high efficiency of the process and equipment design, the total energy consumption (evaluated as feeds + fuel + steam import from package boiler and steam export to urea) is about 6.7 Gcal/metric ton of produced methanol. Very high capacities are achievable in single-train plants, with one synthesis reactor capacity approaching 10,000 metric tpd.

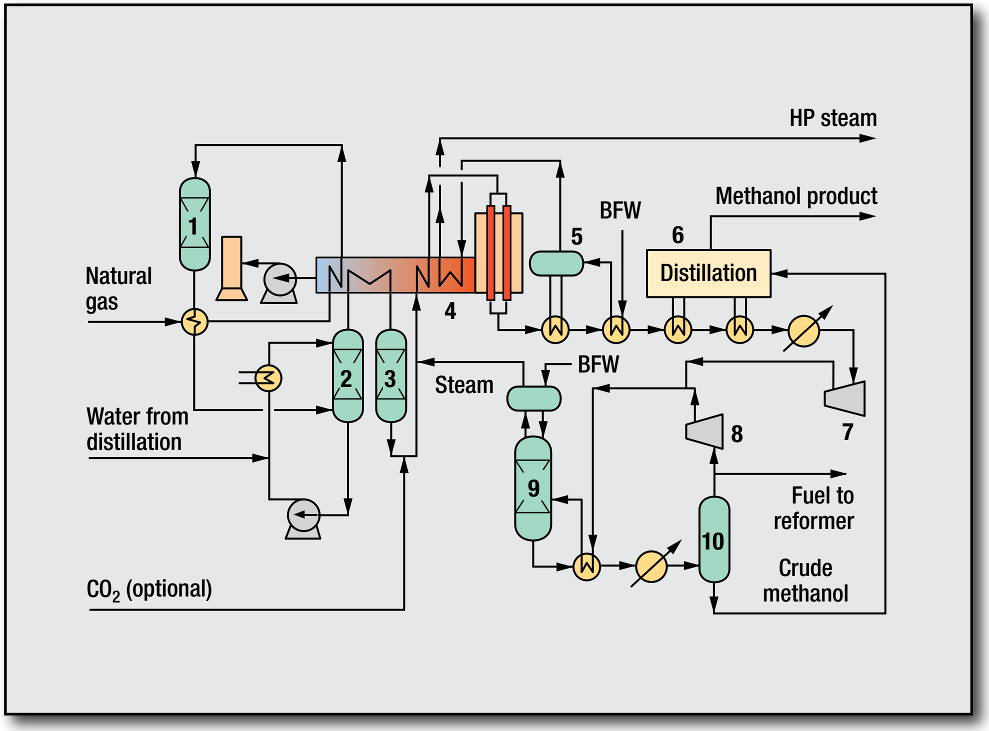
Commercial plants: Four ATR plants are in operation, one 7,000 metric tpd plant is under construction, and seven plate-cooled converters are in operation.

Licensor: Methanol Casale SA, Switzerland - CONTACT

Methanol

Application: The Davy Process Technology–Johnson Matthey process is a low-pressure methanol process. The process produces methanol from natural or associated gas via a reforming step or from syngas generated by the gasification of coal, coke or biomass. The reforming step, also available from this licensor, may be conventional steam reforming (SMR), compact reforming, autothermal reforming (ATR), combined reforming (SMR + ATR) or gas-heated reforming (GHR + ATR). The reforming or gasification step is followed by compression, methanol synthesis and distillation (one, two or three column designs) Capacities up to 7,000 metric tpd, are practical in a single stream and flowsheet options exist for installation of the process offshore on FPSO vessels.

Description: The following description is based on the SMR option. Gas feedstock is compressed (if required), desulfurized (1) and sent to the optional saturator (2) where most of the process steam is generated. The saturator is used where maximum water recovery is important and it also has the benefit of recycling some byproducts. Further process steam is added, and the mixture is preheated and sent to the optional pre-reformer (3), using the Catalytic-Rich-Gas (CRG) process. Steam raised in the methanol converter is added, along with available carbon dioxide (CO_2), 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 50 bar 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 saturator water, 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. Also, 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 light ends such as ethers, esters, acetone and dissolved noncondensable gases. The second column removes water, higher alcohols and similar organic heavy ends.

Continued ▼

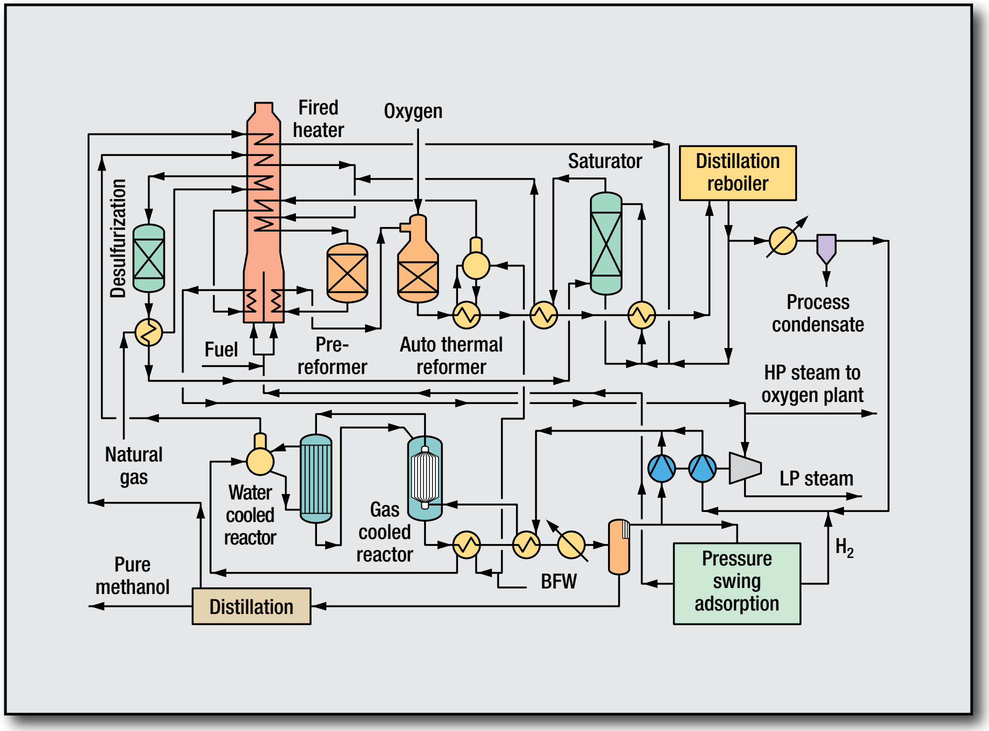
Economics: Outside of China, recent trends have been to build methanol plants in regions offering lower cost gas (such as North Africa, Trinidad and the Arabian Gulf). In these regions, total economics favor low investment rather than low-energy consumption. Recent plants have an energy efficiency of 7.2 Gcal/ton–7.8 Gcal/ton. Choice of both synthesis gas generation and synthesis technologies is on a case-by-case basis. In China, the trend has been for coal-gasification based methanol production to be built. However, where gas based production has been built, the higher gas costs favor higher energy efficiency.

Offshore opportunities globally continue to create interest in order to access low-cost gas reserves, facilitate oil/condensate extraction and avoid flaring.

Commercial plants: Seventy-five licensed plants with 12 current projects in design and construction, 6 of which are based on coal-derived syngas. Five of the licensed plants are at capacities above 5,000 metric tpd.

Licensor: Davy Process Technology with Johnson Matthey Catalysts, both subsidiaries of Johnson Matthey Plc. - CONTACT

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 under composed steam. The reformed gas leaving the autothermal reformer represents a considerable amount of heat, which is recovered as HP steam for preheating energy and energy for providing heat for the reboilers in the distillation section.

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

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

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

Continued ▼

Methanol, *continued*

Economics: Energy consumption (natural gas) 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: Forty-nine methanol plants have been licensed applying Lurgi's Low-Pressure methanol technology. Six MegaMethanol licenses are in operation; two are under construction and a MegaMethanol license has been awarded with capacities up to 6,750 metric tpd of methanol.

Licensor: Lurgi GmbH, a member of the Air Liquide Group - CONTACT

Methanol

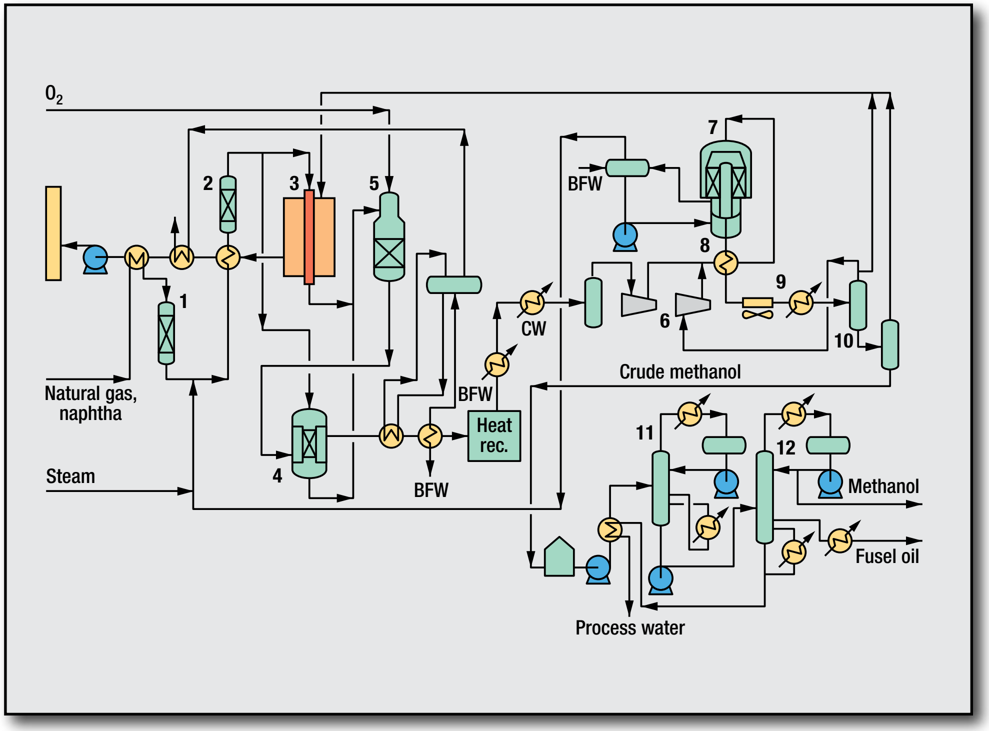
Application: To produce federal-grade AA refined methanol from natural gas-based synthesis gas and naphtha using Toyo Engineering Corp.'s (TOYO's) Synthesis Gas Generation technologies and proprietary MRF-Z reactor. In a natural gas-based plant, the synthesis gas is produced by reforming natural gas with steam and/or oxygen using high-activity steam reforming ISOP catalyst.

Description:

Syngas preparation. 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. Part of the feed is reformed adiabatically in pre-reformer TAS-R (2). Half of the feedstock-steam mixture is distributed into catalyst tubes of the steam reformer (3) and the rest is sent to TOYO's proprietary heat exchanger reformer, TAF-X (4), installed in parallel with (3) as the primary reformer. The heat required for TAF-X unit 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. The synthesis loop comprises a circulator combined with compressor (6), MRF-Z reactor (7), feed/effluent heat exchanger (8), methanol condenser (9) and separator (10). At present, the MRF-Z reactor is the only reactor in the world capable of producing 5,000 tpd–6,000 tpd of methanol in a single-reactor vessel. The operation pressure is 5 MPa–10 MPa. The syngas enters the MRF-Z reactor (7) at 220°C–240°C and leaves at 260°C–280°C normally.

The methanol synthesis catalyst applied is purchased from authorized catalyst vendor(s) by TOYO and is packed in the shell side of the reactor. Reaction heat is recovered and used to efficiently generate steam on 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 taken from the recycling gas can be used as fuel in the reformer (3).



Methanol purification. The crude methanol is fed to a 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.

Commercial plants: TOYO has accumulated experience with 20 methanol plant projects.

Reference: US Patent 6100303.

Licensor: Toyo Engineering Corp. (TOYO) - CONTACT

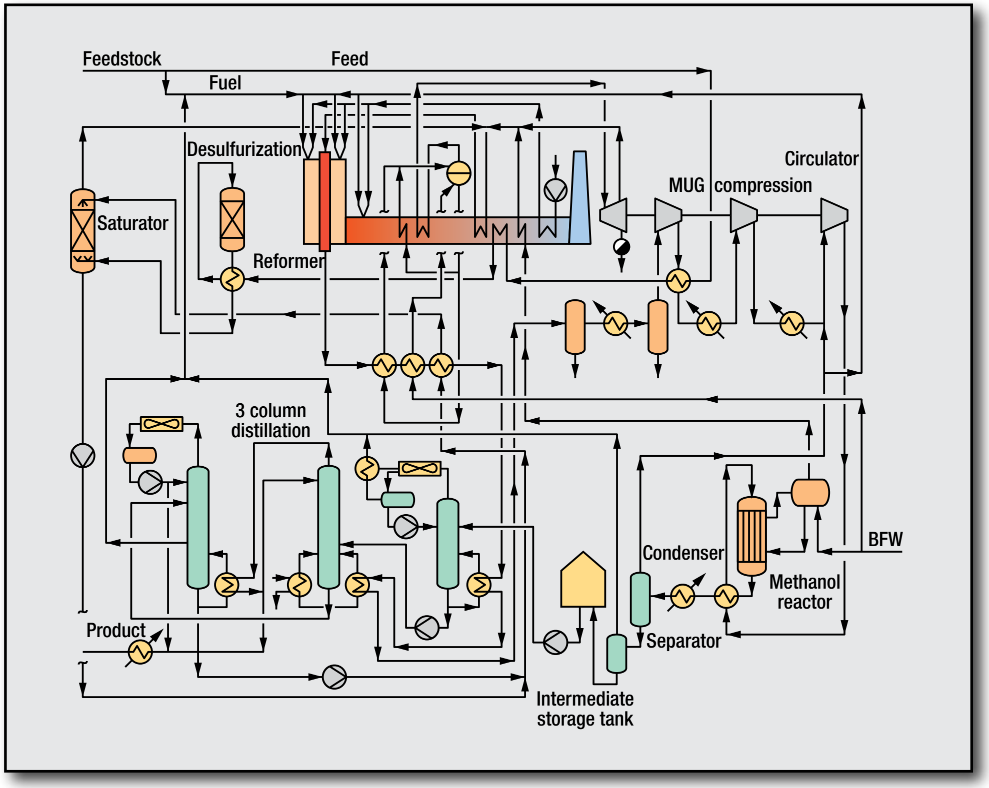
Methanol

Application: Production of high-purity methanol from hydrocarbon feedstocks such as natural gas, process offgases and LPG up to heavy naphtha. The process uses conventional steam-reforming synthesis gas generation and a low-pressure methanol synthesis loop technology. It is optimized with respect to low energy consumption and maximum reliability. The largest single-train plant built by Uhde has a nameplate capacity of 1,250 mtpd.

Description: The methanol plant consists of the process steps: feed purification, steam reforming, syngas compression, methanol synthesis and crude methanol distillation. The feed is desulfurized and mixed with process steam before entering the steam reformer. This steam reformer is a top-fired box type furnace with a cold outlet header system developed by Uhde. The reforming reaction occurs over a nickel catalyst. Outlet-reformed gas is a mixture of H_2, CO, CO_2 and residual methane. It is cooled from approximately 880°C to ambient temperature. Most of the heat from the synthesis gas is recovered by steam generation, BFW preheating, heating of crude methanol distillation and demineralized water preheating.

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

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



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

Continued ▼

Methanol, *continued*

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

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

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

Methanol—two-step reforming

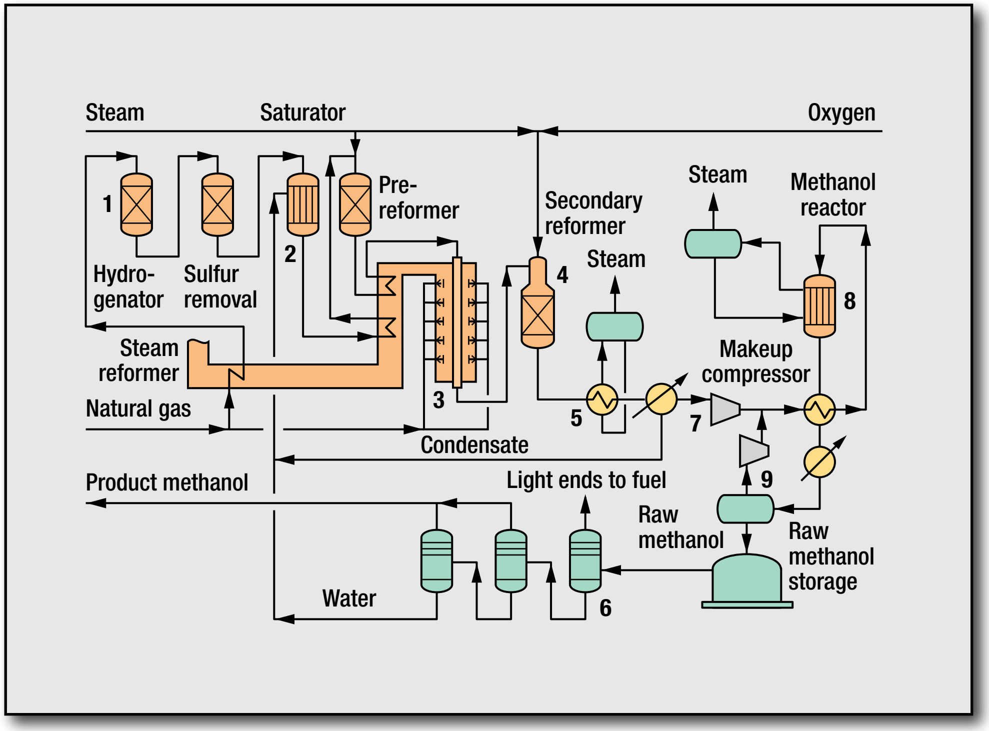
Application: To produce methanol from natural or associated gas feedstocks using two-step reforming followed by low-pressure synthesis. This technology is well suited for world-scale plants. Topsøe also offers technology for smaller as well as very large methanol facilities up to 10,000 tpd, and technology 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/cm^{2}g.

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.

Commercial plants: The most recent large-scale plant is a 5,000-tpd facility in Saudi Arabia. This plant was commissioned in 2008.

Licensor: Haldor Topsøe A/S - CONTACT

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.

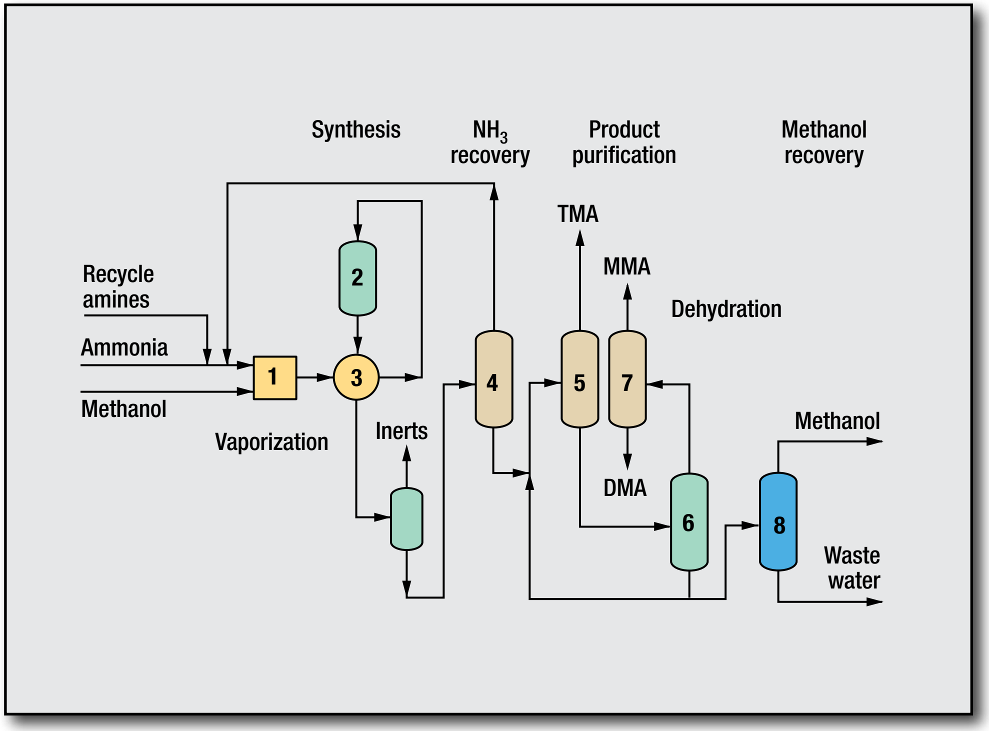
Methanol recovery (8) improves efficiency and extends catalyst life by allowing greater methanol slip exit from the converter. Addition of a methanol-recovery column to existing plants can help to increase production rates.

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 $^1/_3 : {}^1/_3 : {}^1/_3$

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



Commercial plants: Twenty-seven companies in 19 countries use this process with a production capacity exceeding 350,000 metric tpy. Most recent start-up (2010) was a 50,000-metric tpy plant in Saudi Arabia.

Licensor: Davy Process Technology, UK - CONTACT

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).

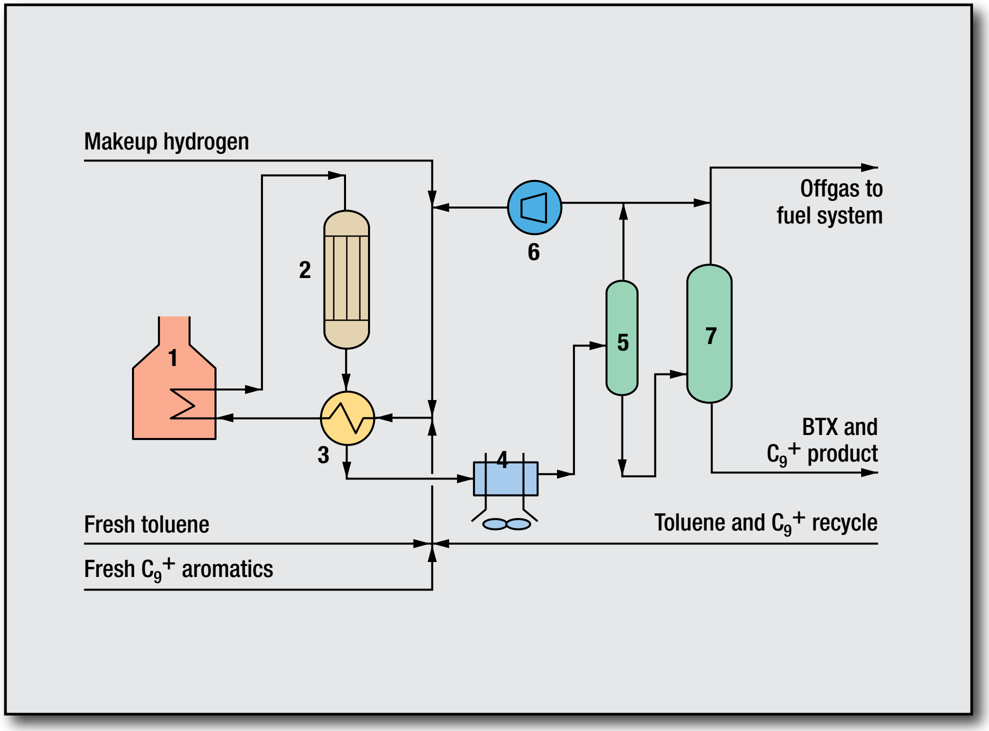
Primary reactions occurring are the dealkylation of alkylaromatics, transalkylation and disproportionation, producing benzene/toluene and C_8 aromatics. The thermodynamic equilibrium of the resulting product aromatics is mainly dependent on the ratio of methyl groups to aromatic rings in the reactor 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. There are 16 TransPlus references.

Licensor: ExxonMobil Chemical Technology Licensing LLC, (retrofit applications)
Axens (grassroots applications) - CONTACT



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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.

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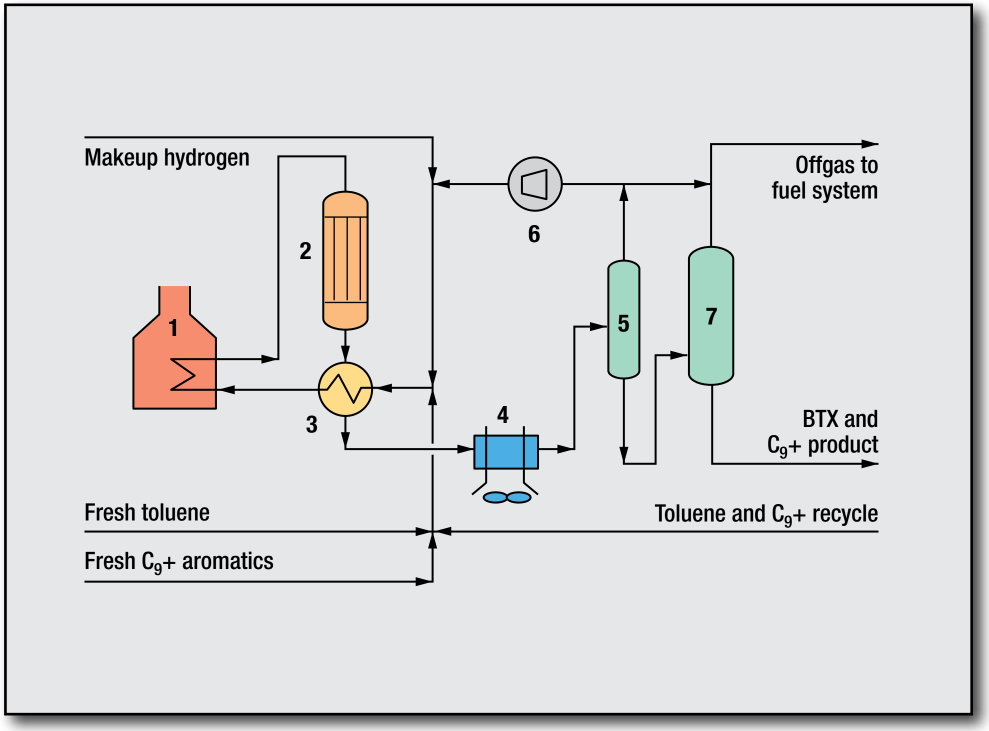


Economics: Favorable operating conditions, relative to other alternative technologies, will result in lower capital and operating costs for grassroots units and higher throughput potential in retrofit applications.

Commercial plants: The first commercial unit was started up in Taiwan in 1997. There are seven TransPlus units currently in operation.

Licensor: ExxonMobil Chemical Technology Licensing LLC, (retrofit applications) - CONTACT
Axens (grassroots applications)

Mixed xylenes

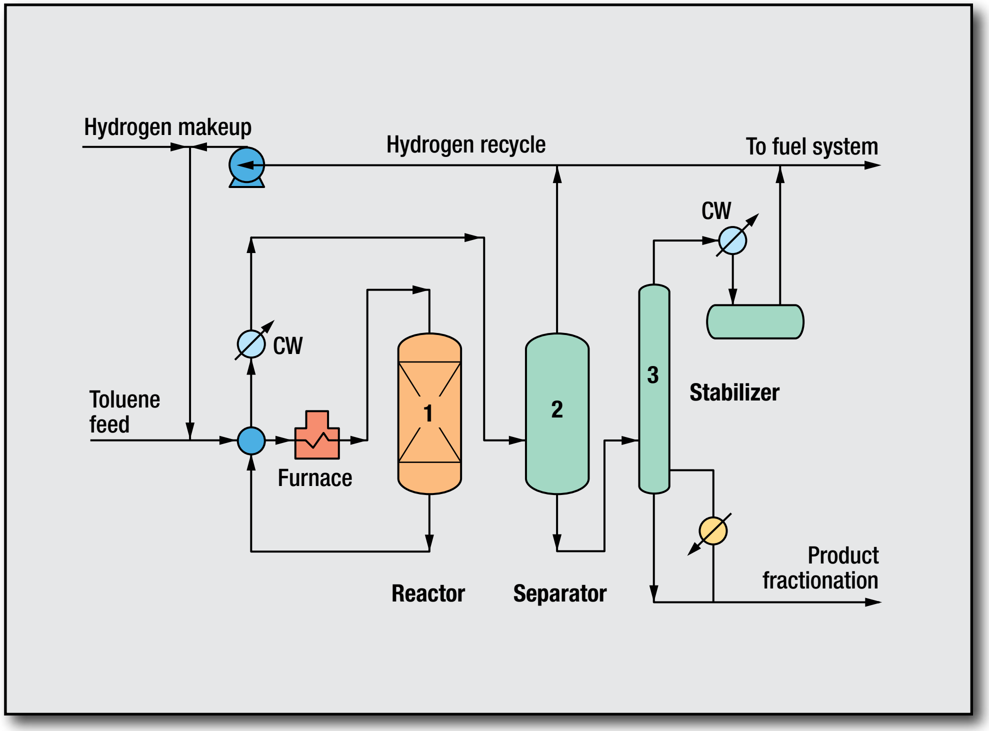
Application: To selectively convert toluene to mixed xylene and high-purity benzene using ExxonMobil Chemical's Toluene DisProportionation 3rd Generation (MTDP-3) process.

Description: Dry toluene feed and up to 25 wt% C_9 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 H_2/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.



Commercial plants: Four MTDP-3 licensees since 1995.

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

Licensor: ExxonMobil Chemical Technology Licensing LLC (retrofit applications) - CONTACT
Axens (grassroots applications)

Mixed xylenes

Application: The Tatoray process produces mixed xylenes and petrochemical grade benzene by disproportionation of toluene and transalkylation of toluene and C_9+ aromatics.

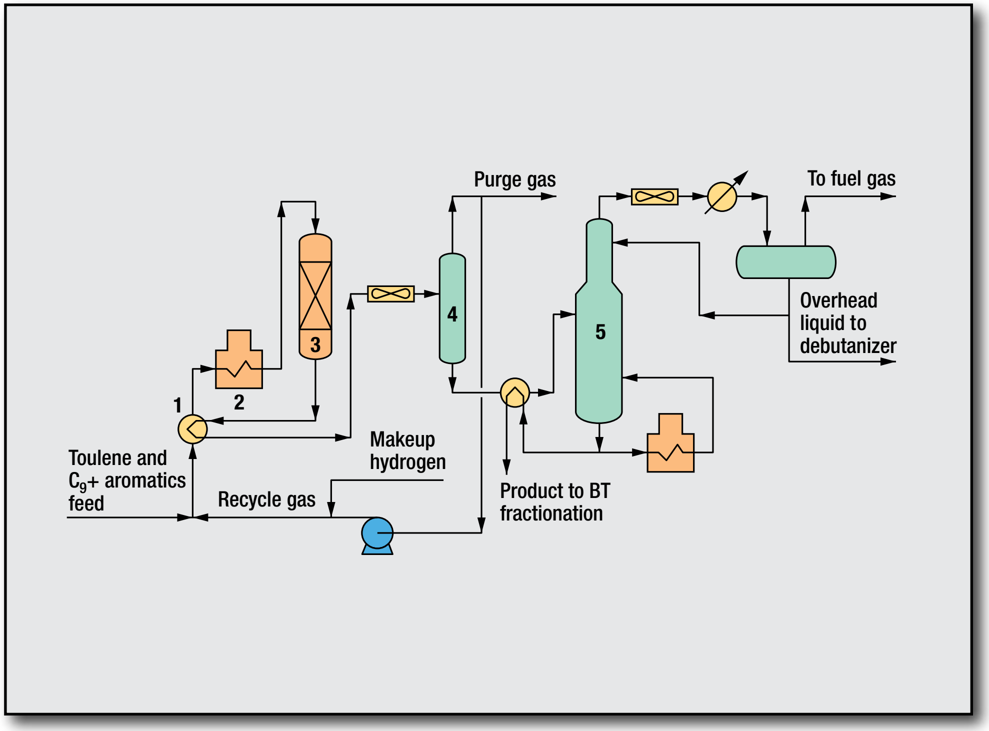
Description: The Tatoray process consists of a fixed-bed reactor and product separation section. The fresh feed is combined with hydrogen-rich recycle gas, preheated in a combined feed exchanger (1) and heated in a fired heater (2). The hot feed vapor goes to the reactor (3). The reactor effluent is 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.

With modern catalysts, the Tatoray process unit is capable of processing feedstocks ranging from 100 wt% toluene to 100 wt% A_9^+. The optimal concentration of A_9^+ 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.

Economics: The process is designed to function at a high level of conversion per pass. 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 1.92 million metric tpy (US Gulf Coast site in 2009):

Investment, US$ million	36



Utilities (per metric ton of feed)

Electricity, kWh	6.7
Water, cooling, m^3	0.1
Fuel, MMkcal	1.19

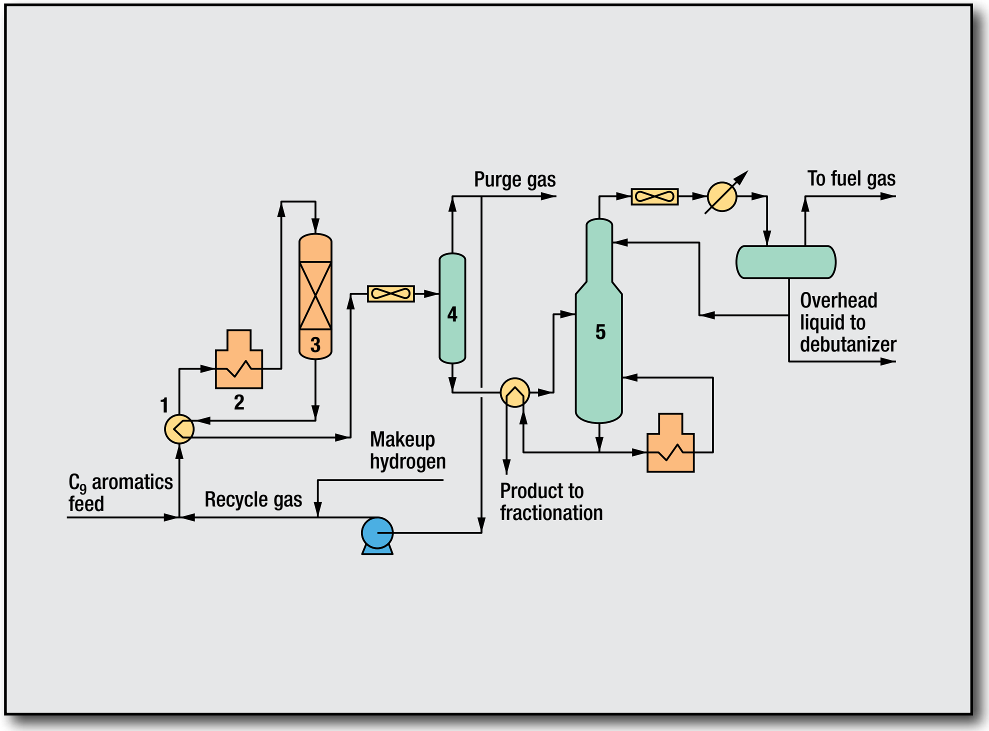
Commercial plants: UOP has licensed a total of 54 Tatoray units; 46 of these units are in operation and 8 are in various stages of construction.

Licensor: UOP LLC, A Honeywell Company - CONTACT

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 380,000 metric tpy of feed consisting of 100 wt% $C_9–C_{10}$ (US Gulf Coast site in 2006):

Investment, US$ million	14
Utilities (per mt of feed)	
Electricity, kWh	6.7
Water, cooling, m^3	0.08
Fuel, MMkcal (credit)	1.2

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

Licensor: UOP LLC, A Honeywell Company - CONTACT

Mixed xylenes and benzene, Toluene selective to paraxylene

Application: GT-STDP produces paraxylene-rich mixed xylene along with high-purity benzene streams from toluene. GT-STDP features a commercially-proven proprietary catalyst with high activity and selectivity to paraxylene (PX).

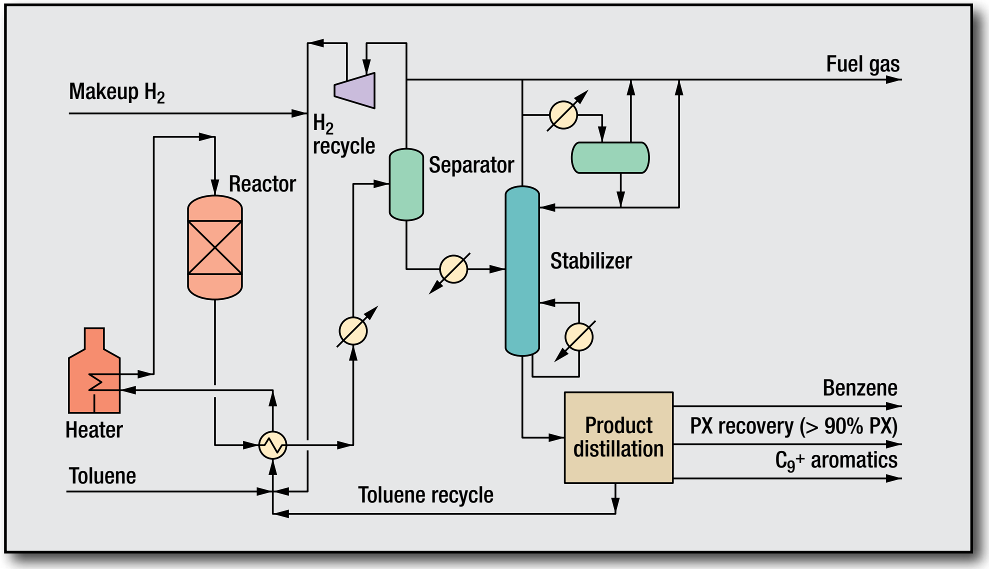
Description: The technology encompasses three main processing areas: reactor section, product distillation and PX recovery. Fresh toluene and recycled toluene from the product distillation area are mixed with hydrogen. The hydrogen to toluene ratio is about 1 to 1.5. The mixed stream is then heated against reactor effluent and sent through a process furnace. This heated vapor stream flows to the reactor, which produces the benzene and xylenes. The toluene disproportionation reactions are mildly exothermic.

The reactor effluent is cooled and flows to the separator, where the hydrogen-rich vapor phase is separated from the liquid stream. A small portion of the vapor phase is purged to control the purity of the recycle hydrogen. The recycle hydrogen is then compressed, mixed with makeup hydrogen, and returned to the reactor.

The liquid stream from the separator is pumped to the stripper to remove light hydrocarbons. The liquid stream from the stripper bottoms contains benzene, toluene, mixed xylenes and a small quantity of C_9^+ aromatics. This liquid stream is sent to the product distillation section to obtain benzene product, toluene for recycle to the reactor, mixed xylenes to the PX recovery section and C_9^+ aromatics. The PX in the mixed-xylenes stream has over 90% purity, which permits low-cost crystallization technology to be used for the PX purification.

Advantages:

- Simple, low-cost fixed-bed reactor design
- Drop-in catalyst replacement for existing hydroprocessing reactors



- PX enriched to over 90% in the xylene stream
- On-specification benzene with traditional distillation
- Physically stable catalyst
- Low hydrogen consumption
- Moderate operating parameters; catalyst can be used as replacement for traditional toluene disproportionation unit, or in grassroots designs
- Efficient heat integration scheme, reduced energy consumption
- Turnkey package for high-purity benzene and paraxylene production available from licensor.

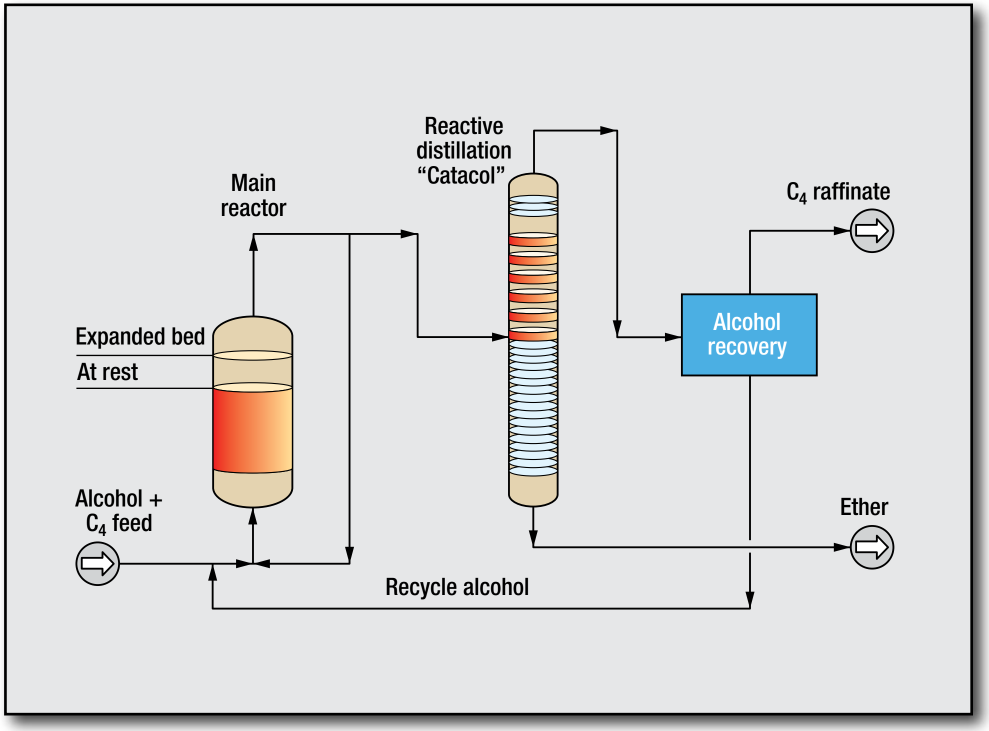
Economics:

Basis	1 Millon tpy (22,000 bpsd) feedrate
Erected cost	$25 million (ISBL, 2009 US Gulf Coast basis)

Commercial plants: GTC markets this technology on a select, regional basis. There are two commercial applications of the STDP process.

Licensor: GTC Technology - CONTACT

MTBE/ETBE and TAME/TAEE: Etherification technologies



Application: Ethers, particularly methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME), have long been used in reformulated gasoline, owing to their attractive blending and engine burning characteristics. Although in North America ethers are being removed gradually from the gasoline pools, they remain the additives of choice in other regions not having groundwater contamination issues.

Another approach now viewed as an option for sustainable development is to add ethanol to gasoline pools. However, direct blending of ethanol in the gasoline pool gives rise to potential problems such as increased Rvp, volume reduction, phase separation and logistics (mixing at terminals). Indirect incorporation of ethanol via the etherification routes producing ethyl tertiary butyl ether (ETBE) or tertiary amyl ethyl ether (TAEE) is an interesting option for sustainable gasoline production as these materials boast excellent blending and engine burning properties. Pioneered by IFP in the 1990s, these processes complement Axens' technology strategy for providing high-quality reformulated and renewable fuels.

Besides, Axens offers a full set of technologies to produce high-purity, polymer-grade butene-1 from cracked C_4s, which involves selective hydrogenation of butadiene, purification stages, high-conversion MTBE and butene-1 superfractionation.

Description: Our experience includes the design and operation of a large number of units since the 1980s. At present, more than 30 units are in operation worldwide. Design configurations applicable to all units include:

- Main reaction section where the major part of the reaction takes place on an acidic catalyst. Fixed-bed reactors or expanded bed reactors may be used depending upon operating severity.
- Fractionation section for separating unconverted raffinate from produced ethers. This separation column may be filled with several beds of conventional etherification catalyst to allow thermodynamic equilibrium and increase conversions. This reactive distillation concept is called Catacol and is well-suited for ethers production maximization or isobutylene extinction (99.9%$^+$ conversion) when locating a MTBE unit upstream of a butene-1 recovery section.
- Alcohol recovery section consisting of a raffinate washing column and alcohol recovery column for recycling unconverted alcohol to the main section to improve reaction selectivity. This is optional in the ethanol mode.

Economics: Typical economics for medium- and high-reactive olefin conversion etherification units are:

Continued ▼

MTBE/ETBE and TAME/TAEE, *continued*

	MTBE	ETBE	TAME	TAEE
C_4 cut feedstock, tpy	329,000	275,000	369,000	355,000
Investment, US$ million	12	10	13	13
Utilities per ton of ether				
Electrical power, kWh	18	14	20	20
Steam, tons	1	0.9	1.2	1.2
Water, cooling m^3	65	57	73	70

Basis: 2010 Gulf Coast unit producing 100,000 tpy of ether from an FCC stream containing either 20% isobutylene or 20% of isoamylenes.

Commercial plants: Forty-two etherification units have been licensed.

Licensor: Axens - CONTACT

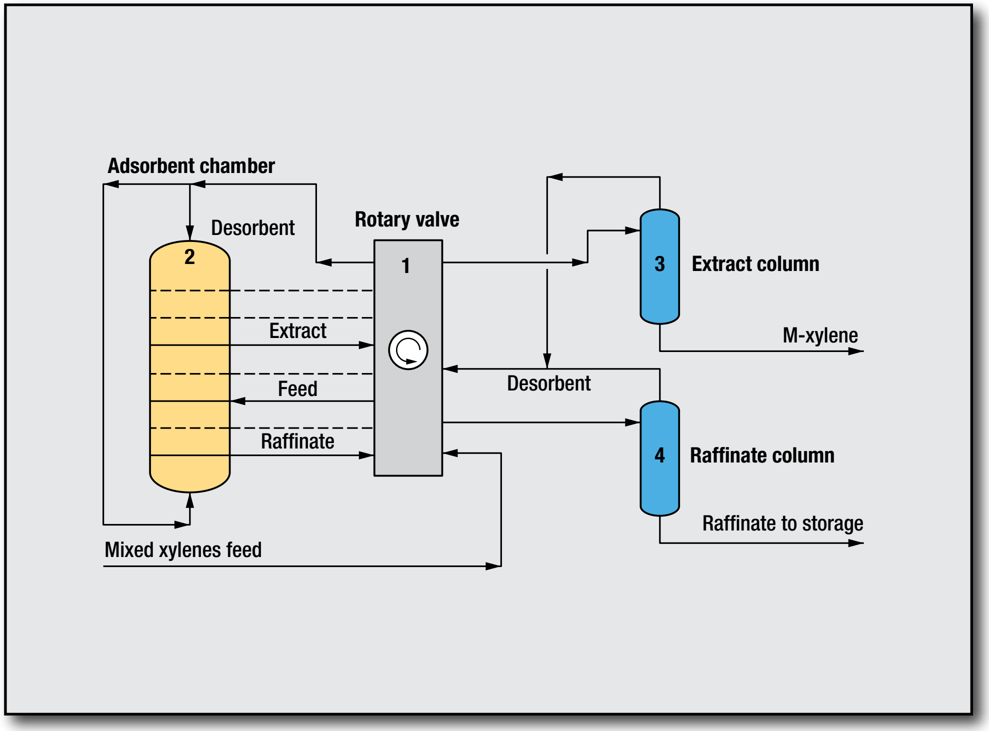
m-Xylene

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	67
Utilities (per mt of *m*-xylene produced)	
Electricity, kWh	134
Water, cooling, m^3	7.4
Fuel fired, MMkcal/hr	3.0

Commercial plants: Seven MX Sorbex units are currently in operation and two units are in design. These units represent an aggregate production of 555,000 metric tpy of *m*-xylene.

Licensor: UOP LLC, A Honeywell Company - CONTACT

Natural detergent alcohols

Application: To produce natural detergent alcohols from fatty acids using esterification, hydrogenolysis and refining.

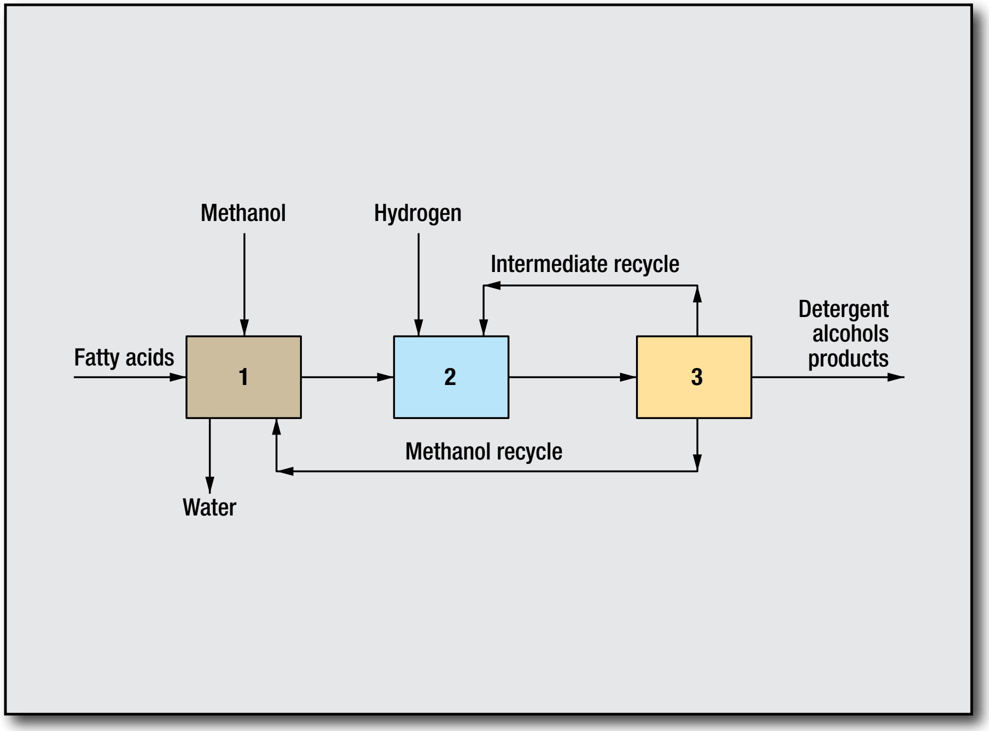
Description: Fatty acids are fed to the esterification section (1) where they are esterified to methyl esters in a reactive distillation column. Water released by this reaction is removed by excess methanol, which is treated in a methanol purification column. This column produces a clean water effluent and recycles methanol to the reactive distillation column.

Methyl esters are fed to a low-pressure, vapor-phase hydrogenation section (2) where the esters are vaporized into a circulating hydrogen stream followed by conversion to fatty alcohol over a fixed catalyst bed. Crude alcohol product is condensed, and the gas is re-circulated with a low-head centrifugal compressor.

Crude alcohol passes to the refining section (3) where low levels of residual methyl esters are converted to wax esters and recycled to the hydrogenation section (2). A refining column removes light and heavy impurities, and the refined fatty alcohol product is polished to convert any residual carbonyls to alcohols.

Economics: Feedstock and utility consumption are heavily dependent on feedstock composition; thus, each must be evaluated on a case-by-case basis.

Commercial plants: The first commercial scale plant (30,000 metric tpy) to use the Davy process was started up in the Philippines in 1998. A further project for a 50,000-metric tpy plant was licensed and designed. This plant was moved to Indonesia and expanded by a further 20,000 metric tpy. In 2005/2006, four plants were licensed, which are now all in operation with production capacities ranging from 70,000 metric tpy to 120,000 metric tpy for C_{12} to C_{18} material.



Reference: Brochure, "Lions share of NDA plants," Davy Process Technology Ltd., www.davyprotech.com

Licensees: Six licensees since 1998.

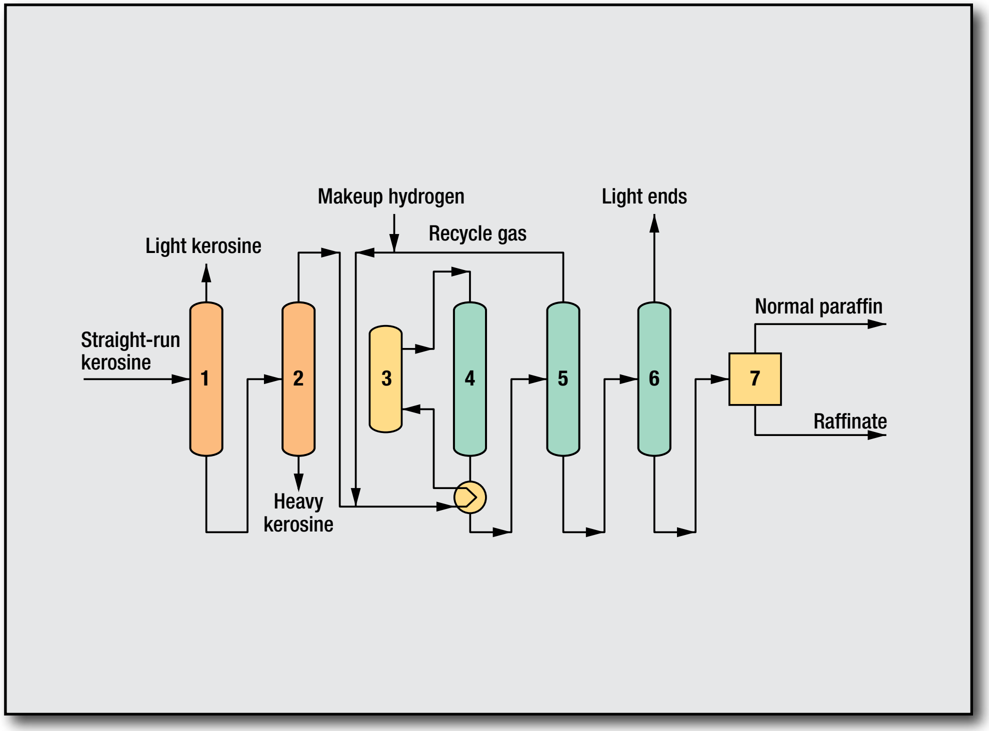
Licensor: Davy Process Technology, UK - CONTACT

Normal paraffins, C_{10}–C_{13}

Application: The Molex process recovers normal C_{10}–C_{13} 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 Unionfining 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 inside battery limits for the production of 100,000 tpy of normal paraffins: 1,000 $/tpy

Commercial plants: Thirty-two Molex units have been built.

Licensor: UOP LLC, A Honeywell Company - CONTACT

n-Paraffin

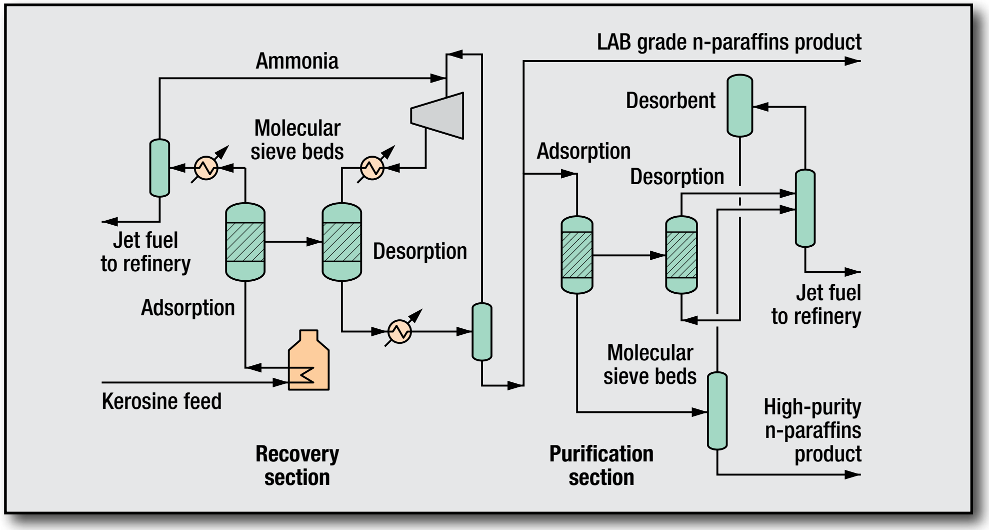
Application: Efficient low-cost recovery and purification processes for the production of linear alkylbenzene (LAB)-grade and/or high-purity normal-paraffin (n-paraffin) products from kerosine.

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 proprietary ENSORB recovery process developed by ExxonMobil Chemical, wherein the long-chain aliphatic normal paraffins are selectively removed from the kerosine stream in vapor phase by adsorption onto a molecular sieve. Isoparaffins, cycloparaffins, aromatics and other components not adsorbed are typically returned to the refinery kerosine pool. The cyclical process uses a low pressure ammonia desorbate to recover the n-paraffins from the sieve for use as LAB-quality product or for further purification.

Significant savings in capital cost are achieved by minimizing the need for feed pretreatment before the kerosine enters the recovery system. The ENSORB process exhibits a high tolerance to feed impurities, up to 400 ppmwt sulfur and 80 ppmwt nitrogen. For feedstocks with higher sulfur and nitrogen content, only mild hydrotreating is needed to reduce the impurity levels in the kerosine feed to an acceptable range. The robust adsorbent is able to last long cycle lengths with a total life up to 20 years, as commercially demonstrated by ExxonMobil.

The LAB-grade product from the recovery process is further processed in an optional purification section, where residual aromatics and other impurities are further reduced to below 100 ppmwt. 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 ENSORB adsorbent offers a high recovery of n-paraffins and a tolerance for sulfur and nitrogen that is unparalleled in the industry. Process conditions can be optimized for a targeted range of molecular weights, and an optimized post-recovery fractionation section allows for fine-tuning of product compositions. The need for a sharp cut in a front-end fractionation section is eliminated, thereby reducing the energy consumption of the process.



Product quality: The technology produces n-paraffins suitable for LAB production and other specialty applications. The typical product quality is:

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

Yield: The highly selective proprietary molecular sieves offer recovery of 99 wt% n-paraffin for LAB quality product.

Commercial plants: EMCC was the first commercial producer of n-paraffins and one of the world's largest producers for over 40 years, operating a single train plant in Baytown, Texas, with a capacity of 400,000 metric tpy.

Licensor: Kellogg Brown & Root LLC - CONTACT

Octenes

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

Description: Butenes from fluid catalytic cracking (FCC) or steam cracking are dimerized into a liquid-phase oligomerization unit comprising three sections. In the reaction 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 for safe disposal (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.

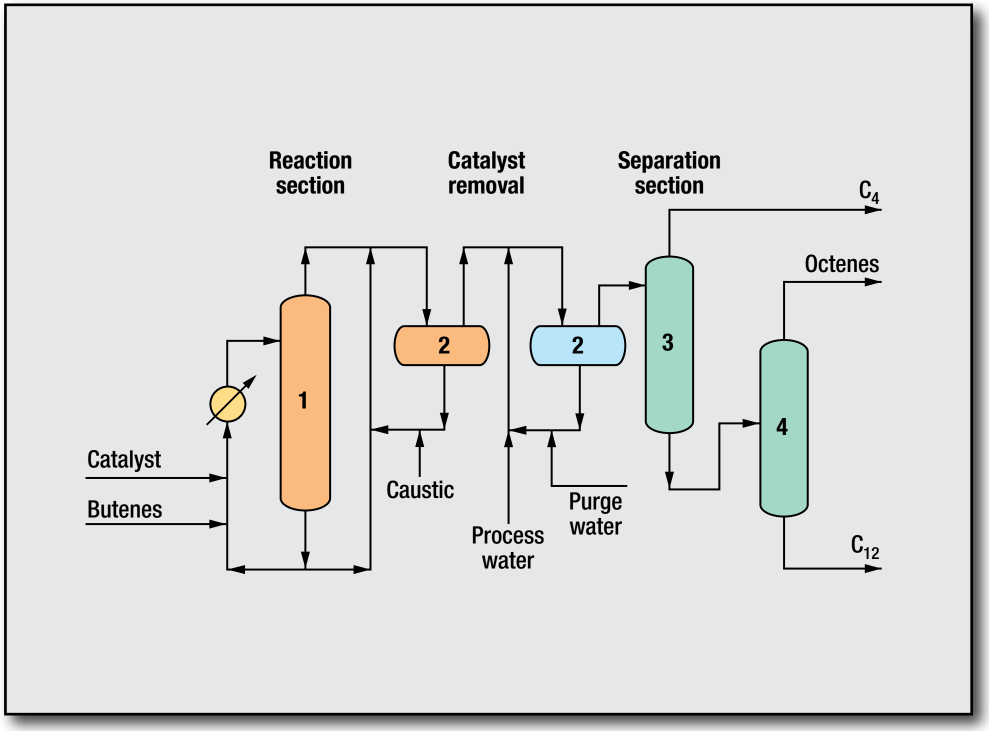
Yields: Nearly 80% conversion of n-butenes can be attained and selectivities toward octenes are about 85%. The typical C_8 product is a mixture having a minimum of 98.5% octene isomers with the following distribution:

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 2010 for a Gulf Coast location using 50,000 tpy of a raffinate-2 C_4 cut containing 75% n-butenes.

Investment, US$ million	8
Typical operating cost, US$	60 per metric ton of octenes



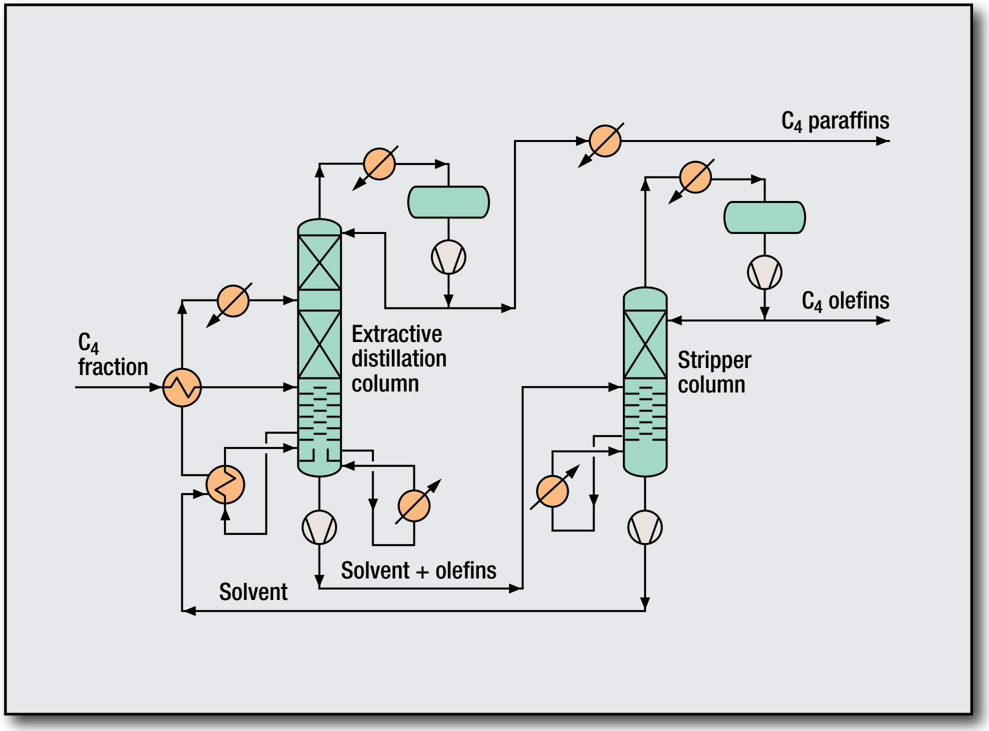
Commercial plants: Thirty-six Dimersol units treating various olefinic C_3 and C_4 cuts have been licensed. Typical octenes production capacities range from 20,000 tpy up to 90,000 tpy.

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

Licensor: Axens - CONTACT

Olefins—butenes extractive distillation

Application: Separation of pure C_4 olefins from olefinic/paraffinic C_4 mixtures via extractive distillation using a selective solvent. BUTENEX is the Uhde technology to separate light olefins from various C_4 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 C_4 fraction feedstock:

Steam, t/t	0.5–0.8
Water, cooling (ΔT = 10°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 - CONTACT

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.

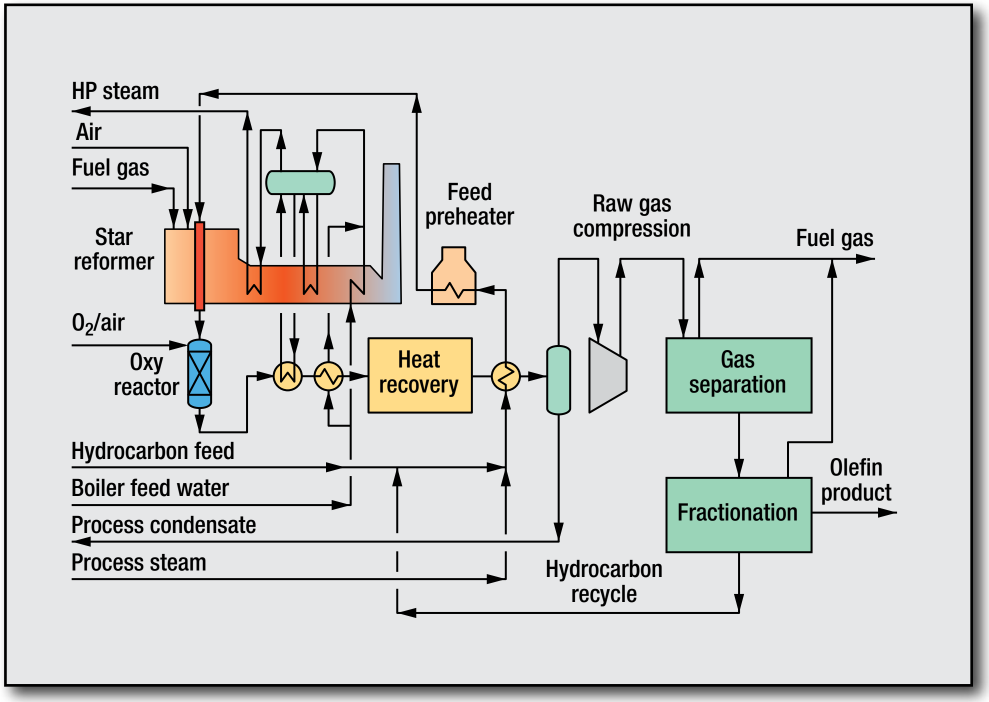
Feed: Liquefied petroleum gas (LPG) from gas fields, gas condensate fields and refineries.

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 recoverd 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

Continued ▼

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 C_3- and C_4-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.

Licensor: Uhde GmbH - CONTACT

Olefins—Catalytic

Application: To selectively convert vacuum gasoils, paraffinic residual feedstocks and resulting blends of each into C_2–C_5 olefins, aromatic-rich, high-octane gasoline and distillate using the Deep Catalytic Cracking (DCC) process.

Description: The DCC process selectively cracks a wide variety of feedstocks into light olefins, with a reactor/regenerator configuration similar to traditional fluid catalytic cracking (FCC) units (see figure). Innovations in catalyst development and process variable selection lead to synergistic benefits and enable the DCC process to produce significantly more olefins than an FCC that is operated for maximum olefins production.

The DCC process was originally developed by the Research Institute of Petroleum Processing (RIPP) and Sinopec in the People's Republic of China. Shaw's Energy and Chemicals Group is the sole engineering contractor licensed to offer DCC technology outside of China.

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

The reaction temperature in DCC is higher than that of conventional FCC but much lower than that of steam cracking. Propylene yields over 20 wt% are achievable with paraffinic feeds. Ethylene yield is much higher than the conventional FCC process. The DCC-mixed C_4s stream also contains increased amounts of butylenes and iso-C_4s as compared to an FCC. The high olefin yields are achieved by deeper cracking into the aliphatic components of the naphtha and LCO. The dry gas produced from the DCC process contains approximately 50% ethylene. The cracking reactions are endothermic, and compared to FCC, a higher coke make is required to satisfy the heat balance. Table 1 summarizes typical olefins yields for DCC with FCC.

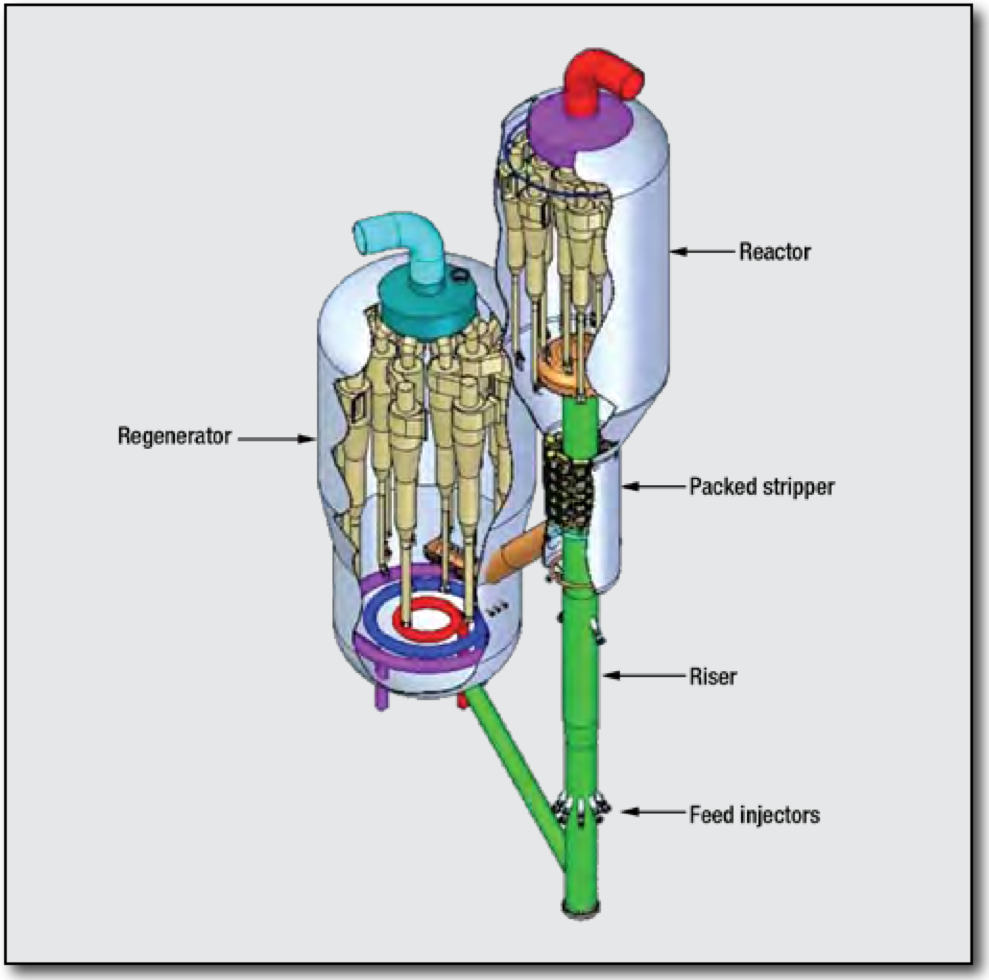


Table 1. Olefin yields for DCC modes

Products, wt% fresh feed	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
in which Isobutylene	5.4	6.1	3.3

Continued ▼

This technology is suitable for revamps as well as grassroots applications. The DCC process is very suitable for integration with an ethylene plant—refer to "HOFCC and Ethylene Plant Integration" for the benefits of capital reduction and production efficiency.

Commercial plants: At present, eight units are in operation: six in China, one in Thailand and one in Saudi Arabia. Another six plants are in design or construction. The unit in Saudi Arabia is the largest DCC unit in the world.

Reference: Dharra, et al., "Increase Light Olefins Production," *Hydrocarbon Processing*, April 2004.

Licensor: The Shaw Group - CONTACT

Paraxylene

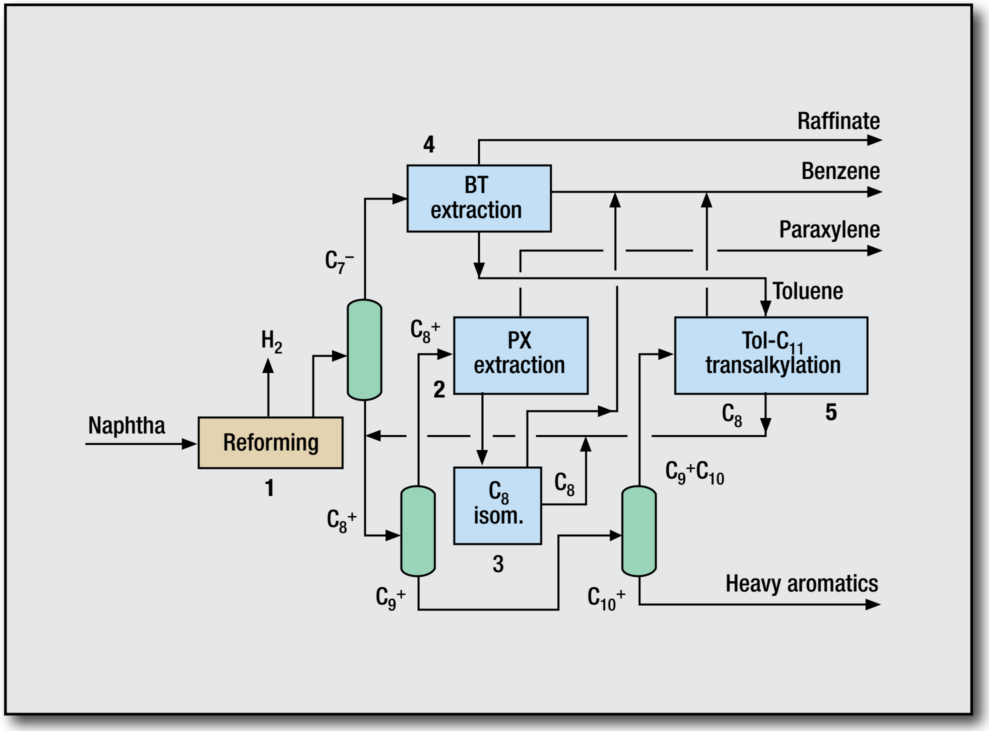
Application: Suite of advanced aromatics technologies combined in the most effective manner to meet customers' investment and production objectives for paraxylene (PX) and benzene and are licensed under the name ParamaX.

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% PX via simulated countercurrent adsorption. The PX-depleted raffinate is isomerized back to equilibrium in the isomerization section (3) with either ethylbenzene (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 C_9 to C_{11} aromatics are converted to higher valued benzene and mixed xylenes in the TransPlus* process (5), leading to incremental PX production.

Eluxyl technology has the industrially proven ability to meet ultimate single-train PX purity and capacities as high as 840,000 metric tpy. Proprietary hybrid Eluxyl configurations integrate an intermediate purity adsorption section with single-stage crystallization, ideal for retrofits. Axens is the licensor of all the technologies involved in the ParamaX suite.

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

Commercial plants: Eleven ParamaX integrated plants have been licensed, accounting for more than 10 million tpy of PX. Three ParamaX integrated plants are in operation. Ten Eluxyl units are in commercial operation with single-line capacity ranging from 180,000 metric tpy to 840,000 metric tpy of PX. Oparis has been selected in 17 plants in both retrofits and grassroots applications. There are 18 XyMax and 16 TransPlus references.



Reference: Leflour,T., N. Yomoji and J. Rault "Fast-track ParamaX implementation at Kashima Oil Refinery," ERTC Petrochemical Conference, Rome 2009.

Licensor: Axens - CONTACT

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

Paraxylene

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

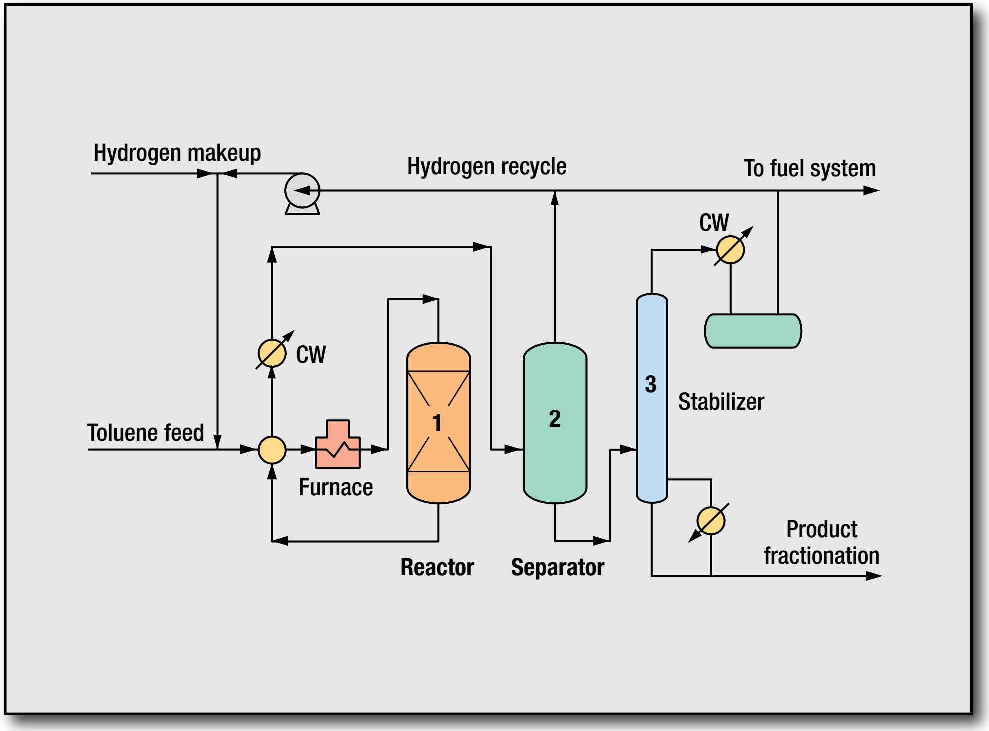
Description: Dry toluene feed and hydrogen-rich recycle gas are pumped through feed/effluent exchangers and charge heater and into the reactor (1). Selective toluene disproportionation (STDP) occurs in the vapor phase to produce the paraxylene-rich xylene and benzene co-product. Byproduct yields are 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-purity paraxylene 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 four MSTDP units (predecessor technology to PxMax), and ASTDP and eight 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 Technology Licensing LLC (retrofit applications)
Axens (grassroots applications) - CONTACT

Paraxylene

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

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.

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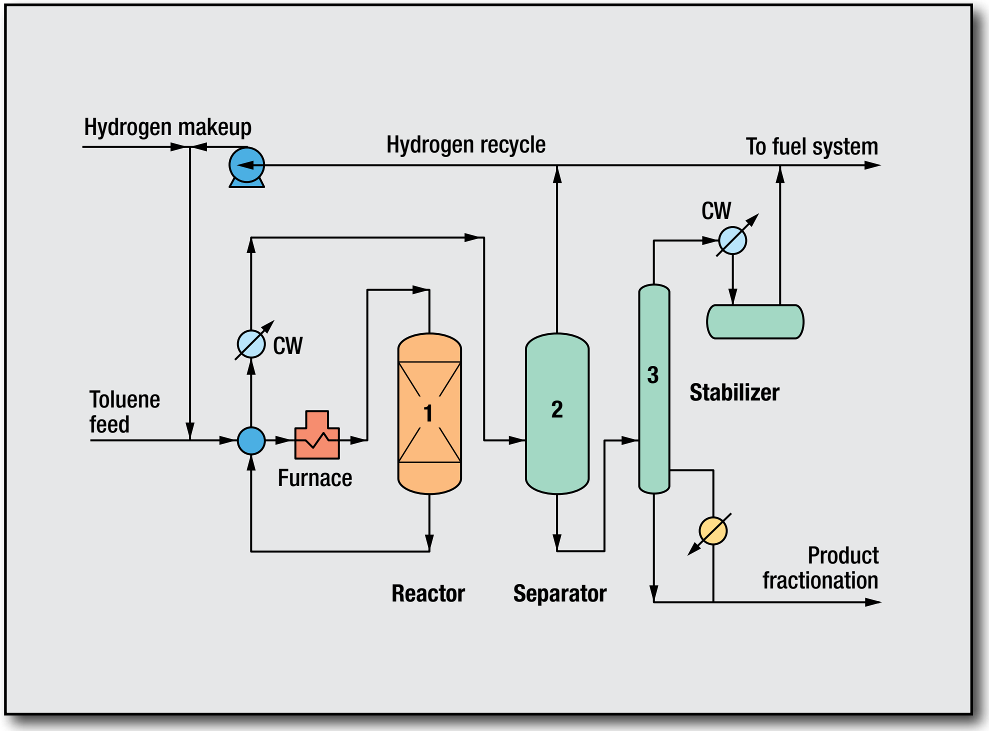
Operating conditions: PxMax operates at lower start-of-cycle temperatures and lower hydrogen to hydrocarbon recycle ratios than other STDP technologies, resulting in longer cycles and lower utilities. By eliminating the in-situ selectivation step, the PxMax technology results in simplified operation and lower capital costs. The catalyst offers long operating cycles and is regenerable.

Commercial plants: There are three MSTDP units (predecessor technology to PxMax) and ten PxMax units are currently in operation. 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 Technology Licensing LLC (retrofit applications) - CONTACT
Axens (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.

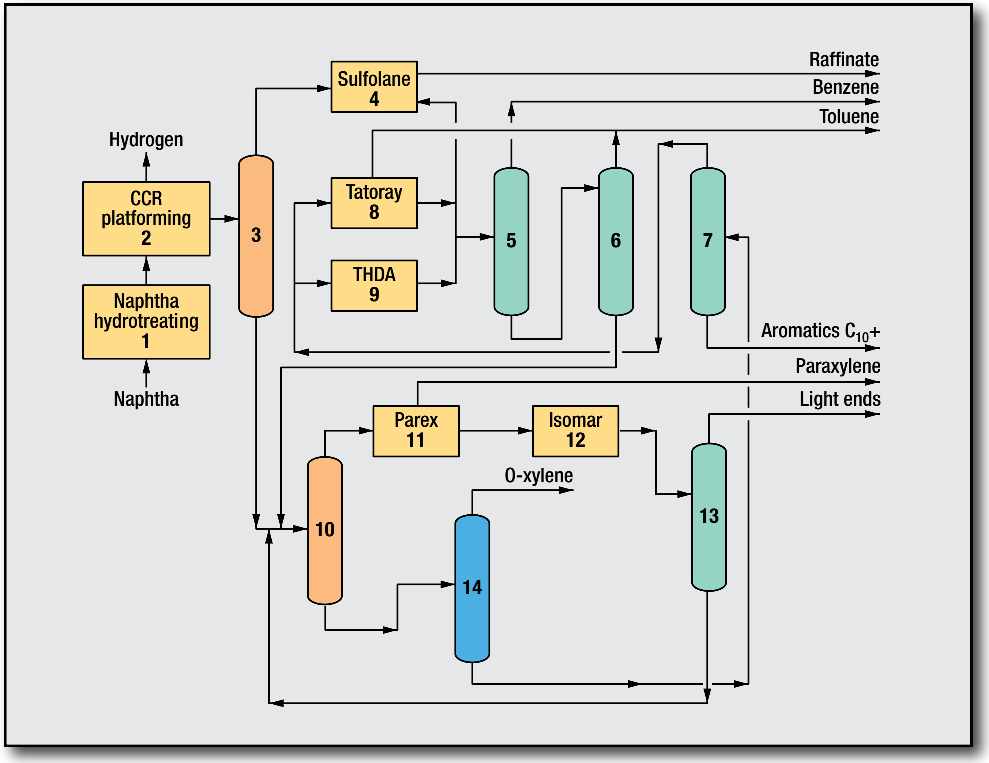
Description: The configuration of an aromatics complex depends upon the available feedstock, the desired product slate, and the balance between performance and capital investment. A fully integrated modern complex contains a number of UOP process technologies.

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

The reformate produced in the CCR Platforming unit is sent to a stabilizer column, which strips off the light ends. The stabilizer 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 UOP 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 paraxylene aromatics complex to process 1.5 million meric tpy of naphtha feed is indicated below. The estimated ISBL erected cost for the unit assumes construction on a US Gulf coast site in 2009.

Continued ▼

Paraxylene, *continued*

Investment, US$ million	363
Products, metric tpy	
Raffinate	252,000
LPG	68,000
Benzene	264,000
Paraxylene	700,000
Pure hydrogen	49,000
Utilities, per metric ton of feed	
Electricity, kWh	64.3
Steam, metric ton	(–0.37)
Water, cooling, m^3	5.7
Fuel, Gcal	1.6

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 260 CCR Platforming units, 139 Sulfolane units, 93 Parex units, 75 Isomar units, 54 Tatoray units and 38 THDA units.

UOP has designed 93 integrated aromatics complexes, which produce both benzene and paraxylene. These complexes range in paraxylene production capacity from 21,000 to 1.7 million metric tpy.

Licensor: UOP LLC, A Honeywell Company - CONTACT

Paraxylene

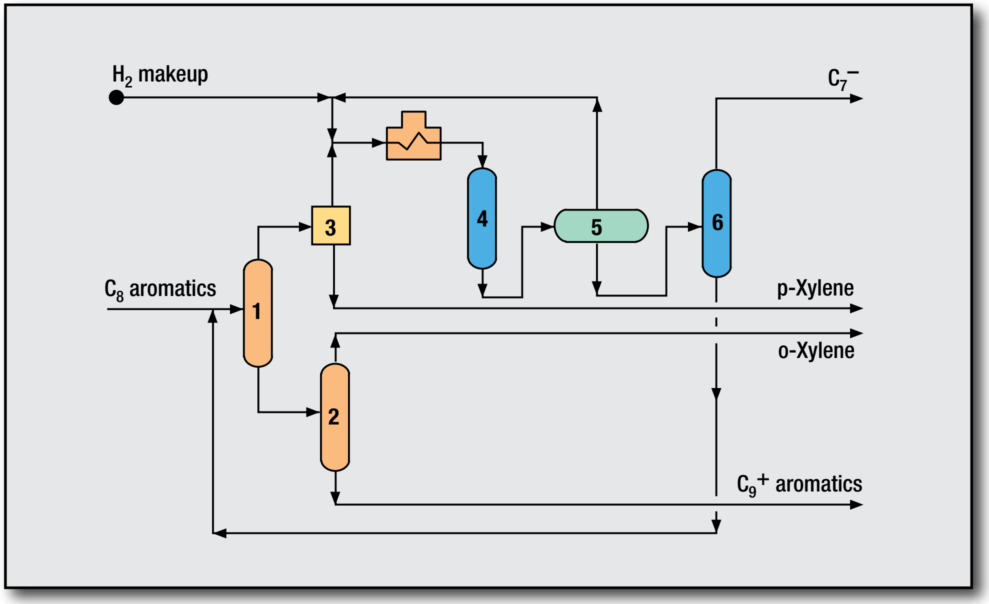
Application: To produce a desired xylene isomer (or isomers) from a mixture of C_8 aromatics using the UOP Isomar and Parex processes.

Description: Fresh feed containing an equilibrium mixture of C_8 aromatic isomers is fed to a xylene splitter (1). Bottoms from the splitter are then separated (2) into an overhead product of o-xylene and a byproduct of C_9^+ aromatics. Overhead from the splitter is sent to a UOP Parex process unit (3) 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 C_8 aromatic isomers. Hydrogen-rich recycle gas is separated (5) from the reactor effluent before fractionation (6) to remove light-cracked byproducts overhead. The remaining C_8 aromatics are then combined with the fresh feed and sent to the xylene splitter (1).

The feedstock consists of a mixture of C_8 aromatics typically derived from catalytically reformed naphtha, hydrotreated pyrolysis gasoline or an LPG aromatization unit. The feed may contain up to 40% ethylbenzene, which is converted either to xylenes or benzene by the Isomar reactor at a high-conversion rate per pass. Feedstocks may be pure solvent extracts or fractional heartcuts containing up to 25% nonaromatics. Hydrogen may be supplied from a catalytic reforming unit or any 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 yields of key products from a Parex-Isomar complex:

Composition	Fresh feed, wt. units	Product, wt. units
Benzene	–	–
Ethylbenzene	17.2	–
p-Xylene	18.3	78.8
m-Xylene	41.8	–
o-Xylene	22.7	10

Economics: Estimated inside battery limits (ISBL) erected and utility costs are given for a Parex-Isomar complex which includes the xylene column, US Gulf Coast site in 2009.

Investment, US$ per metric ton of feed	150–200
Utilities, US$ per metric ton of p-xylene product	30

Commercial plants: Since 1971, UOP has licensed 93 Parex units and 75 Isomar units.

Licensor: UOP LLC, A Honeywell Company - CONTACT

Paraxylene

Application: The UOP 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

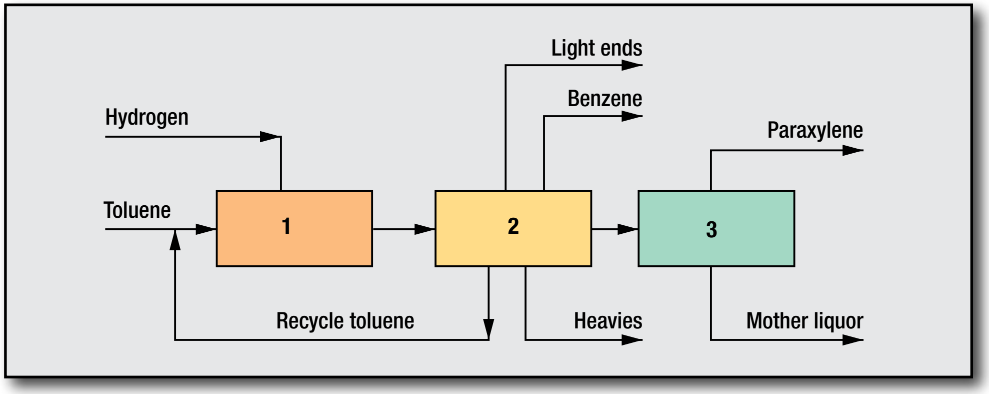
(3) The Badger/Niro paraxylene crystallization process, where single-stage crystallization and crystal wash columns are used.

In the PX-Plus technology, fresh toluene is combined with recycle gas, heated and fed to a fixed-bed reactor. The paraselective 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%	36
Benzene yield, wt%	43
Light ends, wt%	< 8
Paraxylene recovery	93.5%
Paraxylene purity, wt%	99.9

Economics: Capital investment per metic tpy of paraxylene product

EEC, US$	285
Utilities per mt of paraxylene product	
Electricity, kWh	172
Steam, HP, metric ton	2.48
Steam, LP, metric ton	3.76
Water, cooling, m^3	27
Fuel, MMkcal	0.5

Commercial plants: Three PX-Plus units have been brought online. Two Badger/Niro licensed and process packages were produced for three Badger/Niro crystallization projects.

Licensor: UOP LLC, A Honeywell Company, The Shaw Group, Inc., and Niro Process Technology B.V. - CONTACT

Paraxylene, crystallization

Application: CrystPX is a modern suspension crystallization technology for production of paraxylene (PX). The process can be applied in a single-stage for concentrated PX feedstock or in two stages for equilibrium xylenes feed. The technology has fewer pieces of equipment, simplified flow schemes, and a more reliable operation compared to traditional crystallization methods.

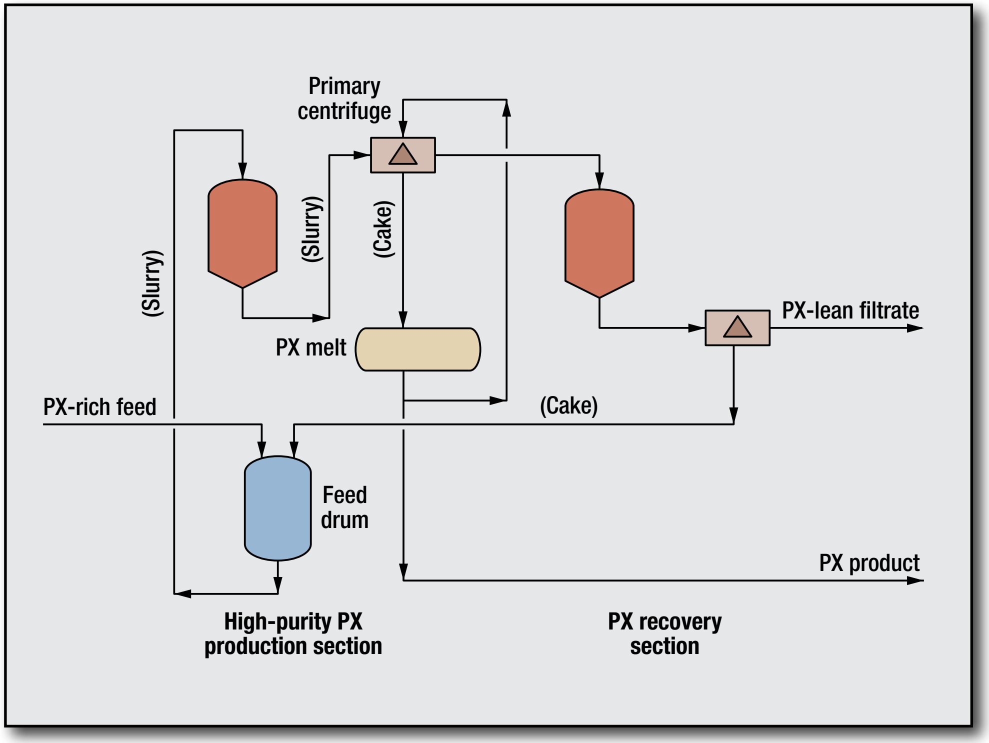
Description: Suspension crystallization of PX in the xylene isomer mixture is used to produce PX crystals. The technology utilizes an optimized arrangement of equipment to obtain the required recovery and product purity. Washing the paraxylene crystal with the final product in a high-efficiency pusher-centrifuge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

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

The design uses only crystallizers and centrifuges in the primary operation. High-purity PX is produced in the front section of the process at warm temperatures, taking advantage of the high concentration of PX already in the feed. At the back end of the process, high PX recovery is obtained by operating the crystallizers at colder temperatures. This scheme minimizes the need for recycling excessive amounts of filtrate, thus reducing overall energy requirements.

Process advantages:

- High-purity PX 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
- Operation is flexible to meet market requirements for PX purity
- System is easily amenable to future requirement for incremental capacity increases
- Feed concentration of PX is used efficiently
- Technology is flexible to process a range of feed concentrations (75 wt%–95 wt% PX) using a single refrigeration system
- Design variations are used to recover paraxylene efficiently from feedstocks (~22% PX) in a multi-stage system, competitive with adsorption-based systems.

Continued ▼

Paraxylene, crystallization, *continued*

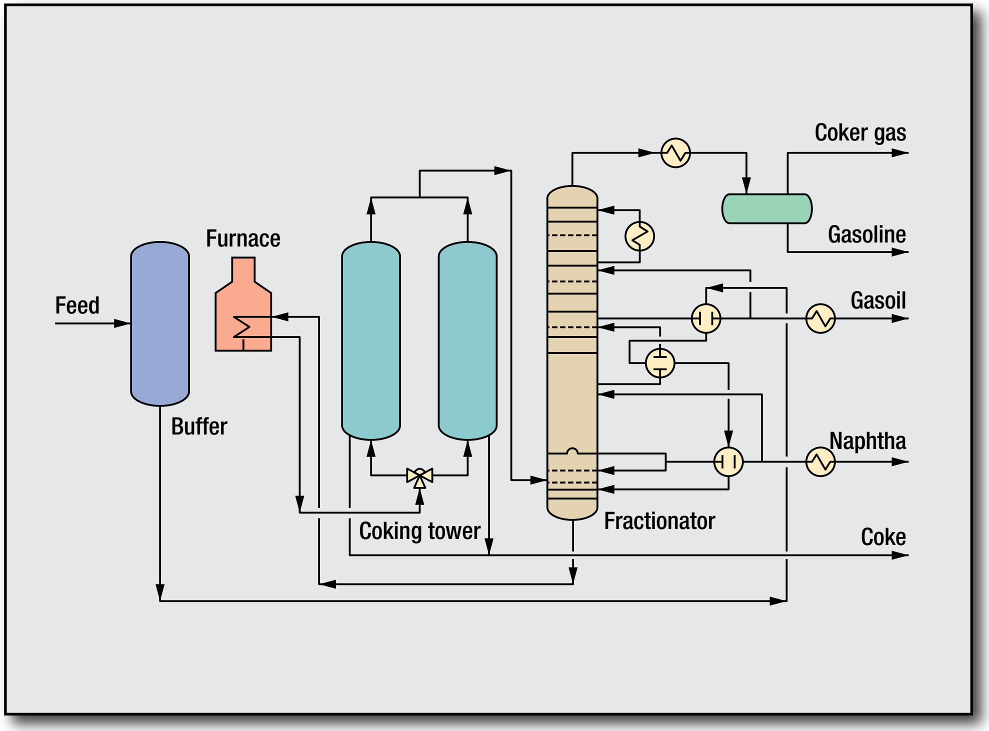
Economics: (400,000 tpy Capacity from concentrated feed)

ISBL investment cost	$35 million
Paraxylene recovery	95%
Electricity consumption	50 kWh/ton PX
Operation mode	Continuous

Commercial plants: Three commercial licenses.

Licensor: CrystPX is a proprietary process technology marketed and licensed by GTC Technology Inc., in alliance with LyondellBassell - CONTACT

Petroleum coke, naphtha, gasoil and gas



Application: The delayed coking technology is a thermal-cracking process to upgrade and convert petroleum residue, asphalt, or slop oil into gas, naphtha, gasoil and petroleum coke. It mainly consists of heater (furnace), coking drums, fractionating section and gas-recovering section.

Description: Key points for the delayed coking technology include:

- Premium petroleum coke (needle coke) can be produced.
- Double-fired, multi-point steam (or water) injection, online spalling, bi-direction steam/air decoking and other techniques enable a three-year run length for the heater and 5% savings.
- The automation and safety interlock design techniques for steam stripping, water quench, coke cooling, hydraulic decoking and oil/gas preheating operations of the coke drums not only reduce work intensity and ensure safe operation, but also create conditions to reduce the drum-cycle time to 16–18 hours.
- The quench oil injection and anti-foaming agent injection with proper position and volume control prevent foaming of the coke drum and fines carry-over into the fractionator.
- During the process from steam stripping to water quench, the oil vapor and steam enter a blowdown system, which treats the vapor and steam in closed mode by stages. The blowdown system can not only recover oil and water and reduce environmental pollution, but it also can process the similar oil and wastewater of the whole refinery.
- The oil/gas preheating process of coke drum with no-coke parking valve improves the oil/gas preheating flow scheme, reduces deformation of the coke drum during oil/gas preheating and shortens preheating time for the oil/gas.
- Equipment improvements of the coke drum include an overhead elliptical head instead of a spherical head, thus increasing the effective volume of the coke drum. The transition section between the skirt and shell connection uses a forged piece structure instead of overlay structure, thereby extending fatigue life. Alloy steel and cladding are used instead of carbon steel, thus improving corrosion resistance.
- The high-efficiency internals improve separation accuracy and enable operation flexibility; coke fine carry-over is reduced.

Continued ▼

- The fractionator recycle oil upper circulation washing and lower spraying washing techniques lower coke fine carry-over in HCGO and other products, thus improving the feed properties for downstream units. The low recycle-ratio operation and flexible recycle ratio adjustment are achieved as well.
- The coke cooling water and coke cutting water are treated separately in closed systems and recycled for reuse. All the treated coke cooling water is recycled for reuse to protect the environment.
- Due to large-scale unit engineering techniques, a single-unit capacity can reach 1.4 metric tpy to 1.6 metric tpy.

Commercial plants: SINOPEC has independently designed and erected more than 50 units with a total processing capacity of 36 million metric tpy over the last 50 years. Thirty-three units have been designed (including revamped units) and constructed in the last 10 years. There are four units with a total processing capacity exceeding 1.6 million metric tpy and are in operation. A 5.2 million metric tpy delayed coking unit is under design and construction.

Licensor: China Petrochemical Technology Co., Ltd. - CONTACT

Phenol

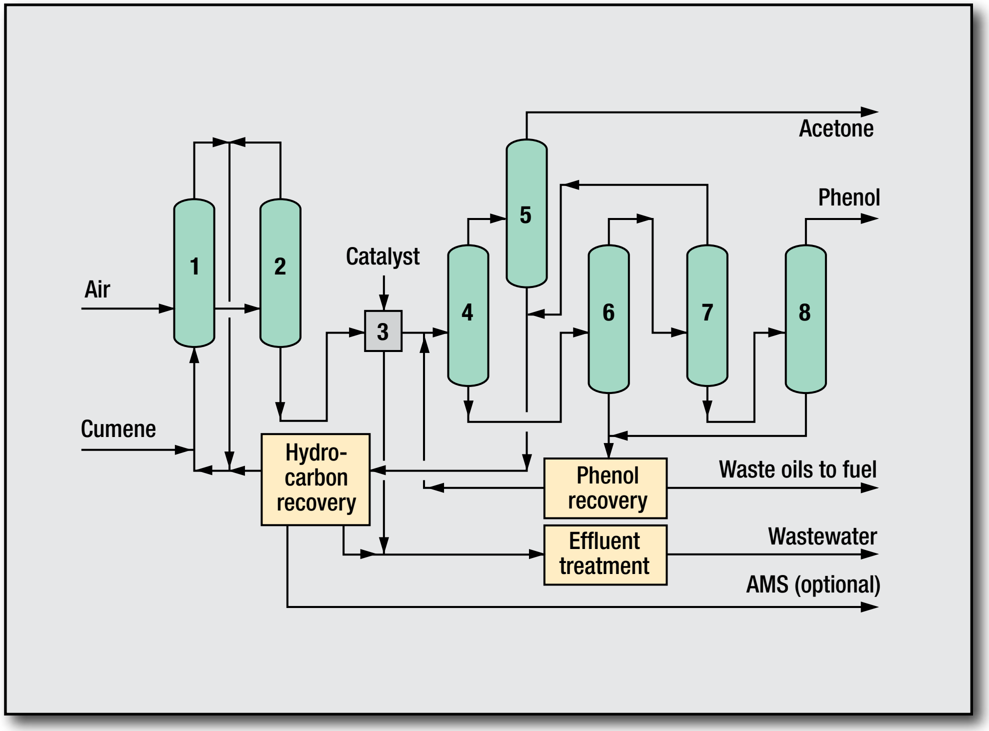
Application: A high-yield process to produce high-purity phenol and acetone from cumene with optional byproduct recovery of alpha methylstyrene (AMS) and acetophenone (AP).

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 cleavage mixture is neutralized and 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.

With AMS hydrogenation, 1.31 tons of cumene will produce 1 ton of phenol and 0.616 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.

Product quality: Typical properties of phenol product:

Property	Specification
Appearance	Clear
Purity (dry basis), wt%	99.99 min.
Total organic impurities, ppm wt	< 30
Water, ppm wt	< 200
Color (APHA)	< 5
Solidification point (dry material), °C	40.85 min.
Total carbonyls, ppm wt	< 10
2-Methylbenzofuran (2-MBF), ppm wt	< 2
Sulfuric acid discoloration (SAD) test, %	95 min.
Iron, ppm wt	< 0.2



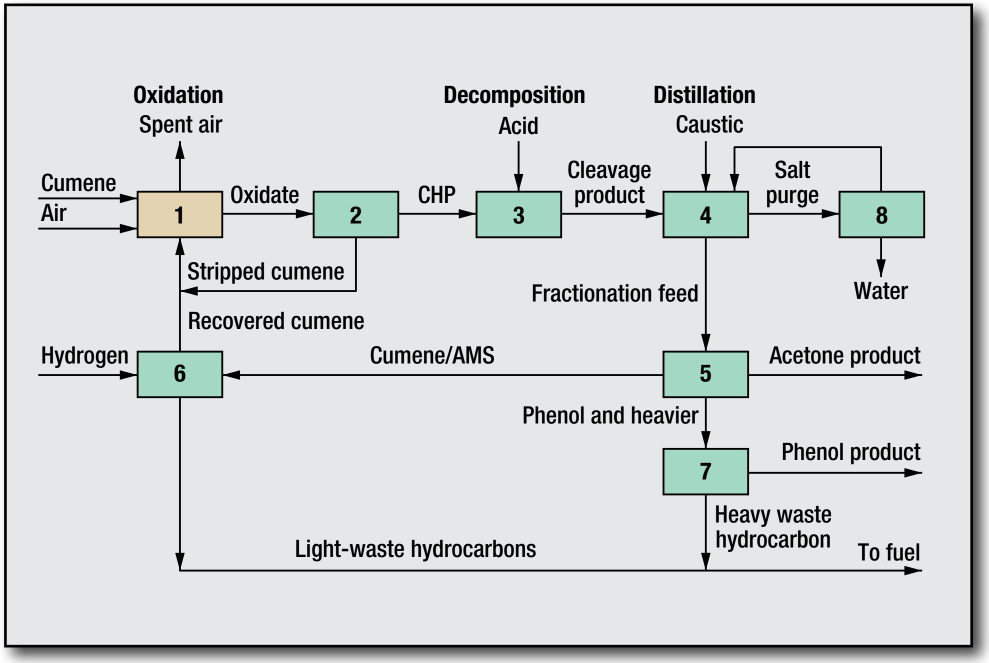
Commercial plants: The KBR Phenol technology has been licensed to 25 producers, and the technology is well-proven commercially at nearly 300,000 metric tpy for single-train operations. In the last five years, KBR was awarded four grassroots phenol plants including two in China and two in Saudi Arabia. More than 50% of the world's licensed phenol capacity is produced via the KBR process.

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

Meyers, R. A., *Handbook of Petrochemical Production Processes*, New York, McGraw Hill, 2005.

Licensor: Kellogg Brown & Root LLC - CONTACT

Phenol



Application: The Polimeri/Lummus process is used to produce high-quality phenol and acetone products from cumene. Alphamethylstyrene (AMS) and pharmaceutical-grade acetone can be produced as byproducts if required.

Description: The process is based on air oxidation of cumene to cumene hydroperoxide (CHP) followed by acid-catalyzed decomposition of CHP to phenol and acetone.

Fresh and recycle cumene is oxidized with air to produce CHP in a series of oxidizers (1) having a unique internal design that improves selectivity and enhances safety. Oxidate is then concentrated in two evaporation stages (2) and fed to a two-stage cleavage section (3) in which CHP is decomposed to phenol and acetone under precisely controlled conditions. AMS is also formed in this section from certain precursors present in the oxidate. The cleavage section effluent is neutralized (4) and then fractionated (5).

Acetone, cumene and AMS are taken overhead in a first distillation column and pure acetone is recovered from this stream. (If desired, acetone containing less than 50 ppm methanol can be produced for pharmaceutical applications.)

Cumene/AMS are fed to a hydrogenation system (6) in which AMS is hydrogenated to cumene. The hydrogenated hydrocarbons are recycled to the oxidizers.

The bottoms from the first distillation column is further fractionated to reject heavies. Extractive distillation (7) using a non-aqueous solvent is used to separate out the carbonyl impurities, producing high-purity phenol.

The technologies for both cumene oxidation and CHP decomposition minimize heavies formation and maximize conversion of by products into recyclable material. The process features flexible, integrated wastewater (8) and vent gas treatment systems, allowing the plant to conform to a wide variety of local, regional, national or international environmental regulations. Polimeri's proprietary simulation software—CheOpe Phenol—allows for the monitoring and optimization of the oxidation and cleavage sections.

Yields and product quality: The consumption of cumene (100%) per metric ton of phenol product is 1.308 metric ton. Phenol purity is higher than 99.99 wt% with less than 10 ppm of carbonyl impurities.

Economics:

Typical utilities, per metric ton of phenol	
High- and medium-pressure steam, metric ton	2.3
Power, kWh	190

Commercial Plants: The process is used in Polimeri Europa's phenol plants at Mantova and Porto Torres, Italy. Two licenses have been granted.

Licensor: Lummus Technology - CONTACT

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 alphamethylstyrene (AMS), catalyzed by mineral acid. This unique design achieves a very high selectivity to phenol, acetone and AMS without using recycle acetone. Decomposed catalyst is neutralized.

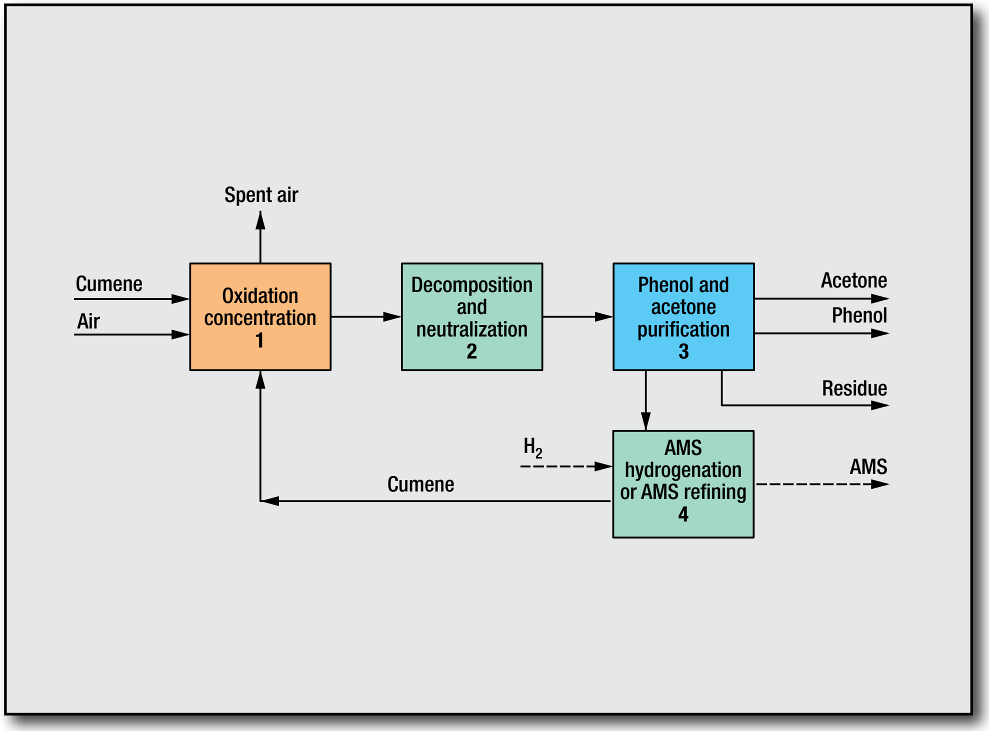
Phenol and acetone purification (3): Phenol and acetone are separated and purified. A small amount of byproduct is rejected as heavy residue.

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). 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. No acetone recycle to the decomposition section and simplified neutralization make the Sunoco/UOP Phenol process easier to operate.

Economics: Basis: ISBL US Gulf Coast

Investment, US$/tpy (200,000 tpy of phenol) 435



Raw materials and utilities, per metric ton of phenol	
Cumene, tons	1.31
Electricity kWh	152
Steam, tons	3.2
Water, cooling, m^3	209

Commercial plants: Fourteen Sunoco/UOP Phenol process units have been licensed with a total phenol capacity of more than 2 million metric tpy.

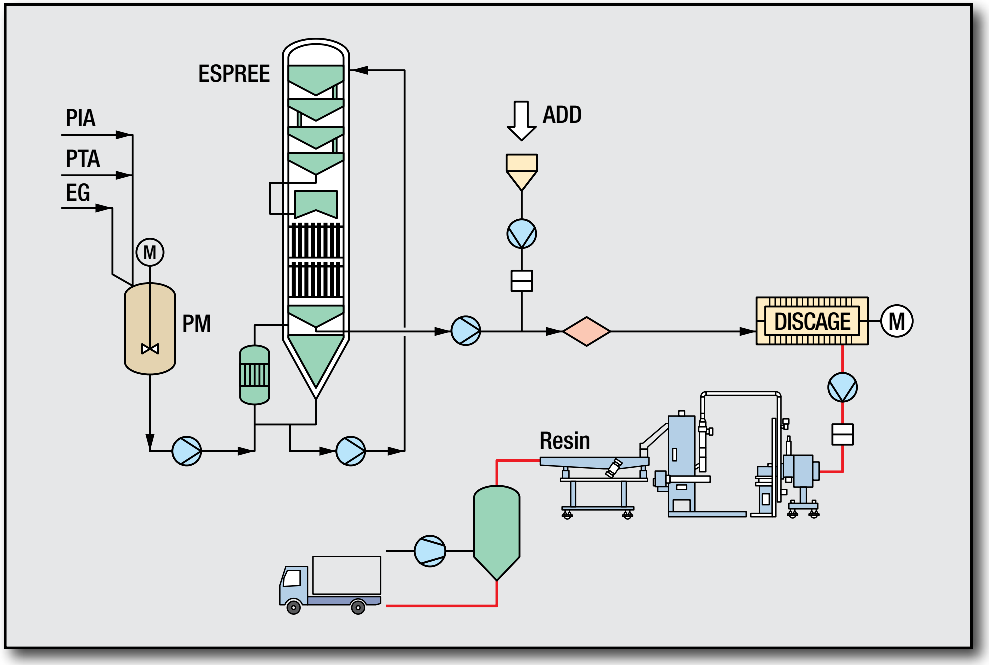
Licensor: Sunoco and UOP LLC, A Honeywell Company - CONTACT

Polyalkylene terephthalates—melt-to-resin (MTR)

Application: New process for directly producing polyesters from all the polyalkylene terephthalate family for bottle-grade resins, based on terephthalic acid (PTA) or dimethyl terephthalate (DMT) and diols using the UIF proprietary two-reactor (2R) process consisting of the tower reactor ESPREE and DISCAGE finisher without a solid-stating post-condensation.

Description: Based on the innovative and patented design modifications to the ESPREE and DISCAGE finisher, which is provided in the medium (MV) or high-viscosity (HV) version. Improved polymer line design, die-face granulation, AA-conditioning, and gentle processing conditions allow to obtain, directly from the melt, highest viscosities of up to 1,500 Pas having a low crystallinity of less than 35% and an AA content below 1 ppm without using a scavenger. The high i. V. polymer melt for bottle-grade PET resins obtained from the DISCAGE finisher is surface cooled and cut by an underwater granulation system in hot water. After separation of pellets and water, the resin is tempered within a few minutes at drying temperatures to avoid stickiness. Later on, the pellets are stored for some hours in a hot air flushed silo to reduce the AA-content to less than 1 ppm.

Economics: The solid state process (SSP) for bottle-grade resins is deleted when applying this new process. The conversion costs are reduced by more than 28% due to lower investment, energy, labor costs and raw material savings. Additionally, the PET resin quality is improved due to low thermal-stress treatment throughout the entire process rendering the lowest polymer degradation, polydispersity, improved color and no core/shell viscosity structure. AA regain during preforming is minimized, as low crystallinity requires significantly less remelting energy.



Commercial plants: Five commercial units with a design capacity of more than 200,000 metric tpy each have been in operation since 2006. A pilot unit is producing 2.4 metric tpd on a semi-industrial scale.

References: "Melt-To-Resin MTR® technology: Benefits for converters," Polyester World Congress, Zürich, 2009.

"OCTAL Petrochemicals opens the world's largest rigid PET sheet plant," 2009.

"Keeping ahead of the market with MTR® technology," Creon PET conference, Moscow, 2009.

"USA: World's First Melt-To-Resin MTR® Plant inaugurated," 2007.

"Melt-To-Resin (MTR®). A new method to produce PET-resin economically without SSP," *Int'l Fiber Journal*, 2006.

Licensor: Uhde Inventa-Fischer - CONTACT

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

Application: 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 the tower reactor ESPREE and the DISCAGE finisher, for textile applications, engineering applications or precursor.

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.

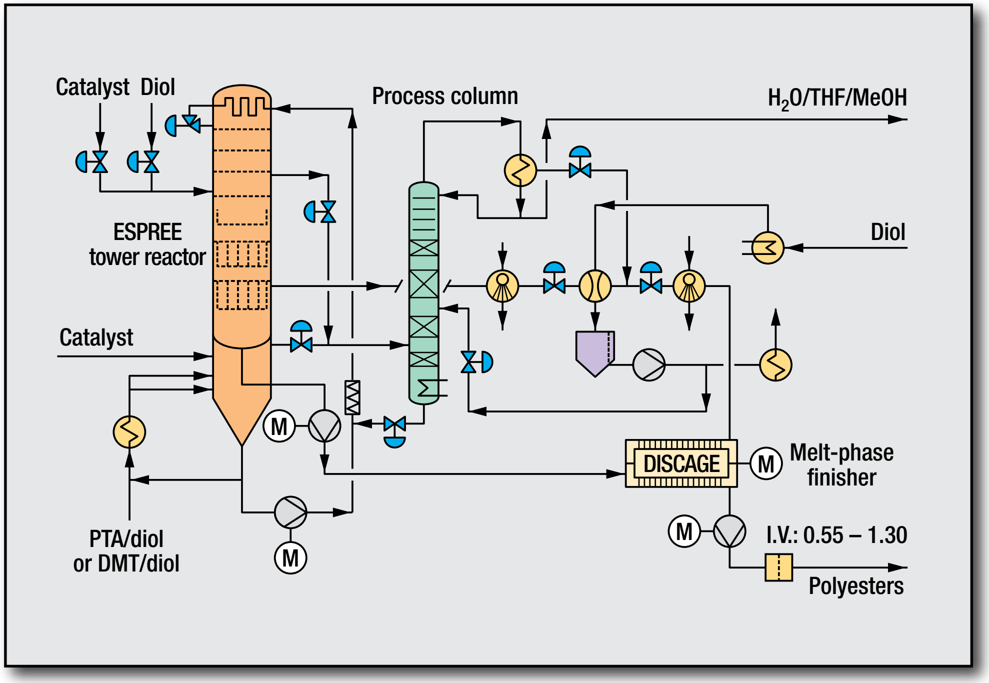
Monomer is transferred via a pressurized pipe to the reactor top where reaction side products are flashed out. Higher conversion rates (97%–99%) are achieved by a cascade of four to six reaction cups at decreasing pressures and increasing temperatures.

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.

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: Ten commercial units with a total operating capacity of > 3,000 metric tpd and one pilot unit of 1 metric tpd.

References: "Textile polyester plant in Mogilev (Belarus) successfully put into operation," 2009.

"Vietnam: Textile Polyester plant for PVTex," 2009.

"Germany: Uhde Inventa-Fischer technology for BASF SE," 2008.

"A new highly economic Polyester Technology > 2R single-stream PET process," *Chemical Fibers Int'l and Int'l Fiber Journal*, 2004.

Licensor: Uhde Inventa-Fischer - CONTACT

Polycaproamide

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

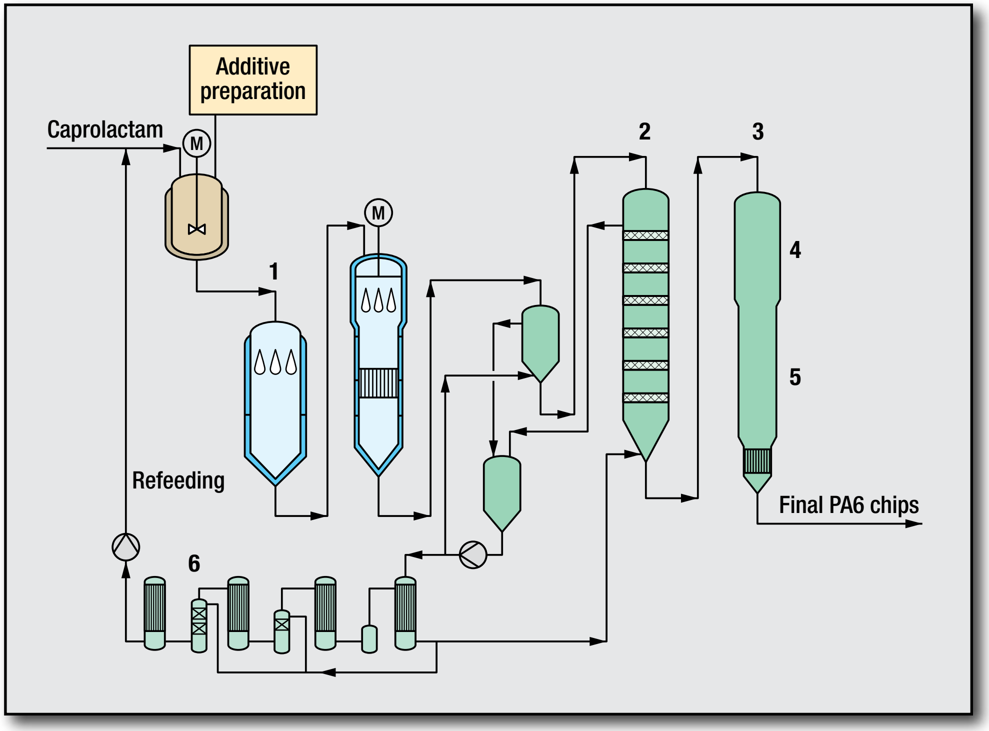
Description: Liquid LC is continuously polymerized in a polymerization unit (one- or two-stage) (1) in the presence of water, stabilizer and modifying additives at elevated temperatures. The polymerization process has proven to be very reliable, easy to operate and economical. Prepolymerization is available to reduce reactor volume for large capacity units. The polycaproamide chips are formed from the melt using strand pelletizing systems 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 consumptions 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.



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 - CONTACT

Polyethylene

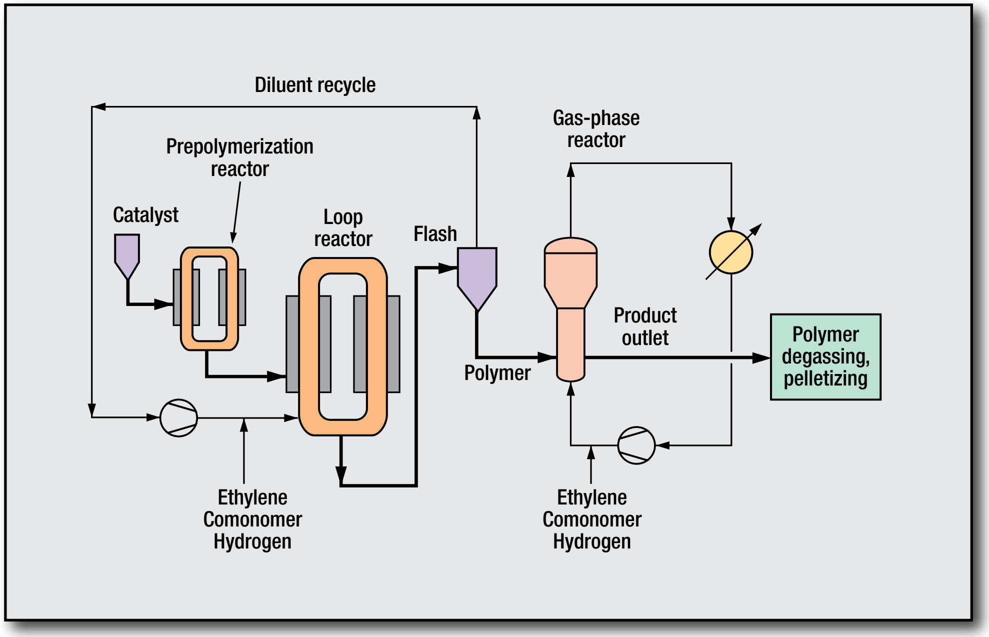
Application: The Borstar polyethylene (PE) process can produce a broad range of bimodal and unimodal linear-low-density polyethylenes (LLDPE), medium-density polyethylenes (MDPE) and high-density polyethylenes (HDPE). The Borstar PE consists of a loop reactor and a gas-phase reactor in series.

Description: PEs with densities of 918–970 kg/m^3 and melt flowrate of 0.1–100 can be produced. Ziegler Natta catalysts are used, but single-site catalysts will be introduced for PE processing.

Catalyst is mixed with a propane diluent and fed to the compact prepolymerization reactor. Cocatalyst, ethylene and hydrogen are also fed into this reactor. The pre-polymerized slurry is sent to the loop reactor, which is designed for supercritical conditions and operates at 75–100°C and 55–65 bar. Typically, lower molecular weight and higher density components of the bimodal polymers are produced in the loop reactor.

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

Polymer from the flash tank polymerizes further in a fluidized-bed gas-phase reactor. No fresh catalyst is needed. The polymer continues to grow on the same catalyst particles, resulting in a homogeneous polymer. The gas-phase reactor operates at 75–100°C and 20 bar. Fresh ethylene, comonomer and hydrogen are fed into the reactor. Typically, high molecular weight components are produced in this step, thus broadening the molecular weight distribution (MWD) and providing strength to the polymer. The production rate ratio between the reactors can be adjusted to meet the targeted product properties. After removing hydrocarbon residuals, the polymer powder is transferred to extrusion.



Products: A wide range of bimodal and unimodal products with a full control of comonomer distribution, can be produced, with densities ranging from 918 kg/m^3 to 970 kg/m^3 and melt flowrate from less than 0.1 to over 100. The MWD can be controlled from narrow to broad. Advanced properties are tailor-made for different applications such as pipe strength, film-bubble stability as well as high ESCR and stiffness in blow molding. Other special applications include extrusion coating and wire and cable.

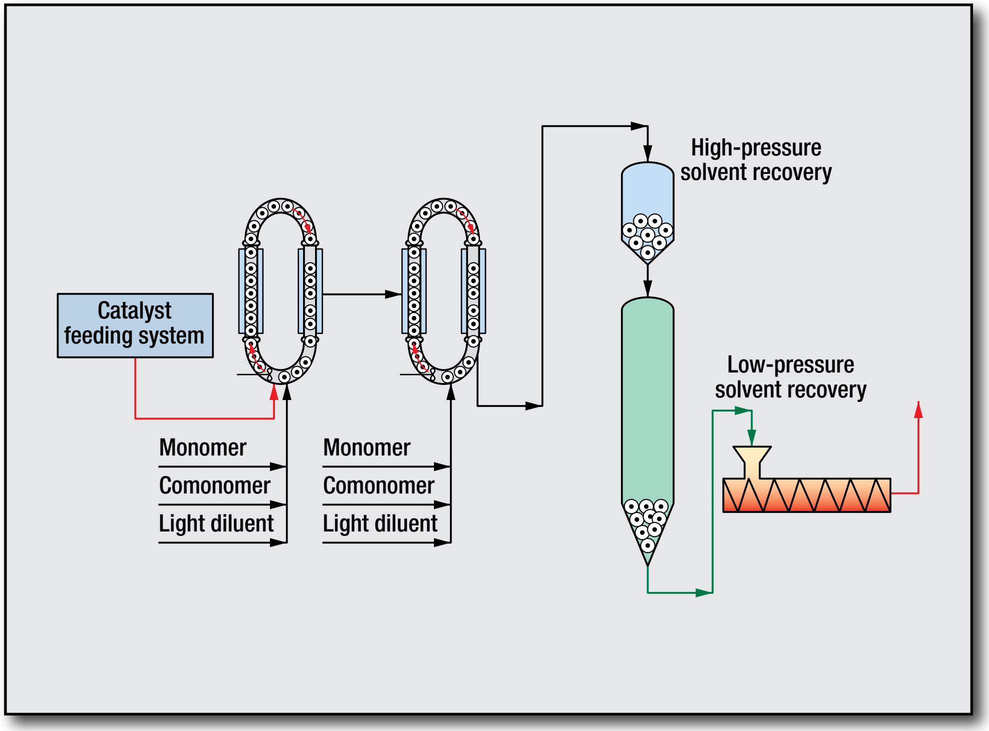
Commercial plants: The first commercial scale Borstar PE plant is a 160,000-tpy facility operating at Borealis in Finland since 1995. A retrofitted HDPE Borstar plant at Stenungsund, Sweden, added 225,000-tpy capacity in 2000. A 250,000-tpy plant started up in 2002 in China for Shanghai Petrochemicals (SPC). In July 2010, Borouge, a joint-venture between the Abu Dhabi National Oil Co. and Borealis, formally signed

Continued ▼

three major engineering, procurement and construction contracts valued at approximately US$ 2.6 billion for its Borouge 3 strategic expansion in Ruwais, Abu Dhabi, in the UAE. The first contract worth US$ 1.255 billion for the construction of two Borstar enhanced polyethylene units and two Borstar enhanced polypropylene units, as well as the second contract worth US$ 400 million for the construction of a 350,000 tpy low-density polyethylene (LDPE) unit. The annual capacity of the new polyethylene units is 1.080 million tpy and the new polypropylene unit is 960,000 tpy. These significant investments will quadruple Borouge's production capacity to over 4.5 million tpy 2013, making it the largest integrated polyolefins site in the world. Maximum single-line design capacity is 350,000 tpy.

Licensor: Borealis A/S - CONTACT

Polyethylene



Application: INEOS Technologies is offering a slurry high-density polyethylene (HDPE) process (INNOVENE S) for license. This technology is based on a process developed by Solvay. The technology was used by the BP/Solvay joint venture in 2002 and acquired by BP when they bought out Solvay's share of their joint venture company in early 2005. It became part of INEOS's portfolio through its acquisition of Innovene at the end of 2005. INNOVENE S is now the most successful HDPE technology in the market with more than 2.3 million metric tons sold since this entry in the licensing arena.

Process description: The INNOVENE S process utilizes a proprietary vertical slurry-loop reactor, as shown in the flow diagram. Two reactors are used for bimodal capability. Isobutane is normally used as the hydrocarbon diluent in the process, although hexane may be used as an alternative. The diluent is used as a catalyst carrier and as the polymerization reactor suspension and heat transfer medium. Hexene-1 and/or butene-1 can be used as a comonomer. Hydrogen is used for molecular weight control when using the Zieglerg catalyst platform. Titanium-based and chromium-based catalysts are both used.

The polymerization reactor is made of large diameter pipes assembled in a long vertical loop configuration. Early designs consisted of four- or six-leg loops. The reactor walls are made of carbon steel and are equipped with water jackets to control temperature in the isothermal reactor. Ethylene is polymerized under a total pressure of about 25 bars to 40 bars and at a temperature between 75°C and 110°C (167°F and 230°F). The recycle diluent, fresh monomer, comonomer, hydrogen, catalyst and co-catalyst (when required), are fed to the reactor. Polyethylene is formed as discrete particles in a rapidly circulating diluent-polymer slurry. On average, 98% of the ethylene is polymerized.

The concentrated withdrawn polymer slurry is flashed to separate the powder from the diluent and unreacted monomers. The polymer flows from the bottom of the flash tank, with the condensed overheads being recycled directly to the reaction system. Residual hydrocarbons are removed from the polymer using a countercurrent nitrogen purge flow. The polymer is then pneumatically transferred to either the extruder feed tank or storage silos.

Product coverage: INNOVENE S technology is capable of producing a full MDPE/HDPE product coverage with Ziegler or chromium catalyst, using monomodal and bimodal configuration with market leading products such PE100.

Continued ▼

Polyethylene, *continued*

High added-value products, in addition to the lowest investment and operational costs allow INNOVENE S technology to make a winning MDPE/HDPE business.

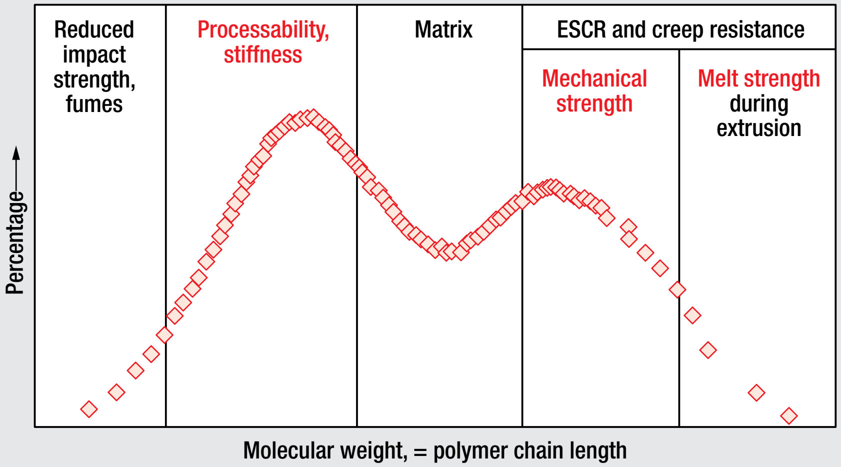
Process advantages:

- Low investment costs (low equipment count)
- Operating costs
- Proven two-reactor bimodal technology
- High onstream times with no reactor fouling or cleaning
- No wax generation and no oligomers
- Safe and environmentally clean operation

Product advantages:

- Broad MDPE and HDPE product range based
- Monomodal and biomodal capability
- Chromium and Ziegler product coverage with demonstrated catalyst transitions
- Easy product transitions
- Proprietary technology to achieve outstanding bimodal products Properties

Licensor: INEOS Technologies - CONTACT



Polyethylene

Application: The SCLAIRTECH[1] technology process produces the full range of linear polyethylene (PE) products, including linear-low-density, medium-density and high-density grades with narrow to broad molecular weight distribution. It is the most efficient PE swing process that allows for economical production across the full spectrum of PE grades from a single train.

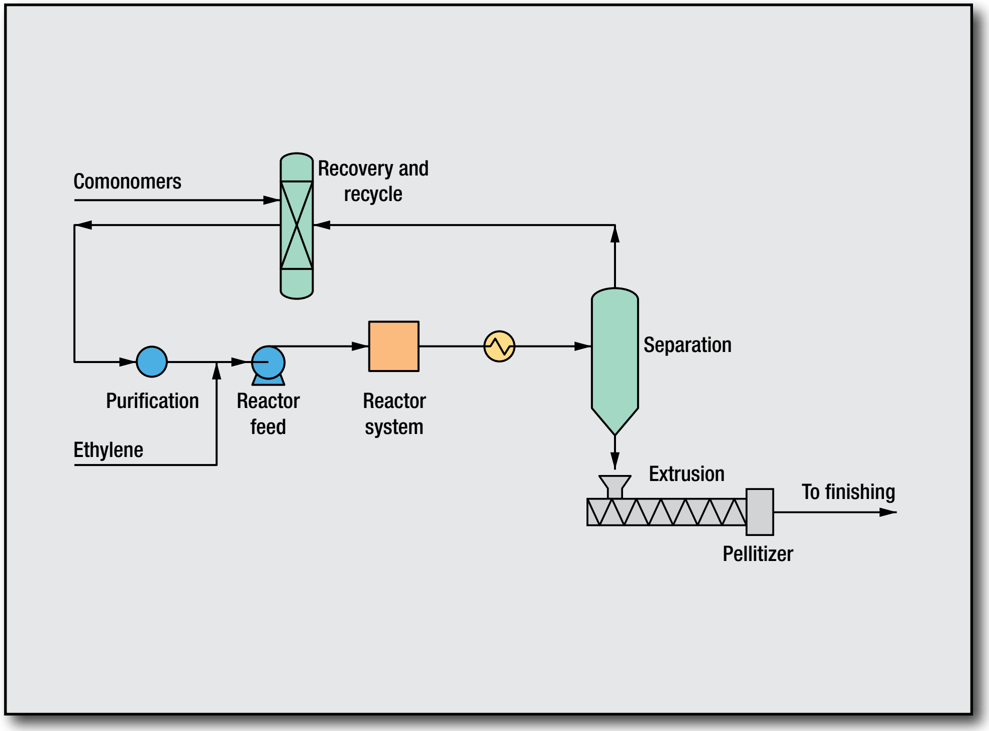
Description: Ethylene and comonomer are dissolved in solvent then fed into a reactor. Butene-1, octene-1 or both together can be used as comonomer. The reactor system operates in a solution phase, and, due to inherent low residence time (less than 2 minutes), it offers a tremendous flexibility for grade 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/m^3, 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 comonomers 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 in Canada and the latest is starting-up in India in 2010. Including this new facility, there are 12 plants operating worldwide with this technology, representing 2.8 million metric tpy of total capacity.

Licensor: NOVA Chemicals (International) S.A. - CONTACT

[1] SCLAIRTECH is a trademark of NOVA Chemicals.

Polyethylene

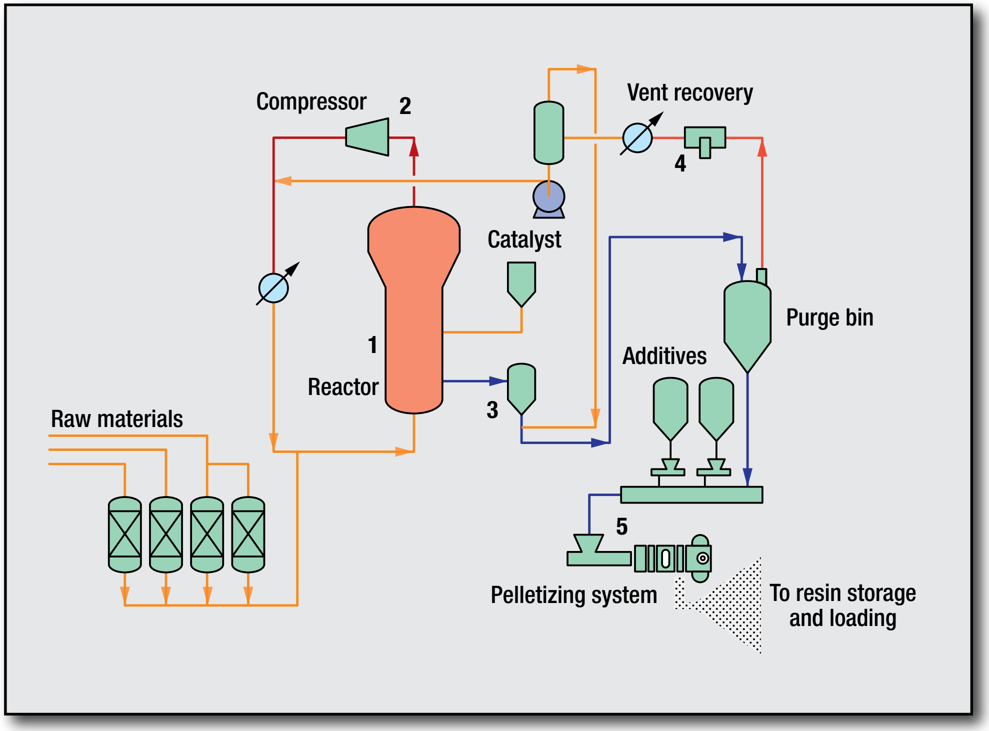
Application: The UNIPOL Polyethylene (PE) Process produces the widest array of linear low-density polyethylene (LLDPE), medium-density polyethylene (MDPE) and high-density polyethylene (HDPE) having unimodal or bimodal molecular weight distribution (MWD) using a single, low-pressure, gas-phase reactor.

Description: The UNIPOL PE Process provides licensees proven flexibility to use a single process with the capability to produce a broad product mix that can be adapted to changing market needs.

Ethylene, comonomer, hydrogen and nitrogen enter the circulation loop that delivers reactants, cooling and mixing in a fluidized bed gas phase reactor (1). Ziegler-Natta, chromium-based or metallocene catalyst is fed into the reactor, which operates at low pressure (< 25 bar) and low temperature (approximately 90°C) and is capable of producing products with either unimodal or bimodal MWD. Adjusting and controlling gas composition and temperature allows for a broad product range to be made with each catalyst. A second reaction system is not required for bimodal products.

The reactor dome efficiently separates the solids from the circulating gas, and the robust design of all equipment avoids the complexity and fouling risk of secondary separation devices such as cyclones or filters. The low head compressor (2) sends the circulation gas through a single conventional external cooler, removing the heat of reaction and compression. The UNIPOL PE Process pioneered the use of "Condensing Mode" and now "Super Condensing Mode" where a portion of the heavier components of the circulation are condensed and carried into the reactor bed as well-dispersed droplets without the need for separators or pumps. The evaporative cooling allows for higher production rates and smoother operation using smaller reactors.

The product discharge system (3) uses the effect of solids displacing gas to minimize reactant discharge and avoid a costly recycle compressor. The granular PE powder is conveyed up to a settled bed purge bin where a drying gas removes the residual reactants. The mixed gas from the purge bin is compressed and cooled in the vent recovery system (4) so condensed reactants can be easily pumped back to the reactor without any distillation or purification. The drying and recovery is inherently simple since no diluent or solvent is used in the process.



In one low-investment configuration, the granular powder from the purge bin flows by gravity to the pelletizing system (5) where additives are incorporated. Low gel pelletizing is achieved across the product slate. Univation Technologies' attention to process design provides a simple and cost effective process for polyethylene manufacture.

Products: A broad range of LLDPE, MDPE and HDPE products can be produced using butene or hexene comonomer with a density range of

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0.915 g/cm to 0.970 g/cm and a narrow, broad or bimodal MWD. Melt index varies from less than 0.1 to greater than 200. Grades produced are suitable for film, blow molding, pipe (PE-100), injection molding, rotational molding and extrusion applications.

Economics: The simplicity of the UNIPOL PE Process offers low investment and operating costs while providing the flexibility to quickly adapt product mix to changing market needs. The manufacture of bimodal products in a single reactor reduces investment when compared against multiple reactor processes. With a low operating pressure and no diluent or solvent, the gas-phase process has low usage of steam and electricity, and provides efficient use of monomer, nitrogen and water.

Commercial plants: The UNIPOL PE Process has over 40 years of proven capability with over 100 reactor lines in operation or under construction that range in capacity from 40 million tpy to 650 million tpy.

Licensor: Univation Technologies, LLC - CONTACT

Polyethylene, HDPE

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

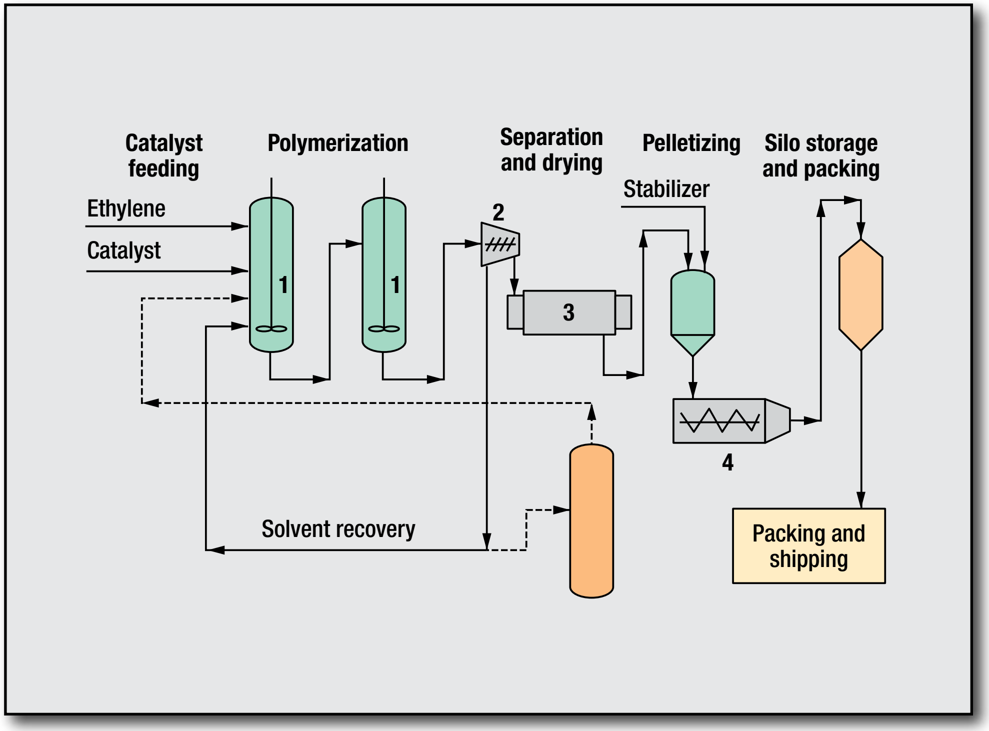
Description: The CX process uses two polymerization reactors in series. The products have bimodal molecular-weight distribution (MWD), where MWD and composition distribution is freely and easily controlled by adjusting the operating conditions of two reactors without changing the catalyst.

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, comonomer and 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 fed to the separation system (2). The wet cake is dried into powder in the dryer system (3). The solvent is separated from the slurry and as much as 90% of separated solvent is directly recycled to the reactors without any treatment. The dry powder is pelletized in the pelletizing system (4) along with required stabilizers.

Products: A broad range of homopolymer and copolymer can be produced including PE-100+ pipe grade.

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



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

Ethylene and comonomer, kg	1,012
Electricity, kWh	315
Steam, kg	305
Water, cooling, ton	210

Commercial plants: Forty-six reactor lines are in operation, engineering design or construction worldwide with a total production capacity of over 5.8 million tpy.

Licensor: Mitsui Chemicals, Inc. - CONTACT

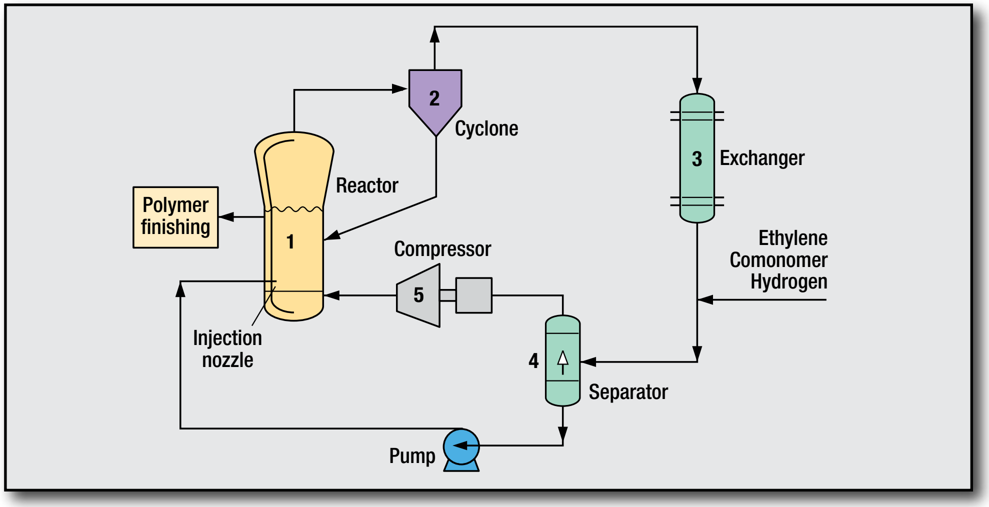
Polyethylene

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

Description: Ziegler-Natta and metallocene catalysts are directly injected into the reactor from storage where as chromium catalysts are injected following activation of the catalyst via INEOS proprietary technology. The INEOS 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 product properties, such as density and melt index (MI), 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 barg, 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 are 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. mLLDPE are high peformance linear low film grade products based on metallocene catalyst using hexene-1 or octene-1 as comonomer. The performance of this product are key differentiator in several film markets segments like food packaging, lamination and stretch film.

Commercial plants: Thirty-two licenses are operating, in design or under construction worldwide representing around 8 million tpy production with capacities ranging from 50,000 tpy to 450,000 tpy. Designs up to 600,000 tpy are also available.

Licensor: INEOS Technologies - CONTACT

Polyethylene, LDPE, autoclave reactor

Application: The high-pressure *Lupotech* A autoclave reactor process is used to produce low-density polyethylene (LDPE) homopolymers, EVA and various acrylic type copolymers. Single-train capacity of up to125,000 tpy can be provided.

Description: Ethylene, initiator and, if applicable, comonomers are fed to the process and compressed to pressures up to 2,400 bar before entering the autoclave reactor.

The polymer properties (MI, density, 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* A process, including standard LDPE grades to EVA copolymers or n-butyl-acrylate modified copolymer. The products can be applied in (shrink) film extrusion, extrusion coating, 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 autoclave reactor design with low residence time are easy and quick transitions, startup and shutdown.

Reactor grades from MI 0.15 to 400 and from density 0.913 to 0.932 g/cm^3, with comonomer content up to 40% can be prepared.

Economics: Consumption, per metric ton of PE:

Ethylene, ton	1.008
Electricity, kWh	900–1,300 (homopolymer grades)
Steam, ton	0.2
Nitrogen, Nm^3	4

Commercial plants: *Lupotech* A plants with a total installed capacity of approximately 1.5 million tpy have been licensed.

Licensor: Equistar (legal entity) LyondellBasell - CONTACT

Polyethylene, LL/MD/HDPE

Application: New generation *Spherilene* gas-phase technology with simplified process flow scheme, to produce the full range of linear-low-density polyethylene (LLDPE), medium-density polyethylene (MDPE) and high-density polyethylene (HDPE) The technology features process simplicity, best in class monomer efficiency as well as catalyst and process options and is able to meet all product portfolio requirements.

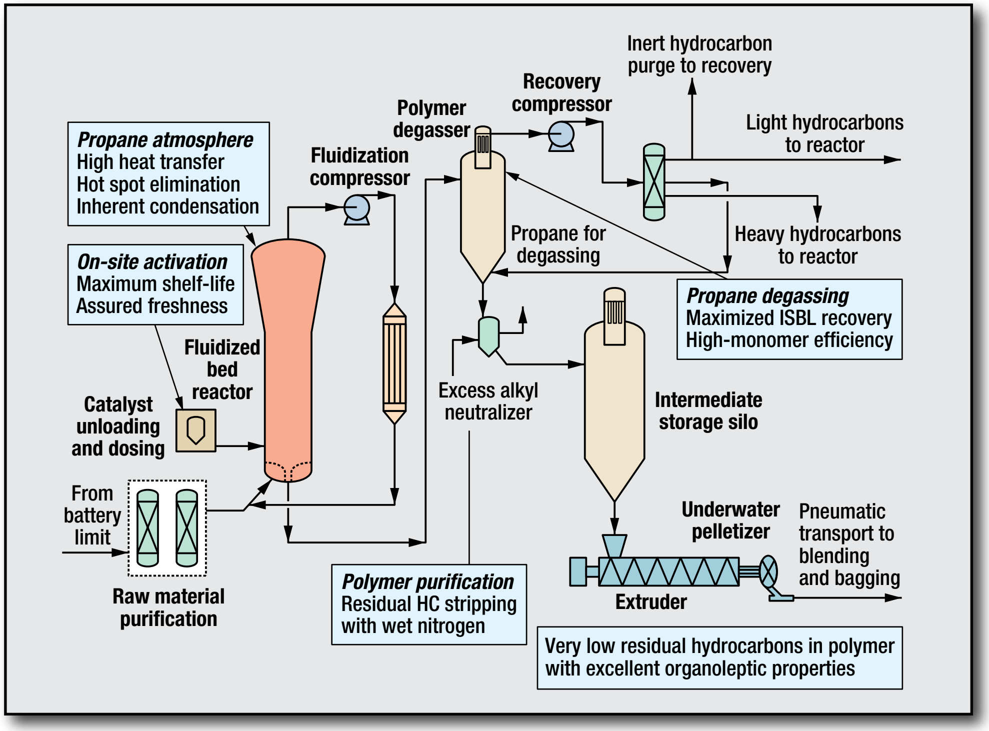
Description: Solid catalyst, alkyls and donor are brought into contact in the pre-contact vessels, where the catalyst is activated. Activated catalyst stream from the pre-contact vessel flows directly into the gas phase reactor and is dispersed in the fluidized reacting bed. The spherical morphology *Avant Z* catalysts can be introduced directly into the reactor, even when empty. Chromium or other specialty catalysts are introduced when there is a seed bed in the reactor.

Ethylene, comonomer and hydrogen are fed to the reactor according to the required production capacity and proportions needed for the target product. Propane is used as the inert medium of reaction and provides an independent means of controlling the reaction kinetics while providing a heat removal capability far superior to that of inorganic inerts (such as nitrogen). The heat of the reaction is removed from the fluidizing gas in a water cooled vertical heat exchanger.

The polymer is withdrawn continuously from a specially designed outlet at the bottom of the reactor and sent to a degassing vessel where monomer unreacted, comonomer and hydrogen are removed from the polymer with the help of a counter-current propane gas flow.

The recovered gas is sent to the hydrocarbon recovery section, where the reaction components are separated from propane and both fractions are recycled inside BL as appropriate. Thus, the hydrocarbon efficiency is kept very high.

Polymer from the propane degassing vessel is fed by gravity to a deactivation vessel where the dissolved hydrocarbons are removed from the polymer by counter-current stripping with nitrogen assisted by a small amount of steam. Steam also ensures that any residual activity of catalyst system components is neutralized completely.



From the bottom of the deactivation vessel, the polymer is conveyed pneumatically to the powder silo located on top of the extruder. The silo is provided with nitrogen purging to ensure that no residual hydrocarbons accumulate in the silo. Polymer from the silos is mixed with required additives before being fed to the extruder.

The *Spherilene* process can also be designed with two gas-phase reactors in series to allow production of bimodal products. In addition, a *Spherilene* process plant built with one reactor can also be expanded in the future by the addition of a second reactor circuit to increase capacity and expand product capability. Thus, Spherilene provides a

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proven and unique, future-proof technology platform to assure long term success for a plant.

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. From a simple cost-effective single reactor configuration, traditional LLDPE, MDPE and HDPE grades for film, blow molding, injection molding, rotomolding, geomembranes, textile, raffia and extrusion applications, a full range of LLDPE products for cast and blown film, extrusion coating are available. Further, the dual reactor configuration 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.

Economics: Consumption, per metric ton of LLDPE:

Ethylene and comonomer, ton	1.005
Electricity, kWh	410
Steam, kg	200
Water, cooling, $\Delta T = 10°C$, metric ton	150

Commercial plants: Licensed from 1992, 12 plants using *Spherilene* process and technology have been licensed, with a total capacity of 3 million tpy. In addition, LyondellBasell operated two plants with a total capacity of 300,000 tpy. Single-line capacities in operation range from 100,000 tpy to 370,000 tpy, with current process design available for plants up to 600,000 tpy in single-line capacity.

Licensor: LyondellBasell - CONTACT

Polyethylene, HDPE

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

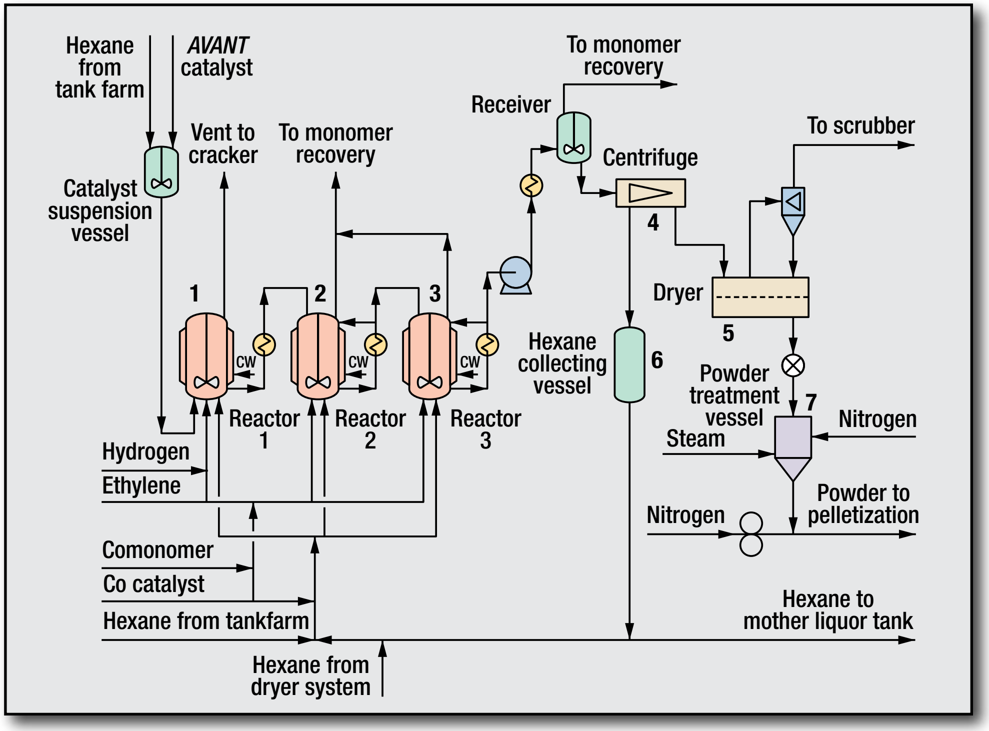
Description: The *Hostalen* ACP process is a slurry polymerization method with three reactors in series. The reaction in cascade enables producing top quality unimodal, bimodal and multimodal polyethylene (PE) from narrow to broad molecular weight distribution (MWD) with the same catalyst family.

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 HDPE production the catalyst, the dispersing medium, monomer and hydrogen are fed to the reactor (1,) where the first polymerisation step occurs.

The second and third step polymerization occurs under different reaction conditions with respect to each reactor. No further catalyst only ethylene, butene and further dispersing medium are fed to the second (2) and third reactor (3). Reactor conditions are controlled continuously, thus HDPE with very high properties is manufactured.

Finally, the HDPE slurry from the third reactor is sent to the decanter (4) and the polymer is separated from the dispersing medium. The polymer containing the remaining hexane is dried in a fluidized bed dryer (5) and catalyst/cocatalyst residuals are removed in the powder treatment vessel (7).

The powder is 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 advanced cascade technology enables the manufacturing of tailor-made products with a definite MWD from narrow to broad MWD, including bimodal and multimodal molecular design. The melt flow index may vary from below 0.2 (multimodal 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, ton	1.015
Electricity, kWh	450 including extrusion
Steam, kg	450
Water, cooling water, ΔT = 10°C, metric ton	175

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Polyethylene, HDPE, *continued*

Commercial plants: There are 41 Hostalen and Hostalen ACP plants in operation or under construction, with a total licensed capacity of 8 million tpy. Individual capacity can range up to 400,000 tpy for a single-line installation.

Licensor: LyondellBasell - CONTACT

Polyethylene, LDPE, Tubular Reactor

Application: The high-pressure *Lupotech* T tubular reactor process is used to produce low-density polyethylene (LDPE) homopolymers and EVA copolymers. Single-train capacity of up to 450,000 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.

The polymer properties (MI, density, 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.

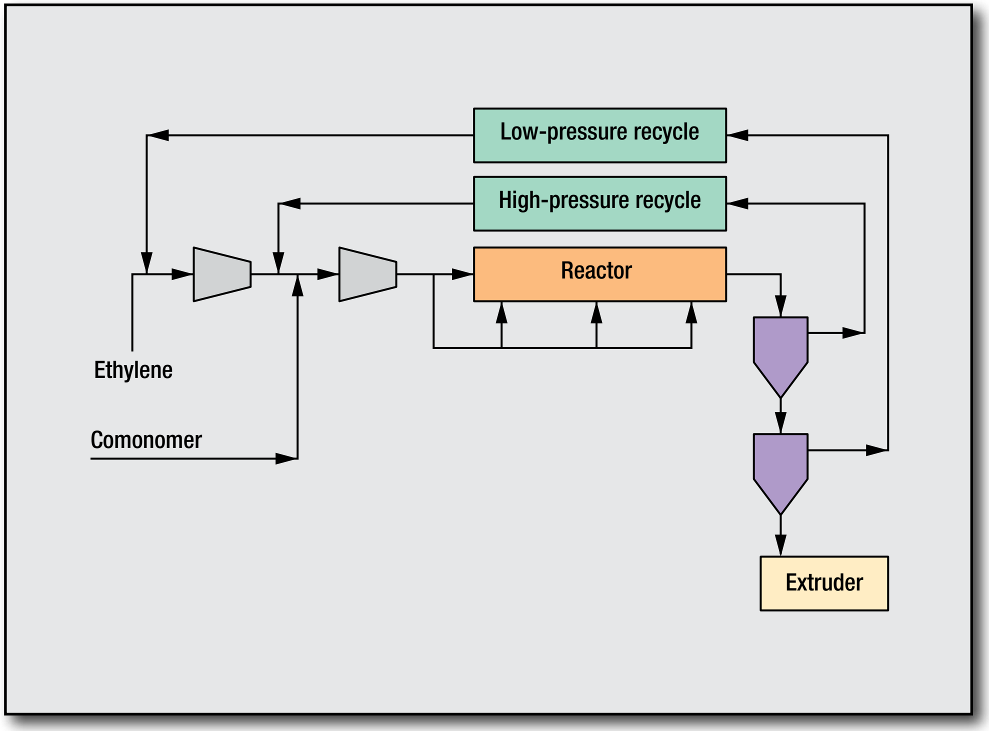
A range of products can be obtained using the *Lupotech* T process, including standard LDPE grades to EVA copolymers or n-butyl-acrylate modified copolymer. The products can be applied in (shrink) film extrusion, injection molding, extrusion blow molding, pipe extrusion, pipe coating, tapes and monofilaments.

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 shutdown.

Reactor grades from MI 0.15 to 50 and from density 0.917 to 0.934 g/cm^3, with comonomer content up to 30% can be prepared.

Economics: Consumption, per metric ton of PE:

Ethylene, ton	1.006
Electricity, kWh	700–900
Steam, ton	–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 9 million tons. LyondellBasell operates LDPE plants in Europe with a total capacity of close to 1 million tpy. The newest state-of-the-art *Lupotech* T unit at Al-Jubail, KSA, was commissioned in 2009; with a capacity of more than 400,000 tons, it is the largest single-line LDPE plant.

Licensor: Basell Polyolefins and LyondellBasell - CONTACT

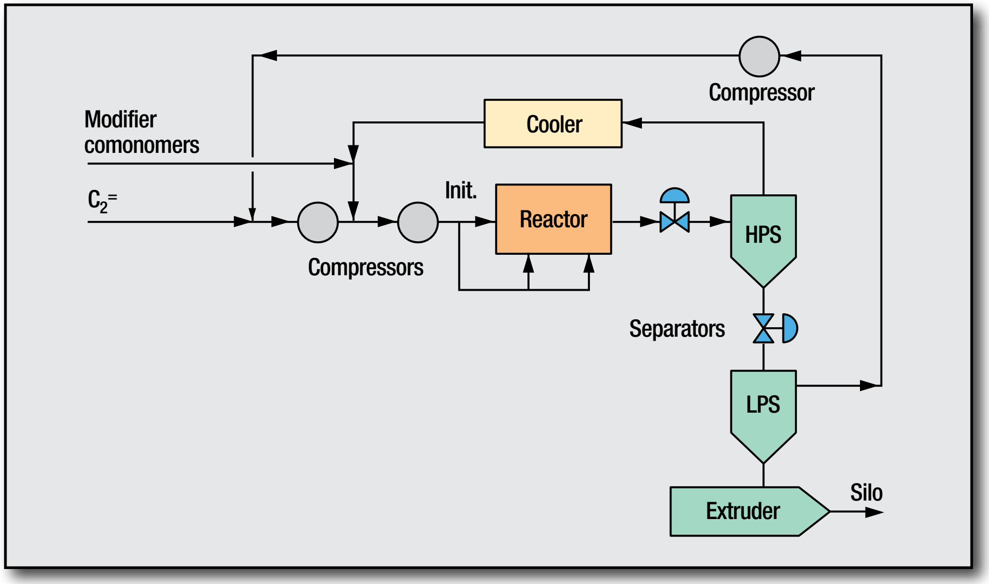
Polyethylene-LDPE

Application: To produce low-density polyethylene (LDPE) homopolymers and ethylene vinyl acetate (EVA) copolymers using the high-pressure free radical process. Large-scale tubular reactors with a capacity in the range of 130,000 tpy–425,000 tpy, as well as stirred autoclave reactors with capacity around 125,000 tpy 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 (MWD) are controlled with temperature profile, pressure, initiator and comonomer concentration. Autoclave reactors can give narrow or broad MWD, depending on the selected reactor conditions, whereas tubular reactors are typically used to produce narrow MWD 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 times 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. Vinyl acetate content up to 30 wt%.

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

Ethylene, ton/ton	1.007
Electricity, kWh	800
Steam, ton/ton	0.3
Nitrogen, Nm^3/t	3

Commercial plants: Affiliates of ExxonMobil Chemical Technology Licensing LLC operate 18 high-pressure reactors on a worldwide basis with a capacity of approximately 1.75 million tpy. Homopolymers and a variety of copolymers are produced. Since 1996, ExxonMobil's LDPE process has been licensed to 10 licensees with a total installed capacity (either in operation or under construction) of approximately 1.9 million tpy.

Licensor: ExxonMobil Chemical Technology Licensing LLC - CONTACT

Polypropylene

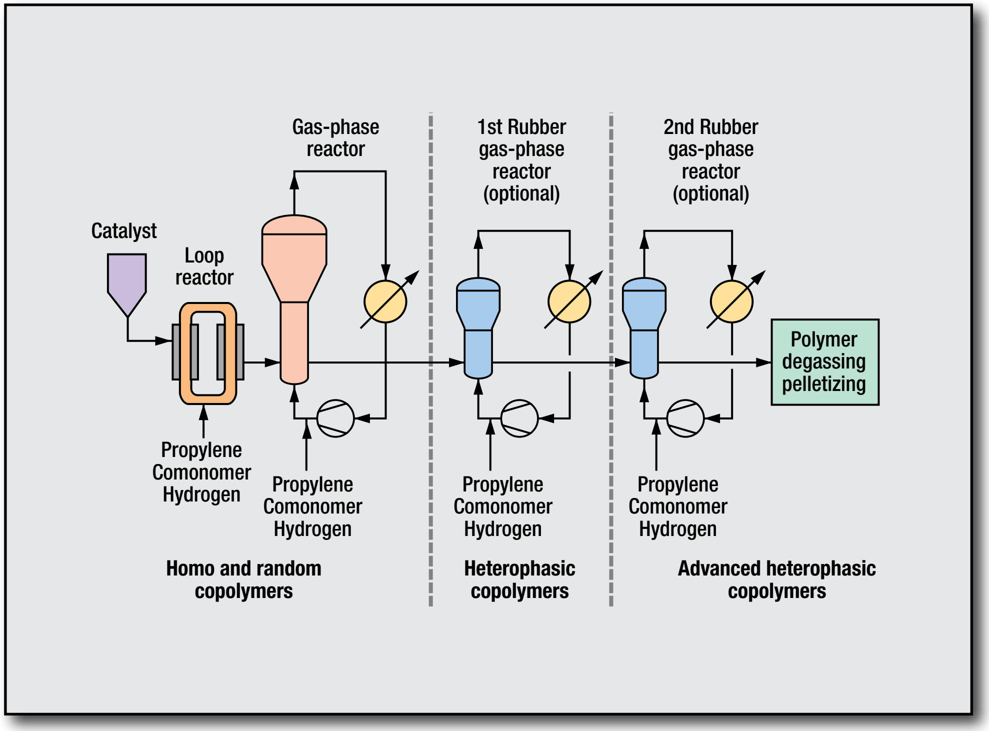
Application: The Borstar polypropylene (PP) process can produce homopolymers, random copolymers, heterophasic copolymers, and very high-rubber-content heterophasic copolymers. It is a modular process; consisting of a loop reactor/gas-phase reactor combination.

Description: PP with a melt flowrate ranging from 0.1 to 1,200 can be produced. Borstar PP uses a Ziegler Natta catalyst, but single-site catalysts can be used in the future. When producing homopolymers and random copolymers, the process consists of a loop reactor and a gas-phase reactor in series. One or two gas-phase reactors are combined to manufacture heterophasic copolymers.

Propylene, catalyst, cocatalyst, donor, hydrogen, and comonomer (for random copolymers) are fed into the loop reactor; propylene is used as the polymerization medium (bulk polymerization). The loop reactor is designed for supercritical conditions and operates at 80–100°C and 50–60 bar. The propylene/polymer mixture exits the loop reactor and is sent to a fluidized-bed, gas-phase reactor, where propylene is consumed in polymerization. This reactor operates at 80–100°C and 25–35 bar. Fresh propylene, hydrogen and comonomer (in case of random copolymers) are fed into the reactor. After removing hydrocarbon residuals, the polymer powder is transferred to extrusion.

For heterophasic copolymers, polymer from the gas-phase reactor is transferred to another, smaller gas-phase reactor where the rubbery copolymer is made. After this processing step, hydrocarbon residuals are removed, and the powder is transferred for extrusion.

The basic module, loop/gas-phase reactor combination, enables high once-through conversion (minimized recycle), since unreacted monomer from loop reactor is consumed in the gas-phase reactor. Polymerization conditions in each reactor can be independently controlled, enabling production of both standard unimodal and broad-molecular-weight multimodal grades. The production rate ratio between the reactors can be adjusted to meet the targeted product properties.



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

Commercial plants: The first Borstar PP plant has successfully operated since May 2000 in Schwechat, Austria, with 200,000-tpy capacity. Maximum single-line design capacity can achieve 400,000 tpy. In July 2010, Borouge, a joint-venture between the Abu Dhabi National Oil

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Co. and Borealis, formally signed three major engineering, procurement and construction contracts valued at approximately US$ 2.6 billion for its Borouge 3 strategic expansion in Ruwais, Abu Dhabi, in the UAE. The first contract worth US$ 1.255 billion for the construction of two Borstar enhanced polyethylene units and two Borstar enhanced polypropylene units, as well as the second contract worth US$ 400 million for the construction of a 350,000 tpy low-density polyethylene (LDPE) unit. The annual capacity of the new polyethylene units is 1.080 million tpy and the new polypropylene unit is 960,000 tpy. These significant investments will quadruple Borouge's production capacity to over 4.5 million tpy 2013, making it the largest integrated polyolefins site in the world.

Licensor: Borealis A/S - CONTACT

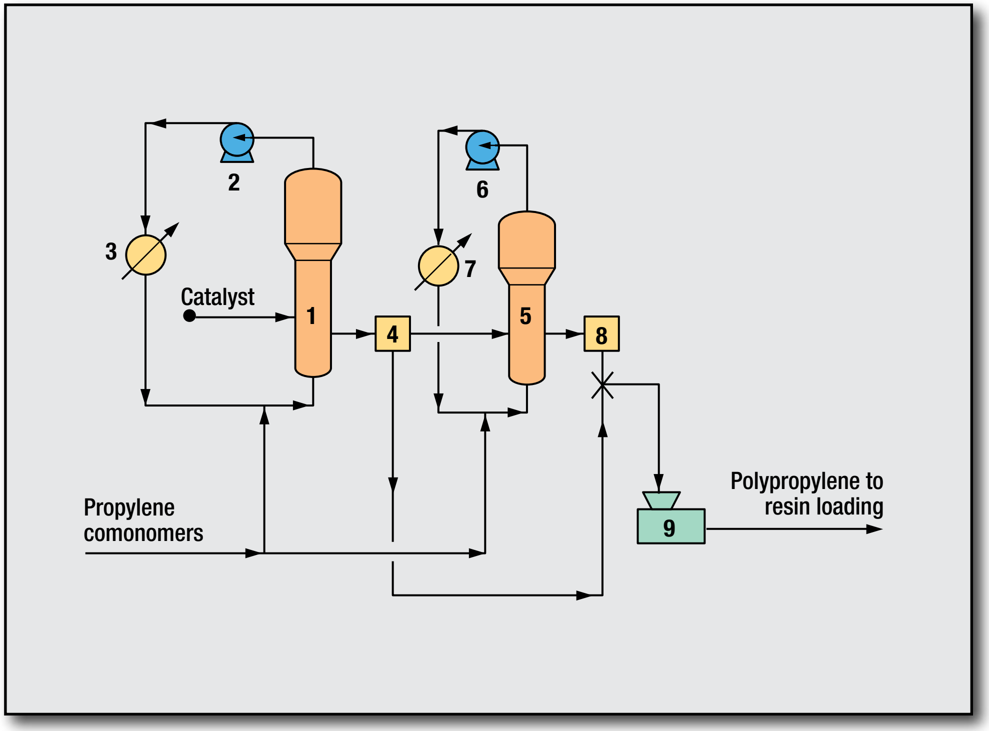
Polypropylene

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/cm^2 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 pelleting 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).

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A 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 with proven advantage for film injection, molding, blow molding, extrusion and textile applications.

Proprietary catalyst and donor systems: The Dow Chemical Co. manufactures and provides a family of polypropylene catalysts (SHAC catalyst) and a family of external electron donors (SHAC ADT) for use in the UNIPOL PP process. SHAC catalyst offers high catalyst activity (up to 35 kg/g-hr using conventional external donor and up to 60 kg/g-hr using a SHAC ADT) and competitive polymer properties. SHAC ADT performs three functions:

1) Controlling polymer isoctaticity similar to conventional external donors, such as D donor or C donor
2) Further improving process continuity by preventing agglomeration of polymer particles
3) Enhancing polymer properties.

The combination of SHAC catalyst and SHAC ADT enables Dow's catalyst systems to achieve low cost and easy production of polypropylene polymer with superior properties. The exceptional performance of the SHAC catalyst systems also finds applications in other PP processes.

Commercial plants: Nearly 45 reaction lines are in operation, with capacities ranging from 80,000 tpy to 650,000 tpy. Approximately seven additional plants are in design and construction. UNIPOL PP offers single-reaction-line systems capable of producing the full range of PP products at capacities up to 650,000 tpy. Total worldwide licensed production of polypropylene with this technology is nearly 12 million tpy.

Licensor: The Dow Chemical Co. Univation Technologies is the licensor of the UNIPOL PP process. - CONTACT

Polypropylene

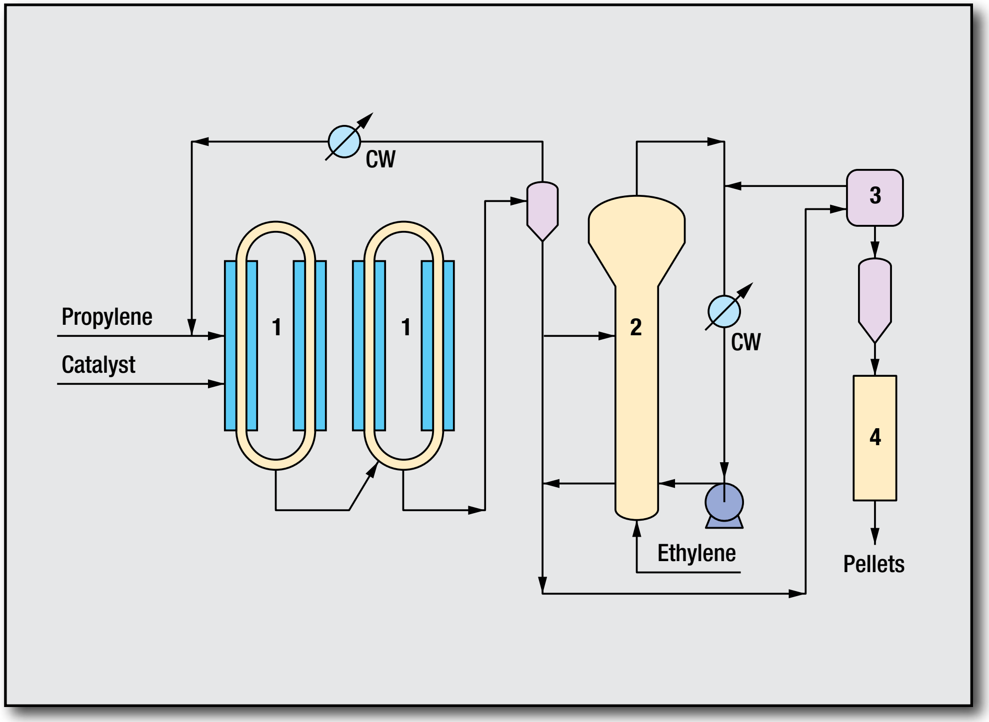
Applications: To produce the full range of polypropylene (PP), including homopolymer, random copolymer and impact copolymer PP, using the ExxonMobil PP Process.

Description: The ExxonMobil PP process utilizes series, bulk-liquid loop reactors (1) for the production of homopolymer and random copolymer PP, plus a gas phase reactor (2) in combination with the loop reactors to production impact copolymer PP. The use of series loop reactors allows the production of different products, as necessary, in each reactor to tailor the final product properties for specific end-use applications. Advancements in the design, chemistry and operation of the gas-phase reactor, in combination with ExxonMobil proprietary catalyst system technology, allows the production of impact copolymer PP with industry leading impact/stiffness balance properties with excellent operational reliability. Additionally, the design allows production of impact copolymer PP with a broad range of impact resistance, including very high-impact resistance grades in a single gas-phase reactor.

The ExxonMobil PP Process has been demonstrated to handle a wide range of supported catalyst solids, which permits the manufacturer to select a catalyst solid that delivers the optimum in product performance and economics.

A unique feature of the ExxonMobil PP Process is the monomer recovery system (3) that utilizes indirect heating and residence time to remove the remaining unreacted monomer without exposing the granules directly to a large steam flow. The result is no mixing of hydrocarbon and steam, which then requires additional equipment for separation and recovery of the hydrocarbon. This approach lowers the capital investment as well as significantly reducing steam and electricity consumption vs. other PP technologies.

The ExxonMobil PP process lines are in operation using both chemical-grade and polymerization-grade propylene as feed.



PP granules plus the final product additive package are finished in a twin screw extrusion system (4) including any post-reactor modification of the polymer molecular weight and molecular weight distribution required by the specific product application, typically referred to as controlled rheology (CR) technology.

Products: The ExxonMobil commercial grade slate covers a wide range of homopolymer, random copolymer and impact copolymer PP for volume and specialty applications. ExxonMobil PP products are known for their quality and lot-to-lot consistency. Key consumers of PP products consider ExxonMobil PP products to be the industry's leader in many important applications including OPP film; nonwoven fiber; durable goods including automotive and appliance applications; consumer products; rigid packaging; and materials handling applications.

Continued ▼

Polypropylene, *continued*

Economics: Typical consumption per metric ton of PP:

	Polymerization		Finishing
	Homopolymer	**Copolymer**	
Electricity, kWh	50–60	70–80	150–200
Steam, kg	160	130	25
Water, cooling m^3	60	80	40

Commercial plants: Four lines are in operation, with a fifth line to be completed in 2010. Two of the four operating lines have a capacity of more than 400,000 tpy. The fifth line will have a capacity in excess of 450,000 tpy. Single train lines with a capacity of 600,000+ tpy have been designed and are available for license.

Licensor: ExxonMobil Chemical Technology Licensing LLC - CONTACT

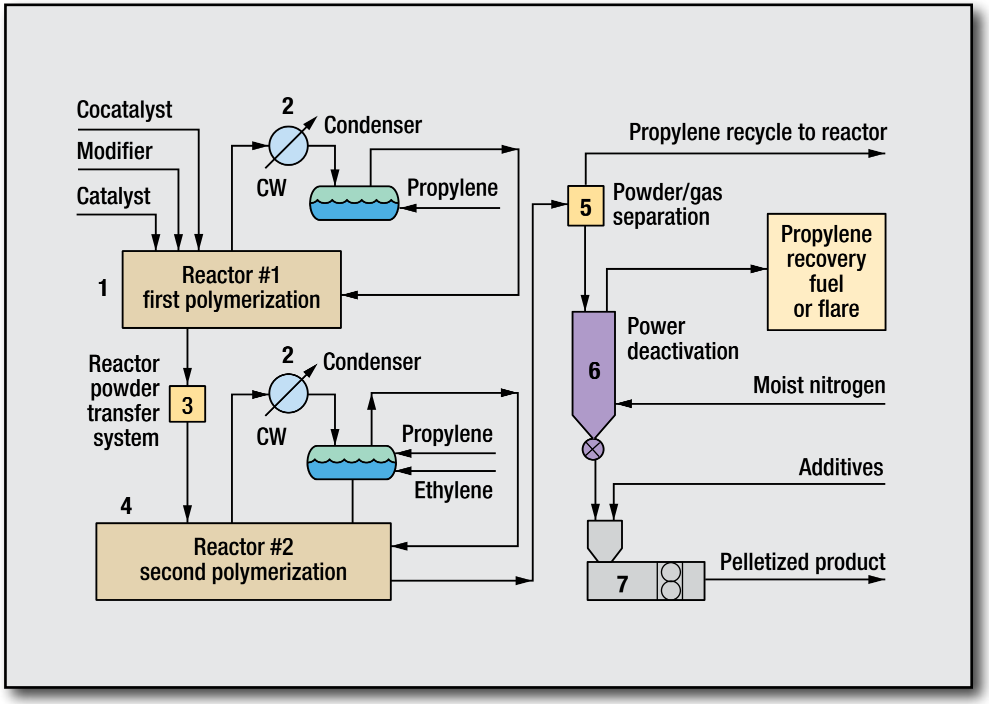
Polypropylene

Application: To produce polypropylene (PP) homopolymer, random copolymer and impact copolymer using the Innovene PP 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 INEOS has controlled morphology, super-high activity and very high sterospecifity. 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: Twenty-two plants are either in operation or in design/construction worldwide with capacities ranging from 65,000 to 450,000 metric tpy.

Licensor: INEOS Technologies - CONTACT

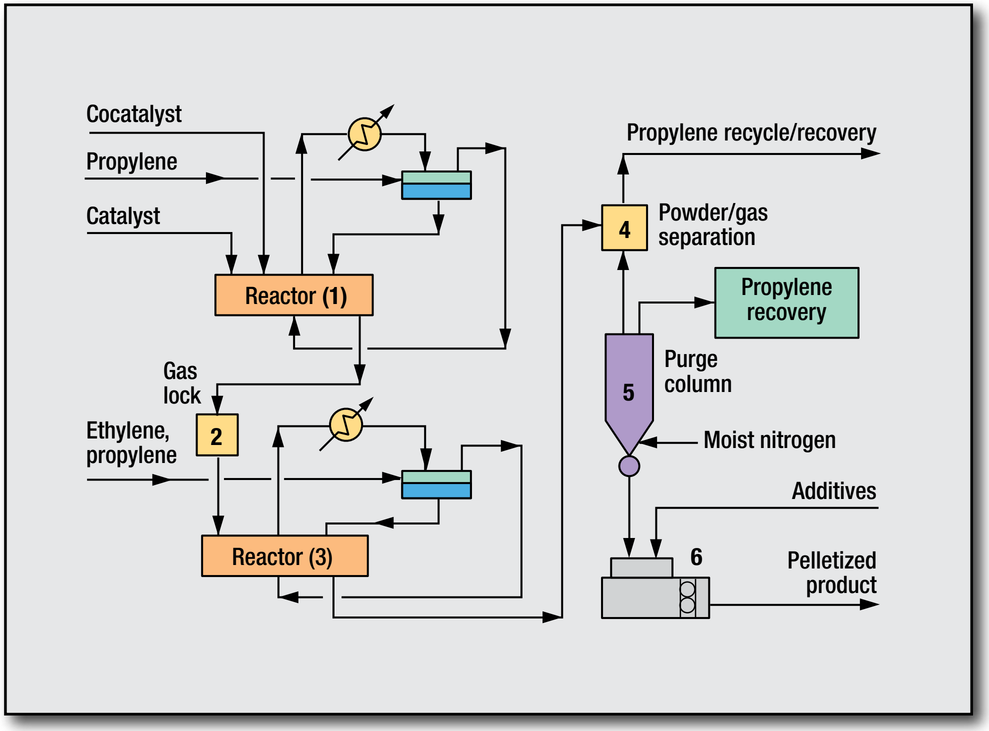
Polypropylene

Application: A process to produce homopolymer polypropylene and ethylene-propylene random and impact co-polymers Japan Polypropylene Corp. (JPP) HORIZONE Technology (formerly known as 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 narrowness of residence time distribution contributes to higher product quality.

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: Eleven polypropylene plants are in operation or under construction, with capacities ranging from 65,000 tpy to 300,000 tpy. JPP offers processing designs for single-production with capacities reaching 400,000 tpy.

Licensor: Japan Polypropylene Corp. (JPP) - CONTACT

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

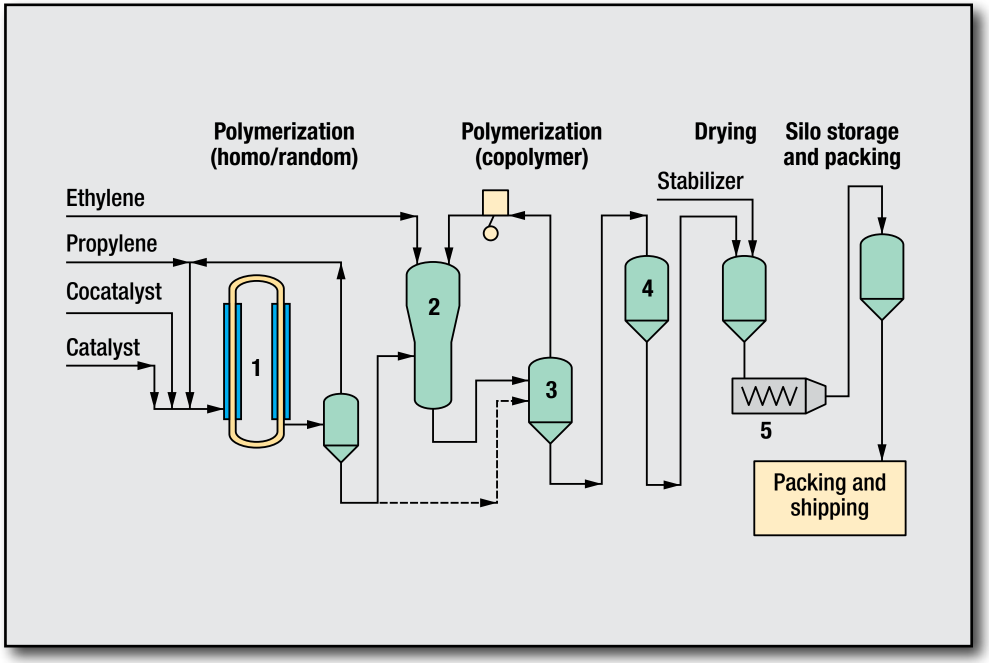
Application: To produce polypropylene (PP) including homopolymer, random copolymer and impact copolymer.

Description: The process, with a combination of the most advanced high-yield and high-stereospecificity catalyst, is a nonsolvent, non-deashing process. 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 kg/kg 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 (fifth-generation catalyst, RK-Catalyst and RH-Catalyst), the process can produce wider melt index ranged polymers 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 gas-phase reactor, no fouling is observed during the operation, and, consequently, reactor cleaning after producing impact copolymer is not required. In addition, the combination of the flexibility of the gas-phase reactor and high-performance catalysts allow processing impact copolymer with high ethylene content.

In the process, homopolymer and random copolymer polymerization occurs in the loop-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.



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

Commercial plants: Twenty-seven reactor lines are in operation, engineering design or under construction worldwide, with a total production capacity of over 3.4 million tpy.

Licensor: Mitsui Chemicals, Inc. - CONTACT

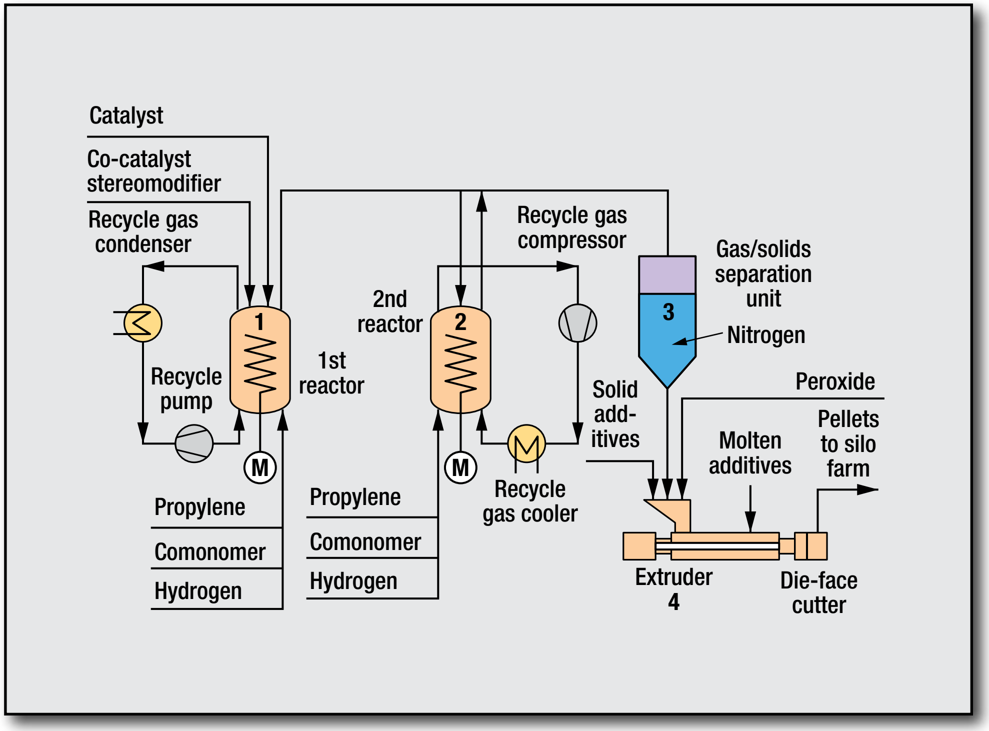
Polypropylene

Application: To produce polypropylene (PP) homopolymer, random copolymers and impact copolymers, including Metallocene PP in the Novolen process.

Description: In the Novolen process, polymerization is conducted in one or two gas-phase reactors, (1) and (2). The reactors contain a bed of polypropylene powder, which is agitated below the fluidization point by a helical agitator to keep the bed in motion and prevent powder agglomeration. A wide range of products can be produced with, at most, two reactors connected in series, including super-high-impact copolymers. The second reactor is used either to incorporate rubber into the homopolymer matrix produced in the first reactor, or the reactors are configured in parallel while producing homopolymers or random copolymers at capacities up to 600,000 metric tpy. It is also possible to switch between parallel and cascade mode in one line—Versatile Reactor Concept (VRC)—providing great flexibility with respect to capacities and product production capability.

Polymerization heat is removed from the reactors by external cooling circuits. Polymer powder is continually withdrawn from the reactors. The powder transfer from the first to the second reactor and from the second reactor to the gas/solids separation unit (3) is pressure driven. In this gas/solids separation unit polymer powder is separated from unreacted monomer and directly fed to the extruder (4) for pelletizing. The unreacted monomer is recovered and recycled. Removal of catalyst residues or amorphous polymer is not required.

Products: The process can produce a wide variety of homopolymers, random copolymers including terpolymers and pentene copolymers, and impact copolymers with up to 50% rubber content. Product range also includes metallocene PP based on a simple drop-in technology.



Commercial plants: The capacities range from 60,000 to 450,000 metric tpy for single lines. Over 50 production lines are in operation, engineering or under construction. The total licensed capacity worldwide for the Novolen process is in excess of 8 million tons.

Licensor: Lummus Novolen Technology GmbH - CONTACT

Polypropylene, Metallocene upgrade

Application: *Metocene* polypropylene (PP) technology upgrades existing and newly built PP plants by extending plant capability to cover specialty PP products with specific and unique features that can be produced with single-site catalysis, in addition to the existing conventional product portfolio.

Description: *Metocene* PP technology can be implemented to PP processes where polymerization takes place in either liquid phase, including such as *Spheripol*, or in gas phase. The retrofit required for implementing *Metocene* technology into *Spheripol* plants and other PP process technologies is dependent on the specific plant design. It relates to adaptations of the plant to specific requirements of such single-site catalysis and related PP products. Plants that have implemented *Metocene* technology can continue to produce conventional PP products based on Ziegler-Natta catalysts in addition to *Metocene*-based operation with metallocene-based catalysts. The addressable portfolio of specialty products covers all typical product fields, i.e. propylene homo-polymers and propylene co-polymers.

Products: The main driver of *Metocene* implementation is the desire to generate differentiated products with new and/or improved properties. Major property highlights of *Metocene*-based PP products include: high purity, high uniformity, high transparency, in addition to a broad range of peroxide-free reactor grades including very high melt-flow grades, and special suitability for high-performance processing in injection molding and fiber spinning.

Commercial plants: *Metocene* polypropylene technology is applied worldwide in the developed polymers markets, i.e., Europe, US and Asia. At present, *Metocene* technology has been implemented into five *Spheripol* plants and one gas plant. The current capacity of the PP plants upgraded with *Metocene* range between 60,000 tpy and 220,000 tpy.

Licensor: LyondellBasell - CONTACT

Polypropylene

Application: *Spheripol* process technology produces propylene-based polymers including homopolymer polypropylene (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 one or two tubular loop reactors (1) in cascade. Heterophasic impact copolymerization can be achieved by adding a gas-phase reactor (3) in series.

Unreacted monomer is flashed in a two-stage pressure system (2, 4) and recycled back to the reactors mostly by condensation with CW and pumping. 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 (93% to 95%) or the typical polymerization-grade (99.5%).

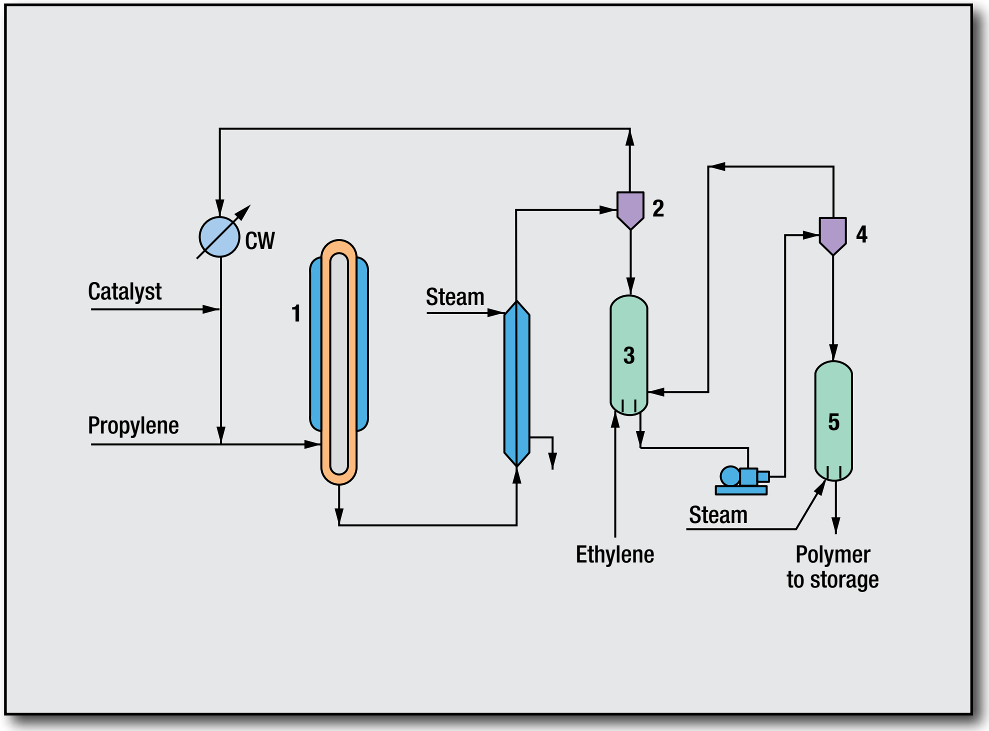
Yields: Polymer yields of 40,000–60,000 kg / kg of supported catalyst are obtained. The polymer has a controlled particle size distribution and an isotactic index of 90%–99%.

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 (polymerization):

Propylene and comonomer, ton	1.001
Catalyst, kg	0.016–0.025
Electricity, kWh	80*
Steam, kg	280
Water, cooling, metric ton	90

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 and high-clarity copolymers.



Commercial plants: *Spheripol* technology is used for about 40% of the total global PP capacity. There are more than 100 *Spheripol* process plants licensed or operating worldwide with total capacity of about 21 million tpy. Single-line design capacity is available in a range from 40,000 tpy to 550,000 tpy.

Licensor: LyondellBasell - CONTACT

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

Polypropylene

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

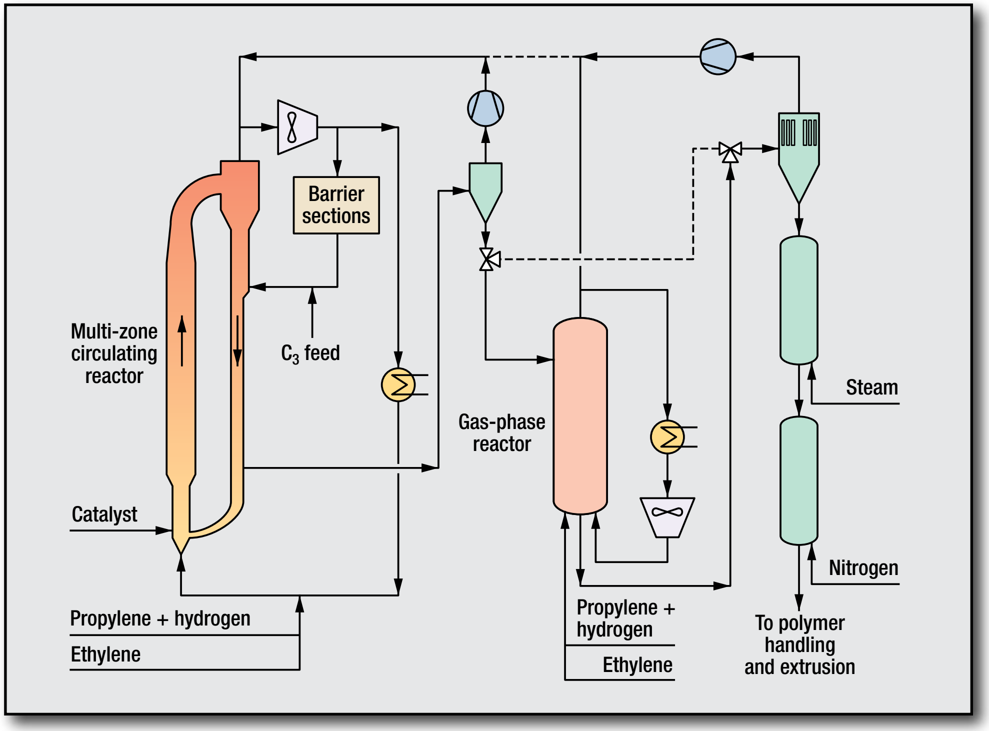
Description: The *Spherizone* process is LyondellBasell's new proprietary gas-loop reactor technology based on a Multi-Zone Circulating Reactor (MZCR) concept. Inside the reactor (1) the growing polymeric granule is continuously recirculating between two interrelated zones, where two distinct and different fluodynamic 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 gas composition with respect to the chain terminator (hydrogen) and to the comonomer can be altered between the two zones of the MZCR. 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 superior homogeneity of the final product. Unreacted monomer is mostly recovered at intermediate pressure (3) and recycled back to the MZC reactor through a compressor, 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 (polymerization):

Propylene (and comonomer for copolymers), kg	1,001
Catalyst, kg	0.025
Electricity, kWh	120*
Steam, kg	120
Water, cooling, m^3	85

Continued ▼

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 copolymer/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 LyondellBasell site in Brindisi since 2002, and 10 licenses for a total capacity of 3.25 million ton have been granted since 2004. The largest unit licenses are two 450,000-tpy single-line plants operating since 2009 and 2010 respectively.

Licensor: LyondellBasell - CONTACT

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

Polystyrene

Application: The INEOS polystyrene (PS) technology is based on a bulk continuous process giving access to a wide range of general purpose polystyrene (GPPS) also known as crystal polystyrene and high-impact polystyrene (HIPS), which incorporates rubber particles for high shock absorbance.

Products and economics: The process yields a variety of superior products with attractive investment and conversion costs. These products are sold and well accepted worldwide. INEOS offers commercially proven swing-line technology, capable of producing both GPPS and HIPS grades, with capacities ranging from 60,000 tpy up to 200,000 tpy that provide a turndown capability of 60%.

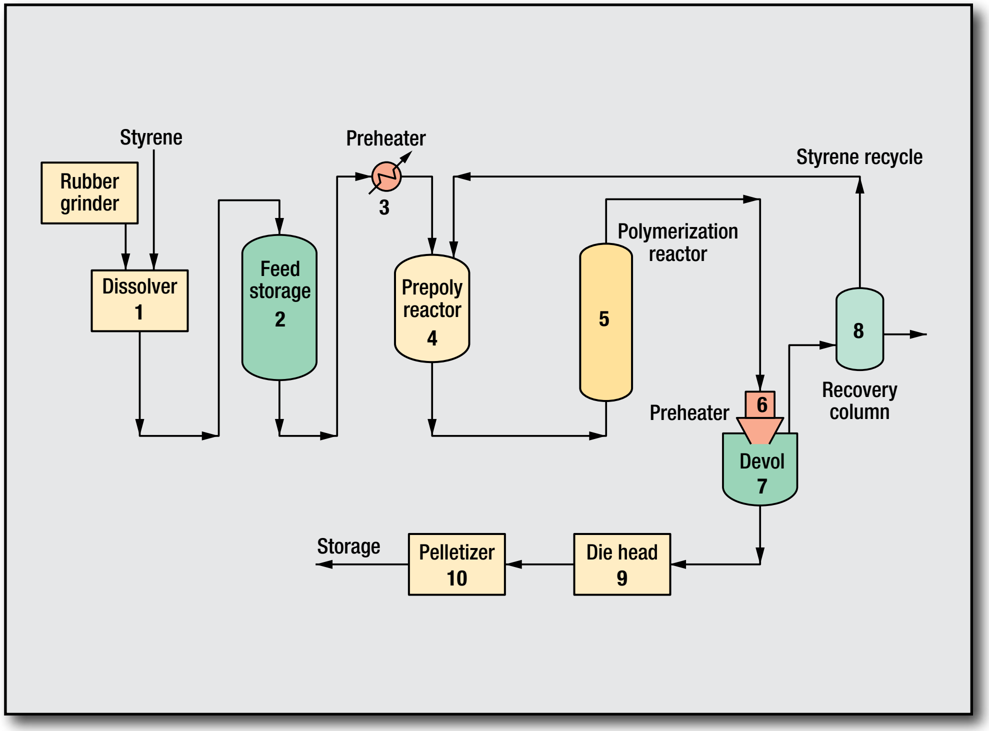
Description: The INEOS PS technology can be divided into several key processing operations as follows:

Rubber dissolving (1): Polybutadiene rubber, in bale form, is chopped into crumbs. To enhance dissolving, preheated styrene is introduced into a high-shear in-line mixer. This operation allows high capacity production of dissolved rubber at a high rubber concentration.

Prepolymerization (4): Prepolymerization is conducted in the first two reactors that are CSTR-type with proprietary agitator designs. Prepolymerization may be thermally or chemically initiated depending on the desired product. For HIPS, this is a critical phase of the process since this is where the rubber morphology and physical properties of the resultant product are controlled.

Polymerization (5): Polymerization is conducted in the last reactor, which is a plug-flow type of proprietary design allowing high efficiency heat removal and temperature control on viscous media.

Devolatilization (7): This is a two-step operation under high vacuum, to remove lights components such as unreacted styrene and diluent, which is enhanced with the addition of a foaming agent in the second stage. The stripping effect of the foaming agent reduces the residual monomer content to as low as 200 ppm.



Recycle recovery (8): Unreacted styrene and diluents from the devolatilization operation are distilled and recycled to the front end of the process. The distillation of the recycle stream ensures that only styrene and ethylbenzene are recycled back to the first pre-polymerization reactor to ensure that the styrene purge is minimized and the oligomer concentration in the reactor system is kept low. Two purges are provided to control the accumulation of light and heavy components in the PS unit: a lights purge consisting of styrene and ethylbenzene and a heavy purge consisting of oligomers and other heavy organics. These purges are used as fuel for the hot oil heater.

Continued ▼

Finishing: This section consists of filtering the polymer melt, extruding it into strands, cutting them into cylindrical pellets of prescribed size, sorting the resultant pellets from fines and oversize pellets and conveying the product pellets to a quality control silo.

Process features:

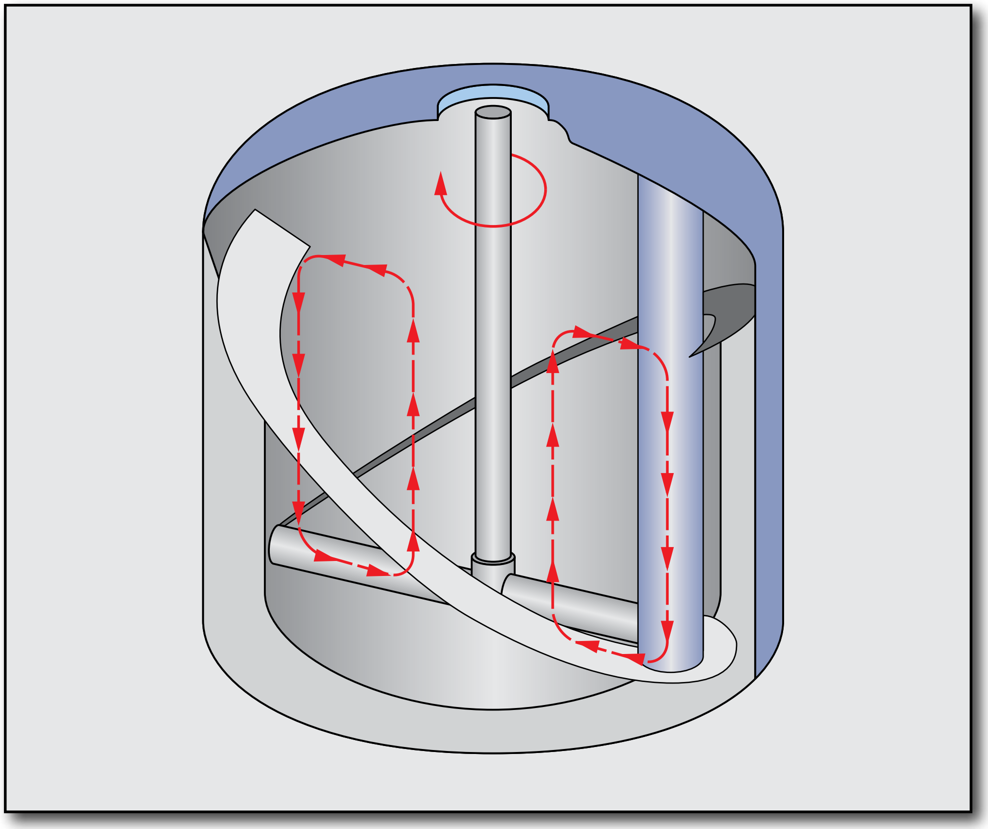
- Proprietary rubber grinding and dissolving unit
- Catalyzed polymerization:
  - o Enhanced polymer/rubber grafting
  - o Reduced oligomers byproducts
- Proven proprietary prepoly reactor design allowing temperature and morphology control
- Proprietary plug-flow reactor design => outstanding temperature control, highest conversion rates, rubber morphology preservation
- High-efficiency devolatilization system
- LP steam generation system
- Ongoing development of new and improved formulations.

Client benefits:

- High rubber efficiency
- Low-investment cost and inventory on the rubber section
- Excellent rubber yields
- High consistency and high product quality thanks to rubber morphology control
- Minimized capital investment
- High reliability
- Best in class residual SM on final product
- Fast transitions, high prime quality yields
- Consistent, high quality products
- Lowest utility consumption among licensed technologies
- Market penetration into new applications.

Commercial plants: At present, nearly 1.3 million metric tpy world-scale capacities have been awarded through seven different projects using INEOS proprietary technology.

Licensor: INEOS Technologies - CONTACT



Polystyrene, expandable

Application: For the production of regular and flame-retardant expandable polystyrene, INEOS offers the "one-step" suspension process.

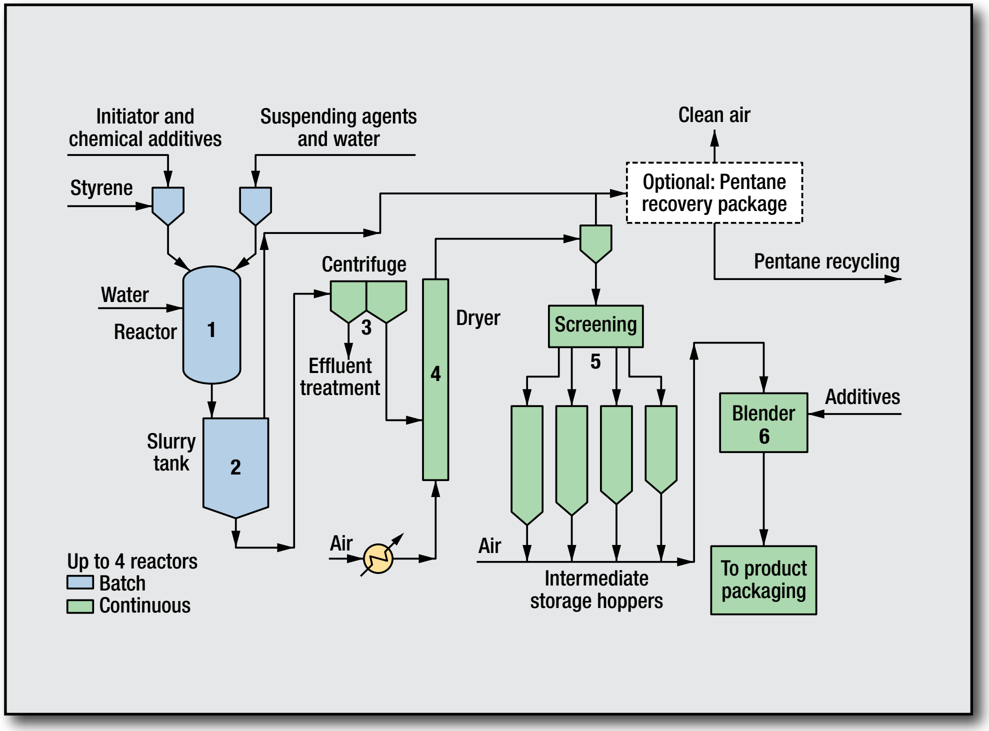
Products and economics: This state-of-the-art technology offers a wide range of products with an attractive capital investment and operational costs. Computer control and monitoring ensure consistent products with capacity up to 100,000 tpy per line.

Description: Depending on the formulation, styrene, blowing agent, water, initiators, suspending agents and other additives are injected into the reactor (1). The reactor contents are then subjected to a time-temperature profile under agitation. The combination of suspending agent and agitation disperse the monomer to form beads. Polymerization is then continued to essentially 100% conversion. This unit operation is fully DCS controlled through an automated sequence. After cooling, the polystyrene beads and water are discharged to a slurry tank (2).

The downstream slurry tank process becomes fully continuous. The bead/water slurry is centrifuged (3) so that most of the "suspension water" is removed. The beads are conveyed to a pneumatic-type flash dryer (4) where surface moisture is removed.

The dry beads are then screened (5) yielding two targeted product cuts out of four possible options. Such segregation is achievable thanks to the mineral suspension, which increases the yield for a targeted cut. With organic suspensions, the four product cuts are produced at the same time. Fig. 2 shows the effects of mineral vs. organic suspension in terms of product size distribution. Narrower distributions allow targeting more specifically product cut in line with market needs. Typically, the fine to medium cuts target the packaging market, whereas the medium to big cuts target the insulation market.

Process advantages:



- Regular and flame-retardant grades available
- Narrow-bead size distribution thanks to the mineral suspension system
- High reactor productivity/high capacity design (up to 100,000 metric tpy on a single line)
- Proven and easy to operate technology
- Optional volatile organic compound (VOC) recovery system
- The process includes batch reactions automatically controlled followed by a fully continuous downstream section
- Continuous low residence time coating process.

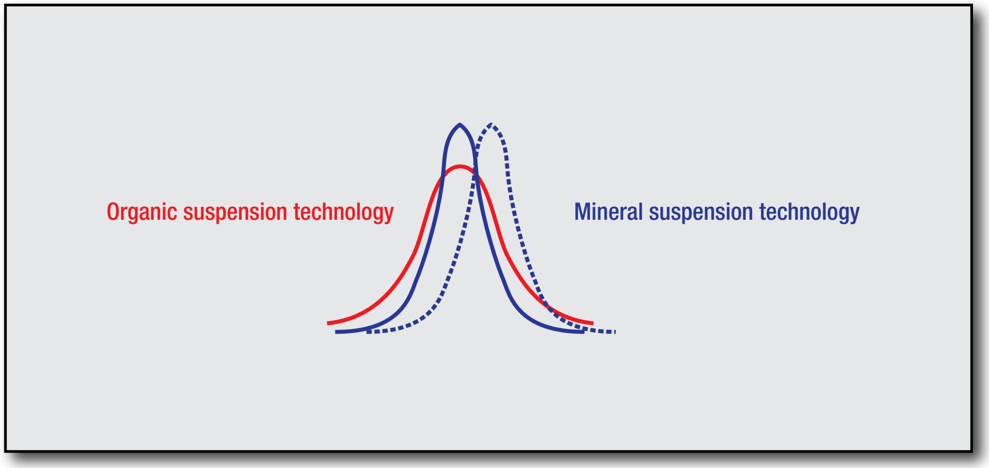
Market advantages:

- Outstanding raw material and utility yields
- Consistent high-quality products widely accepted in the marketplace

Continued ▼

Polystyrene, expandable, *continued*

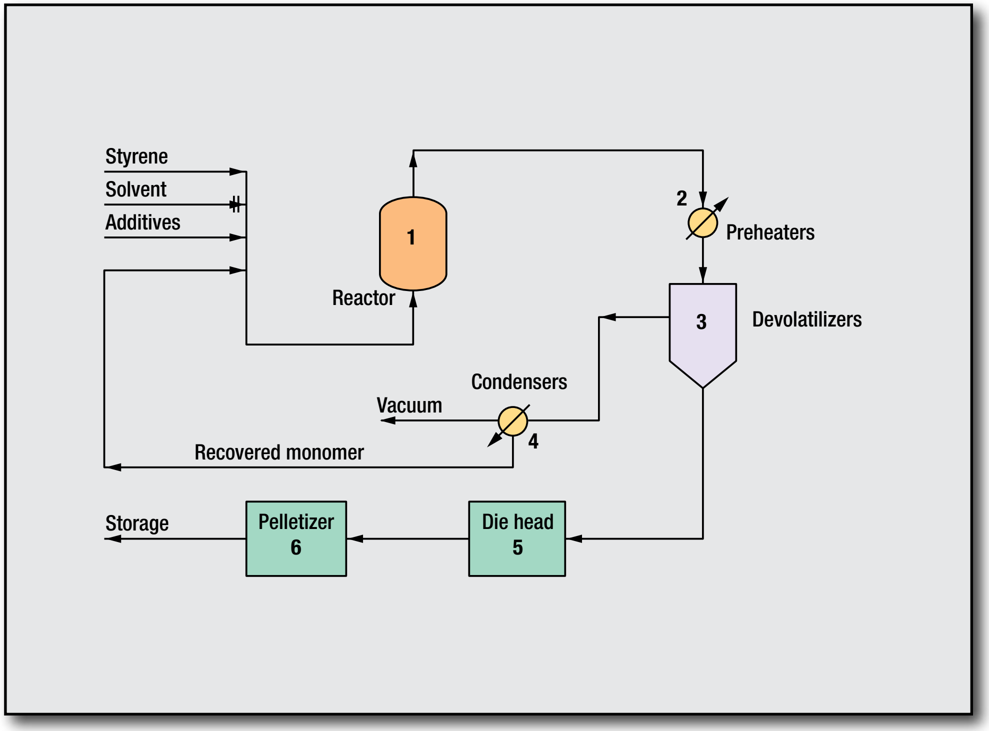
- Best packaging grade offer of the market and universal flame-retardant product range
- Clean process
- High quality yields (above 99% prime)
- High selectivity allowing to fit market demand
- High reliability
- Ongoing development of new and improved, market-specific formulations
- Excellent technical support from INEOS.



Commercial plants: The technology has been selected three times with the award of a 40,000 metric tpy capacity plant in 1997; a 50,000 metric tpy plant in 2004; and 50,000 metric tpy facility in 2007.

Licensor: INEOS Technologies - CONTACT

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. (TOYO)/Mitsui Chemicals Inc. technology.

Description: Styrene monomer, small amount of solvent and additives are fed to a specially designed reactor (1) where the polymerization 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 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 metric tpy GPPS

Raw materials consumption per metric ton of GPPS, kg	1,009
Utilities consumption per metric ton of GPPS,US$	10.5

Commercial plants: 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. (TOYO)/Mitsui Chemicals Inc.
- CONTACT

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. (TOYO)/Mitsui Chemicals Inc. technology. The process provides a swing production feature and is also capable of producing general purpose polystyrene (GPPS).

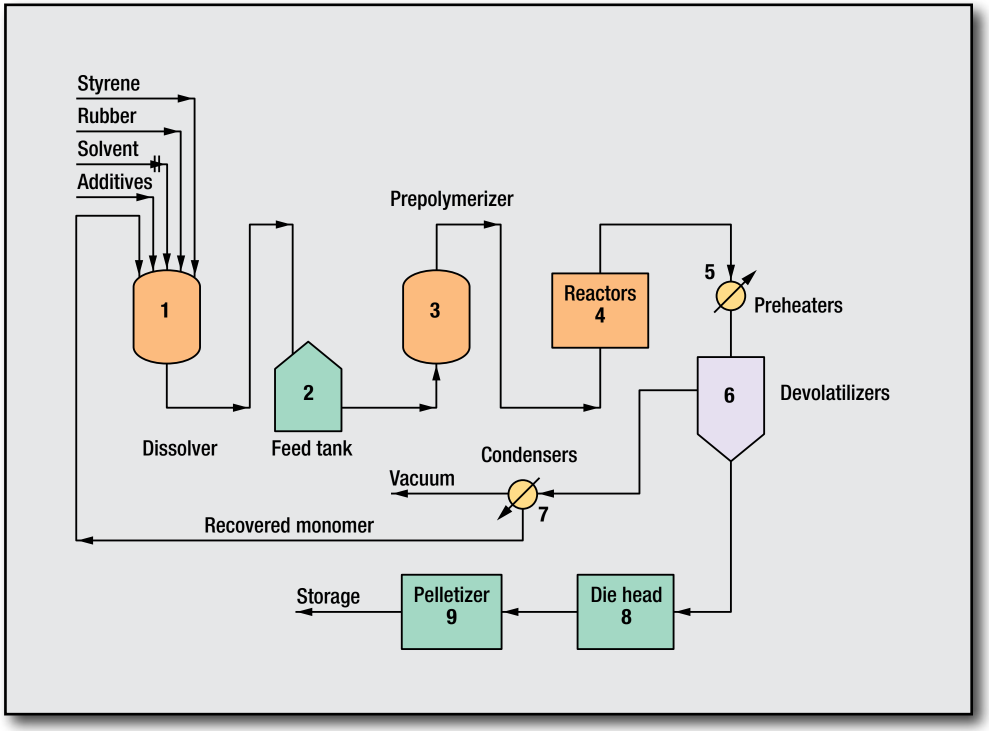
Description: Styrene monomer, ground rubber chips and small amount of additives are fed to the rubber dissolver (1). The rubber chips are completely dissolved in the styrene. This rubber solution is sent to a rubber-solution-feed tank (2). The rubber solution from the tank is sent to the prepolymerizer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

Raw materials consumption per metric ton of HIPS, kg	1,009
Utilities consumption per metric ton of HIPS, US$	8



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

Licensor: Toyo Engineering Corp. (TOYO)/Mitsui Chemicals Inc.
 - CONTACT

Propylene

Application: The worldwide demand for gasoline, diesel and petrochemicals is shifting toward a greater emphasis on diesel and propylene, and flexibility to meet changing demands will be vital for refinery profitability. Axens has developed the new FlexEne technology to expand the capabilities of the fluid catalytic cracking (FCC) process, which is the main refinery conversion unit traditionally oriented to maximize gasoline and at times propylene.

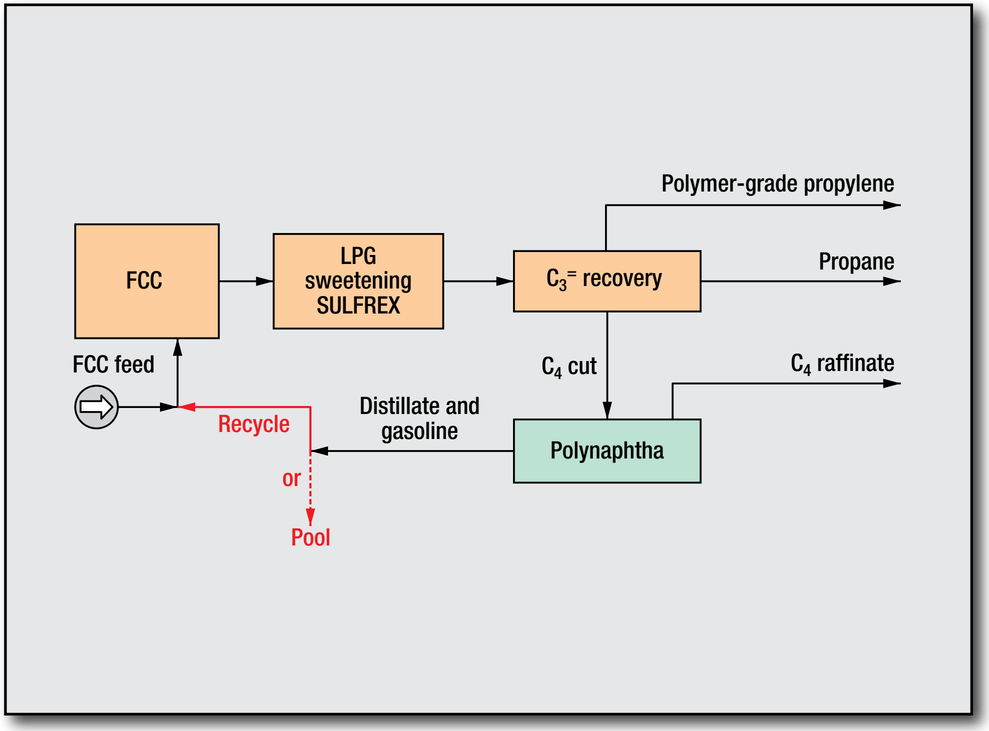
Description: FlexEne relies on the integration of an FCC and an oligomerization unit called Polynaphtha to process light FCC olefins and to deliver good molecules back to the FCC and to provide product flexibility required by the marketplace.

By adjusting the catalyst formulation and operating conditions, the FCC process is able to operate in different modes: *maxi distillate*, *maxi gasoline* and *high propylene*. The combination with Polynaphtha delivers the flexibility expected by the market.

In a *maxi gasoline* environment, the olefin-rich C_4 FCC cut is usually sent to an alkylation unit to produce alkylate and to increase the overall gasoline yield. In most recent max gasoline production schemes, alkylation has been advantageously substituted by Polynaphtha, which delivers high-quality gasoline at a much lower cost.

For greater distillate production, Polynaphtha technology may be operated at higher severity to produce distillates from C_4 olefins. Additional diesel production may be supplied by operating the FCC unit in the *maxi distillate* mode.

For greater propylene production, Axens/IFP R&D has shown that either the Polynaphtha gasoline or distillate fractions can easily crack in the FCC unit to produce Propylene. Consequently, depending upon market conditions, gasoline or diesel can be recycled to the FCC to produce high-value propylene and C_4 olefins.



Thanks to optimized combination of FCC and oligomerization, FlexEne delivers the largest market product flexibility when targeting production of propylene and/or gasoline and/or distillates.

Commercial plants: Two FlexEne units have been licensed for new R2R/Polynaphtha projects.

Licensor: Axens - CONTACT

Propylene

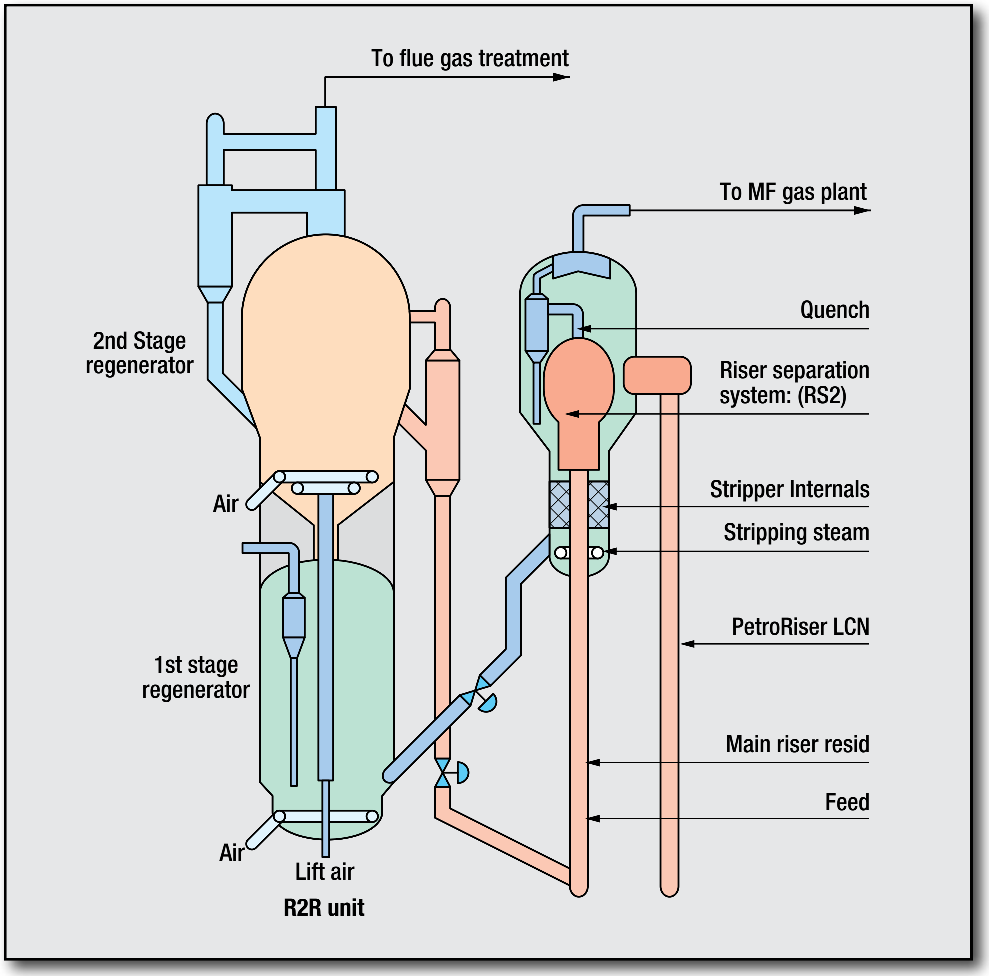
Application: When the process objective is maximum propylene production, specific technology features must be added to the fluid catalytic cracking (FCC)/resid FCC (RFCC) unit. The challenge is particularly great when the feedstock contains residue.

Description: ZSM-5 additive is able to crack only C_7 to C_{10} olefins to LPG. Consequently, most of the C_5 and C_6 cut are not converted by ZSM-5 in the main riser. To convert this cut, it has been published by IFP and others that the optimum catalytic system is a recycle in a separate riser operating under more severe conditions—a PetroRiser.

Indeed, recycling with the feed does not allow converting this light naphtha since the temperature is too low in the main riser. If the naphtha recycle is injected before the feed zone where the catalyst temperature is above 700°C, production of fuel gas is very high due to thermal cracking as well as detrimental side reactions specific to this thermal level. In addition, injecting light naphtha below the main feed alters the riser conditions at the point of injection of the main resid feed resulting in less than optimum performance.

The conclusion of the R&D work is that recycling light naphtha to a separate riser at a temperature higher than the main riser allows cracking C_5 and C_6 olefins and also enables paraffins to produce more LPG and less C_5–70°C naphtha.

An additional feedstock for propylene production is the indirect recycle of C_4 olefins. As with light naphtha, the C_4 olefins will not crack in the main riser, and a simple recycle to the PetroRiser will result in nonselective conversion of C_4 olefins. The easiest and most selective way to recycle crack the C_4 olefins into propylene is to use the benefit of a C_4 oligomerization unit (Polynaphtha) to produce longer olefins (C_8 and C_{12} olefins). These longer chain olefins will crack very selectively in the PetroRiser, thus producing more propylene as well as good quality gasoline. This integration is called FlexEne and presented in more details in a dedicated paragraph of the handbook.



Reference: R. Roux, "Resid to petrochemicals technology," 12th ARTC Petrochemical Conference, Kuala Lumpur, 2009.

Commercial plants: PetroRiser has been licensed in Abu Dhabi for the largest RFCC unit (127,000 bpsd).

Licensor: Axens - CONTACT

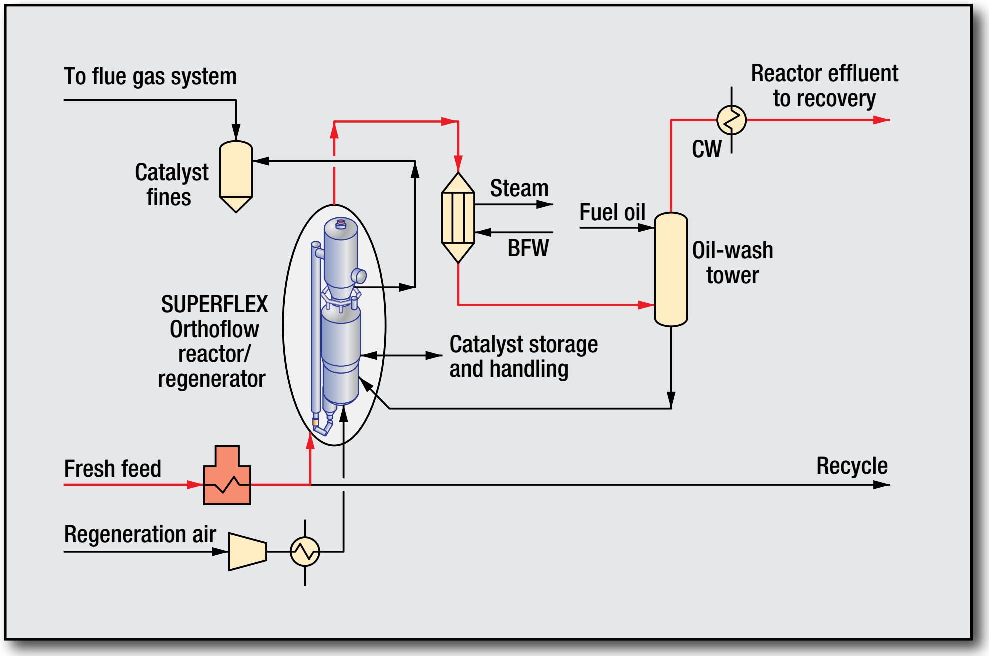
Propylene

Application: To produce propylene and ethylene from low-value, light (C_4 to C_{10}) hydrocarbon olefins-containing streams from ethylene plants and refineries. Suitable feeds include C_4/C_5 streams from a steam cracker, light cat-cracker C_4s and naphtha and coker gasolines.

Description: The SUPERFLEX process is a proprietary technology patented by ARCO Chemical Technology, Inc. (now LyondellBasell) and exclusively offered worldwide for license by KBR. It uses a fluidized catalytic reactor system with a proprietary catalyst to convert low-value feedstocks to predominantly propylene and ethylene products. The catalyst is very robust; thus, no feed pretreatment 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_4s, 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. Because this is a catalytic process, the CO_2 footprint per ton of product is lower than conventional steam cracking.

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. Depending on the final use of the ethylene byproduct, the recovery section costs may be reduced via use of an absorption process to produce dilute ethylene product rather than polymer grade.



Yields: The technology produces 50 wt%–60 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	**Olefin-rich C_4s**	**Olefin- rich C_5s**	**FCC LCN**	**Coker LN**
Ultimate yield, wt%*				
Fuel gas	7.2	12.0	13.6	11.6
Ethylene	22.5	22.1	20.0	19.8
Propylene	48.2	43.8	40.1	38.7
Propane	5.3	6.5	6.6	7.0
C_6^+ gasoline	16.8	15.6	19.7	22.9

*Ultimate yield with C_4s and C_5s recycled.

Continued ▼

Propylene, *continued*

Commercial plants: The first SUPERFLEX licensee with a propylene production capacity of 250,000 metric tpy is Sasol Technology; this plant has been in operation since December 2006. Two additional SUPERFLEX units have been licensed.

Licensor: Kellogg Brown & Root LLC - CONTACT

Propylene

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

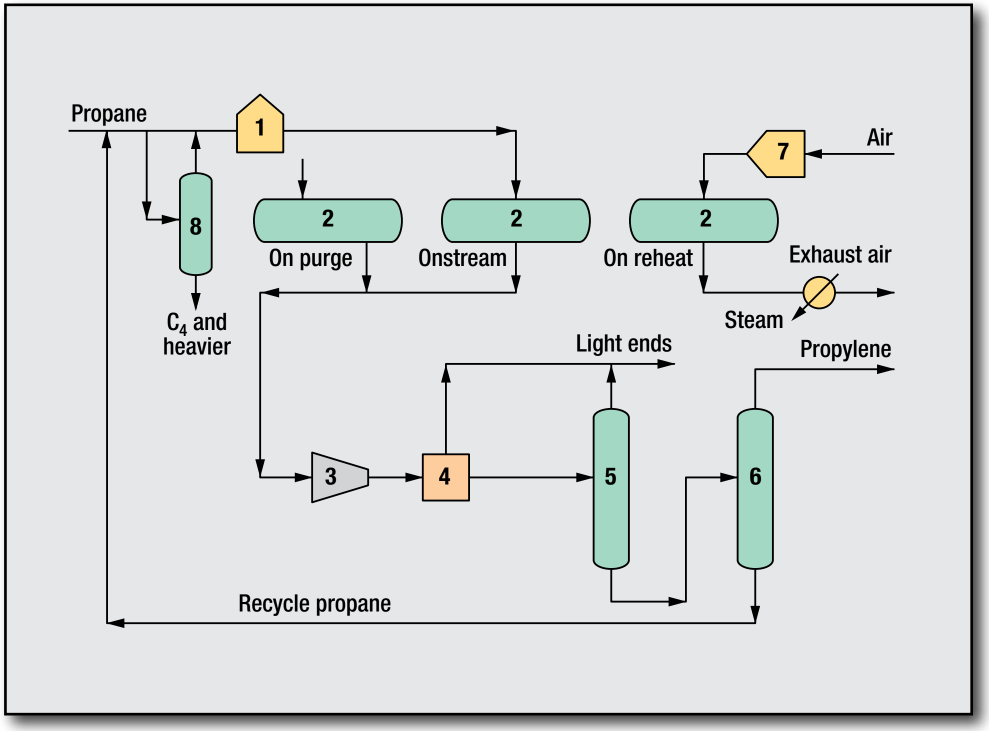
Description: The CATOFIN reaction system consists of parallel fixed-bed reactors and a regeneration air system. The reactors are cycled through a sequence consisting of reaction, regeneration and evacuation/purge steps. Multiple reactors are used so that the reactor feed/product system and regeneration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

Fresh propane feed is combined with recycle feed from the bottom of the product splitter (6). The total propane feed is then vaporized and 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. A purge stream, taken from the total propane feed, is passed through a deoiler (8) to remove C_4 and heavier components.

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. 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.

The low operating pressure and temperature of the CATOFIN reactors, along with the robust Süd-Chemie catalyst, allows the CATOFIN technology to process propane feedstock from a variety of sources. The simple reactor construction, with its simple internals, results in a very high onstream factor.



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 (>99.5%). 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 650,000 metric tpy propylene) minimizes the investment cost/mt of product.

Continued ▼

Propylene, *continued*

Raw material and utilities, per metric ton of propylene

Propane, metric ton	1.16
Power, kWh	50
Fuel, MWh	1.2

Commercial plants: Currently eight CATOFIN dehydrogenation plants are on stream producing over 1,800,000 metric tpy of isobutylene and 1,160,000 metric tpy of propylene. There are now two CATOFIN propane dehydrogenation units in operation with a design capacity of 455,000 metric tpy propylene. These are the world's largest single-train units. Both plants have successfully met their guarantees and continue to operate well above design capacity.

Licensor: Lummus Technology - CONTACT

Propylene

Applications: The Total Petrochemicals/UOP Olefin Cracking Process (OCP) is used to primarily produce propylene from C_4 to C_8 olefins supplied by steam crackers, refineries and/or methanol-to-olefins (MTO) plants.

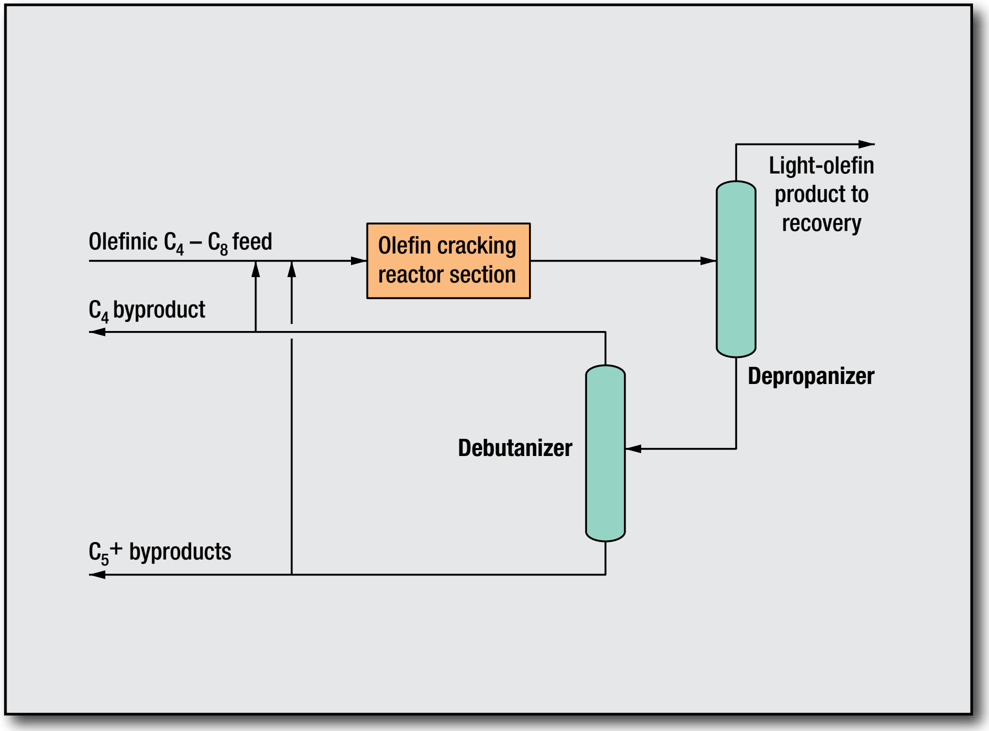
Description: The Olefin Cracking Process was jointly developed by Total Petrochemicals (formerly ATOFINA) and UOP to convert low-value C_4 to C_8 olefins to propylene and ethylene. The process features fixed-bed reactors operating at temperatures between 500°C and 600°C and pressures between 1 and 5 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.



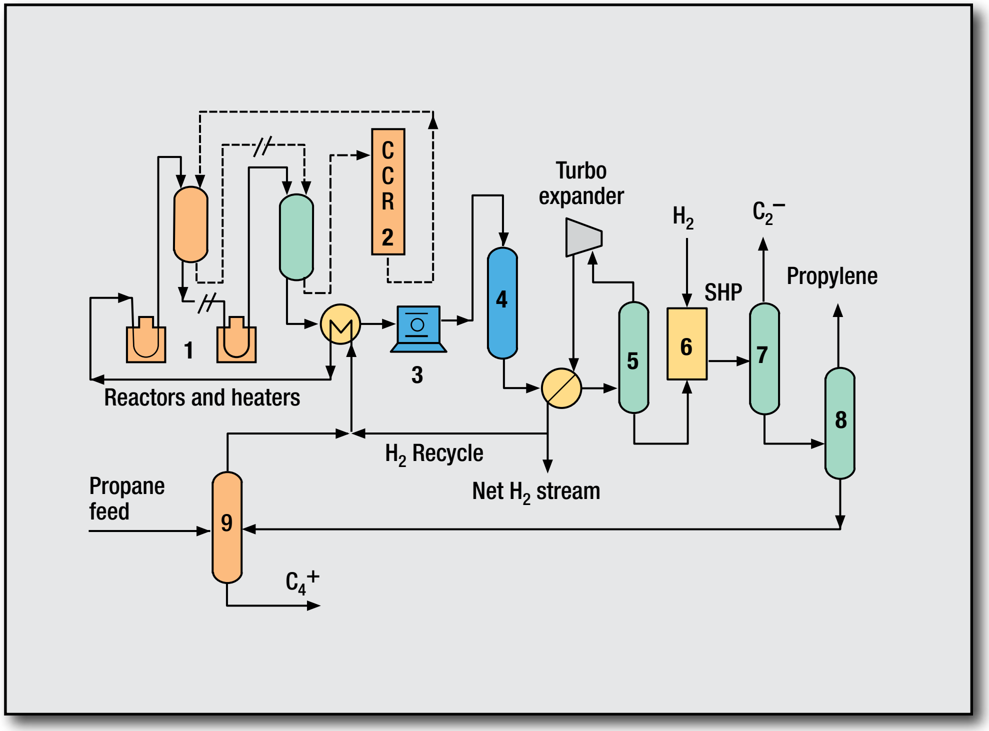
Commercial plants: Total Petrochemicals operate a demonstration unit that was installed in an affiliated refinery in Belgium in 1998. Total installed a second demonstration unit in 2009 that is integrated with a semi-commercial MTO/OCP process demonstration unit.

Licensor: UOP LLC, A Honeywell Company - CONTACT

Propylene

Application: The Oleflex process is used to produce polymer-grade propylene from propane.

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: The US Gulf Coast inside battery limits investment for the production of a 450,000 tpy polymer-grade propylene facility is approximately $600/tpy.

Inside battery limits investment, $ million	600

Commercial plants: Thirteen Oleflex units are in operation to produce propylene and isobutylene. Eight of these units produce propylene. These units represent 2.1 million metric tpy of propylene production. Three additional Oleflex units for propylene production are in design or under construction.

Licensor: UOP LLC, A Honeywell Company - CONTACT

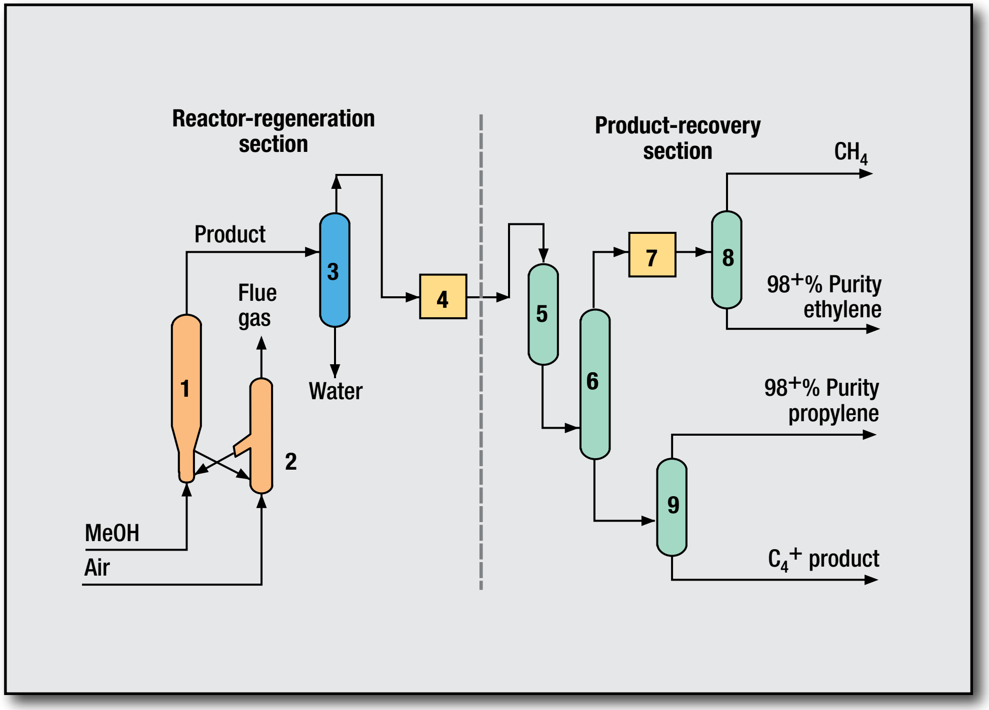
Propylene and ethylene

Application: The UOP/HYDRO Methanol-to-Olefins (MTO) Process produces ethylene and propylene from methanol derived from raw materials such as natural gas, coal, petroleum coke or biomass.

Description: This process consists of a reactor section, including a catalyst regenerator and product recovery section. One or more fluidized-bed reactors (1) are used with catalyst transfer to and from the catalyst regenerator (2). The robust MTO-100 catalyst is based on a nonzeolitic molecular sieve. Methanol is fed to a low-pressure reactor (1), where it is converted (99%) to olefins with a very high selectivity to ethylene and propylene. The recovery section design depends on product use, but it contains a product water and oxygenate recovery and recycle system (3), a CO_2 removal system (4), a dryer (5), a deethanizer (6), an acetylene converter (7), a demethanizer (8) and a depropanizer (9). The process can produce polymer-grade ethylene and propylene by including C_2 and C_3 splitter columns in the recovery section. The MTO process is combined with an Olefin Cracking Process (OCP) unit to further increase yields by converting C_4^+ byproducts into ethylene and propylene.

Yields: The MTO process consumes 3 tons of methanol feed per ton of light olefin (ethylene + propylene) produced. The weight ratio of propylene product to ethylene product can be selected within the range of 0.8 to 1.3. When combined with OCP, the Advanced MTO process consumes 2.6 tons of methanol feed per ton of light olefin (ethylene + propylene) produced. The weight ratio of propylene product to ethylene product for Advanced MTO can be selected within the range of 1.2 to 1.8.

Economics: The capital cost for the MTO process units (including light olefin recovery and purification) are about 10% lower than conventional steam crackers based on producing the same amount of light olefin product. MTO projects typically include upstream process units to convert raw materials into syngas and then to methanol as well as downstream units to produce olefin derivatives. The overall project capital costs for MTO (including upstream and downstream process units) vary significantly depending on the type of raw materials to be utilized and the types of olefin derivative products to be produced. In general, when MTO projects are linked to cost-advantaged raw materials, the projects offer low cash costs for production and attractive returns on investment compared to conventional steam crackers. The economic advantage for MTO typically becomes greater as crude oil prices increase.



Commercial plants: INEOS (formerly Hydro) operate a demonstration unit that was installed in Norway in 1995. Total Petrochemicals operates a semi-commercial demonstration unit that was installed in Belgium in 2009.

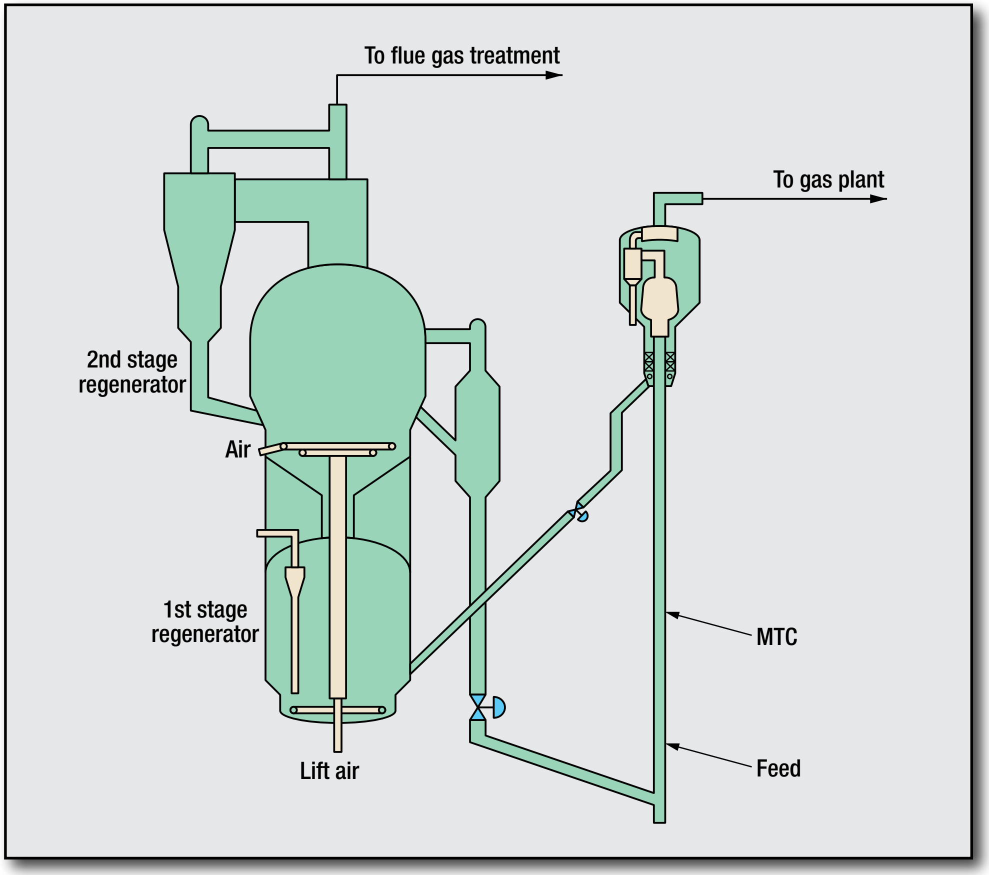
Licensor: UOP LLC, A Honeywell Company - CONTACT

Propylene or iso-olefin

Application: Deep-catalytic cracking (DCC) is a catalytic conversion technology that uses heavy hydrocarbon feedstocks, such as vacuum gasoil (VGO), vacuum resid (VR) or VGO blended with deasphalted oil (DAO) to produce light olefins (ethylene, propylene and butylenes), LPG, gasoline, middle distillates, etc. The technology targets maximizing propylene production (DCC-I) and maximizing iso-olefins production (DCC-II).

Description: The DCC process overcame the limitations of conventional fluid catalytic cracking (FCC) processes. The propylene yield of DCC is 3–5 times that of conventional FCC processes. The processing scheme of DCC is similar to that of a conventional FCC unit consisting of reaction-regeneration, fractionation and gas concentration sections. The feedstock, dispersed with steam, is fed to the system and contacted with the hot regenerated catalyst either in a riser-plus fluidized dense-bed reactor (for DCC-I) or in a riser reactor (for DCC-II). The feed is catalytically cracked. Reactor effluent proceeds to the fractionation and gas concentration sections for stream separation and further recovery. The coke-deposited catalyst is stripped with steam and transferred to a regenerator where air is introduced and coke on the catalyst is removed by combustion. The hot regenerated catalyst is returned to the reactor at a controlled circulation rate to achieve the heat balance for the system.

The DCC has two reactor operating modes: DCC-I (Riser-plus fluidized dense-bed reactor, maximum propylene mode) and DCC-II (Riser reactor, maximum iso-olefins mode). The DCC can process different heavy feeds—VGO, DAO, coker gasoil, atmospheric residue, VR, etc. Paraffinic feedstocks are the best feeds for DCC. In DCC maximum propylene operation mode, over 20 wt% propylene yield can be obtained from paraffinic feedstocks. The naphtha and middle distillates streams from the DCC unit can be used as blending components for high-octane, commercial gasoline and fuel oil, respectively.



Using a specially designed and patented zeolite catalysts, the reaction temperature in the DCC process is higher than that of conventional FCC, but much lower than that of steam cracking. Other processing benefits include:

- **Flexibility of process operation.** Easy to obtain the shift of DCC operation modes by regulating the operating conditions and catalyst formulations.

Continued ▼

Propylene or iso-olefin, *continued*

- **Easy separation and recovery of product streams through a similar absorption/fractionation of conventional FCC.** Cryogenic separation for separating and recovering DCC product stream is not necessary.
- **Contaminants found in the hydrocarbons are at trace levels** in DCC lighter olefin products; thus, hydrotreating is not needed.

Commercial plants: The first commercial DCC unit came onstream in 1990, and 10 DCC units have been licensed. The largest unit is 4.50 million tpy facility. It is estimated that a total of 13 units will be fully operational by the end of 2010.

Licensor: China Petrochemical Technology Co., Ltd. - CONTACT

Propylene glycol

Application: To produce propylene glycol from glycerine, using hydrogenation and refining.

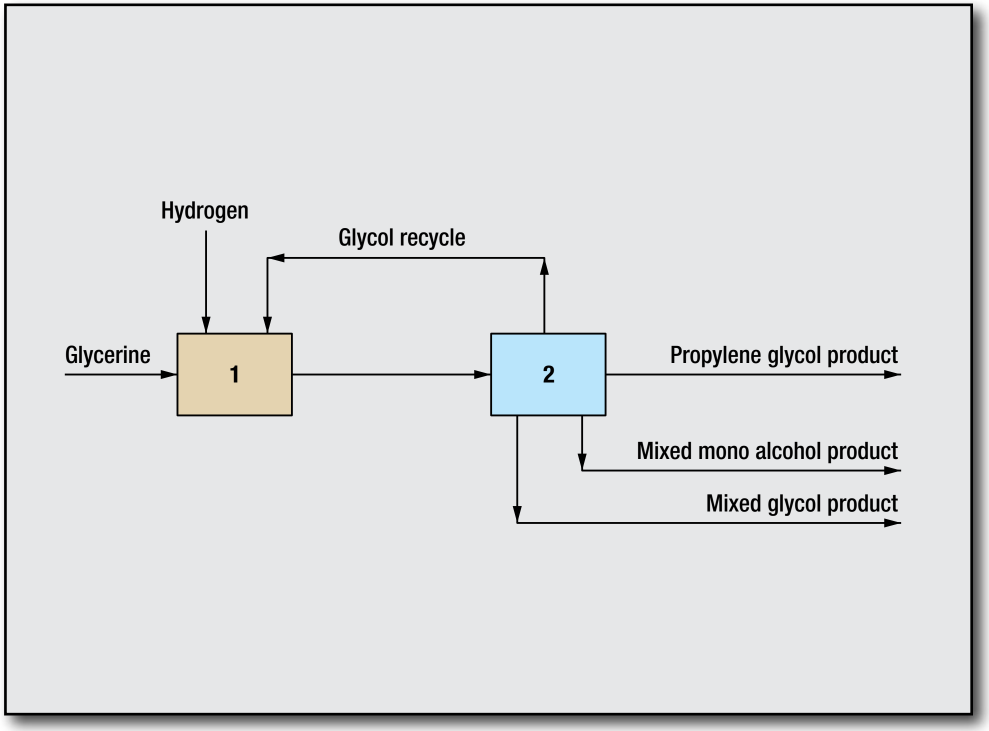
Description: Glycerine is fed to a low-pressure, vapor-phase hydrogenation section (1) where the glycerine is vaporized into a circulating hydrogen stream followed by conversion to propylene glycol over a fixed catalyst bed. Crude propylene glycol product is condensed, and the gas is recirculated with a low-head centrifugal compressor.

Crude propylene glycol from hydrogenation section (1) is polished and it passes to the refining section (2). The refining section (2) recovers mixed mono alcohols (methanol, ethanol and propanol) and mixed glycols (mainly ethylene glycol) byproducts, and produces a final-product propylene glycol. Residual glycerine is also recovered and recycled to the hydrogenation section (2).

Economics: Feedstock and utility consumption are heavily dependent on feedstock composition; thus, each must be evaluated on a case-by-case basis.

Commercial plants: At present, there are no operating propylene glycol plants using this technology.

Licensor: Davy Process Technology, UK - CONTACT



Propylene via metathesis

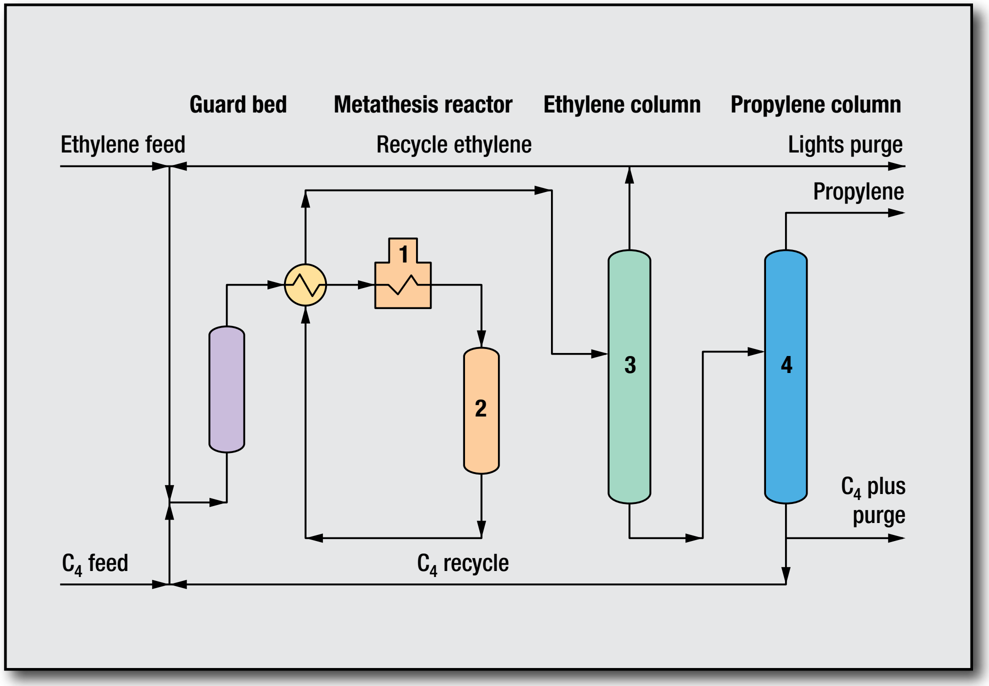
Application: To produce polymer-grade propylene from ethylene and butenes using Lummus' olefins conversion technology (OCT). This technology can be used with a variety of C_4 streams, including the mixed C_4s produced in steam cracking, raffinate C_4s from MTBE or butadiene extraction, and C_4s produced in FCC units.

Description: Two chemical reactions take place in the OCT process: propylene is formed by the metathesis of ethylene and butene-2; and butene-1 is isomerized to butene-2 as butene-2 is consumed in the metathesis reaction.

Ethylene feed plus recycle ethylene are mixed with the butenes feed plus recycle butenes and heated (1) prior to entering the fixed-bed metathesis reactor (2). The catalyst promotes the reaction of ethylene and butene-2 to form propylene, and simultaneously isomerizes butene-1 to butene-2. The beds are periodically regenerated using nitrogen-diluted air. The ethylene-to-butene feed ratio to the reactor is controlled at a value to minimize C_5^+ olefin byproducts and maintain the per-pass butene conversion.

The reactor product is cooled and sent to the ethylene column (3) to remove ethylene for recycle. A small portion of this recycle stream is purged to remove methane, ethane and other light impurities from the process. The ethylene column bottoms is fed to the propylene column (4) where butenes are separated for recycle to the reactor and some is purged to remove butanes, isobutylenes and heavies from the process. The propylene column overhead is ultra-high-purity, polymer-grade propylene product.

This process description is for a stand-alone OCT unit that can be added into any refining/petrochemical complex. The utility requirements—which include cooling water, steam, electricity, fuel gas, nitrogen and air—are typically integrated with the existing complex. The process may also be integrated into a grassroots cracker project to either reduce equipment sizes, capital cost and energy requirements; or to increase propylene-to-ethylene ratio to as high as 1.1:1.



Yields and product quality:

Typical yields

	Metric ton/metric ton Propylene	
Feed		
Raffinate-3 (80% n-butenes)	1.00	
Polymer-grade ethylene	0.33	
Main products		
Polymer-grade propylene	1.00	
C_4^+ byproduct	0.33	
Typical product quality		
Propylene	99.9 mol%	min

Continued ▼

Propylene via metathesis, *continued*

Economics:

Typical utilities, per metric ton propylene

Fuel gas (fired), MMKcal	0.15
Electricity, kWh	19
Steam, metric ton	1.1

Commercial plants: The OCT process has been licensed in 25 plants, 16 of which are currently operating and producing almost 3 million metric tpy of propylene. By 2013, total worldwide propylene capacity via OCT is expected to reach almost 6 million metric tpy.

Licensor: Lummus Technology - CONTACT

Propylene, Advanced Catalytic Olefins

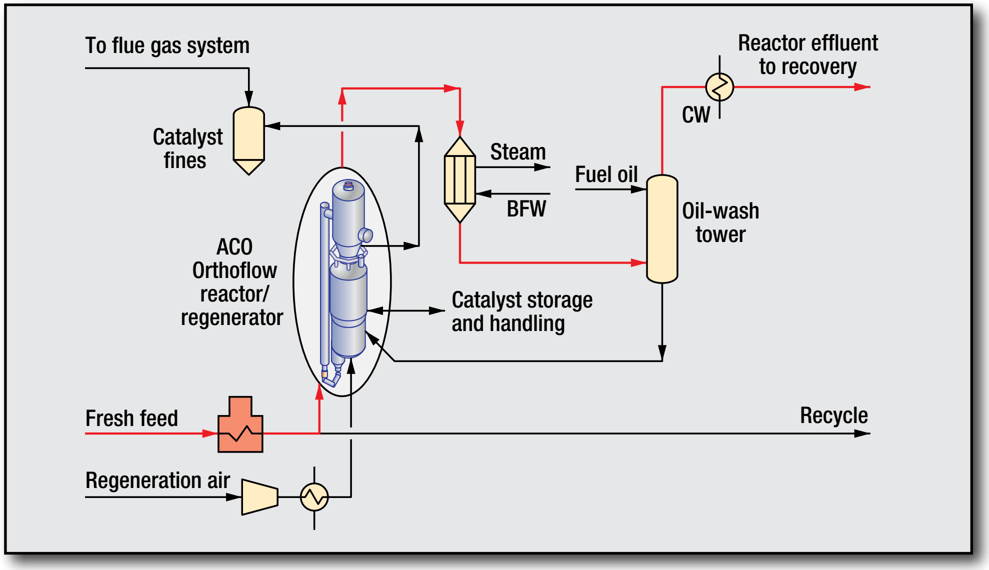
Application: An alternative to steam cracking to crack straight run feeds such as light and full-range naphthas to produce greater quantities of propylene and total light olefins, but with much higher propylene/ethylene (P/E) ratio of 1.0.

Description: The most predominant feed used to produce ethylene today is naphtha, as more than half of the world's ethylene is currently derived from cracking naphtha feed. The Advanced Catalytic Olefins (ACO) process is an alternative process that catalytically converts naphtha feed and is thus able to produce higher ultimate yields of light olefins (propylene plus ethylene) and at a higher P/E production ratio relative to steam cracking, typically about 1:1.

ACO is a process co-developed by KBR and SK Energy in Korea and offered for license worldwide exclusively by KBR. SK Energy developed and patented the catalyst used in the process, which is geared specifically to cracking paraffinic streams such as naphthas and condensate. The fluidized reactor system is designed by KBR and is similar to a refinery fluid catalytic cracking (FCC) unit consisting of a fluidized reactor/regenerator vessel, air compression, catalyst handling, flue-gas handling and feed and effluent heat recovery. Use of a catalytic system to crack the feed allows operating at much less severe conditions relative to a cracking furnace, and the system uses less fuel, meaning that the CO_2 footprint is reduced.

The ACO recovery section is very similar to KBR's ethylene plant recovery section design and is capable of production of polymer-grade olefins. Proprietary know-how is included to remove specific contaminants in the ACO process gas resulting from the FCC-type cracking process.

Yields: Light olefins yields are greater than in a steam cracker, and the P/E ratio is about 1:1 as opposed to 0.5. Fig. 2 is a comparison of steam cracker and ACO ultimate yields for a typical naphtha.



Energy: Fuel consumption is lower for the ACO process relative to a steam cracker. However, steam import is higher since there is less waste heat available for recovery. Overall cost of production is approximately US$90/ton ethylene lower for ACO due to the improved product slate.

Commercial plants: SK Energy is installing the first commercial application of the ACO process in its facilities in Ulsan, Korea, and this demonstration unit is expected to be in operation by October 2010.

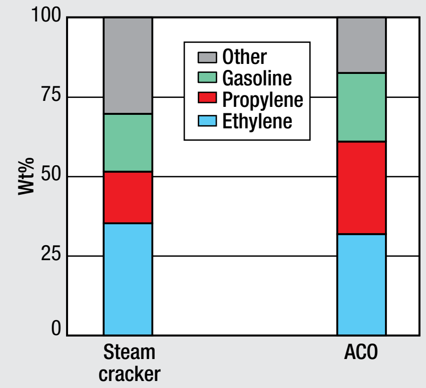


Fig. 2 Comparison of naphtha cracking yields.

Licensor: Kellogg Brown & Root LLC - CONTACT

Purified terephthalic acid (PTA)

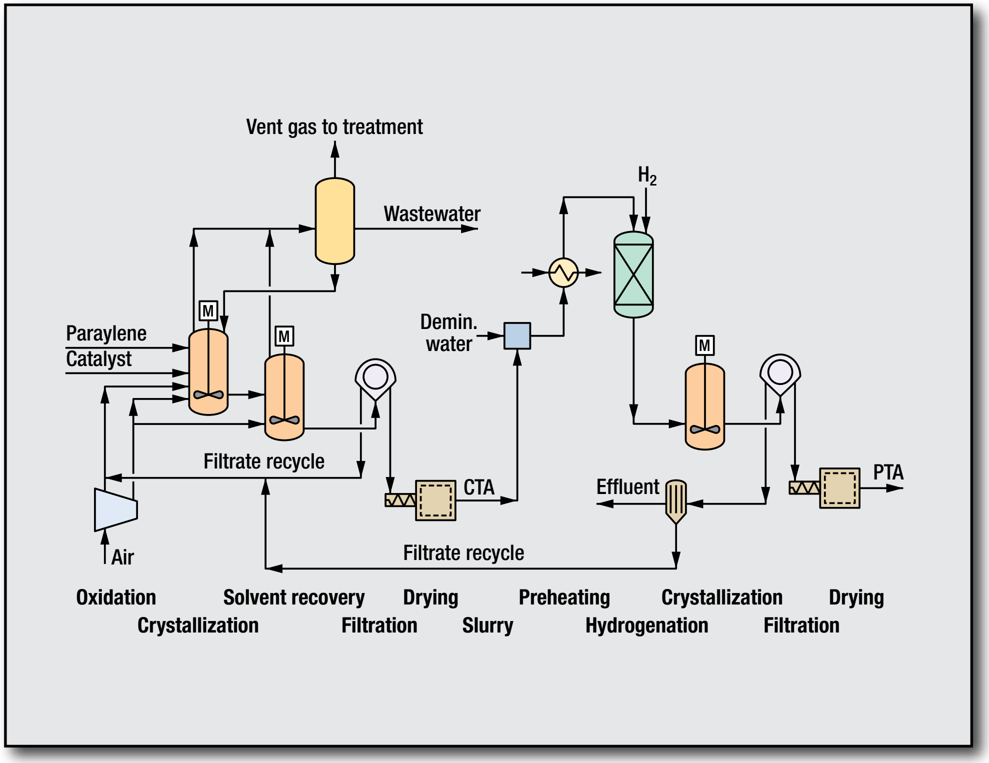
Application: The production of purified terephthalic acid (PTA) for use across all downstream polyester products. The process offered by The Dow Chemical Co. (Dow) and Davy Process Technology (DPT) has undergone a substantial upgrade to meet the high hurdles for investment, quality and environmental protection essential for success in this industry. The result is COMPRESS PTA.

Description: Following a PTA joint licensing agreement in 2008, DPT and Dow established a comprehensive technology development program to streamline and modernize the former Inca/Technimont PTA technology.

The production of PTA occurs in two stages. First, paraxylene is reacted with oxygen in the presence of a catalyst in an acetic acid solvent to yield crude terephthalic acid (CTA). This crude product is then filtered and re-slurried prior to polishing in a hydrogenation reaction after which it is crystallized, filtered and dried prior to export as purified terephthalic acid.

There are several intermediate separation and recovery operations within the conventional flowsheet, and a great deal of effort has gone into reducing the numbers of equipment items required to minimize feedstock consumption while maximizing recovery of catalyst, solvent, byproducts and energy in the most cost-effective way. For example, COMPRESS PTA incorporates these benefits:

- Energy-efficient, low-pressure binary distillation offering simpler, safer and more stable operation than conventional systems
- CTA and PTA filtration using rotary pressure filters, proven in commercial operation on PTA since 2007, resulting in a significant reduction in equipment count, improved reliability and lower energy usage.
- Simplified handling of water streams in the purification plant, thus lowering capital and operating costs.



Although based upon the conventional chemistry used on virtually all existing terephthalic acid plants, when compared with traditional technologies, COMPRESS PTA has a much lower main plant equipment count, with significantly reduced capital expenditure, and achieves a significant reduction in the variable cost of production. This reduction will also lead to a much more reliable process with high utilization factors.

COMPRESS PTA is the latest technology available from Davy Process Technology and The Dow Chemical Co. There are some significant improvements, and we are now embarking on further improvements of a fundamental nature so that our licensees will have access to the latest developments in chemistry and engineering.

Continued ▼

Economics: When compared to conventional PTA technology that can be licensed today, implementation of these technology features has resulted in several significant benefits to the proposed design, including:

- 30% reduction of the inside battery limit (ISBL) equipment count on a like-for-like scope of supply basis.
- Estimated 15% reduction on capital investment costs for main plant items (MPI).
- 25% reduction in the ISBL plot plan area.
- Significant improvements in energy efficiency resulting in a 20% reduction in HP steam demand, with no support fuel requirement for the process
- ISBL plant has become a net exporter of electrical power.

Commercial plants: The Dow PTA process has been licensed in 11 plants, the first in 1974, in 6 countries.

Licensor: Jointly licensed by The Dow Chemical Co. and Davy Process Technology - **CONTACT**

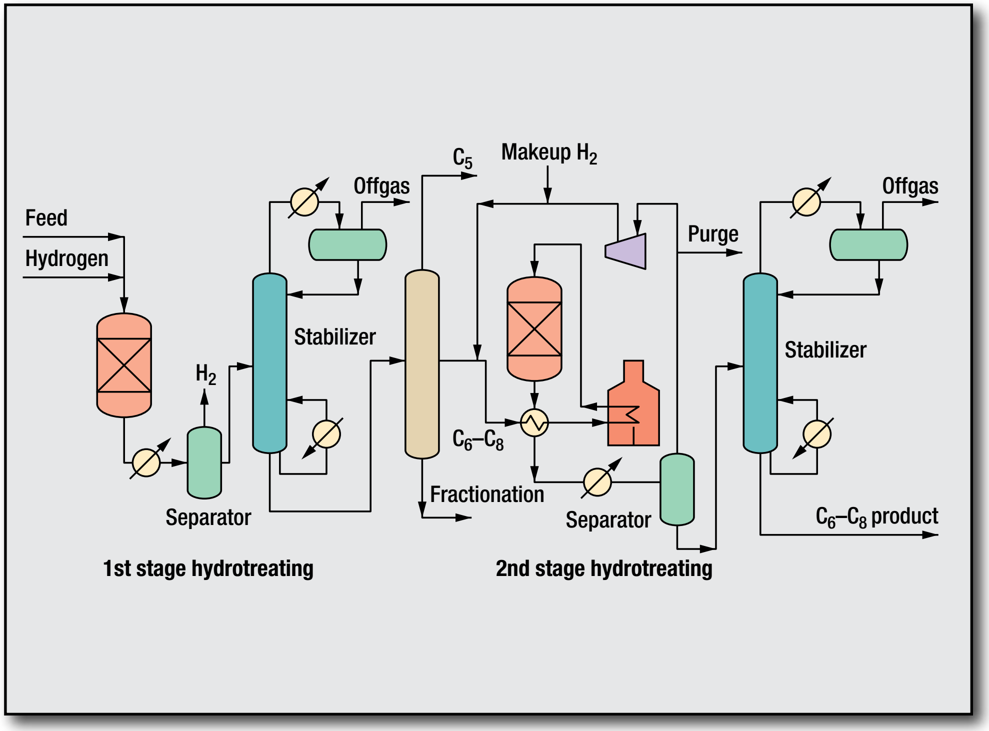
Pygas hydrotreating

Application: GTC offers an optimized technology for two-stage pyrolysis gasoline (pygas) hydrotreating (HDT), where di-olefins, olefins and styrene in the raw pygas feed are saturated. The technology is simple and easy to implement into existing plant requirements. The process is applied to the C_5^+ fraction of raw pyrolysis gasoline.

Description: In GTC's pyrolysis hydrotreating technology process, raw pygas is first fed to the first-stage hydrotreating section. The pygas feed stream along with hydrogen is preheated by the recycle liquid stream to the desired temperature and sent to the first-stage hydrotreating (HDT) reactor where most di-olefins in the feed are selectively saturated to olefins only, preserving the octane value of the hydrotreated stream.

The reactor effluent is sent to the first-stage product separator. Part of the liquid from the bottom of the product separator is recycled back to the front section of the first-stage hydrogenator to control the reactor temperature rise. Excess hydrogen and light hydrocarbons are removed at the top of the separator and sent to the recycle gas compressor. The separator liquid is fed to a first-stage stabilizer column. In the receiver, H_2 and light hydrocarbons are separated and drawn as a vapor product, which is sent as offgas to the battery limit (BL). The liquid from the receiver is fully returned as reflux to the column. The liquid stream from the stabilizer bottoms is C_5^+ gasoline fraction and can be sent to the gasoline pool. To produce benzene, toluene and xylene (BTX), this C_5^+ stream is sent to a fractionation section to obtain a C_6–C_8 heat cut, which will be further hydrotreated to saturate mono-olefins in the second-stage hydrotreating section.

In the second-stage hydrotreating section, the C_6–C_8 heart cut, combined with a recycle vapor stream and makeup hydrogen, is preheated in the second stage feed/effluent heat exchanger before being heated further to the desirable reaction temperature by a charge heater. The feed mixture passes through the fixed catalyst beds in the second-stage HDT reactor where olefin species are saturated and sulfur species are converted to H_2S.



The reactor effluent is then cooled in the second-stage feed/effluent heat exchanger and subsequently in an after-cooler before being routed to a second-stage product separator. In the product separator, the unreacted hydrogen and other light components are separated from the hydrotreated liquid products and recycled to the HDT reactor using a recycle gas compressor. A small vapor stream is purged as offgas to control the level of impurities in the recycle gas.

The hydrotreated liquid stream is fed to the second-stage stabilizer column. The column vapors are partially condensed in the overhead condenser and sent to an overhead receiver. In the receiver, H_2 and light

Continued ▼

hydrocarbons are separated and drawn as a vapor product, which is sent as offgas to the BL. The liquid from the receiver is fully returned as reflux to the column. The bottoms product from the stabilizer, which is the hydrotreated C_6–C_8 cut, is cooled further and sent to BL for further processing for aromatics extraction.

Process advantages:

- Flexibility in prefractionator cut point and a proprietary vaporizer allows control of polymerization potential in the hydrotreaters.
- Reactor operates at high liquid content with mixed phases to minimize polymer byproduct plugging.
- Optimized recycle scheme minimizes hydrocarbon vaporization and thereby extends reactor run length.
- Catalyst exhibits high activity, stability, mechanical strength and poison resistance.
- Aromatics saturation in second-stage reactor is less than 1%.
- Efficient heat integration scheme reduces energy consumption.
- Turnkey package for high-purity benzene, toluene and paraxylene production is available from licensor.

Economics:

Basis	500,000 tpy (11,000 bpsd) feedrate
Erected cost	$26 million (ISBL, 2009 US Gulf Coast basis)

Commercial plants: Commercialized technology available for license.

Licensor: GTC Technology - CONTACT

Styrene

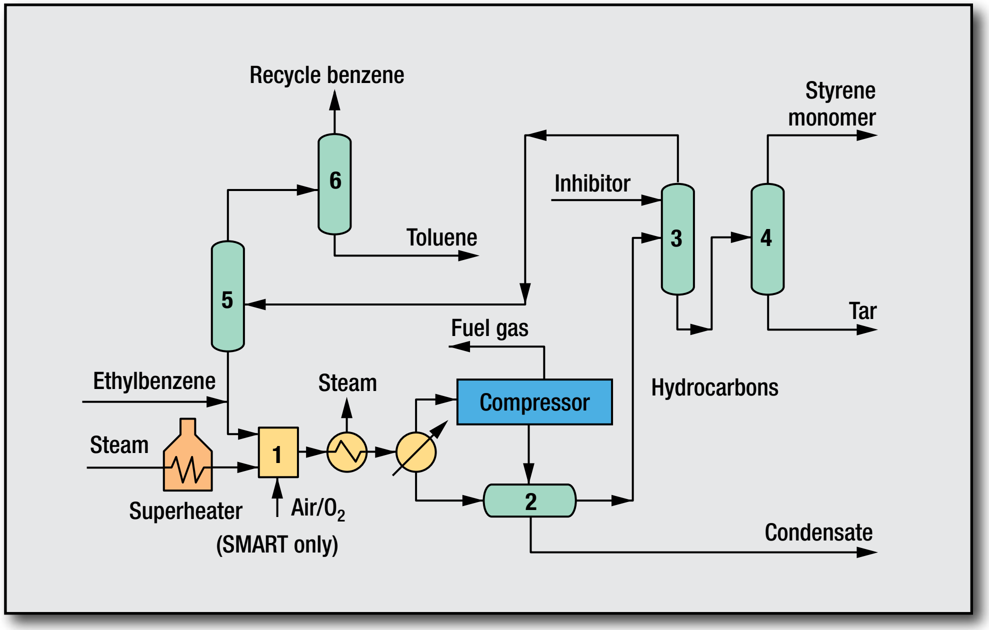
Application: To produce polymer-grade styrene monomer (SM) by dehydrogenating ethylbenzene (EB) using the Lummus/UOP "Classic" styrene process or the Lummus/UOP SMART process (for revamps involving plant capacity expansion).

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 and 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 or recovered as a valuable byproduct. Condensed hydrocarbons from an oil/water separator (2) are sent to the distillation section. Process condensate is stripped to remove dissolved aromatics and then used internally for steam generation.

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. In additional columns (5,6), toluene is produced as a minor byproduct and benzene 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 selectively 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 75% EB conversion per pass, eliminates the costly interstage reheater, and reduces superheated steam requirements. For existing SM producers, revamping to the SMART process may be the most cost-effective route to increased capacity.



Economics:

Ethylbenzene, metric ton/metric ton SM	1.055
Utilities, US$/metric ton SM	29

Commercial plants: Currently, 36 operating plants incorporate the Lummus/UOP Classic styrene technology. The largest single train plant in operation has a capacity of 815,000 metric tpy SM. Nine operating facilities are using the SMART process technology. Many future units using the SMART process are expected to be retrofits of conventional units, since the technology is ideally suited for revamps.

Licensor: Lummus Technology and UOP LLC, A Honeywell Company - CONTACT

Styrene

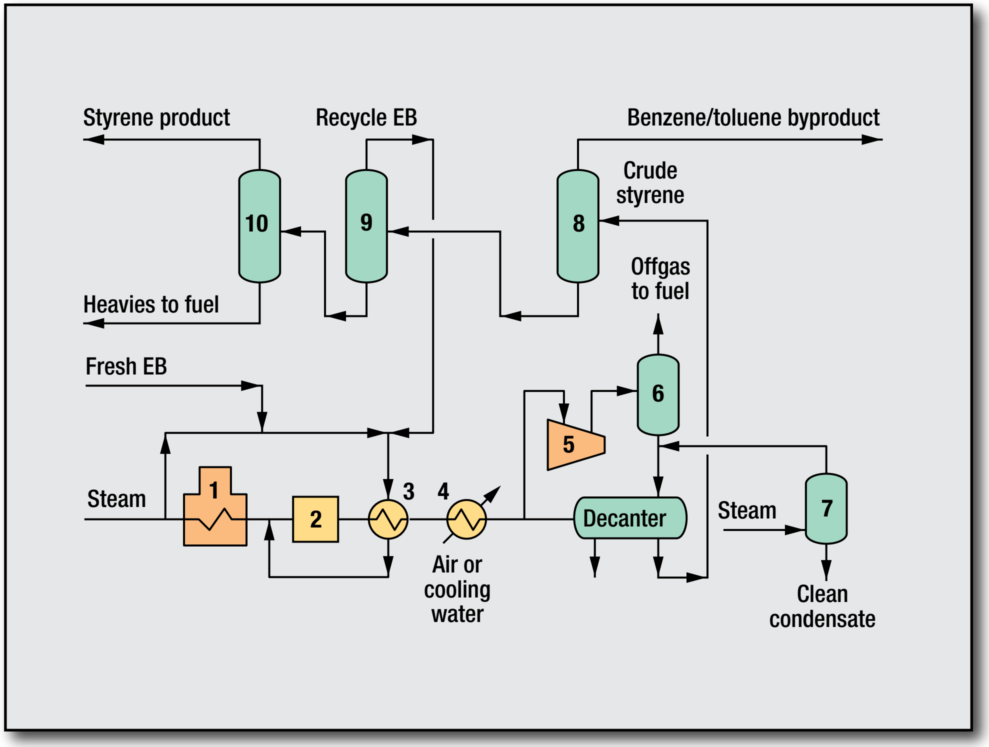
Application: Process to manufacture styrene monomer (SM) by dehydrogenating ethylbenzene (EB) to styrene. Feedstock EB is produced by alkylating benzene with ethylene using the EBMax process.

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 70%. Heat can be added either indirectly using conventional means such as a steam heat exchanger or directly using a proprietary Direct Heating Technology co-developed by Shell Oil, TOTAL and Shaw Energy and Chemicals.

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 C_9 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:

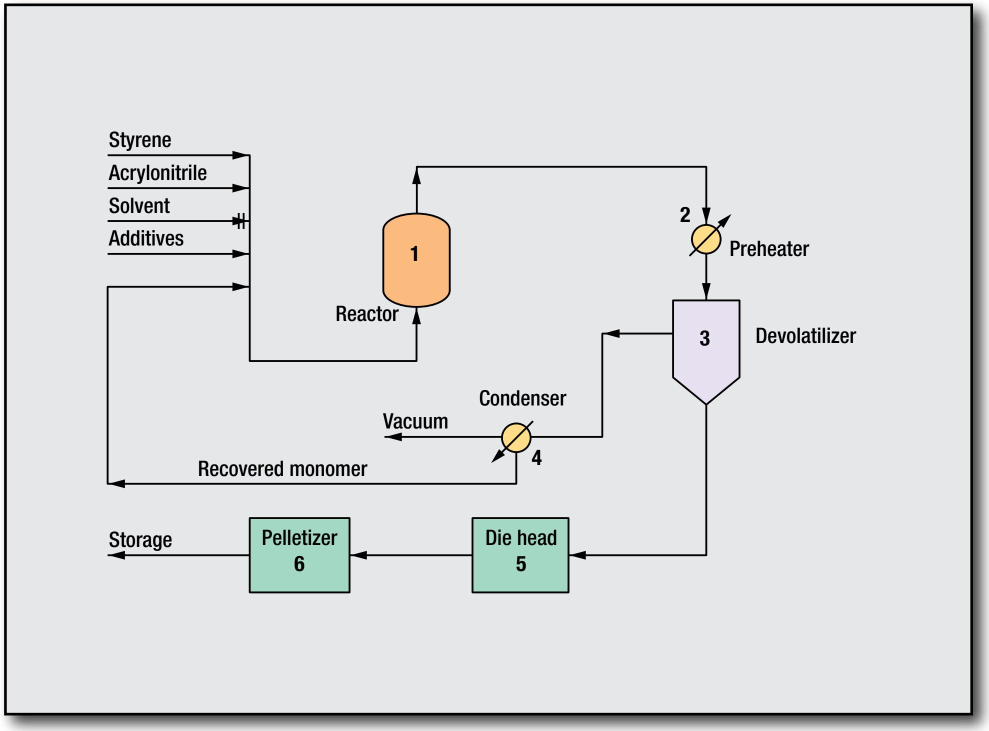
Ethylbenzene consumption, per ton of SM	1.054
Net energy input, kcal per ton of SM	1.25
Water, cooling, m^3 per ton of SM	150

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 50 units having design capacities (single train) up to 720,000 metric tpy. The aggregate capacity of these units is nearly 14 million metric tpy.

Licensor: Badger Licensing LLC - CONTACT

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. (TOYO) 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).

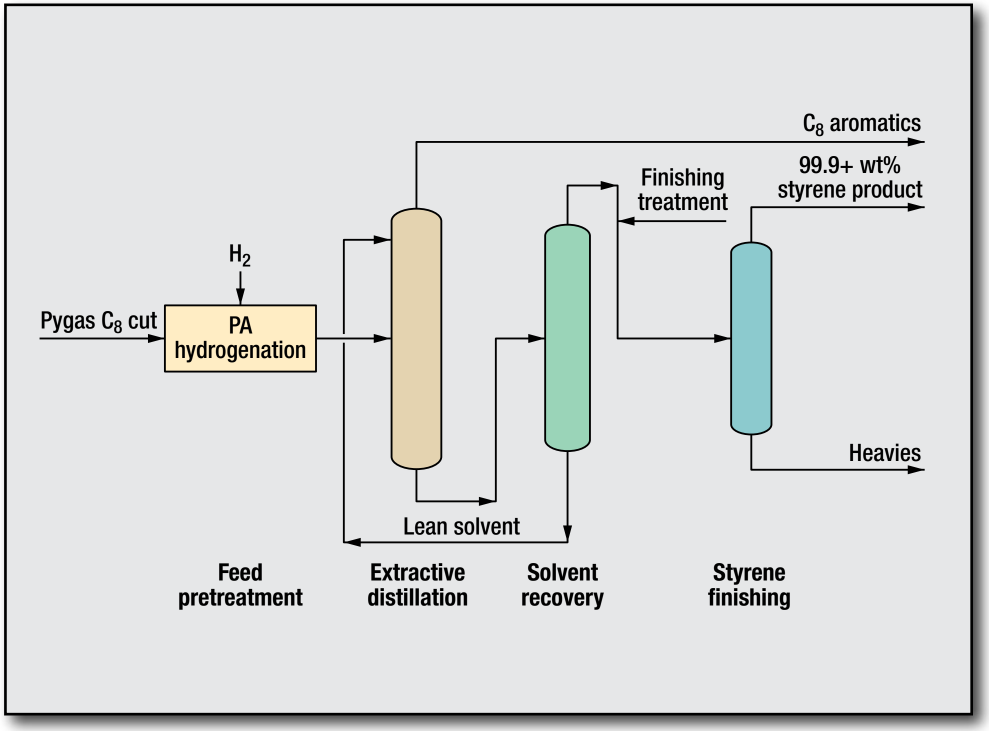
Economics: Basis: 50,000 metric tpy SAN

Raw materials consumption per metric ton of SAN, kg	1,009
Utilities consumption per metric ton of SAN, US$	18

Commercial plants: 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. (TOYO) - CONTACT

Styrene recovery from pygas



Application: GT-Styrene is an extractive distillation process that directly recovers styrene from the raw pyrolysis gasoline derived from the steam cracking of naphtha, gasoils and natural gas liquids (NGLs). The produced styrene is high purity and suitable for polymerization at a very attractive cost compared to conventional styrene production routes. The process is economically attractive for pygas feeds containing more than 15,000 tpy of styrene.

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 the styrene to the tower bottoms. The rich solvent mixture is routed to a solvent recovery column, which recycles the lean solvent back 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 can produce approximately 25,000 tpy of styrene and 75,000 tpy of mixed xylenes from pyrolysis gasoline.

Process advantages:

- Produces polymer-grade styrene at 99.9% purity
- Allows the recovery of isomer-quality mixed xylenes for paraxylene production
- Upgrades pygas stream components to chemical value
- Debottlenecks pygas hydrotreater and extends cycle length
- Reduces hydrogen consumed in hydrotreating
- Optimized solvent system and design provide economical operating costs.

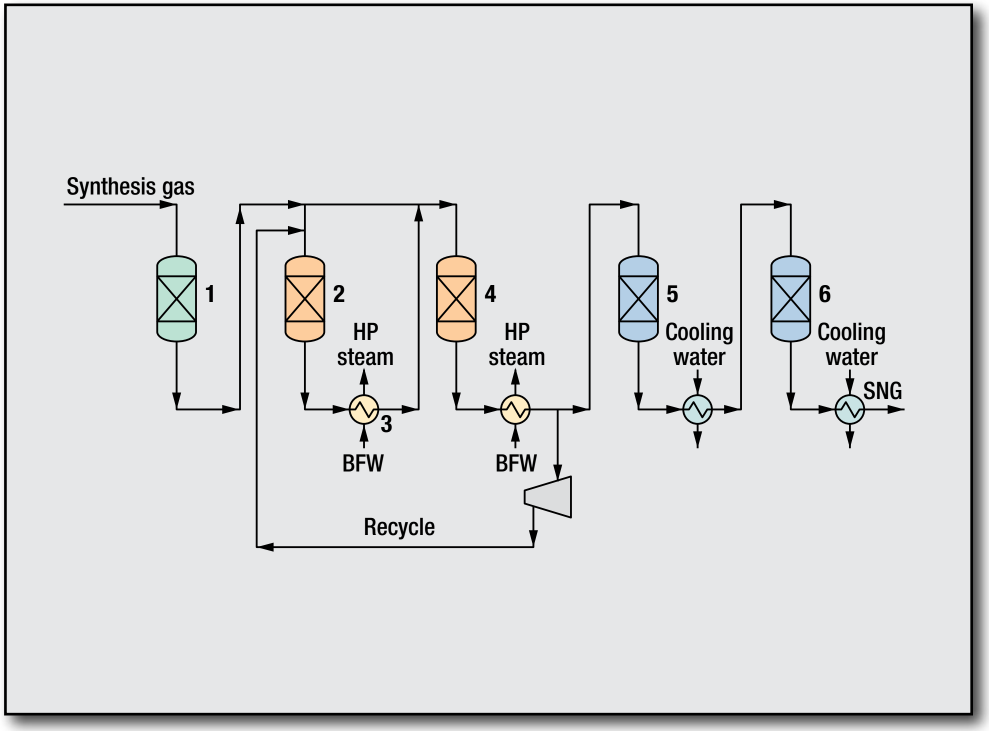
Economics:

Basis	25,000 tpy styrene recovery
Erected cost	$20 million (ISBL, 2009 US Gulf Coast basis)

Commercial plants: Three commercial licenses.

Licensor: GTC Technology - CONTACT

Substitute natural gas (SNG)



Application: To produce substitute natural gas (SNG) from purified synthesis gas produced by coal gasification, using shift and methanation reactions.

Description: The synthesis gas is fed to a sulfur guard vessel (1) to remove residual catalyst poisons, and it is then split into two parts. Part of the feed is mixed with the recycle gas and passed to the first bulk methanator (2) where shift and methanation reactions take place to produce a methane-rich product in an exothermic reaction. Product from the first bulk methanator is cooled by producing high-pressure (HP) steam (3) and is then mixed with the remaining feed gas. The gas mixture is passed to the second bulk methanator (4). After cooling to raise additional HP steam, the product stream from the reactor (4) is split, part providing recycle gas to the first bulk methanator and the remainder passing to the trim methanation stages (5) and (6).

The number of trim-methanation stages required depends on the final product specifications. Generally, two trim-methanation stages are sufficient to produce a high-methane, pipeline-quality gas.

Economics:

Steam production	2 ton/1,000 Nm^3
Power consumption	15 kW/1,000 Nm^3
Feedstock	Stoichiometric conversion of H_2 and CO to CH_4

Commercial plants: In the 1960s, over 40 town-gas and SNG plants were built in the UK based on naphtha feedstocks. More recently, there has been renewed interest, and three coal-based plants have been licensed with a capacity of 4 billion Nm^3/yr of SNG production.

Licensor: Davy Process Technology, UK - CONTACT

Upgrading pyrolysis gasoline

Application: Increase the value of steam-cracker pyrolysis gasoline (pygas) using conversion, distillation and selective hydrogenation processes. Pygas, the C_5–C_9 fraction issuing from steam crackers, is a potential source of products such as dicyclopentadiene (DCPD), isoprene, cyclopentane, benzene, toluene and xylenes (BTX).

Description: To produce DCPD and isoprene, pygas is depentanized and the C_5 fraction is processed thermally to dimerize cyclopentadiene to DCPD, which separates easily (1) from the C_5s via distillation.

Isoprene can be recovered by extractive distillation and distillation. The remaining C_5s and the C_6–C_9 cut are fed to the first-stage catalytic hydrogenation unit (2) where olefins and diolefins are eliminated.

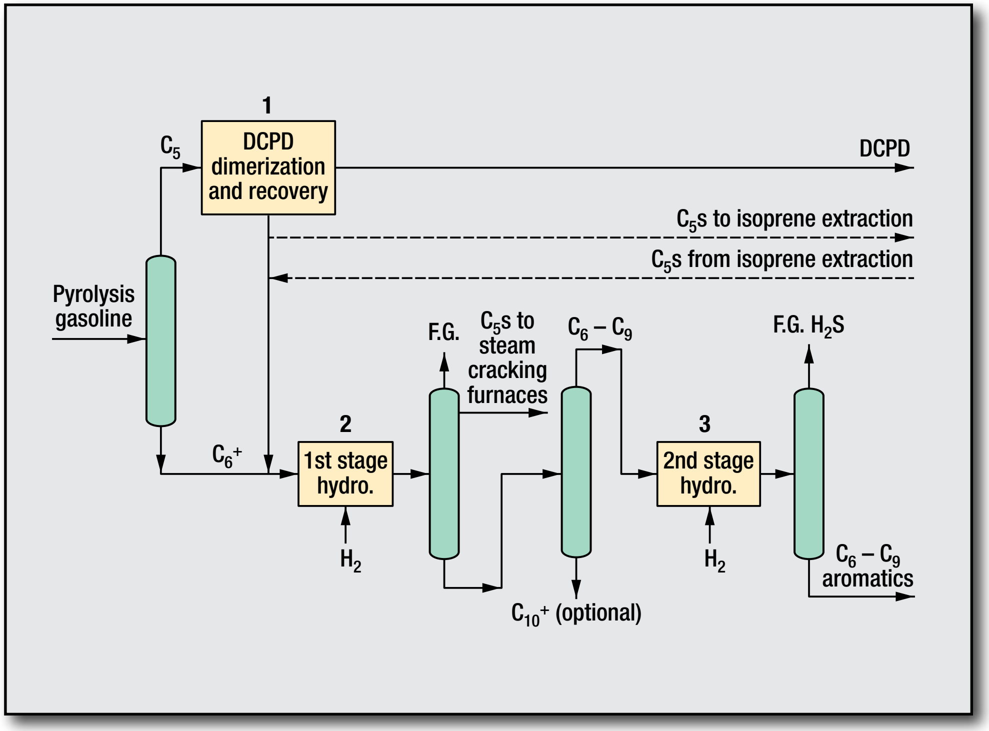
The C_5s are recycled to the steam cracker or an isomerization unit. Sulfur and nitrogen compounds are removed in the second-stage hydrogenation units (3). The BTX cut is ideal for processing in an aromatics complex.

Yields: For the new generation catalysts, recovery and product quality parameters are:

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 2010:

Investment, US$/ metric ton of feed	50
Utilities & catalysts, US$/ metric ton	10



Reference: Debuisschert, Q., "Innovation in Selective Hydrogenation Latest Technologies" 8th Asian Petrochemicals Strategy and Technology Conference, May 2010, Kuala Lumpur.

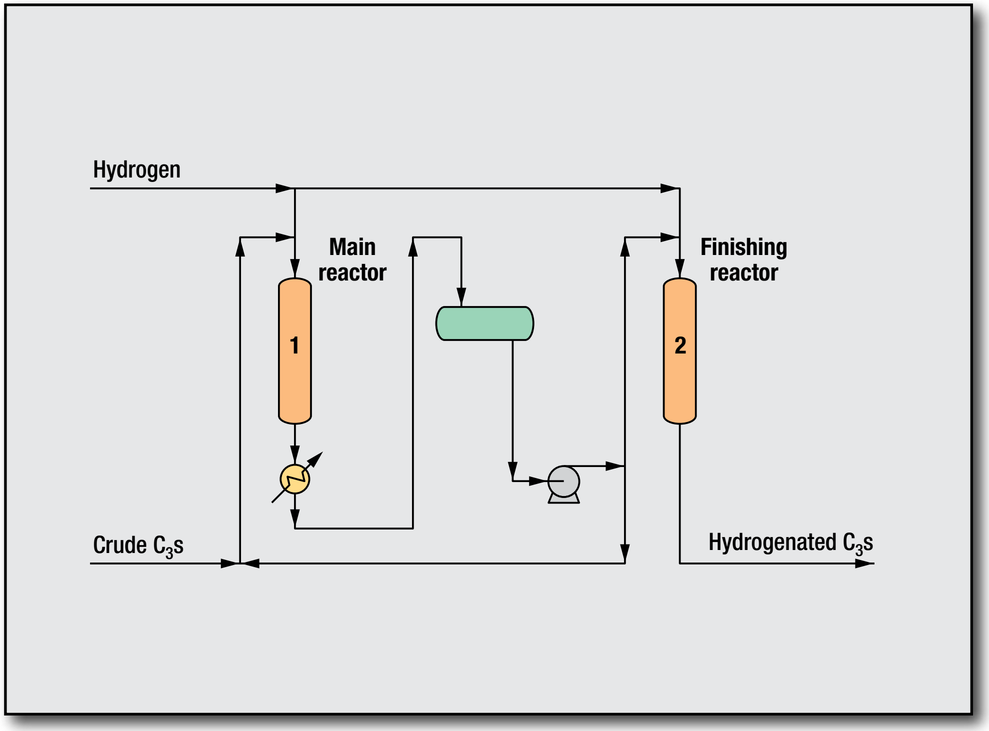
Commercial plants: Over 110 first-stage and 70 second-stage pygas hydrogenation units have been licensed.

Licensor: Axens - CONTACT

Upgrading steam cracker C_3 cuts

Application: To purify propylene-propane cuts from pyrolysis processes via selective catalytic hydrogenation of methylacetylene and propadiene (MAPD) impurities. Steam cracker C_3 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 applied as it not only achieves the tight MAPD specifications, but it also produces more propylene.

Description: The C_3 cut is joined by recycled C_3s and makeup 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 C_3 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 C_3 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%	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**

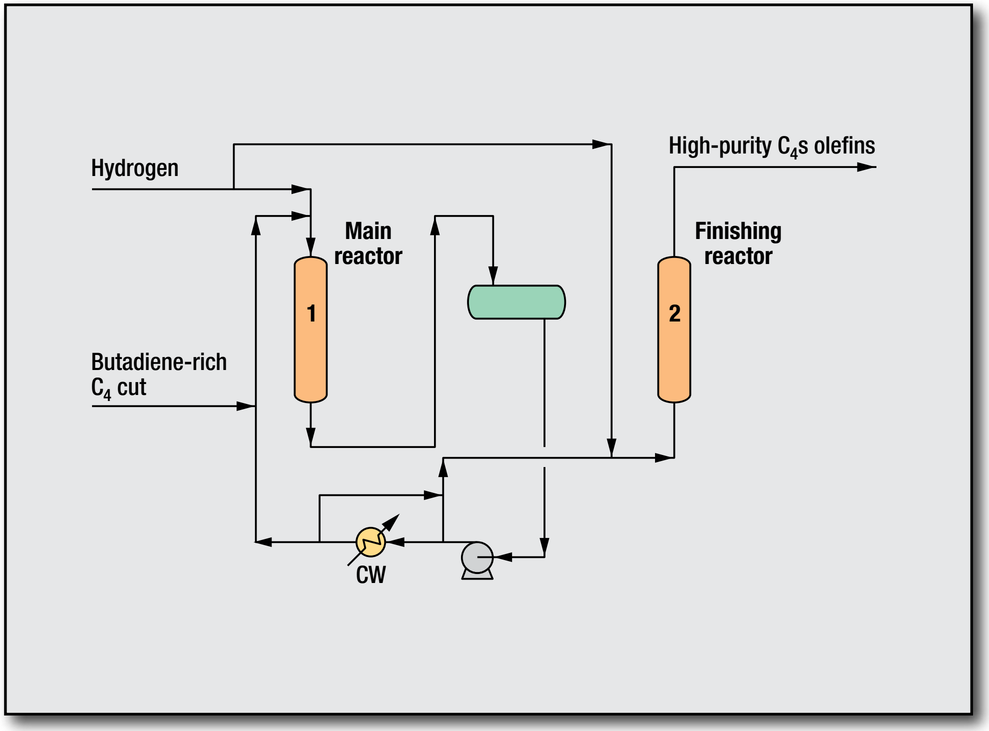
Economics: Based on a 1 million tpy capacity steam cracker, ISBL Gulf Coast location in 2010:

Investment, US$/metric ton of propylene	6.0
Utilities & catalysts, US$/metric ton of propylene	0.24

Commercial plants: Over 110 C_3 hydrogenation units have been licensed.

Licensor: Axens - CONTACT

Upgrading steam cracker C_4 cuts



Application: Increase the value of steam-cracker C_4 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 C_4 cuts; high conversion MTBE and superfractionation to produce polymer-grade butene-1; total C_4 cut hydrogenation; and total hydrogenation of combined C_3/C_4 and C_4/C_5 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 C_4 cut, recycled C_4s, makeup 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 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 C_4 selective hydrogenation process applied to maximize 1-butene. It is typically completed with high-conversion MTBE (using Axens, reactive distillation called Catacol) to convert isobutylene and superfractionation delivering the highest quality butene-1 used as a copolymer in LLDPE.

The process is different in the case of high-purity isobutylene production where a reactor and distillation column operate on the C_4 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):

	Feed	Product with LD-271, wt%
C_3s	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
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

Continued ▼

Upgrading steam cracker C4 cuts, *continued*

Economics: Based on a 160,000-tpy crude C_4 feed, ISBL Gulf Coast location in 2010:

Investment, US$	4.0 million
Utilities & catalysts, Water, cooling, m^3/h	500
Electrical power, kWh/h	250

Commercial plants: Over 100 C_4 hydrogenation units have been licensed for this process application.

A total of 30 etherification units (MTBE, ETBE, TAME and TAEE) have been licensed by Axens.

Licensor: Axens - CONTACT

Urea

Application: To produce urea from ammonia (NH_3) and carbon dioxide (CO_2). The process is based on applying Casale's highly efficient equipment, including:

- Casale full condenser
- Casale-Dente high-efficiency trays
- Casale high efficiency hydrolyzer used in the process condensate treatment unit.

This process is called the Casale split flow loop process, and is an improved CO_2 stripping process.

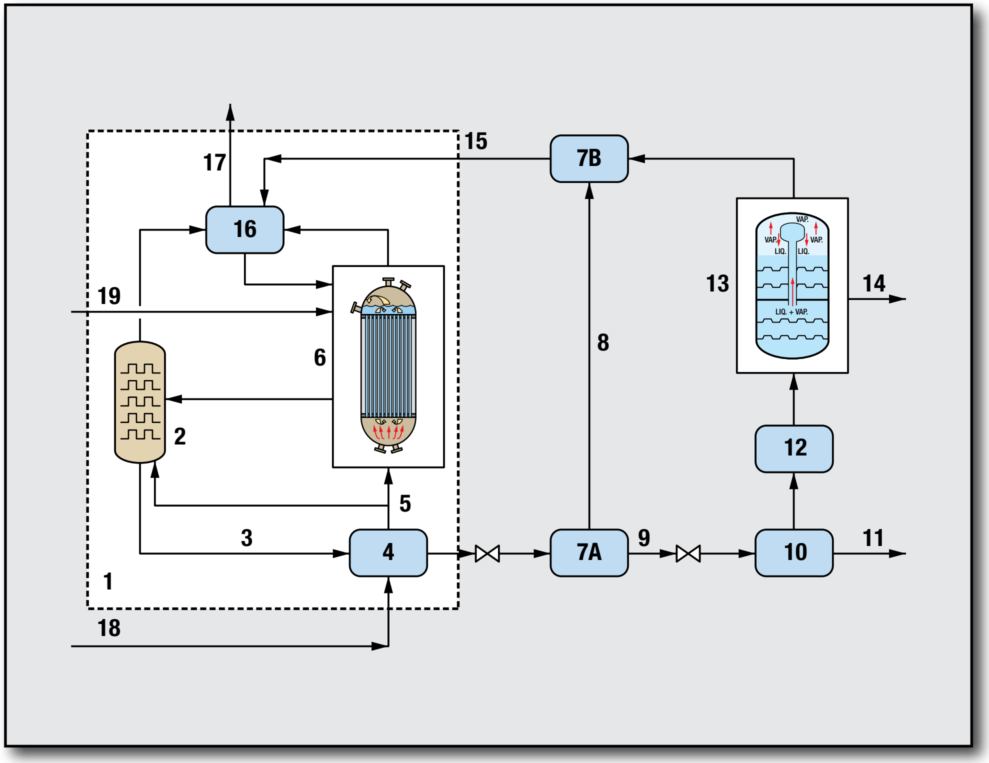
Description: Urea is formed from CO_2 (18) and NH_3 (19) in the HP loop (1) in a reactor (2) fitted with Casale-Dente high-efficiency trays. The urea solution (3) from the reactor (2), which still contains unreacted NH_3 and CO_2, is first treated in a stripper (4), operating at the same pressure as the reactor, heated with steam and using CO_2 (18) as stripping agents to recover most of the unreacted NH_3 and CO_2.

The vapor stream (5) (NH_3, CO_2 and H_2O) generated in the stripper, containing all inerts, is split after leaving the high-pressure (HP) stripper (4). One portion of the vapor stream is sent to the HP carbamate condenser (6) (Casale full condenser), while the rest of the vapors bypass the condenser and go directly to the reactor (2).

The Casale full condenser (6) is practically a submerged condenser and the carbamate flow obtained in this equipment is sent to the reactor.

From the stripper (4), the urea solution, still containing unreacted NH_3 and CO_2, is sent to a low-pressure (LP) single decomposition/condensation stage (7a+7b) where practically all of the remaining unreacted NH_3 and CO_2 is recovered in the form of a carbamate solution (8).

The urea-water solution (9), containing only small quantities of NH_3 and CO_2, is further treated in a vacuum evaporation section (10) to obtain a urea melt (11) for the prilling tower or the granulator.



The process condensate, obtained from the vacuum condensers (12) is purified with two columns and one hydrolyzer (13) to eliminate all NH_3, CO_2 and urea, thus obtaining the purified water (14).

The carbamate solution (15) obtained in the LP section is sent first to the HP scrubber (16), where the inerts (17) leaving the HP loop are washed, and then sent through the Casale full condenser (6) to the reactor (2).

Economics: Thanks to its design, the Casale split flow loop process is highly efficient; for a given capacity, process benefits include low investment due to smaller sized equipment and low medium-pressure steam consumption (22 bar, superheated) of 750 kg/metric tons and almost stoichiometric raw material consumption.

Continued ▼

Commercial plants: Three plants are in operation utilizing the split flow loop process with capacities ranging from 1,300 metric tpd to 2,300 metric tpd. In addition, one plant with 1,000 metric tpd capacity was recently built.

Licensor: Urea Casale SA, Switzerland - CONTACT

Urea

Application: To produce urea from ammonia and carbon dioxide using an ammonia-stripping process.

Description: Ammonia (NH_3) and carbon dioxide (CO_2) react at 150 bar to yield urea and ammonia carbamate. The conversion in the reactor is very high due to a favorable NH_3/CO_2 ratio of 3.3~ 3.5:1 and operating temperature of 185°C to 190°C. These conditions prevent corrosion problems.

Carbamate is decomposed in three stages at different pressures: in the stripper at the same pressure as the reactor, in the medium-pressure decomposer at 18 bar and in the low-pressure decomposer at 4.5 bar. Reactants not transformed into urea are recycled to the reactor by an ejector. Main equipment is installed at ground level. This layout is essential for large plants. Heat recoveries are particularly developed to have low-energy usage.

Any finishing can be coupled with the synthesis: prilling and granulation, both direct or via crystallization. Different product quality (biuret, moisture, hardness and size) are obtained according to client requests.

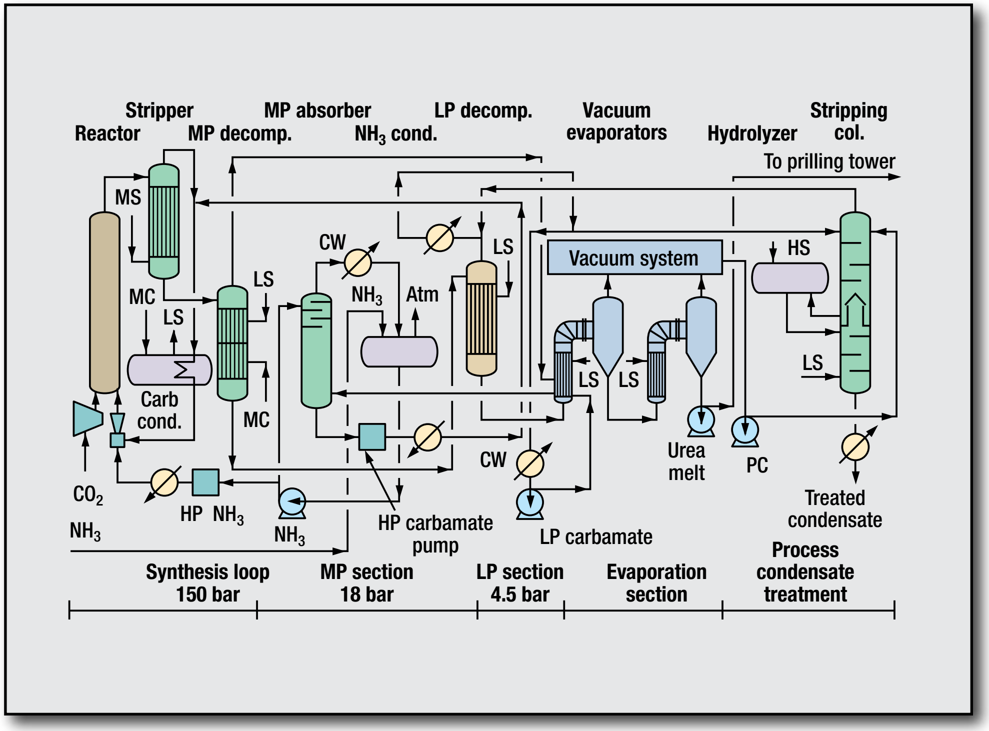
The plant is completely free from pollution problems. All vents are efficiently treated or flared so that they are discharged to atmosphere practically free of ammonia and/or urea. Process wastewater is hydrolyzed within the plant to achieve boiler feedwater specification and to recover ammonia and carbon dioxide.

Snamprogetti granulation technology has been applied in a 1,650-tpd plant operating since 1990.

Economics: Raw materials and utilities per 1,000 kg of urea product are (prilling case):

Ammonia, kg	566
Carbon dioxide, kg	735
Steam, 110 bar, 510°C , kg	730(1)
Electric power, kWh	21
Water, cooling, m^3	80
Condensate, kg	1,045

(1) Includes steam to the CO_2 compressor turbine, as well as all utilities for effluent treatment.



Commercial plants: One hundred and sixteen plants have been licensed, with capacity up to 3,850 tpd on a single line.

Licensor: Saipem - CONTACT

Urea

Application: To produce urea from ammonia (NH_3) and carbon dioxide (CO_2) using the CO_2 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°C–185°C. Unconverted materials in synthesis solution are efficiently separated by CO_2 stripping. The milder operating condition and using two-phase stainless steel prevent corrosion problems. Gas from the stripper is condensed in a vertical submerged carbamate condenser. Using a high-pressure (HP) ejector for internal synthesis recycle, major synthesis equipment is located on the ground level.

The urea solution from synthesis section is sent to a medium-pressure (MP) decomposer at 17 bar and a low-pressure (LP) decomposer at 2.5 bar for further purification. No pure ammonia recycle is required due to the high separation efficiency in the stripper.

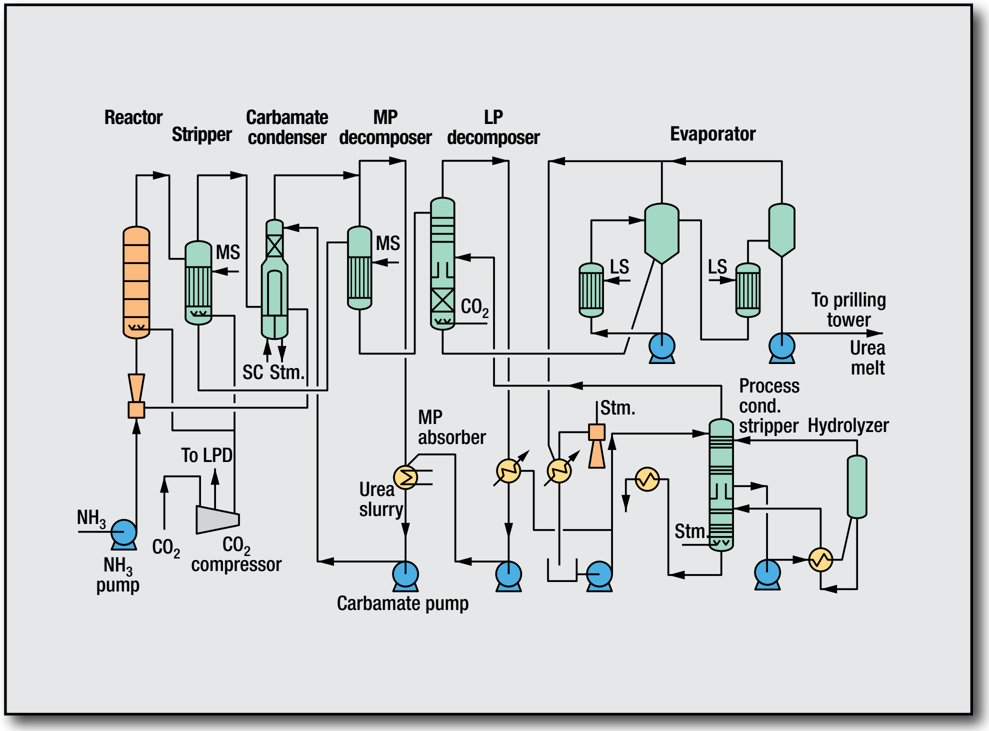
The vacuum evaporator unit produces urea melt at the required concentration either for prilling or granulation.

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. (TOYO) has a spout-fluid bed granulation technology to produce granular urea—typically 2 mm–4 mm size. Due to proprietary granulator, electric power consumption is the lowest among granulation processes.

Economics: Raw material and utilities consumptions per metric ton of prilled urea are:

Ammonia, kg	566
Carbon dioxide, kg	733
Steam, 110 bar, 510°C	690*
Electric power, kWh	20
Water, cooling, m^3	75



Commercial plants: More than 100 plants, including urea granulation plants, have been designed and constructed based on TOYO technology.

Licensor: Toyo Engineering Corp. (TOYO) - CONTACT

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* Includes steam for CO_2 compressor turbine and steam for process condensate treatment

Urea, 2000plus

Application: To produce urea from ammonia (NH_3) and carbon dioxide (CO_2) using the Stamicarbon CO_2 stripping urea technology. Urea finds its application for 90% as fertilizer; further, urea is used as base material for the production of resins, melamine, as cattle feed and as a NO_x reducing agent "Ad Blue."

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, the internal recycle is based on gravity flow. This results in very low electrical energy requirement. Synthesis gas condensation in the pool condenser or 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 a vacuum condensation system produces urea melt with the required concentration either for the Stamicarbon fluidized-bed granulation or prilling.

Process water produced in the plant is treated in a desorption/hydrolyzer section. This section produces an effluent, which is suitable for use as boiler feedwater.

With Stamicarbon's pool condenser technology, condensation can be done very efficiently by reversing the former high-pressure carbamate condenser's process and steam side. The entire heat exchanging part is submerged in condensed carbamate. This pool-type condensation enables higher heat transfer, while staging two-thirds of the entire synthesis section's urea conversion in its liquid holdup. Thus, the urea reactor can be much smaller, and the plant will be smaller. Stamicarbon's Urea 2000plus technology can be offered for capacities up to 5,000 metric tpd–6,000 metric tpd.

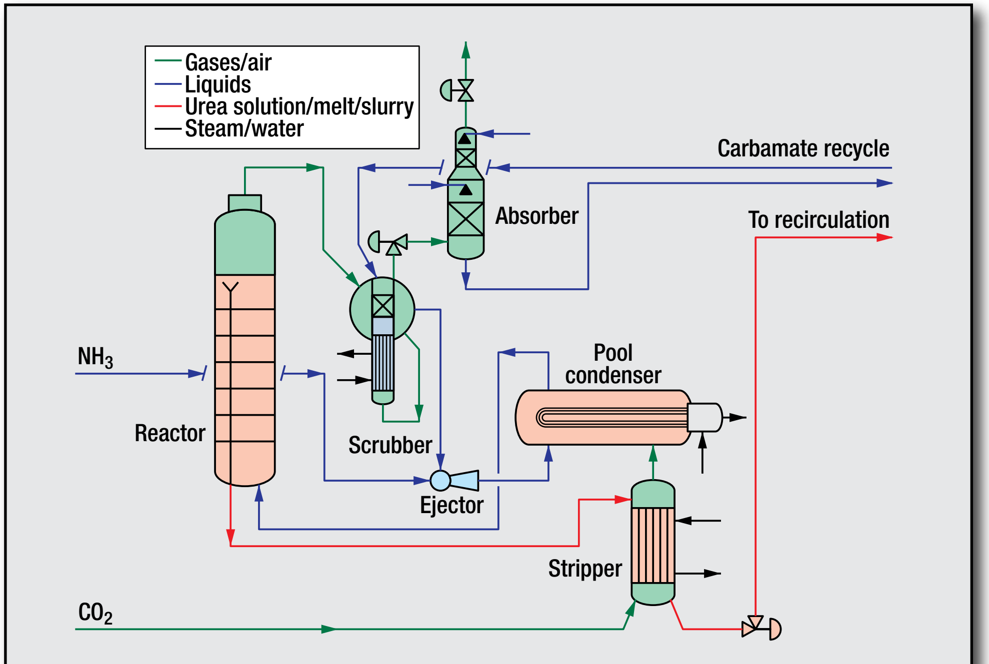


Fig. 1. Synthesis section Urea 2000Plus Pool condenser Process.

Taking this a stage further, Stamicarbon invented the pool reactor (Fig. 2), which effectively combines the pool condenser and the downstream urea reactor into a single piece of high-pressure equipment. Pool reactor type of urea plants are currently offered for capacities up to 2,300 metric tpd.

Economics: Depending on the various heat exchange options within the design, the raw material and utility consumptions per metric ton of urea product typically are:

Continued ▼

Urea, 2000plus, *continued*

	Urea	
	Granulation	**Prilling**
Ammonia, kg	564	567
Carbon dioxide, kg	730	733
Nitric acid (56%), kg	–	–
Steam, 23 bar, 330°C*, kg	770	785
Electric power, kWh	56	20
Water, cooling (ΔT= 10°C), m^3	64	71
Steam export, 4 bar, saturated, kg	50	50
Steam condensate export, kg	415	385
Process condensate export, kg	300	650

*Excluding steam for CO_2 compressor drive

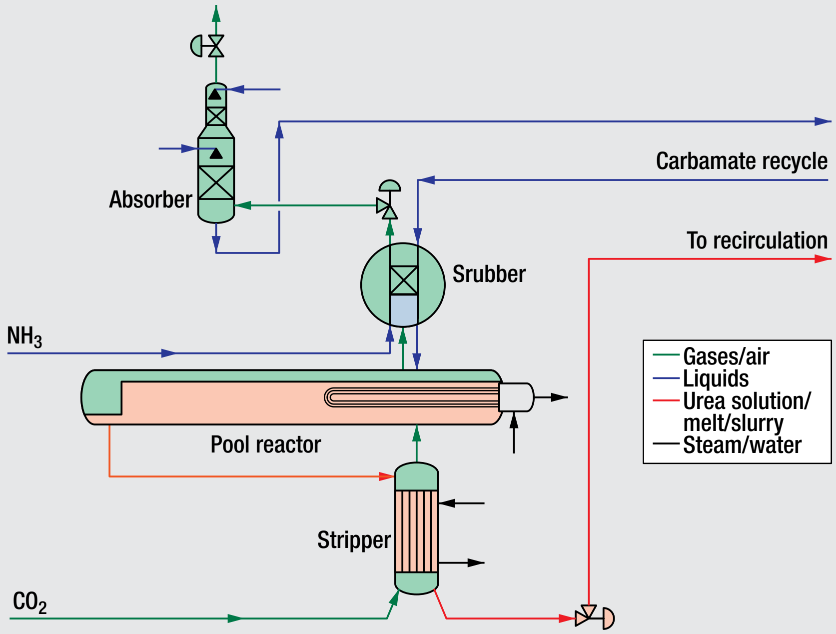


Fig. 2. Synthesis section Urea 2000Plus Pool reactor Process.

Commercial plants: More than 150 plants based on Stamicarbon's CO_2 stripping urea technology are in operation. The largest single-line unit with Urea 2000plus technology produces more than 3,600 metric tpd.

Licensor: Stamicarbon B.V. - CONTACT

Urea, AVANCORE process

Application: To produce urea from ammonia (NH_3) and carbon dioxide (CO_2) using the Stamicarbon CO_2 stripping urea technology. Urea finds its application for 90% as fertilizer; further urea is used as base material for the production of resins, melamine as cattle feed, and as a NO_x reducing agent "Ad Blue."

Description: Ammonia and carbon dioxide are introduced to the high-pressure (HP) synthesis using a HP ammonia pump and carbon dioxide compressor (Fig. 1). The NH_3, together with the carbamate solution from the downstream recirculation section, enters the pool condenser.

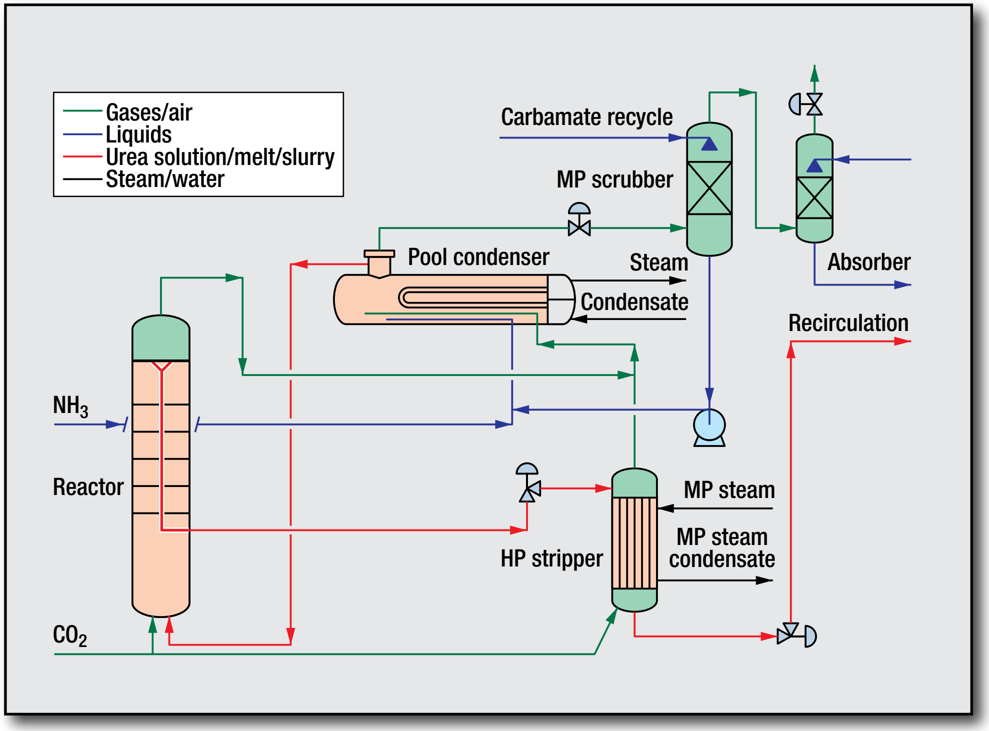
The major part of the CO_2 enters the synthesis through the HP stripper counter-current to the urea/carbamate solution leaving the reactor. On the shell side, the HP stripper is heated with steam. The offgas of the HP stripper, containing the CO_2, together with NH_3 and CO_2 resulting from dissociated carbamate, is fed into the pool condenser.

The minor part of the CO_2, entering the synthesis as a feed, enters the urea reactor at the bottom in order to produce sufficient heat for the endothermic urea reaction.

In the pool condenser, NH_3 and CO_2 are condensed to form carbamate, and a substantial part of the conversion to urea is already established here. The heat released by condensation and subsequent formation of carbamate is used to produce re-usable low-pressure (LP) steam.

Downstream from the pool condenser, the urea-carbamate liquid enters the vertical reactor, if required, located at ground level. Here, the final part of the urea conversion takes place. The urea solution then leaves the top of the reactor, all by gravity flow via an overflow funnel, before being introduced into the HP stripper. Gases leaving the urea reactor are directed to the pool condenser.

Gases leaving the pool condenser are fed into the scrubber operating at a reduced pressure. Here, the gases are washed with the carbamate solution from the LP recirculation stage. The enriched carbamate solution is then fed into the pool condenser. This enriched carbamate flow contains no more water than in earlier generations of Stamicarbon CO_2-stripping plants, meaning that the conversions in the synthesis section are as high as ever. Inert gases leaving the scrubber at reduced pressure containing some NH_3 and CO_2 are then released into the atmosphere after treatment in an LP absorber.



Economics: Depending on the various heat exchange options within the design, the raw material and utility consumptions per metric ton of urea product typically are:

Continued ▼

	Urea	
	Granulation	**Prilling**
Ammonia, kg	564	567
Carbon dioxide, kg	730	733
Nitric acid (56%), kg	–	–
Steam, 23 bar, 330°C*, kg	770	785
Electric power, kWh	56	20
Water, cooling ($\Delta T = 10°C$), m^3	64	71
Steam export, 4 bar, saturated, kg	50	50
Steam condensate export, kg	415	385
Process condensate export, kg	300	650

*Excluding steam for CO_2 compressor drive

Commercial plants: The AVANCORE urea process is a new urea synthesis concept that incorporates all the benefits of Stamicarbon's earlier proven innovations. The AVANCORE urea process combines the advantages of Urea 2000Plus technology, Safurex and innovations and experiences gained from many revamp projects. No AVANCORE Urea plants are yet in operation.

Licensor: Stamicarbon B.V. - CONTACT

Urea, Mega plant

Application: To produce urea from ammonia (NH_3) and carbon dioxide (CO_2) using the Stamicarbon CO_2 stripping urea technology.

Urea finds its application for 90% as fertilizer; further urea is used as base material for the production of resins melamine, as cattle feed, and as a NO_x reducing agent "Ad Blue."

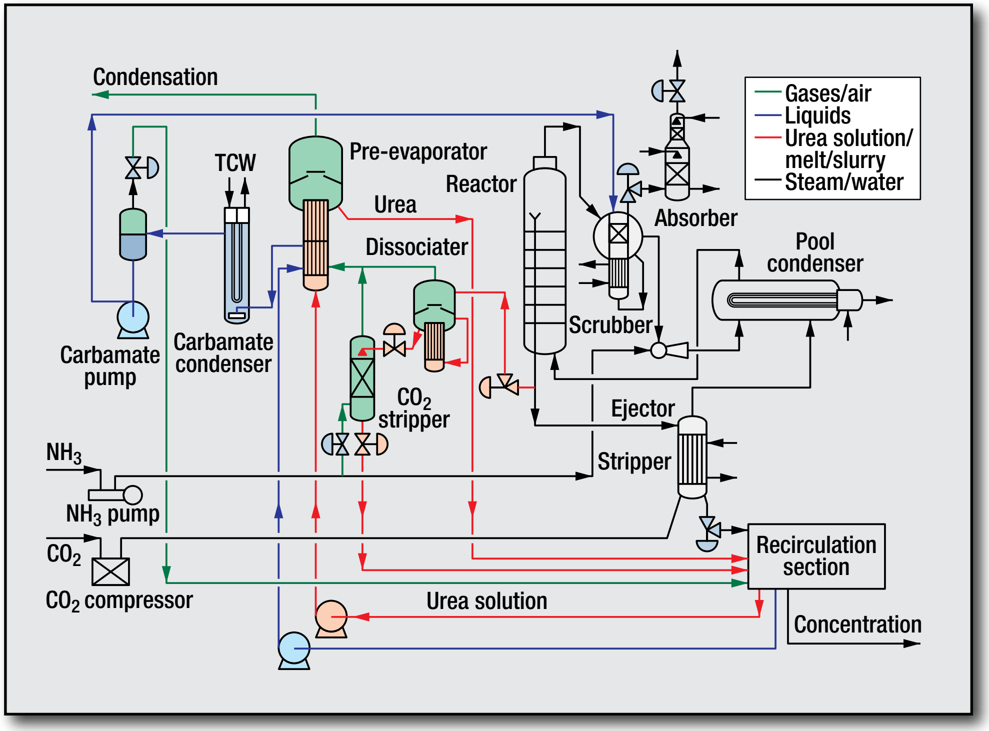
Description: Large urea plants require large high-pressure (HP) equipment that is difficult and costly to manufacture. To reduce costs, Stamicarbon has developed a Mega plant concept for single-line urea plants producing 5,000 metric tpd of urea.

In the Stamicarbon Mega plant concept, a portion of the liquid effluent from the urea reactor is diverted to a medium-pressure (MP) recycling section, thereby reducing the size of the HP vessels needed. Thanks to the Mega plant concept, the size of the required HP equipment and lines will not exceed the size of equipment needed for a 3,500 metric tpd pool condenser type CO_2-stripping urea plant. A Mega plant can be built with both the Stamicarbon AVANCORE or the Stamicarbon Urea 2000Plus technology.

About 70% of the urea solution leaving the urea reactor flows to the HP CO_2 stripper. The remainder is fed into a MP recirculation section. The reduced liquid feed to the stripper, in turn, reduces not only the size of the stripper, but also the heat exchange area of the pool condenser. The degree of stripping efficiency is adjusted to ensure that as much low-pressure (LP) steam is produced by the carbamate reaction in the pool condenser as is needed in the downstream sections of the plant.

About 30% of the urea solution that leaves the reactor is expanded and enters a gas/liquid separator in a recirculation stage operating at a reduced pressure. After expansion, the urea solution is heated by MP steam. By heating the urea solution, the unconverted carbamate is dissociated into NH_3 and CO_2.

Stamicarbon's Mega plant concept does not need the NH_3 recycle section or the NH_3 hold-up steps that are commonly seen in competitors, total recycle urea plants. This is because the low NH_3:CO_2 molar ratio in the separated gases allows for easy condensation as carbamate only.



The operating pressure in this MP recirculation stage is about 20 bars. After the urea solution leaves the MP dissociation separator, it flows into an adiabatic CO_2 stripper, which uses CO_2 to strip the solution.

As a result of this process, the NH_3:CO_2 molar ratio in the liquid leaving the MP recirculation section is reduced, thus facilitating the condensation of carbamate gases in the next step. Vapors leaving the MP dissociation separator together with the gases leaving the adiabatic CO_2 stripper are condensed on the shell side of the evaporator. The carbamate formed in the LP recirculation stage is also added to the shell side of this evaporator. The heat released by condensation is used to con-

Continued ▼

centrate the urea solution. Further concentration of the urea solution is achieved using LP steam produced in the pool condenser.

The remaining uncondensed NH_3 and CO_2 leaving the shell side of the evaporator are sent to a MP carbamate condenser. The heat released by condensation in this condenser is dissipated into a tempered cooling water system. This process forms MP carbamate that contains only 20 wt%–22 wt% water. The carbamate is transferred via a HP carbamate pump to the HP scrubber in the urea synthesis section. The urea solution leaving the adiabatic CO_2 stripper and the HP stripper are expanded together in the LP recirculation section.

Economics: Depending on the various heat exchange options within the design, the raw material and utility consumptions per metric ton of urea product typically are:

	Urea	
	Granulation	**Prilling**
Ammonia, kg	564	567
Carbon dioxide, kg	730	733
Nitric acid (56%), kg	–	–
Steam, 23 bar, 330°C*, kg	770	785
Electric power, kWh	56	20
Water, cooling ($\Delta T = 10°C$), m^3	64	71
Steam export, 4 bar, saturated, kg	50	50
Steam condensate export, kg	415	385
Process condensate export, kg	300	650

*Excluding steam for CO_2 compressor drive

Commercial plants: At present, five urea plants using Stamicarbon's Mega technology are in operation.

Licensor: Stamicarbon B.V. - CONTACT

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 JX Nippon Oil and Energy Corp. (NOE), the license being available from Toyo Engineering Corp. (TOYO).

Description: Conventional wet oxidation processes adopt a plug-flow type of reactor system,which usually has problems such as:

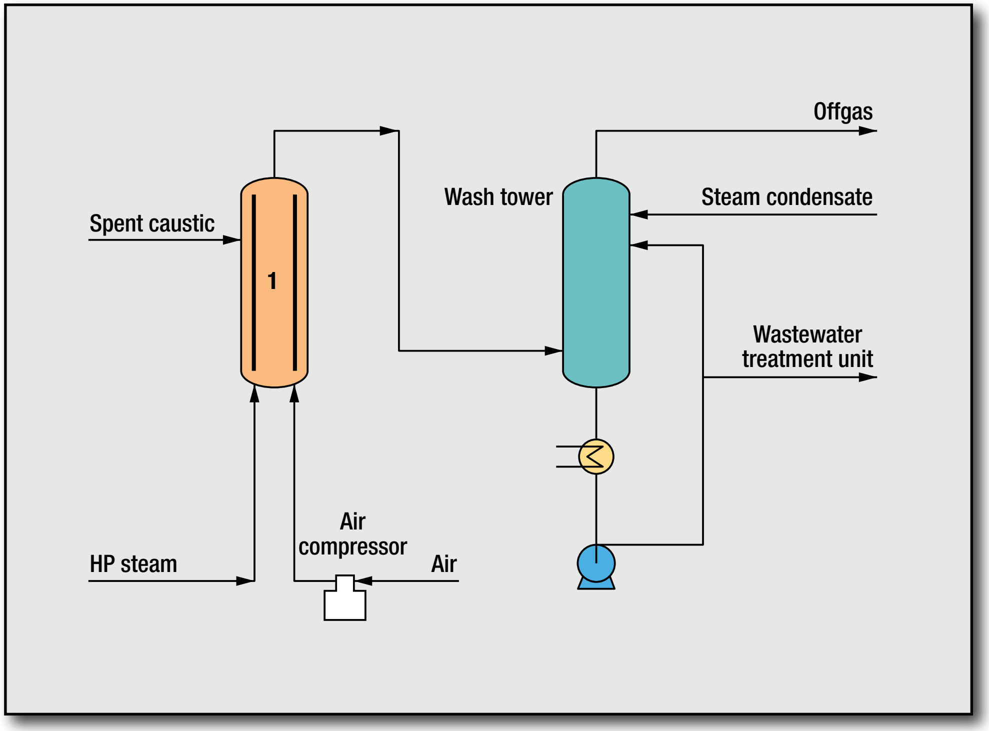
- Plug-flow reactors require higher reaction temperature for the oxidation reaction and need a feed preheater. Clogging problems in the outlets of the reactor and preheater often occur.
- High processing temperatures cause corrosion problems. High-grade construction materials such as nickel or nickel alloy are needed for the reactor.

The NOE 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,m³/h	55
	Washwater, m³/h	2



Commercial plants: Many olefins plants worldwide use this WAO process. Thirteen processing units have been designed by TOYO since 1989.

Licensor: JX Nippon Oil and Energy Corp. - CONTACT

Xylene isomerization

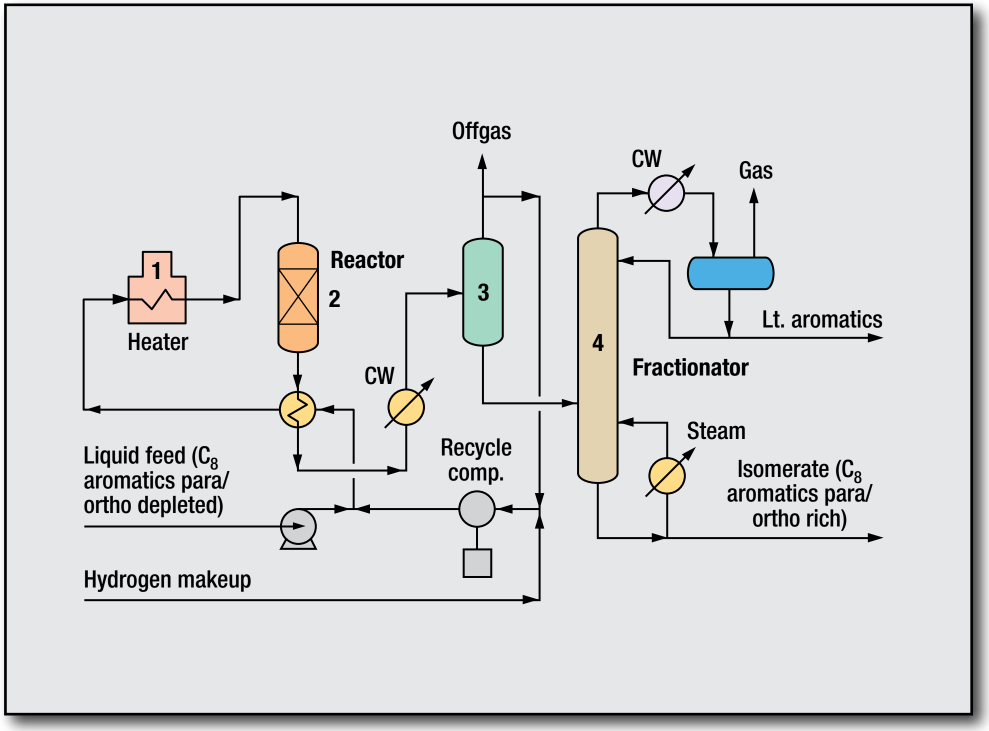
Application: To selectively isomerize a paraxylene-depleted C_8 aromatics mixture to greater than equilibrium paraxylene (PX) concentration using ExxonMobil Chemical's XyMax and Advanced MHAI processes. Simultaneously, ethylbenzene (EB) and non-aromatics in the feed are converted to benzene and light paraffins, respectively. Conversion of EB is typically 60%–80%.

Description: The para-depleted liquid C_8 aromatics raffinate stream from the PX 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 lower xylene loss.

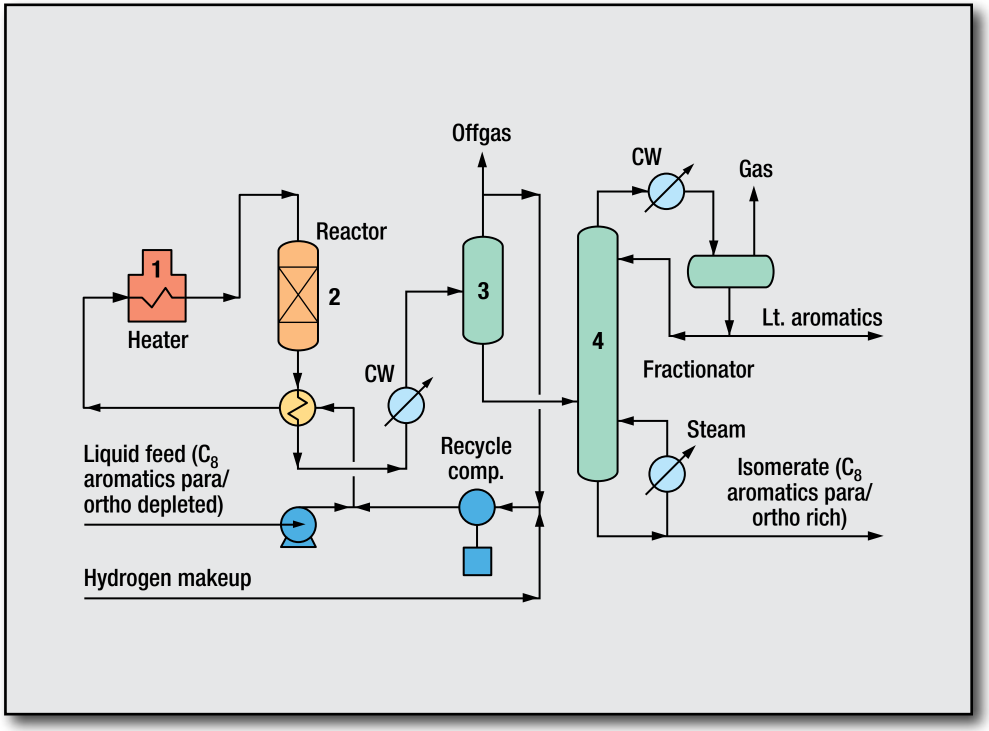
Operating conditions: XyMax and AMHAI units operate with a high space velocity and a low hydrogen-to-hydrocarbon ratio, which results in increased debottlenecking potential and decreased utilities costs. By converting a high portion of EB in the feed, these technologies can provide significant savings in associated paraxylene recovery facilities. Both technologies offer long operating cycles.



Commercial plants: The AMHAI process was first commercialized in 1999. Six AMHAI units are currently in operation. The first commercial unit using XyMax technology was brought onstream in 2000. Since then, 17 additional applications of the XyMax technology have been licensed.

Licensor: ExxonMobil Chemical Technology Licensing LLC (retrofit applications)
Axens (grassroots applications) - CONTACT

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 AMHAI 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.

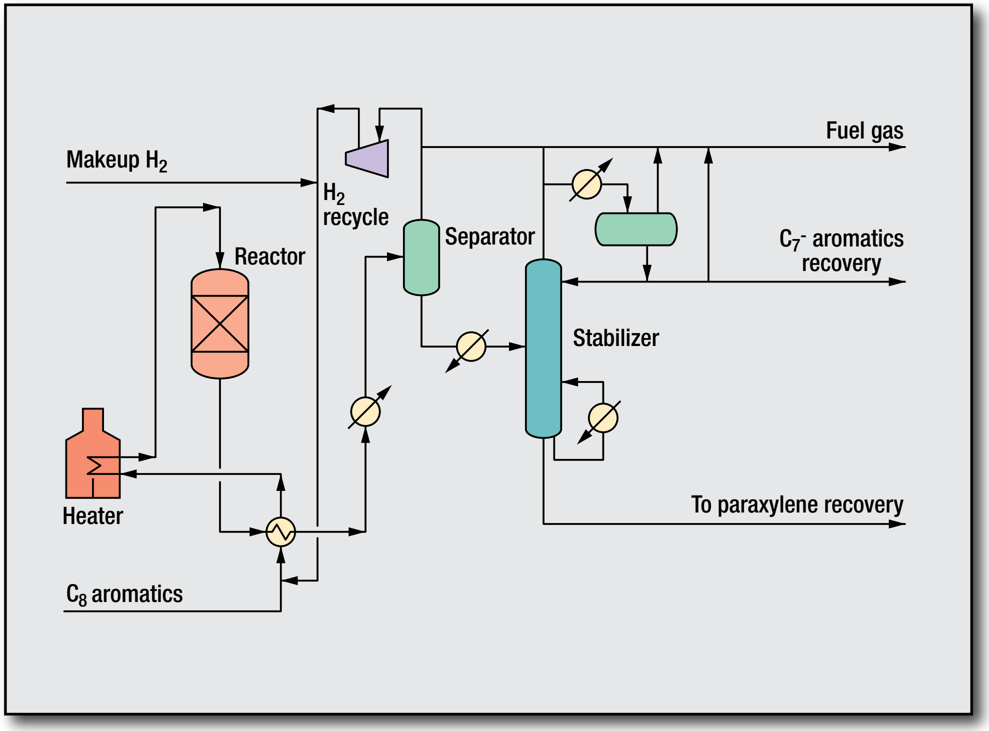
Two enhanced isomerization catalyst technologies have been developed by ExxonMobil Chemical. The first technology, referred to as Advanced Mobil High Activity Isomerization (AMHAI), provides higher selectivity and lower operating costs compared to isomerization processes used in the past. The AMHAI technology 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. There are ten XyMax units currently in operation.

Licensor: ExxonMobil Chemical Technology Licensing LLC (retrofit applications) - CONTACT
Axens (grassroots applications)

Xylene isomerization



Application: GT-IsomPX is GTC's xylene isomerization technology available in two versions: ethylbenzene (EB) isomerization and EB dealkylation. Both versions gain high ethylbenzene conversion rates while producing equilibrium mixed xylenes—meta-xylene (MX), ortho-xylene (OX) and paraxylene (PX).

Description: For an EB dealkylation type of isomerization, the technology encompasses two main processing areas: *reactor section* and *product distillation* section. In this process, PX-depleted feed stream is first mixed with hydrogen. The mixed stream is then heated against reactor effluent and sent through a process furnace. The heated mixture is fed into isomerization reaction unit, where MX, OX and PX are isomerized to equilibrium and EB is de-alkylated to benzene.

The reactor effluent is cooled and flows to the separator, where the hydrogen-rich vapor phase is separated from the liquid stream. A small portion of the vapor phase is purged to control the purity of the recycle hydrogen. The recycle hydrogen is then compressed, mixed with makeup hydrogen, and returned to the reactor.

The liquid stream from the separator is pumped to the deheptanizer to remove light hydrocarbons. The liquid stream from the deheptanizer overhead contains benzene and toluene and is sent to the distillation section to produce high-purity benzene and toluene products. The liquid stream from the deheptanizer bottoms contains mixed xylenes and a small amount of C_9^+ aromatics. This liquid stream is returned to the PX recovery section.

Process advantages:

- PX in xylenes reaches thermodynamic equilibrium after the reaction
- With the EB-dealkylation catalyst, byproduct benzene is produced at high purity by simple distillation.
- Low H_2/HC ratio, high WHSV, and low xylenes loss
- Long cycle length
- Efficient heat integration scheme reduces energy consumption
- Turnkey package for high-purity benzene, toluene and PX production available from licensor.

Economics:

Basis	4 million tpy (88,000 bpsd) feedrate
Erected cost	$29 million (ISBL, 2009 US Gulf Coast basis)

Commercial plants: Two commercial licenses.

Licensor: GTC Technology - CONTACT

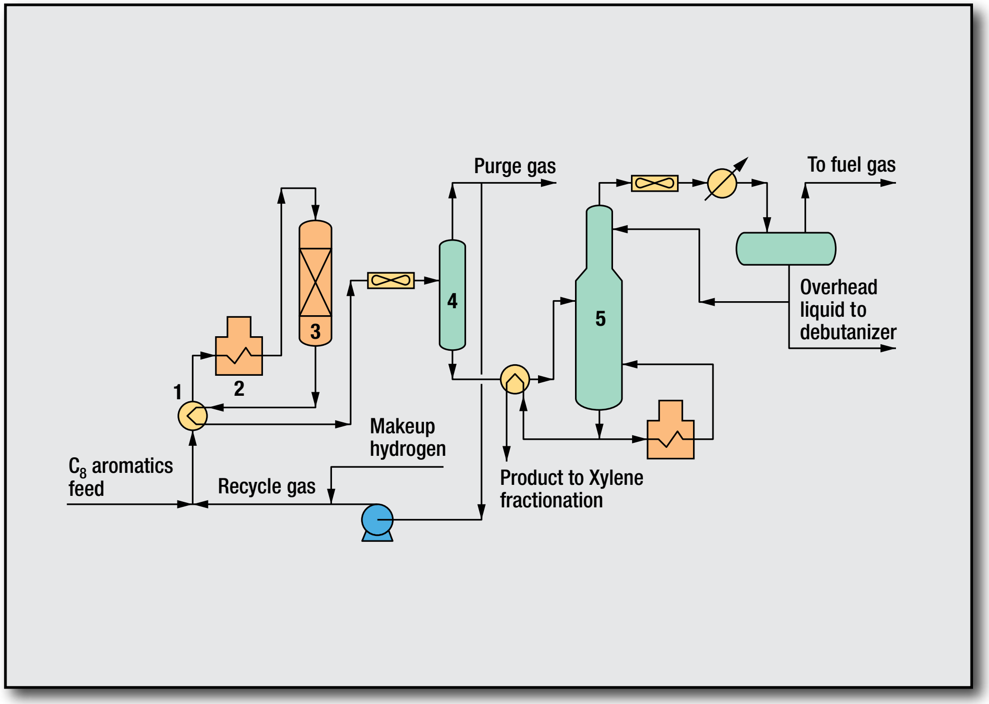
Xylene isomerization

Application: The UOP 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 3.56 million metric tpy) is shown below. The estimated inside battery limits (ISBL) erected cost for the unit assumes construction on a US Gulf Coast site in 2009:

Investment, US$ million	44
Utilities (per mt of feed)	
Electricity, kWh	4.2
Steam, mt	0.004
Water, cooling, m^3	0.26
Fuel, Gcal	0.17

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 75 Isomar units.

Licensor: UOP LLC, A Honeywell Company - CONTACT

Xylenes and benzene

Application: The S-TDT process can produce mixed xylenes and benzene in an aromatics complex through disproportionation of toluene and transalkylation of toluene and C_9^+ aromatics (C_9^+ A) using toluene and C_9^+ A as feedstocks.

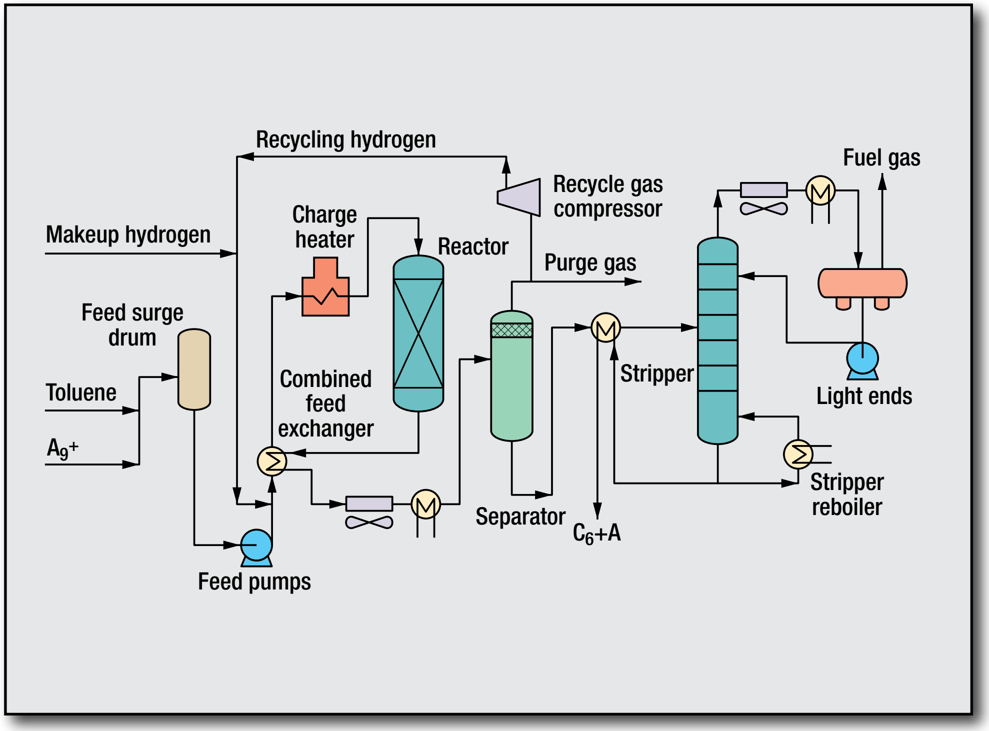
Description: The commercially proven HAT series catalysts are the core of the S-TDT process. The catalyst provides high activity, high selectivity, good operation stability and feedstock flexibility. The excellent performance of HAT series catalysts provides technological supports for some aromatics complexes to expand their capacities without a reactor revamp, increase in catalyst inventory and hydrogen compressor replacement.

Commercial examples: The capacities for two plants were 398,000 metric tpy and 1.007 million metric tpy, respectively. After using the HAT catalysts and operation conditions of the S-TDT process, outputs for both benzene and mixed xylenes increased by 40% without any changes to the reactor, compressor and catalyst inventory for both facilities.

Either pure toluene or high content of C_9^+ A (70 wt%) can be used as feedstocks for the process. In particular, C_{10} aromatics (C_{10}A) in the feedstock can be as much as 10 wt%. C_{10}A can also be converted into lower carbon aromatics, so that more benzene and mixed-xylenes can be produced and plant profitability is increased.

The purity of the benzene product from the benzene and toluene (BT) fractionation section is such that no further extraction is needed. The mixed-xylenes product containing only 1%–4% ethylbenzene is a good feedstock for paraxylene (PX) production.

To reduce operating costs and save energy, the plant's waste heat is utilized as much as possible with heat integration technology and high-efficiency heat exchangers.



Commercial plants: The S-TDT process has been licensed to six plants, among which three were commissioned in China and the Middle East, and the other three are under design.

The HAT series catalysts not only have exhibited excellent performance in the S-TDT process units, but also have been successfully used as a drop-in catalyst in many other company-licensed process units in China.

Licensor: China Petrochemical Technology Co., Ltd. - CONTACT

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Lummus Technology	www.cbi.com

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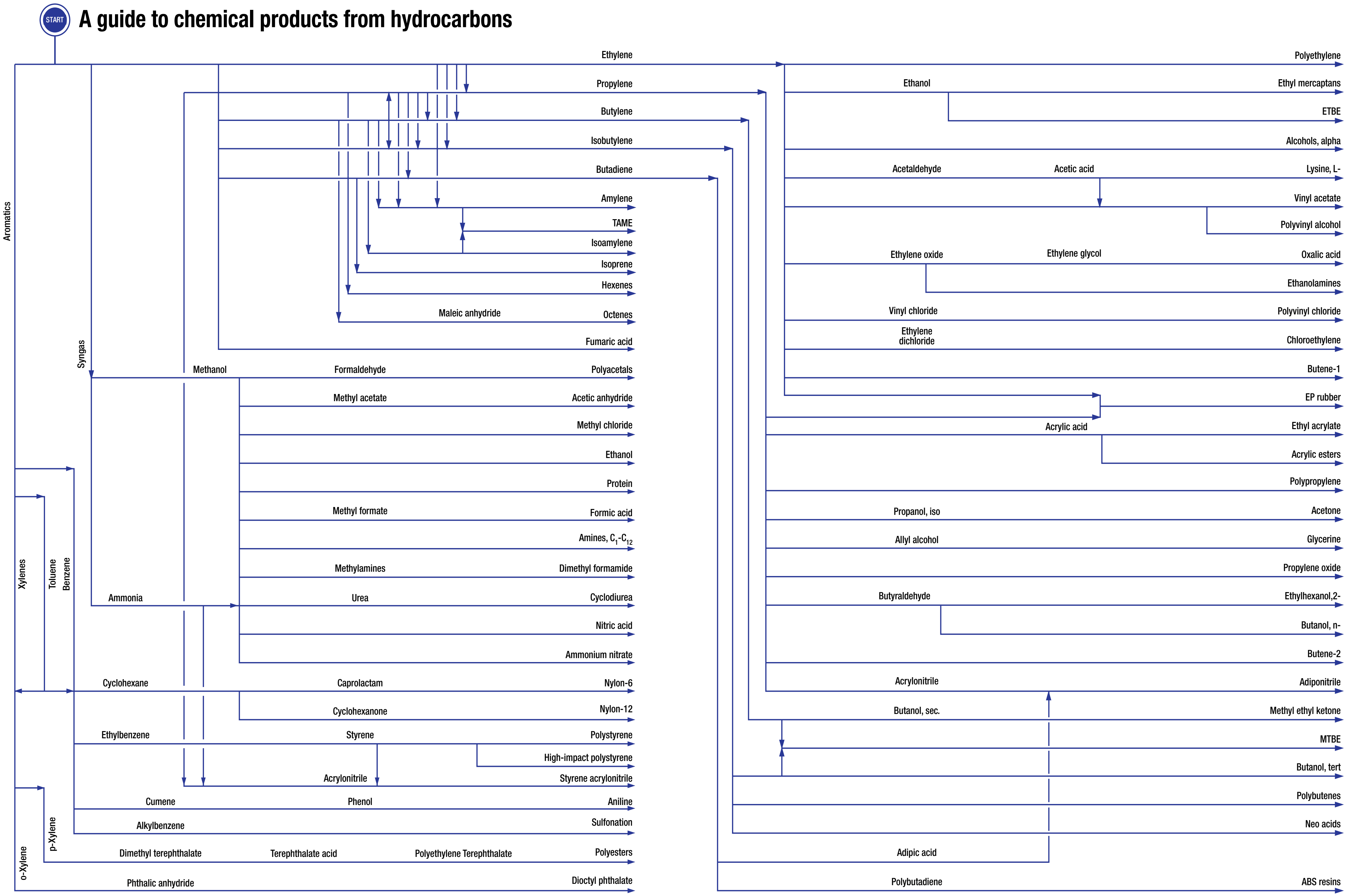
Lummus/CDTECH/Lummus Technology and Chemical Research & Licensing	www.cbi.com
Lurgi GmbH, a company of the Air Liquide Group	www.lurgi.com
LyondellBasell	www.lyondellbasell.com/Technology/
Mitsui Chemicals, Inc.	www.mitsuichem.com/techno/license/index.html
NOVA Chemicals (International) S.A.	www.novachem.com
Saipem S.P.A.	www.saipem.eni.it
Scientific Design Company, Inc.	www.scidesign.com
Shell Global Solutions International B.V.	www.shell.com/home/content/global_solutions/aboutshell/contact_us/
Stamicarbon B.V.	www.stamicarbon.com
Technip	www.technip.com/en/experience-and-technologies/onshore/ethylene
The Shaw Group	www.shawgrp.com
Toyo Engineering Corp (TOYO)	www.toyo-eng.co.jp
Uhde GmbH	www.uhde.eu
Uhde Inventa-Fischer	www.uhde-inventa-fischer.com
Univaton Technologies	www.univation.com
UOP LLC, A Honeywell Company	www.uop.com/secure/8071.asp
Vinnolit GmbH & Co KG	www.vinnolit.de/vinnolit.nsf/id/EN_VinTec_Licensing_Activities

A guide to chemical products from hydrocarbons



Petrochemical Licensor Index

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
OLEFINS					
Lummus Technology	Acetylene extraction	C_2s	Selective adsorption of acetylene with dimethyl form amine (DMF)	4	1991
Shaw Energy & Chemicals	Acetylene extraction	C_2s and C_3s separately	Proven extraction design uses DMF solvent. Complete C_2 acetylene removal. C_3 (MAPD) is separate product.	6+	2000
Linde AG/SABIC	Alpha olefins	Ethylene	Butene-1, hexane-1, octene-1, decene-1, etc., are produced from ethylene in a homogenous catalytic reaction. The a-Sablin process is based on a highly active bifunctional catalyst system operating at mild reaction condtions with highest selectivities to a-olefins	1	NA
CDTECH	Butadiene	C_4^+ from naphtha cracking	Selective hydrogenation of C_4 acetylenes in a distillation column to produce low acetylene feed for butadiene extraction	2	1998
Lummus Technology	Butadiene	Butane-n or mixed C_4s	CATADIENE n-butane dehydrogenation process uses mulitple fixed-bed reactors in cyclic operation to produce butadiene.	18	1986
BASF/Lummus Technology	Butadiene extraction	Butanes/butenes/butadienes/acetylenes	Uses extraction distillation with NMP solvent and conventional distillation	44	2010
Lurgi GmbH	Butadiene, 1,3	C_4 cut from naphtha cracking	Extractive distillation using N-methylpyrrolidone as solvent has high yield, low utilities	24	2001
BASF/Lummus Technology	Butadiene-free C_4 hydrocarbons, mixed	Mixed C_4 hydrocarbons	Selective hydrogenation of butadiene from mixed C_4s stream; product-butadiene-free C_4 stream	28	2009
Axens	Butene-1	Ethylene	Alphabutol uses low investment, low operating cost liquid-phase homogenous catalysts to make high-purity butene-1	27	2009
Lummus Technology	Butene-1	Mixed C_4 hydrocarbons	Super fractionation to produce high-purity (99+%) butene-1	6	2009
Saipem S.p.A.	Butene-1, polymerization grade	Selectively prehydrogenated Raffinate-2 from MTBE	Butene-1 recovery via superfractionation	4	2010
Shaw Energy & Chemicals	C_2–C_5 Olefins	Naphtha, VGO, residue	Deep Catalytic Cracking (DCC) process to make light olefins, C_2–C_5, primarily propylene.	16	2008
Axens	Contaminant-free condensate, naphtha	Condensate, Naphtha	To produce mercury, arsenic and lead-free feedstocks to refineries and steam crackers	20	2004
China Petrochemical Technology Co., Ltd.	Ethylene	Ethane to heavy-vacuum gasoil	CBL cracking technology is a steam-cracking technology developed by SINOPEC.	44	NA
UOP LLC, A Honeywell Co.	Ethylene	Naphtha -cracker feed	MaxEne process increases ethylene yield from naphtha crackers by raising the concentration of normal paraffins (n-paraffins) in the naphtha-cracker feed. The process is the newest application of UOP's Sorbex technology. It uses adsorptive separation to separate C_5–C_{11} naphtha into a n-paraffins rich stream and a stream depleted of n-paraffins	NA	NA
Linde AG	Ethylene	LPG, Naphtha, gas oils and hydrocracker residue	Highly selective furnaces thermally crack hydrocarbons and efficiently recover products	52	NA
Lummus Technology	Ethylene	Ethane/propane/butane/naphtha/gas oils	Low capital cost, high efficiency/reliable/safe operation, SRT heaters	>120	2009
Technip	Ethylene	Ethane to HVGO	Ethylene and propylene production using Technip's High Selective Furnaces and progressive separation at low energy and feedstock consumption	18	2000
Kellogg Brown & Root LLC	Ethylene, SUPERFLEX	Hydrocarbon feedstock	Selective Cracking Optimum Recovery (SCORE) pyrolysis furnace cracks the feed hydrocarbon in the presence of dilution steam into large amounts of ethylene, propylene and byproducts. Furnace effluent is cooled by generating steam and quenched further to remove heavy gasoline, fuel oil and dilution steam	172	NA

Company	**Product**	**Feedstock**	**Process description**	**No. of licenses**	**Date of last license**
Technip	Ethylene/cracking furnaces	Ethane to HVGO	Thermal cracking of hydrocarbons in the presence of steam by highly selective GK and SMK cracking furnaces	500	2001
Shaw Energy & Chemicals	Ethylene/propylene	Ethane, propane, butane & naphtha	Ultra-Selective Conversion, USC types, and ARS/HRS recovery designs selected individually for specific feedstocks.	120+	2010
Axens	Hexene-1	Ethylene	To produce high-purity hexene-1 that is suitable for copolymers in LLDPE production via new AlphaHexol process developed by IFP and based on selective ethylene homogeneous trimerization	NA	NA
Lummus Technology	Hexene-1	Mixed C_4 hydrocarbons	Utilizes isomerization and metathesis to produce high-purity hexene-1 from a mixed C_4 stream	NA	NA
Axens	Isobutane, Isobutylene, 2-Butenes, Butene-1	C_4 Cut	Upgrading C_4s from steam crackers via hydrogenation processes	>100	2010
CDTECH	Isobutylene	Raffinate 1	Selective hydrogenation of butadiene and hydroisomerization of butene-1 to butene-2 via catalytic distilation to recover isobutylene	1	1994
CDTECH	Isobutylene	Raffinate 1	Selective hydrogenation of butadiene and hydroisomerization of butene-1 to butene-2 to produce isobutylene	1	1994
CDTECH	Isobutylene	MTBE	Back-cracking process yields high-purity isobutylene (99.9%) and methanol	8	1997
Lummus Technology	Isobutylene	Isobutane	CATOFIN isobutane dehydrogenation process uses mulitple fixed-bed reactors in cyclic operation to produce isobutylene.	9	1996
Technip	Isobutylene/ butacracking	Butanes (field)	Co-production of propylene and iso-butylene by thermal steam cracking of butane at elevated temperatures	NA	NA
CDTECH	Isobutylene	Mixed C_4 hydrocarbons	Integrated MTBE and MTBE back-cracking processes to selectively recover high-purity (99.9%) isobutylene	7	1991
CDTECH	Isobutylene/isoamylene	n-Butenes and n-pentenes	Skeletal isomerization of n-olefins to iso-olefins	3	2000
Saipem S.p.A.	Isobutylene, high-purity	MTBE	MTBE back-cracking process yields high-purity isobutylene (99.9%)and methanol	6	2009
CDTECH	n-Butenes	Mixed C_4 hydrocarbons	Selective hydogenation of butadiene to n-butenes in catalytic distillation column	4	1997
CDTECH	n-Butenes	Mixed C_4 hydrocarbons	Isobutylene isomerization to produce normal butenes	NA	NA
Axens	Octene	Butenes	Dimersol-X uses low investment, low operating cost liquid-phase homogenous catalysis to make octenes with low braching	36	2007
Axens	Olefins, linear alpha	Ethylene	AlphaSelect process offers flexible product slate, low investment, low operating costs, liquid-phase homogenous catalysis to make high-purity C_4–C_1 linear alpha olefins	NA	NA
Uhde GmbH	Olefins by dehydrogenation	LPG and gas condensates	Steam Active Reforming (STAR) process produces (a) propylene as feedstock for olefins	87	NA
Uhde GmbH	Olefins—butenes extractive distillation	C_4 feedstocks	BUTENEX extractive distillation process uses selective solvents to separate light olefins from various C_4 feedstocks	2	NA
Axens	Polymer Grade Propylene	C_3 Cut	Upgrading steam cracker C_3 cuts by selective hydrogenation	>110	2008
Kellogg Brown & Root LLC	Propylene	Light (C_4 to C_{10}) hydrocarbon olefins-containing streams	The SUPERFLEX process uses a fluidized catalytic reactor system with a proprietary catalyst to convert low-value feedstocks to predominately propylene and ethylene products	3	2006

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
BRICI/Lummus Technology	Propylene	C_3s	Selective hydrogenation of methyl acetylene and propadiene to propylene	>30	2009
CDTECH	Propylene	$C_3{}^+$ steam cracker	Selective hydrogenation of methyl acetylene and propadiene to propylene	3	1999
Lummus Technology	Propylene	Ethylene and mixed C_4s	Highly selective catalyst promotes formation of propylene by metathesis of ethylene and butene-2 while simultaneously isomerizing feed butene-1 to butene-2	25	2010
Lummus Technology	Propylene	Propane	CATOFIN propane dehydrogenation process uses mulitple fixed-bed reactors in cyclic operation to produce propylene.	8	2010
Lummus Technology	Propylene	Ethane	Combination of ethane cracking, dimerization and isomerization/metathesis to produce propylene from ethane	NA	NA
UOP LLC, A Honeywell Co.	Propylene	Propane	Oleflex process produces polymer-grade propylene from propane by catalytic dehydrogenation	11	2010
UOP LLC, A Honeywell Co.	Propylene	C_4 to C_8 olefins	Total Petrochemicals/UOP Olefin Cracking process (OCP) is used to primarily produce propylene from C_4 to C_8 olefins supplied by steam crackers, refineries and/or methanol-to-olefins (MTO) plants	2	2009
UOP LLC, A Honeywell Co.	Propylene and ethylene	Methanol	UOP/HYDRO Methanol-to-olefins (MTO) process produces ethylene and propylene from methanol derived from raw materials such as natural gas, coal, petroleum coke or biomass	2	2009
China Petrochemical Technology Co., Ltd.	Propylene or iso-olefin	Vacuum gasoil (VGO), vacuum resid or VGO blended with deasphalted oil	Deep catalytic cracking (DCC) conversion technology, produces light olefins (ethylene, propylene and butylenes), LPG, gasoline, middle distillates, etc., from hydrocarbon feedstocks	NA	NA
Kellogg Brown & Root LLC	Propylene, Advanced Catalytic Olefins	Light and full-range naphthas	Catalytic conversion of naphtha feed to produce higher ultimate yields of light olefins and at higher P/E production ratio relative to steam cracking, typically about 1:1	1	2010
Axens	Steam Cracker Feedstock	Raw pyrolysis gasoline from SC	Upgrading C_5s from steam crackers via hydrogenation processes	>150	2007
AROMATICS					
UOP LLC, A Honeywell Co.	Alkylbenzene, linear (LAB)	$C_{10}$and C_{13} normal paraffins of 98+% purity	UOP/CEPSA process uses a solid, heterogeneous catalyst to produce linear alkylbenzene (LAB) by alkylating benzene with linear olefins made by UOP Pacol, DeFine and PEP processes	33	NA
UOP LLC, A Honeywell Co.	Aromatics extraction	Reformate, pyrolysis gasoline or coke oven light oil	UOP Sulfolane process recovers high-purity C_6–C_9 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	139	NA
UOP LLC, A Honeywell Co.	Aromatics extractive distillation	BT Reformate	UOP Extractive Distillation (ED) Sulfolane process recovers high-purity aromatics from hydrocarbon mixtures by extractive distillation. Extractive Distillation is a lower cost, more suitable option for feeds rich in aromatics containing mostly benzene and/or toluene	139	2010
Uhde GmbH	Aromatics extractive distillation	Reformate, pyrolysis gasoline or coke-oven light oil	Extractive distillation Morphylane process, a single-compound solvent, N-formylmorpholine, alters the vapor pressure of the components being separated	55	NA
ExxonMobil Chemical Technology Licensing LLC	Aromatics treatment	Heavy reformate or aromatic extract	Liquid-phase aromatics treatment for olefins removal	8	2008
GTC Technology	Aromatics, Transalkylation	Toluene and/or C_9/C_{10} aromatics streams	Production of benzene and xylenes through transalkylation of the methyl groups from toluene and/or heavy aromatics streams using proprietary zeolite catalyst	4	2008
Axens	Benzene	Toluene, C_8A, C_9A$^+$	No catalyst is needed with hydrodealkylation process; onstream time exceeds 95%	36	2009
Lummus Technology	Benzene	Toluene-rich stream, or pyrolysis gasoline, or light coke-oven gases	Single-step hydrodealkylation produces high-purity product, without hydrotreating (Detol/Pyrotol/Litol, for respective feedstocks)	29	1998
China Petrochemical Technology Co., Ltd.	Benzene and toluene	Pyrolysis gasoline, reformate or coal tar oil	Sulfolane extractive distillation (SED) process uses a complex solvent system composed of sulfolane (as main solvent) and a co-solvent	12	2005

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
GTC Technology	Benzene, ethylbenzene dealkylation	Pygas C_8 or reformer C_8 streams	Conversion of EB contained in the C_8 aromatic feedstocks to high-purity benzene plus ethans, and upgrade the mixed xylenes to premium grade. The technology features a proprietary catalyst with high activity, low ring loss and superior long catalyst cycle length.	NA	NA
Axens/Uhde	Benzene, Toluene	Reformate and/or hydrotreated Pyrolysis gasoline BT cuts	In extractive distillation, the addition of a selective solvent modifies the vapor pressures of the hydrocarbons in the feed in such a way that paraffinic and naphthenic components can be separated from the aromatics by distillation.	65	2009
Lurgi GmbH	Benzene/toluene	Pyrolysis gasoline, reformate, coke oven benzole	Extractive distiliation using N-methylpyrrolidone as solvent has high yield, low utilities	22	2000
ExxonMobil Chemical Technology Licensing LLC	Benzene/xylene	Toluene and up to 25% aromatics	Disproportionation converts toluene and C_9 aromatics into high-purity benzene and mixed xylenes	2	2007
Badger Licensing LLC	Bisphenol-A	Phenol, acetone	High purity suitable for polycarbonate and epoxy resin applications	5	2009
Chiyoda Corp.	BTX	Light naphtha, LPG and raffinate	Zeolite catalyst and fixed-bed reactor produce petrochemical grade BTX	1	NA
UOP LLC, A Honeywell Co.	BTX aromatics	Propane and butanes	To produce petrochemical-grade BTX via the aromatization of propane and butanes using the BP-UOP Cyclar process	2	NA
UOP LLC, A Honeywell Co.	BTX aromatics	Naphtha and condensate	To produce reformate, 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	263	2010
Axens	BTX aromatics and LPG	Pygas	To produce high-purity BTX that is suitable after simple distillation and without the need for extraction as well as LPG's that by recycling to the steam cracker can significantly enhance ethylene and propylene yields	2	2008
GTC Technology	BTX, extraction	Reformate, pygas, coke oven light oil	Aromatics recovery technology that uses extractive distillation to purify benzene, toluene and xylene (BTX) from refinery or petrochemical aromatics streams	28	2010
Axens	BTX, production	Naphtha	Aromizing maximizes BTX production with high yields of high-quality aromatics	98	2010
Axens	BTX, purification	Reformate	Arofining hydrogenates diolefins reducing or eliminating activated clay consumption	7	2009
UOP/Shell	BTX, purification	Reformate, pyrolysis gasoline	Shell Sulfolane process, Shell technology; liquid/liquid extraction and/or extractive distillation with sulfolane solvent	NA	NA
Axens	BTX, separation	Pyrolysis, reformate, light oils	Highly efficient sulfolane solvent separates BTX from feedstocks	23	2009
Lummus Technology	Cumene	Benzene, propylene	Liquid-phase process attains 99.7% yield, 99.95% product purity using a proprietary zeolite catalyst.	2	2008
Badger Licensing LLC	Cumene	Benzene, propylene (dilute/polymer-grade)	Highly active, selective zeolite catalyst produces high yields and purity	24	2010
CDTECH	Cumene	Crude cumene	Selective hydrogenation of alpha methyl styrene in a distillation column to produce purified cumene distillate	NA	NA
CDTECH	Cumene	Propylene and benzene	Catalytic distillation technology with zeolite catalyst, high yield/quality produce ultra-high purity	1	1995
UOP LLC, A Honeywell Co.	Cumene	Benzene and propylene	Q-Max process produces high-quality cumene (isopropylbenzene) by alkylating benzene with propylene (typically refinery, chemical or polymer-grade) using zeolite catalyst technology	14	NA
Axens/ExxonMobil	Equilibrium xylenes	Para-depleted Xylenes	The feed is a mixture of fresh and recycled C_8 aromatics in which paraxylene (and orthoxylene, if desired) is depleted to less than equilibrium concentrations. The mixed xylene and ethylbenzene feed combined with hydrogen-rich recycle gas is passed through the reactor where ethylbenzene dealkylation and xylenes isomerization occur to produce an equilibrium xylenes mixture.	18	2009
Badger Licensing LLC	Ethylbenzene	Benzene, ethylene (FCC off-gas, chemical-grade, or polymer-grade)	Vapor-phase process: accepts dilute ethylene feedstocks, catalysts highly resistant to poisoning by trace impurities	35	1997

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
Badger Licensing LLC	Ethylbenzene	Benzene, ethylene (chemical-grade or polymer-grade)	EBMax process uses proprietary ExxonMobil zeolite catalysts: high yields and product purity, low capital cost	32	2010
CDTECH	Ethylbenzene	Benzene, ethylene	Patented fixed-bed, catalytic distillation technology uses zeolite catalyst to alkylate benzene with ethylene	NA	NA
Lummus Technology	Ethylbenzene	Ethylene and benzene	Catalytic distillation technology with zeolite catalyst, high yield/quality	4	2003
Lummus Technology/UOP	Ethylbenzene	Ethylene and benzene	Liquid-phase alkylation with zeolite catalyst, high-yield/quality, long catalyst life	35	2010
Axens/ExxonMobil	Mixed Xylenes	Toluene	In the MTDP-3 process, the feed is a mixture of fresh and recycled toluene. The mixed feed is combined with hydrogen-rich recycle gas, preheated and passed through the reactor where disproportionation reactions are promoted. Benzene and equilibrium xylenes are produced as a result of the thermodynamics equilibrium.	3	2007
ExxonMobil Chemical Technology Licensing LLC	Mixed xylenes	Toluene, benzene, C_9^+ aromatics	Transalkylation/disproportionation-based process using benzene, toluene and C_9^+ to produce high-yield mixed xylenes	14	2009
UOP LLC, A Honeywell Co.	Mixed xylenes	Toluene and C_9^+ aromatics	Tatoray process produces mixed xylenes and petrochemical-grade benzene by disproportionation of toluene and transalklyation of toluene and C_9^+ aromatics	54	NA
UOP LLC, A Honeywell Co.	Mixed xylenes	C_9 and C_{10} aromatics	In a modern UOP aromatics complex, the TAC_9 process is integrated into the flow scheme to selectively convert C_9 and C_{10} aromatics into xylenes rather than sending them to the gasoline pool or selling them as a solvent	3	NA
GTC Technology	Mixed xylenes and benzene, toluene selective to paraxylene	Toluene	Process, featuring a commercially-proven proprietary catalyst with high activty and selectivity to paraxylene, produces paraxylene-rich mixed xylene along with high-purity benzene streams from toluene.	2	NA
UOP LLC, A Honeywell Co.	m-Xylene	Mixed xylenes	MX Sorbex process recovers meta-xylene (m-xylene) from mixed xylenes. The process uses adsorptive separation for highly efficient and selective recovery at high purity of molecular species that cannot be separated by conventional fractionation	9	NA
UOP LLC, A Honeywell Co.	Paraxylene	C_8 aromatics	Isomar and Parex processes produce a desired xylene isomer (or isomers) from a mixture of C_8 aromatics	168	NA
UOP LLC, A Honeywell Co.	Paraxylene	Petroleum naphtha and pyrolysis gasoline	Aromatics complex, combination of process units, convert petroleum naphtha and pyrolysis gasoline into benzene, toluene, paraxylene and/or other ortho-xylene	600+	NA
UOP LLC, A Honeywell Co./The Shaw Group/Niro Process Technology B.V.	Paraxylene	Toluene	UOP PX-Plus XP process converts toluene to paraxylene and benzene. The paraxylene is purified to 99.9+ wt% via single-stage crystallization and wash column. The benzene purity is 545-grade by fractionation	3	NA
ExxonMobil Chemical Technology Licensing LLC	Paraxylene	Toluene	Selectively converts toluene to paraxylene-rich xylenes and high-purity benzene	15	2010
Axens	Paraxylene, Benzene, Orthoxylene, Mixed Xylenes	Naphtha, toluene, mixed xylenes, reformate, pygas	Any combination of Aromizing, Arofining, Morphylane, Sulfolane, TransPlus, MTDP-3, PXMax, Eluxyl	14	2009
GTC Technology	Paraxylene, crystallization	Equilibrium mixed xylenes and PX-rich streams	Modern suspension crystallization technology for production of paraxylene	4	2010
Axens/ExxonMobil	Paraxylene-rich Xylenes	Toluene	In the PXMax process, the feed is a mixture of fresh and recycled toluene. The mixed feed is combined with hydrogen-rich recycle gas, preheated and passed through the reactor where disproportionation reactions are promoted. Benzene and paraxylene-rich xylenes are produced as a result of the combined thermodynamics equilibrium and catalyst permanent shape selectivity.	8	2006
GTC Technology	Styrene	Pygas C_8 cut	Extractive distillation process that directly recovers styrene from the raw pyrolysis gasoline derived from the steam cracking of naphtha, gasoils and NGL	3	2009

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
TOTAL/Badger Licensing LLC	Styrene	Ethylbenzene	Two-stage adiabatic dehydrogenation yields high-purity product	50	2008
TOTAL/Badger Licensing LLC	Styrene catalyst stabilization technology	N/A-additive to feeds for styrene dehydogenation	CST adds potassium to styrene dehydrogenation catalyst; increases productivity and extends catalyst service life	12	2008
Lummus Technology/UOP	Styrene monomer	Ethylbenzene	Innovative oxidative reheat technology, 30%-50% expansion of existing SM units with minimal investment for new equipment	9	2004
Lummus Technology/UOP	Styrene monomer	Ethylbenzene	Vapor-phase dehydrogenation of EB to styrene monomer, high-temperature, deep-vacuum design, 99.9% purity	37	2009
TOTAL/Badger Licensing LLC	Styrene/phenylacetylene removal	Crude styrene reduction	Process reduces phenylacetylene (PA) levels in styrene to less than 20 ppm, polystyrene makers require low PA levels	6	2000
Axens/ExxonMobil	Xylene	Toluene and C_9^+ aromatics	In the TransPlus process, the feed is a mixture of fresh and recycled toluene together with fresh and recycled C_9^+ aromatics. The mixed feed is combined with hydrogen-rich recycle gas, preheated and passed through the reactor where transalkylation reactions take place.	16	2009
GTC Technology	Xylene isomerization	PX-depleted mixed xylenes	Xylene isomerization technology available in two versions: EB isomerization type and EB dealkylation type	2	2008
UOP LLC, A Honeywell Co.	Xylene isomerization	C_8 aromatics	Isomar process isomerizes C_8 aromatics to mixed xylenes to maximize recovery of paraxylene in a UOP aromatics complex. Depending on the type of catalyst used, ethylbenzene (EB) is also converted into xylenes or benzene	75	NA
ExxonMobil Chemical Technology Licensing LLC	Xylene isomerization	Paraxylene depleted C_8 aromatics	High EB dealkylation to benzene; over 100% paraxylene approach equilibrium; long operating cycles	26	2009
Axens	Xylene, para	Mixed xylenes	Eluxyl separates purified p-xylene from C_8 aromatic streams	19	2009
Axens	Xylene, para	Mixed xylenes	The xylenes isomerization unit upgrades PX-depleted streams from PX separation units. The reaction takes place under mild operating conditions in a conventional vapor-phase reactor. Ethyl Benzene and Xylenes thermodynamics equilibrium is restored	17	2010
China Petrochemical Technology Co., Ltd.	Xylenes and benzene	Toluene and C_9^+ A	S-TDT process produces mixed xylenes and benzene in a aromatics complex through the disproportionation of toluene and transalkylation of toluene and C_9^+ aromatics (C_9^+ A)	6	NA
POLYMERS					
INEOS	Acrylonitrile	Propylene, ammonia	Fluid-bed reactor design and proprietary catalysts significantly reduces product costs	43	2001
INEOS	Innovene "G" Polyethylene Gas Phase	Ethylene, comonomers	Low Capex/Opex fully flexible LL/HD. Zi/chrome and metallocene. C_4/C_6 or C_8 comonomers.	36	2009
INEOS	Innovene "S" Polyethylene Slurry HD	Ethylene, comonomers	Dedicated HDPE Zi and chrome catalysts. Mono and Bi-modal products including PE 100 pipe	17	2009
Uhde Inventa-Fischer	Polyamide 6	Caprolactam	Two-stage or single-stage continuous polymerization process to produce PA-6 chips for textiles, film, engineering plastics	79	2009
Uhde Inventa-Fischer	Polyamide 6.6	Acipic acid and hexamethylene diamine	Batch polymerization process to produce PA-66 chips for textiles, film, engineering plastics	8	2010
Uhde Inventa-Fischer	Polybutylene terephthlate (PBT)	Terephthalic acid, I,4-butanediol	2-reactor continuous process to produce PBT chips ready for conversion of filaments, films and engineered plastics	8	2008
NOVA Chemicals (International) S.A.	Polyethylene	Ethylene and comonomer	SCLAIRTECH technology process produces the full range of linear polyethylene (PE) products, including linear-low-density, medium-density and high-density grades with narrow to broad molecular weight distribution	12	2010
Borealis A/S	Polyethylene	Ethylene, butene	Slurry-loop process uses supercritical propane and a series gas-phase reactor to produce tailor-made MW , enhanced LLDPEs, MDPEs and HDPEs	7	2010

Company	**Product**	**Feedstock**	**Process description**	**No. of licenses**	**Date of last license**
Univation Technologies, LLC	Polyethylene	Ethylene	UNIPOL Polyethylene process produces the widest array of linear low-density polyethylene (LLDPE), medium-density polyethylene (MDPE) and high-density polyethylene (HDPE) having unimodal or bimodal molecular weight distribution using single, low-pressure, gas-phase reactor	100	NA
LyondellBasell	Polyethylene, HDPE	Ethylene and comonomer	Stirred-tank, heavy-diluent *Hostalen* ACP process uses a slurry-polymerization method with three reactors in series to produce bimodal and multimodal high-density polyethylene (HDPE)	41	NA
Mitsui Chemicals, Inc.	Polyethylene, HDPE	Ethylene and comonomer	To produce high-density polyethylene (HDPE) and medium-density polyethylene (MDPE) under low-pressure slurry process—"CX process"	46	NA
ExxonMobil Chemical Technology Licensing LLC	Polyethylene, high-pressure LDPE	Ethylene and EVA	State-of-the-art reactor provides broadest scope for LDPE products; including high-clarity films to medium-density polymers	9	1999
LyondellBasell	Polyethylene, LDPE, autoclave	Ethylene	High-pressure *Lupotech A* autoclave reactor process produces low-density polyethylene (LDPE) homopolymers, EVA and various acrylic-type copolymers	NA	NA
LyondellBasell	Polyethylene, LDPE, Tubular Reactor	Ethylene	High-pressure *LupotechT* tubular reactor process produces low-density polyethylene (LDPE) homopolymers and EVA copolymers	NA	2009
LyondellBasell	Polyethylene, LL/MD/HDPE	Ethylene and comonomer	*Spherilene* gas-phase technology with simplified process flow scheme, produces the full range of linear-low-density polyethylene (LLDPE), medium-density polyethylene (MDPE) and high-density polyethylene (HDPE).	14	NA
ExxonMobil Chemical Technology Licensing LLC	Polypropylene	Propylene	Technology provides large-capacity reactors for homopolymer PP and impact copolymers	NA	NA
Mitsui Chemicals, Inc.	Polypropylene	Propylene and ethylene	The process, with a combination of the most advanced high-yield and high-stereospecificity catalyst, is a nonsolvent, nondeashing process. It produces polypropylene including homopolymer, random copolymer and impact polymer	27	NA
Borealis A/S	Polypropylene	Propylene, ethylene	Slurry-loop and a series gas-phase reactor produce tailor-made MW and enhanced PPs, homopolymers, high-comonomers, heterophasic	4	2010
INEOS	Polypropylene	Propylene	Low Capex and Opex for homo, random and impact co-polymers. "Plug" flow reactor gives quick grade changes and excellent impact copolymers	22	2009
Japan Polypropylene Corp. (JPP)	Polypropylene	Propylene and ethylene	Simplified gas-phase process with horizontal reactor and high-performance catalyst	6	2008
LyondellBasell	Polypropylene	Propylene and comonomer	*Spheripol* process produces propylene-based polymers including homopolymer polypropylene (PP) and many families of random and heterophasic impact and specialty impact copolymers	100	NA
LyondellBasell	Polypropylene	Propylene	Gas-loop reactor technology, *Sperizone* process, based on Multi-Zone Circulating Reactor (MZCR) concept, produces polypropylene-based polymers, including homopolymer polypropylene (PP), random, heterophasic impact and specialty dual-composition copolymers	13	2010
Lummus Novolen Technology	Polypropylene homopolymer, random copolymers, impact copolymers, including Metallocene PP	Propylene (and ethylene for production of copolymers)	Polymerization of propylene in one or two gas-phase reactors stirred by helical agitators to produce a wide range of products	27	2010
LyondellBasell	Polypropylene, Metallocene upgrade	Propylene	*Metocene* polypropylene (PP) technology upgrades existing and newly built PP plants by extending plant capability to cover specialty PP products with specific and unique features that can be produced with single-site catalysis, in addition to the existing conventional product portfolio	6	NA

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
The Dow Chemica Co/ Univation Technologies	Polypropylene	Propylene comonomers	Process produces homopolymer, random copolymer and impact copolymer polypropylene using the Dow gas-phase UNIPOL PP process	52	2010
INEOS	Polystyrene	Styrene	Wide range production of GPPS and HIPS using bulk continuous process	7	2007
INEOS	Polystyrene, expandable	Styrene	One-step batch suspension process with high reactor productivity	3	3006
Toyo Engineering Corp. (TOYO)/Mitsui Chemcials Inc.	Polystyrene, general purpose (GPPS)	Styrene monomer	To produce a wide range of GPPS with excellent high clarity and suitable properties to process PS foam via a direct injection extrusion by the continuous bulk polymerization process	6	NA
Toyo Engineering Corp. (TOYO)/Mitsui Chemcials Inc.	Polystyrene, high-impact (HIPS)	Styrene monomer	Continuous bulk polymerization process produces a wide range of HIPS with well-balanced mechanical properties and processability. Swing production feature also capable of producing GPPS	6	NA
INEOS	Polyvinyl chloride (emulsion)	Vinyl chloride monomer	High-productivity, high-quality grades, low residual VCM, effective condenser usage	3	2009
Chisso Corp.	Polyvinyl chloride (suspension)	Vinyl chloride monomer	Batch process manufactures many PVC grades including commodity, high/low K values, matted type and copolymer PVC	25	2010
INEOS	Polyvinyl chloride (suspension)	Vinyl chloride monomer	High productivity, low residual VCM (<1 ppm), flexible operation, no buildup	21	2009
Vinnolit GmbH&CoKG	Polyvinyl chloride (suspension)	Vinyl chloride monomer	Batch process uses two or more reactors (depending on capacity); special coating/buildup suppressant allows many batch operations before cleaning	12	2009
Toyo Engineering Corp. (TOYO)	Styrene acrylonitrile (SAN) copolymer	Styrene monomer and acrylonitrile	Continuous bulk polymerization process produces a wide range of SAN copolymer with excellent chemical resistance, heat resistance and suitable property for compounding with ABS	17	NA
OXYGENATES					
Scientific Design Company, Inc.	Alkoxylates	Propylene oxide/ethylene oxide and various chain starters	Unique reactor - catalyzed liquid phase is finely dispersed into a PO/EO vapor stream	80	2001
Davy Process Technology, UK	Butanediol, 1,4-	Maleic anhydride and hydrogen	Process produces 1,4 butanediol (BDO) from butane via maleic anhydride and hydrogen using ester hydrogenation	11	NA
Toyo Engineering Corp. (TOYO)	Di methyl ether (DME)	Crude methanol	To produce DME from methanol using synthesis technology based on a methanol dehydration process. Feedstocks can be crude and refined methanol	4	2008
CDTECH	DIPE	Refinery C_3 stream	Ether production from propylene and water using Zeolite catalyst	NA	NA
CDTECH	ETBE	Mixed C_4 hydrocarbons	High-conversion catalytic distillation process for ETBE using C_4s and ethanol	5	2000
CDTECH	Ether	Refinery C_4 and C_5 streams	Produces high iso-olefin/ether products by hydrogenation and isomerization	5	1992
Axens	Ethers	Refinery C_4 and C_5 streams	CATACOL technology combines catalysis and distillation separation	42	2009
Uhde GmbH	Ethers—ETBE	C_4 cuts from steam cracker and FCC units with isobutene contents ranging from 12% to 30%	Process combines ethanol and isobutene to produce the high-octane oxygenate ethyl tertiary butyl ether	3	NA
Uhde GmbH	Ethers—MTBE	C_4 -cuts from steam cracker and FCC units with isobutene contents range from 12% to 30%	Catalytic additive reaction for isobutene and methanol	5	NA
Axens	Ethyl tertiary butyl ether (ETBE)	FCC and steam-cracker C_4 cuts and ethanol	CATACOL technology ensures high ETBE yields by combining catalysis and distillation separation	8	2009
Saipem S.p.A./Ecofuel S.p.A.	Ethyl Tertiary Butyl Ether (ETBE)	C_4 streams containing isobutylene, ethanol	Multipurpose plant. High efficiency, flexibility and reliability. Compact and low-investment plants	10	2009
Shell Global Solutions B.V.	Ethylene glycol	Ethylene, oxygen or ethylene oxide	Highly integrated with EO plant fully benefiting from high selectivity catalyst; yielding superior quality glycols	NA	NA

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
Scientific Design Company, Inc.	Ethylene Oxide	Ethylene and oxygen	Efficient process yielding highest product quality. Improved catalyst	48	2009
Union Carbide Corp., a subsidiary of The Dow Chemical Co.	Ethylene oxide	Ethylene	Process produces ethylene oxide (EO) from the direct oxidation of ethylene using the Dow METEOR process	18	NA
Shell Global Solutions B.V.	Ethylene oxide	Ethylene and oxygen	Direct oxidation process using high-selectivity catalyst with high product yields	NA	NA
Scientific Design Company, Inc.	Ethylene Oxide/Ethylene glycols	Ethylene and oxygen	Efficient process yielding highest product quality. Improved catalyst	78	2010
Scientific Design Company, Inc.	Ethylene Oxide/Ethylene glycols	Ethanol and oxygen	Utilizes renewable resources to produce "green" glycol and EO	8	2009
Scientific Design Company, Inc.	Glycol Ethers	Ethylene oxide and alcohols	Process offers high product quality with wide product distribution	2	1974
Davy Process Technology, UK/Johnson Matthey Catalysts	Methanol	Natural gas or associated gas	The process produces methanol from natural gas or associated gas via a reforming step or from syngas generated by gasification of coal, coke or biomass. The reforming/gasification step is followed by compression, methanol synthesis and distillation	87	2010
Methanol Casale SA	Methanol	Natural gas	To produce methanol from natural gas. The process is based on Casale's highly efficient plate-cooled technology for the methanol converter	NA	NA
Methanol Casale SA	Methanol	Natural gas	To produce methanol from natural gas. The process is based on Casale's highly efficient axial-radial pre-reformer, high-efficiency auto-thermal reformer design and plate-cooled technology for the methanol converter	12	2010
Toyo Engineering Corp. (TOYO)	Methanol	Natural gas-based synthesis gas and naphtha	Federal-grade AA refined methanol is produced from natural gas-based synthesis gas and naphtha using Synthesis Gas Generation technologies and proprietary MRF-Z reactor.	20	NA
Lurgi GmbH	Methanol	Natural gas, naphtha, vacuum residue, natural gas	Oxygen-operated syngas generation, two-step isothermal synthesis with maximum yield and very large single-train capacity	40	2000
Uhde GmbH	Methanol	Natural gas, LPG and heavy naphtha	Process uses steam-reforming synthesis gas generation and a low-pressure methanol synthesis loop technology	11	NA
Haldor Topsøe A/S	Methanol—two-step reforming	Natural gas, naphtha, fuel oil	Process produces methanol from natural or associated gas feedstocks using two-step reforming followed by low-pressure synthesis.	NA	NA
Axens	Methyl tertiary butyl ether (MTBE)	FCC and steam-cracker C_4 cuts and methanol	CATACOL technology ensures high MTBE yields by combining catalysis and distillation separation	26	2009
Saipem S.p.A./Ecofuel S.p.A.	Methyl Tertiary Butyl Ether (MTBE)	C_4 streams containing isobutylene, methanol	Multipurpose plant. High efficiency, flexibility and reliability. Compact and low-investment plants	23	2006
CDTECH	Mixed ethers	Mixed C_4–C_7 hydrocarbons	MTBE, TAME and heavier ether production from hydrocarbon feeds containing C_4, C_5, C_6 and C_7 iso-olefins	3	2000
CDTECH	MTBE	Mixed C_4 hydrocarbons	High-conversion catalytic distillation process for MTBE using C_4s and methanol	107	2000
Davy Process Technology, UK	Natural detergent alcohols	Fatty acids	Natural detergent alcohols are produced from fatty acids using esterification, hydrogenolysis and refining	6	NA
Kellogg Brown & Root LLC	Phenol	Cumene	Oxidization of cumene with air at high efficiency (+95%) produces cumene hydroperoxide (CHP) which is concentrated and cleaved under high-yield conditions (+99%) to phenol and acetone in the presence of an acid catalyst	25	NA
Lummus Technology	Phenol	Cumene	Cumene oxidation process with ability to produce alphamethylstyrene and pharmaceutical-grade acetone byproducts	2	2008

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
Sunoco/UOP LLC, A Honeywell Co.	Phenol	Cumene	Process produces high-quality phenol and acetone by liquid-phase peroxidation of cumene	14	NA
Davy Process Technology, UK	Propylene glycol	Glycerine	Process produces propylene glycol from glycerine using hydrogenation and refining	NA	NA
CDTECH	TAEE	Mixed C_5 hydrocarbons	High-conversion catalytic distillation process for TAEE production using C_5s and ethanol	1	1991
CDTECH	TAME	Mixed C_5 hydrocarbons	High-conversion catalytic distillation process fro TAME production using C_5s and methanol	29	2000
Saipem S.p.A.	Tame/LCN etherification	Light cracked naphtha, methanol	More than 90% pentenes and 40–60% reactive isohexenes/20–30%reactive isoheptanes etherified into TAME and higher ethers	NA	NA
Saipem S.p.A.	Tertiary Amy Methyl Ether (TAME)	C_5 streams containing isoamylenes, methanol	High efficiency and reliability, compact and low-investment plants	1	1988
Axens	Tertiary amyl methyl ether (TAME)	FCC and steam-cracker C_4 cuts and methanol	Olefinic C_5 cuts are upgraded to high-octane blending value, low Rvp TAME/TAEE	8	2009
ALDEHYDE/KETONES					
Lummus Technology	Dimethyl Carbonate	Methanol, carbon monoxide and oxygen	Produces DMC via oxidative carbonylation of methanol, avoiding the use of phosgene	3	1995
Lummus Technology	Diphenyl Carbonate	Dimethyl carbonate, phenol	DMC and phenol react to produce phenylmethyl cabonate (PMC), which is then disproportionated to produce DPC and DMC that can be recylced back to the DMC unit.	3	1995
Uhde Inventa-Fischer	Formaldehyde	Methanol	Silver process	60	1989
ACIDS/SALTS					
Chiyoda Corp.	Acetic acid	Methanol and carbon monoxide (CO)	In the ACETICA process, methanol and CO are reacted with the carbonylation reaction using a heterogeneous Rh catalyst	1	NA
Lurgi GmbH /Nippon Kayaku	Acrylic acid–glacial and acrylates	Propylene	Advanced oxidation process, cost-effective fixed-bed tubular reactor, largest single-train, high-yield catalyst	1	2008
GTC Technology	Carboxylic acid	Acid-containing aqueous steams	Liquid-liquid extraction technology is combined with distillation to recover and concentrate carboxylic acids from wastewater. Economic for any aqueos stream generated by producing DMT, PTA, pulp/paper, furfural and other processes	2	NA
GTC Technology	DMT	PX, methanol	Series of process enhancements including oxidation, esterification, distillation and crystallization for dimethyl terephthalate (DMT) production	7	1995
Davy Process Technology, UK	Ethyl acetate	Ethanol	Ethanol is dehydrogenated to form ethyl acetate and hydrogen. Heat exchanger separates hydrogen from crude product before it is polished in second catalytic reactor. Polished product is then passed through distillation train to produce unreacted ethanol (which is recycled) and ethyl acetate.	3	NA
Scientific Design Company, Inc.	Maleic anhydride	n-Butanes	Fixed-bed technology; efficient product recovery systems; high product quality	9	2007
INEOS	Maleic anhydride	n-Butane	Fluid-bed catalytic oxidation process with an aqueous-based recovery and purification	3	2005
Lummus Technology/ Polynt	Maleic anhydride	Butane	Fluidized bed technology, organic solvent product recovery	9	2000
The Dow Chemical Co./ Davy Process Technology, UK	Purified terephthalic acid (PTA)	Paraxylene	COMPRESS PTA process reacts paraxylene with oxygen in the presence of a catalyst in a acetic-acid solution to yield crude terephthalic acid. This crude is filtered and re-slurried prior to polishing in a hydrogenation reaction after which it is crystallized, filtered and dried.	11	NA

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
NITROGEN COMPOUNDS					
Ammonia Casale SA	Ammonia	Natural gas (NG)	Process produces anhydrous ammonia from natural gas by applying Casale's high-efficiency secondary reformer design, axial-radial technology for shift conversion, ejector ammonia wash system, axial-radical technology for ammonia converter and advanced waste-heat boiler design in the synthesis loop.	5	2010
Haldor Topsøe A/S	Ammonia	Natural gas, naphtha, fuel oil	Low-energy ammonia technology produces ammonia from a variety of hydrocarbon feedstocks ranging from natural gas to heavy naphtha	60	NA
Linde AG	Ammonia	Light hydrocarbons	LCA process simplifies conversion of light hydrocarbons to ammonia. It consists of a modern hydrogen plant, standard nitrogen unit and high-efficiency ammonia synthesis loop	4	NA
Udhe GmbH	Ammonia	Natural gas, LPG, naphtha	Process uses conventional steam reforming synthesis gas generation (front-end) and an ammonia synthesis loop	15	NA
Kellogg Brown & Root, Inc.	Ammonia, KAAP*plus*	Hydrocarbons	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	200	2010
Kellogg Brown & Root, Inc.	Ammonia, KBR Purifier	Hydrocarbons	To produce ammonia from hydrocarbon feedstocks and air. Process features include a mild primary reforming, secondary reforming with excess air, cryogenic purification of syngas, and synthesis of ammonia over magnetite catalyst in a horizontal converter	200	NA
Kellogg Brown & Root, Inc.	Ammonia, PURIFIER*plus*	Hydrocarbons	To produce ammonia from hydrocarbon feedstocks using a high-pressure heat exchange-based steam reforming process integrated with cryogenic purification of syngas	200	NA
Udhe GmbH	Ammonia—Dual pressure process	Natural gas, LPG, naphtha	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	2	NA
Kellogg Brown & Root LLC	Aniline	Mononitrobenzene	Mononitrobenzene (MNB), produced through nitration of benzene with nitric acid, is hydrogenated to produce high-quality aniline	8	2004
Davy Process Technology, UK	Dimethylformamide (DMF)	Dimethylamine (DMA) and carbon monoxide (CO)	DMA and CO are fed to specialized reactor containing a catalyst dissolved in solvent. A separation system then separates the spent catalyst. Excess DMA and catalyst solvent are stripped from the crude product. Next, vacuum distillation followed by purification produces fiber-grade DMF	15	2010
Davy Process Technology, UK	Ethanolamines	Ethylene oxide and ammonia	Ammonia solution, recycled amines and ethylene oxide are fed continuously to a reaction system that simultaneously produces MEA, DEA and TEA	1	NA
Scientific Design Company, Inc.	Ethanolamines	Ethylene oxide and ammonia	Process offers high product quality with wide product distribution	5	2008
Lurgi GmbH	Melamine	Urea	LP technology in combination with gaseous quench, excellent product quality, high yield	1	2007
Davy Process Technology, UK	Methylamines	Methanol and ammonia	Anhydrous liquid ammonia, recycled amines and methanol are continuously vaporized, superheated and fed to a catalyst-packed converter. The converter utilizing a high-activity, low-byproduct amination catalyst simultaneously produces mono-, di- and triethylamines	20	2010
Toyo Engineering Corp. (TOYO)	Urea	Ammonia (NH_3) and carbon dioxide (CO_2)	Process produces urea from NH_3 and CO_2 using CO_2 stripping process	100+	NA
Urea Casale SA	Urea	Ammonia (NH_3) and carbon dioxide (CO_2)	The Casale split flow loop process is an improved CO_2 stripping process. It produces urea from NH_3 and CO_2 by applying Casale's highly efficient full condenser, Casale-Dente high-efficiency trays and Casale high-efficiency hydrolyzer used in the process condensate treatment unit.	4	NA
Stamicarbon bv	Urea	Ammonia and carbon dioxide	CO_2 stripping technology using proven, innovative Urea 2000 Plus or Avancore synthesis process for urea melt	115	2001

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
Saipem S.p.A.	Urea (Snamprogetti Urea Technology)	Ammonia and carbon dioxide	Process is pollution-free, and energy-efficient	116	2009
Stamicarbon bv	Urea granules	Urea melt	Fluidized bed granulation technology using film dpraying, producing high-quality urea granules	NA	NA
Stamicarbon bv	Urea prills	Urea melt	Prilling technology producing low-cost, high-quality urea prills	NA	NA
CHLORIDES					
INEOS	BICHLOR Electrolyzers	NaCl, H_2O, electricity	Production of chlorine, hydrogen and 32% NaOH solution by electrolysis of NaCl solution. 97%+ efficiency, very low-power consumption due to zero-gap electode design and modular design provides low-maintenance cost. Bipolar electrolyzer design	33	2009
INEOS	BICHLOR Electrolyzers	KCl, H_2O, electricity	Production of chlorine, hydrogen and 32% KOH solution by electrolysis of NaCl solution. 98%+ efficiency, very low-power consumption due to finite gap electode design Bipolar electrolyzer design.	3	2008
INEOS	Chlorine	Brine, Electricity	Chlor-alkali electrochemical technology & electrode coatings providing increased efficiency, flexibility and operability	83	2010
INEOS	Direct chlorination, high-temperature chlorination	Ethylene, chlorine	Energy-efficient process, product purity of 99.95%, low-maintenance, no EDC washing	12	2008
INEOS	Direct chlorination, low-temperature chlorination	Ethylene, chlorine	Well established system and extensively licensed converts lower purity C_2 in gaseous stream	29	2008
Vinnolit GmbH&CoKG	Ethylene dichloride (EDC) via direct chlorination	Ethylene, chlorine	Direct chlorination process producess EDC cost-effectively with an exothermic reaction, heat integration with EDC purification, own catalyst based process	15	2010
Vinnolit GmbH&CoKG	Ethylene dichloride (EDC) via lean oxychlorination	Ethylene, Hydrogenchloride and oxygen	Oxychlorination process producess EDC cost-effectively with an exothermic reaction, steam generation, cooper catalyst-based process	15	2010
INEOS	Ethylene dichloride (EDC),	Ethylene, chlorine	Well established system and extensively licensed converts lower-purity C_2 in gaseous stream	29	2008
INEOS	Ethylene dichloride (EDC), high-temperature	Ethylene, chloride	Energy-efficient process, product purity of 99.95%, low-maintenance, no EDC washing	12	2008
INEOS	Fixed-bed oxygen-based oxychlorination	Ethylene, oxygen, hydrogen chloride	Environmentally attractive process; simple design offers high selectivity and capacity; energy-efficient	26	2008
INEOS	FM1500 Electrolyzers	NaCl, H_2O, electricity	Production of chlorine, hydrogen and 32% NaOH solution by electrolysis of NaCl solution. 97%+ efficiency, low-power consumption due to novel finite gap electrode design. Monopolar electrolyzer design	54	2009
INEOS	FM1500 Electrolyzers	KCl, H_2O, electricity	Production of chlorine, hydrogen and 32% KOH solution by electrolysis of NaCl solution. 98%+ efficiency, low-power consumption due to novel finite gap electrode design. Mono polar electrolyzer design.	1	1989
Vinnolit GmbH&CoKG	VCM (Vinyl chloride monomer)	EDC	EDC Cracking process produces VCM (Vinyl chloride monomer) and hydrochloride as couple product	13	2010
Chisso Corp.	VCM Removal	PVC slurry with unreacted VCM	Stripping process for PVC plants to recover VCM from PVC slurry;VCM can be reused without deteriorating polymer quality	49	2010

Company	Product	Feedstock	Process description	No. of licenses	Date of last license
INEOS	Vinyl chloride monomer	Ethylene, chlorine and air/oxygen	Fixed-bed oxygen-based oxychlorination, low temperature, direct chlorination	43	2008
CYCLO-COMPOUNDS					
Axens	Cyclohexane	Benzene	Liquid-phase homgeneous catalysis hydrogenation offers low-investment and operating costs than vapor-phase processes	33	2007
NAPHTHA/REFINING					
GTC Technology	Aromatization	Paraffinic or olefinic C_4-C_8 fraction	Aromatization technology for gasoline octane improvement or aromatics production using a proprietary catalyst in fixed-bed reactors with periodic catalyst regeneration	1	2008
GTC Technology	Benzene saturation	Full-range FCC naphtha	Application of extractive distillation technology for simultaneous recovery of BTX and thiophenic sulfur species from refinery or petrochemical aromatic-containing streams	1	2008
GTC Technology	BTX recovery, FCC gasoline	Full-range reformate	Effective benzene management process to allow refiners to meet the stringent benzene content in gasoline blendstock	2	2010
BASF/Lummus Technology	C_4/C_5 hydrogenation	C_4 and C_5 olefins and diolefins	D1-olefins and diolefins are saturated by concurrent/countercurrent flow	25	2009
China Petrochemical Technology Co., Ltd.	Gasoline, high-quality	Naphtha	S Zorb sulfur-removal technology (S Zorb SRT) removes sulfur from full-range naphtha in a one-step process	13	2010
GTC Technology	Isomerization	Light naphtha	Light gasoline isomerization processes using regenerable catalyst with superior tolerance to process impurities and water	7	2008
Saipem S.p.A./CDTech	Iso-octene	Mixed C_4 hydrocarbons	Isobutylene dimerization to produce isooctene in presence of catalytic distillation tower	NA	NA
CDTECH/Saipem	Isooctene/isooctane	Mixed C_4 hydrocarbons	Isobutylene dimerization to produce isooctene. Additional process can hydrogenate isooctene to produce isooctane	2	1999
Saipem S.p.A./Ecofuel S.p.A.	Iso-octene/Iso-octane	C_4 streams containing isobutylene	Multipurpose plant. Flexibility, Isobutylene dimerization and hydrogenation of produced Iso-OctEne	2	2006
UOP LLC, A Honeywell Co.	Noraml paraffins, C_{10}–C_{13}	Kerosine	Molex process recovers C_{10}–C_{13} paraffins from kerosine using UOP's innovative Sorbex adsorptive separation technology	32	NA
Kellogg Brown & Root LLC	n-Paraffin	Kerosine	ENSORB recovery process (developed by ExxonMobil Chemical) removes long-chain aliphatic normal paraffins from the kerosine stream in vapor phase by adsorption onto a molecular sieve. A low-pressure ammonia desorbate recovers the n-paraffins from the sieve for use as LAB-quality product for further purification	1	NA
China Petrochemical Technology Co., Ltd.	Petroleum coke, naphtha, gasoil and gas	Petroleum residue, asphalt or slop oil	Delayed coking, thermal cracking process, upgrades and converts petroleum residue, asphalt or slop oil into gas, naphtha, gasoil and petroleum coke. It mainly consists of heater (furnace), coking drums, fractionating section and gas-recovering section	50	2010
GTC Technology	Pygas hydrotreating	Raw pygas	Optimized technology for two-stage pyrolysis gasoline (pygas) hydrotreatment, where diolefins, olefins and styrene in the raw pygas feed is being saturated	3	2008
GAS PROCESSING					
Davy Process Technology, UK	Substitute natural gas (SNG)	Purified synthesis gas	SNG is produced by coal gasification, using shift and methanation reactions	43	NA
GTC Technology	Sweet gas sulfur treating	Sour gas	A nonaqueous process that has been developed specifically for treating high-pressure sour natural gas in medium-sized sulfur applications	1	2005
JX Nippon Oil & Energy Corp.	Wet air oxidation (WAO), spent caustic	Sent caustic	Oxidation of sodium sulfide (Na_2S) component in the caustic scrubber effluent of olefin plants with air using wet air oxidation	13	NA