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2014 Petrochemical Processes Handbook

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HYDROCARBON PROCESSING®

2014 Petrochemical Processes Handbook

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Sponsors:

Processes Index

(1 / 2 / 3 / 4)

Processes Index, cont.

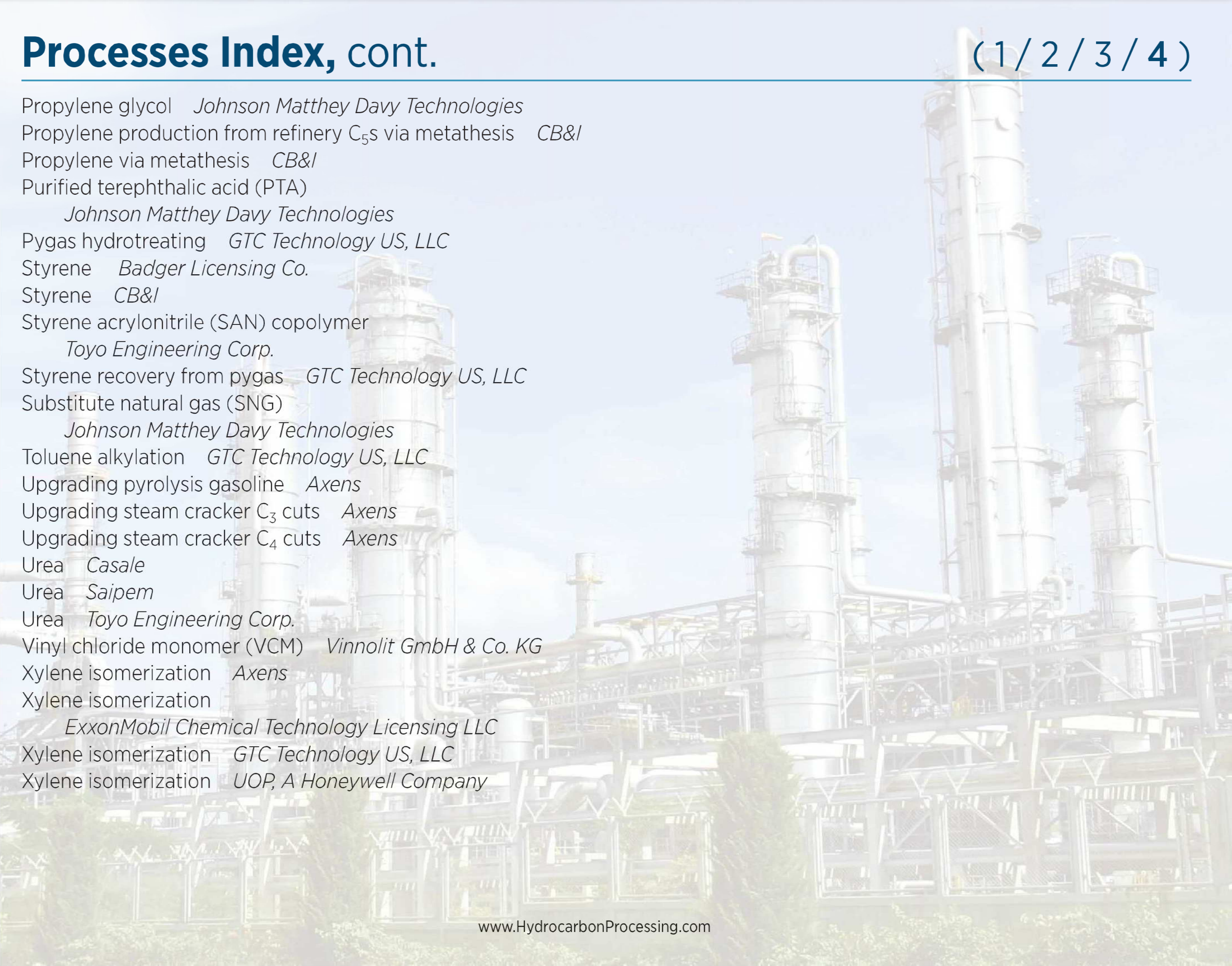
(1 / **2** / 3 / 4)

Processes Index, cont.

(1 / 2 / **3** / 4)

Methanol (exchanger reformer combined)
    Toyo Engineering Corp.
Methanol (steam reforming) *Toyo Engineering Corp.*
Methylamines *Johnson Matthey Davy Technologies*
Mixed xylenes *Axens*
Mixed xylenes *Axens*
Mixed xylenes *ExxonMobil Chemical Technology Licensing LLC*
Mixed xylenes *ExxonMobil Chemical Technology Licensing LLC*
Mixed xylenes *UOP, A Honeywell Company*
MTBE/ETBE and TAME/TAEE: Etheritication technologies
    Axens
n-Paraffin *Kellogg Brown & Root, LLC*
Natural detergent alcohols
    Johnson Matthey Davy Technologies
Normal parafins, C_{10}–C_{13} *UOP, A Honeywell Company*
Octenes *Axens*
Olefins—Deep catalytic cracking
    Technip Stone & Webster Process Technology
Paraffin Isomerization *GTC Technology US, LLC*
Paraxylene *Axens*
Paraxylene *Axens*
Paraxylene *ExxonMobil Chemical Technology Licensing LLC*
Paraxylene *UOP, A Honeywell Company*
Paraxylene *UOP, A Honeywell Company*
Paraxylene *UOP, A Honeywell Company*
Paraxylene, crystallization *GTC Technology US, LLC*

Phenol *CB&I*
Phenol *Kellogg Brown & Root, LLC*
Phenol *UOP, A Honeywell Company*
Polyethylene *INEOS Technologies Ltd*
Polyethylene *INEOS Technologies Ltd*
Polyethylene *Nova Chemicals*
Polyethylene—LDPE
    ExxonMobil Chemical Technology Licensing LLC
Polypropylene *CB&I*
Polypropylene *Dow Chemical Company*
Polypropylene *INEOS Technologies Ltd*
Polypropylene *Japan Polypropylene Corporation*
Polystyrene *INEOS Technologies Ltd*
Polystyrene, expandable *INEOS Technologies Ltd*
Polystyrene, general-purpose (GPPS) *Toyo Engineering Corp.*
Polystyrene—GPPS and HIPS
    Technip Stone & Webster Process Technology
Polystyrene, high-impact (HIPS) *Toyo Engineering Corp.*
Polyvinyl chloride, suspension *Vinnolit GmbH & Co. KG*
Propylene *Axens*
Propylene *Axens*
Propylene *CB&I*
Propylene *UOP, A Honeywell Company*
Propylene *UOP, A Honeywell Company*
Propylene, K-COT *Kellogg Brown & Root, LLC*
Propylene and ethylene *UOP, A Honeywell Company*



Processes Index, cont.

(1 / 2 / 3 / 4)

HOME
PROCESSES INDEX
COMPANY INDEX

Company Index

Air Liquide Global E&C Solutions Germany GmbH
Axens
Badger Licensing Co.
Casale
CB&I
Chiyoda Corporation
Dow Chemical Company
ExxonMobil Chemical Technology Licensing LLC
GTC Technology US, LLC
INEOS Technologies Ltd
Japan Polypropylene Corporation
Johnson Matthey Davy Technologies
Kellogg Brown & Root, LLC
Linde AG
NOVA Chemicals
Saipem
Shell Global Solutions International BV
Technip Stone & Webster Process Technology
Toyo Engineering Corp.
UOP, A Honeywell Company
Vinnolit GmbH & Co. KG

Air Liquide Global E&C Solutions Germany GmbH

1,3 Butadiene
Acrylic acid
Aromatics extractive distillation
Low-pressure melamine process
Methanol

Axens
IFP Group Technologies

Processes

Aromatics recovery
Aromatics treatment
Benzene
BTX aromatics
BTX aromatics and LPG
Butene-1
Cyclohexane
Ethylene feed preatment-mercury, arsenic and lead removal
Hexene-1
Mixed xylenes
Mixed xylenes
MTBE/ETBE and TAME/TAEE: Etheritication technologies
Octenes
Paraxylene
Paraxylene
Propylene
Propylene
Upgrading pyrolysis gasoline
Upgrading steam cracker C_3 cuts
Upgrading steam cracker C_4 cuts
Xylene isomerization

Badger Licensing Co.

Bisphenol A
Cumene
Ethylbenzene
Styrene

Casale

Ammonia
Methanol
Methanol
Urea

CB&I

1,3 Butadiene (Extraction from mixed C_4)
Benzene
Butadiene from n-butane
Butene-1
Butenes (extraction from mixed butanes/butenes)
Cumene
Dimethyl carbonate
Diphenyl carbonate
Ethylbenzene
Ethylbenzene
Ethylene
Hexene-1
Isobutylene
Isomerization
Phenol
Polypropylene
Propylene
Propylene production from refinery C_5s via metathesis
Propylene via metathesis
Styrene

Chiyoda Corporation

Acetic acid

Dow Chemical Company

Butyraldehyde, n and i
Ethylene glycol
Ethylene oxide
Polypropylene

ExxonMobil Chemical Technology Licensing LLC

Aromatics treatment
Mixed xylenes
Mixed xylenes
Paraxylene
Polyethylene—LDPE
Xylene isomerization

GTC Technology US, LLC

Aromatics, transalkylation
Benzene, ethylbenzene dealkylation
Benzene saturation
BTX extraction
BTX recovery from FCC gasoline
C_5 componenets recovery
Isoprene
Paraffin Isomerization
Paraxylene, crystallization
Pygas hydrotreating
Styrene recovery from pygas
Toluene alkylation
Xylene isomerization

INEOS Technologies Ltd

Acrylonitrile
Chlor-alkali
Maleic anhydride
Polyethylene
Polyethylene
Polypropylene
Polystyrene
Polystyrene, expandable

Japan Polypropylene Corporation

Polypropylene

Johnson Matthey Davy Technologies

Butanediol, 1, 4-
Dimethylformamide
Ethyl acetate
Methanol
Methylamines
Natural detergent alcohols
Propylene glycol
Purified terephthalic acid (PTA)
Substitute natural gas (SNG)

Kellogg Brown & Root, LLC

Ammonia, KAAP*plus*
Ammonia, KBR
Ammonia, KBR KAAP
Ammonia, KBR Purifier
Ammonia, PURIFIER*plus*
Bisphenol A
Ethylene, SCORE
Isooctene/Isooctane
Methanol
n-Paraffin
Phenol
Propylene, K-COT

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Linde

Processes

Alpha olefins
Ammonia
Ethylene: Ethane and E/P mix
Ethylene: Liquid feedstocks
Ethylene: Value cracking

NOVA Chemicals

Polyethylene

Saipem

Urea

Shell Global Solutions International BV

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

Technip Stone & Webster Process Technology

ABS—Emulsion process
ABS—Mass process
Ethylene—Cracking furnaces
Ethylene—Steam cracking and product recovery (gaseous feedstocks)
Ethylene—Steam cracking and product recovery (liquid feedstocks)
Ethylene recovery from refinery offgas with contaminant removal
High-olefins FCC and ethylene plant integration
Olefins—Deep catalytic cracking
Polystyrene—GPPS and HIPS

Toyo Engineering Corp.

Acrylonitrile butadiene styrene (ABS) copolymer
Dimethyl ether (DME)
Methanol (autothermal reforming)
Methanol (combined reforming)
Methanol (exchanger reformer combined)
Methanol (steam reforming)
Polystyrene, general-purpose (GPPS)
Polystyrene, high-impact (HIPS)
Styrene acrylonitrile (SAN) copolymer
Urea

UOP, A Honeywell Company

Aromatics extraction
Aromatics extraction
BTX aromatics
BTX aromatics
Cumene
Ethylene
Linear alkylbenzene
m-Xylene
Mixed xylenes
Normal parafins, C_{10}–C_{13}
Paraxylene
Paraxylene
Paraxylene
Phenol
Propylene
Propylene
Propylene and ethylene
Xylene isomerization

Vinnolit GmbH & Co. KG

Direct chlorination (DC)
Polyvinyl chloride, suspension
Vinyl chloride monomer (VCM)

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.

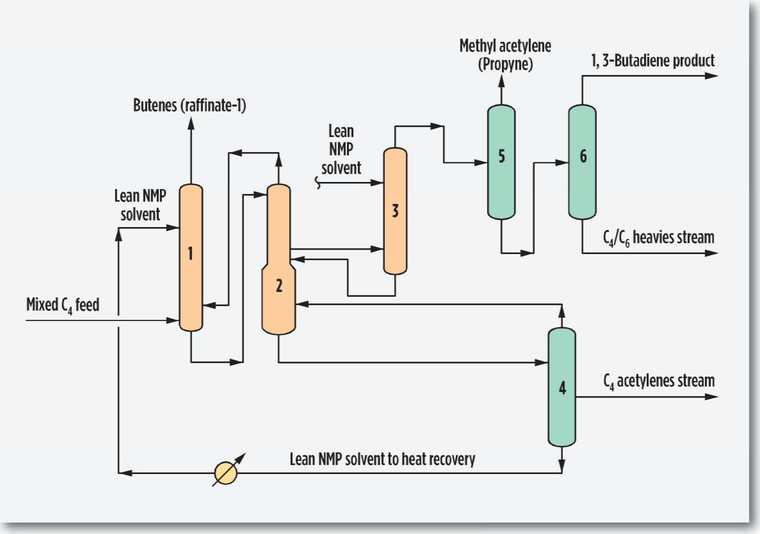
Description: The mixed C_4 feed stream is fed into the main washer, the first extractive distillation column (1), which produces an overhead butanes/butenes stream (raffinate-1) that is essentially free of butadiene and acetylenes.

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

Continued ▼

1,3 Butadiene (Extraction from mixed C_4), cont.

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.

Economics: Typical utilities, per ton BD

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

Commercial plants: Currently, 38 plants are in operation using the BASF butadiene extraction process. Fourteen additional projects are in the design or construction phase.

Licensor: BASF/CB&I CONTACT

1,3 Butadiene

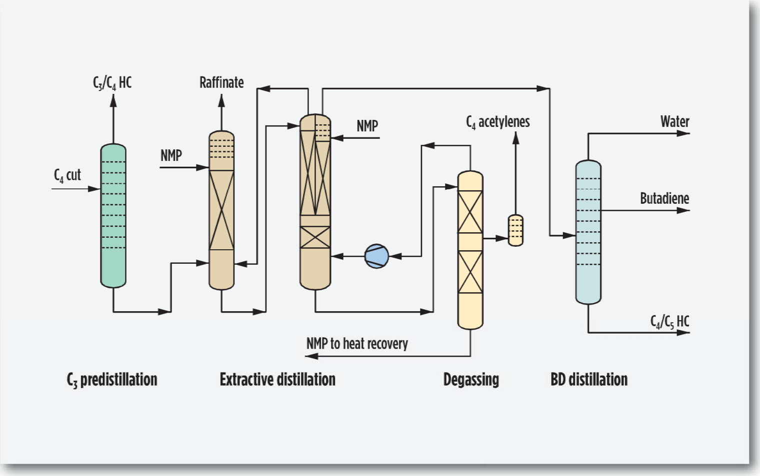
Application: 1,3 Butadiene is recovered from a crude C_4 stream from olefins plants by extractive distillation. N-methylpyrrolidone (NMP) as the selective solvent substantially improves the volatilities of the components. Different process configurations are available.

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 as 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 recycled to the rectifier bottoms via a 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.

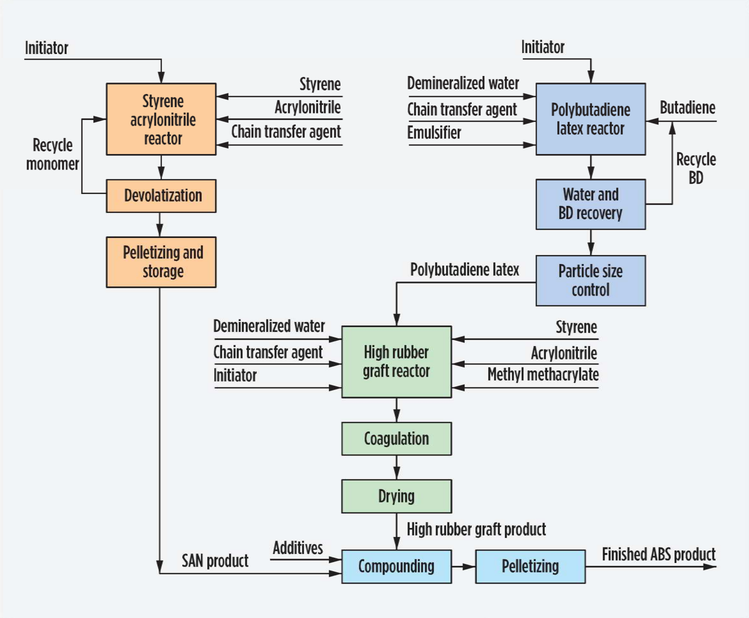
Economics: The BASF process requires less equipment items than other BD extraction technologies and is especially renowned for reliability and availability as well as low operating costs.

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

Commercial plants: Thirty-six units are in operation.

Licensor: BASF SE/Air Liquide Global E&C Solutions Germany GmbH
CONTACT

ABS—Emulsion process



Application: Acrylonitrile butadiene styrene (ABS) is used in the electronics, appliances, building, construction and transportation industries. A wide range of ABS thermoplastic resin products can be produced by SABIC's ABS emulsion process. Composites of styrene acrylonitrile (SAN) copolymer and high butadiene acrylonitrile styrene graft [high rubber graft (HRG)] yield ABS products with exceptional impact strength. The properties of ABS can be widely varied by using different concentrations of butadiene rubber and acrylonitrile in the copolymer.

Description: The ABS process requires the production of four distinct products: SAN copolymer; polybutadiene latex (PBL), an emulsion of polybutadiene rubber in water; HRG resin; and finished ABS product via compounding. The SAN production area includes feed filtration, bulk reaction, devolatization, unreacted monomer recovery and product pelletizing. Styrene, acrylonitrile and additives are continuously charged to the reactor. The SAN polymer is produced in a single stirred reactor that provides sufficient residence time at the controlled reactor conditions to achieve the required monomer conversion, typically operated at 55% to 70% solids. Unreacted volatile materials in the polymer melt are devolatilized by using a flash system operating at controlled vacuum. Recovered monomers are recycled to the reactor. Features of the SAN reactor configuration allow straightforward control of product composition and molecular weight. Waste vapors are scrubbed for recovery. Following devolatization, the polymer melt is pelletized, cooled and sent to storage. A typical design is capable of producing multiple unique SAN grades.

Separately but in parallel with SAN production, PBL is manufactured as a raw material to make resin in the HRG process area. The four main steps to produce PBL are feed preparation, reaction, flash removal of unreacted butadiene, and particle size control. The reactor is charged with demineralized water, emulsifier and butadiene. After heat-up and polymerization, additional butadiene, initiator and chain transfer agent are added on a continuous basis. This unique semi-batch process significantly improves reactor cycle time while minimizing the risk of runaway reaction that is normally present in traditional batch PBL reactors. Butadiene is polymerized to near completion. Reactor contents (crude PBL) are directed to a flash chamber operating under vacuum to remove unreacted butadiene monomer which is recycled to the feed system. Prior to storage and feeding, in the HRG resin production area, crude PBL is sent to a proprietary particle size control step.

Continued ▼

ABS—Emulsion process, cont.

The HRG reaction process, a semi-batch emulsion reaction of styrene and acrylonitrile with PBL, is followed by a continuous coagulation to form resin particles, water removal and drying. Initially, PBL latex solution and demineralized water are added to the reactor. After heating, styrene, acrylonitrile and additives are charged to the reactor. Application of semi-batch operation results in lower monomer inventory and reduced runaway polymerization potential. Prior to transfer from the reactor, to increase monomer conversion, a small amount of methyl methacrylate is added. The HRG latex is next directed to a coagulation system where particle size is controlled by agitation speed and acid addition. The proprietary coagulation process is designed to separate the latex emulsion by creating an HRG resin slurry. The coagulated slurry is then washed and dewatered in a series of proprietary process steps. Finally, the wet resin is dried to less than 1% moisture content in a rotary dryer.

Finished ABS product is formulated in the compounding area using a twin-screw extruder. An automated feed system delivers HRG resin, SAN pellets and pre-blended additives to the extruder. The extruder system includes a screen changer, strand die, water slide pelletizer, pellet dryer, water recirculation system and screener. After screening, the pellet material is transferred to product surge hoppers and packaging.

Products: A broad range of ABS products, including plating, extrusion and fire-retardant grades, are available for license. Emulsion ABS products are well suited for high-gloss automotive, high-heat automotive, refrigeration, medical, food and pipe applications. Cycolac* ABS resins provide an excellent balance of processability, impact, dimensional stability, and high-temperature resistance with a stable light base color.

*Cycolac is a trade name of SABIC Innovative Plastics.

Commercial plants: Licensed plants include two 200-KTA plants in China and a 140-KTA plant in KSA. SABIC operates four ABS facilities: three in the USA and one in Mexico.

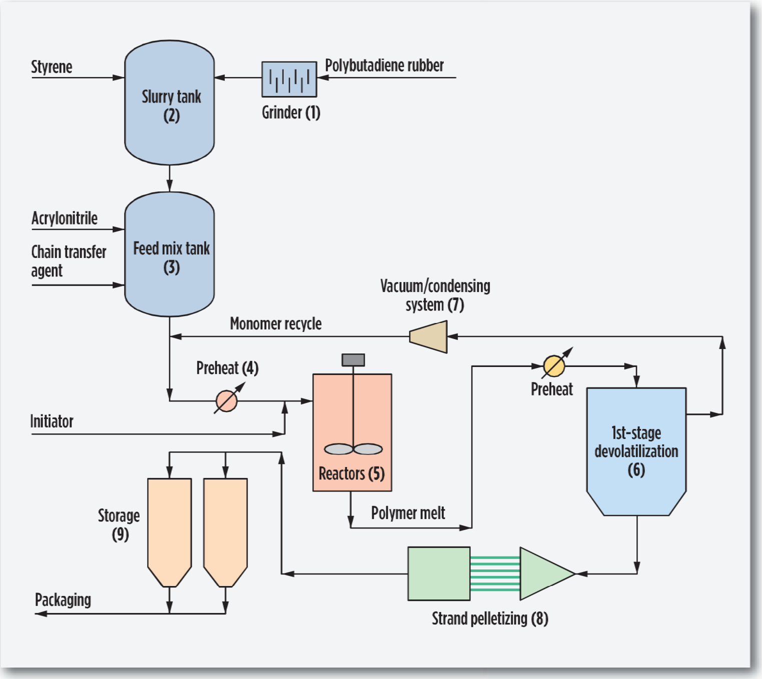
Key features:

- Inherently safe reaction processes, low reaction viscosities
- Competitive capital and operating costs
- High reactor productivity
- Single HRG product results in simplified operation
- Exceptional product quality
- A broad family of products meeting the most demanding application requirements
- Optimized impact-flow performance with low organic volatiles and non-polymer impurities
- Additive flexibility enables specialty products from natural/black/white and custom colors

Licensor: Technip Stone & Webster Process Technology CONTACT

ABS—Mass process

Application: Acrylonitrile butadiene styrene (ABS) is used in the electronics, appliances, building, construction and transportation industries. A wide range of ABS thermoplastic resin products can be produced by SABIC's Mass ABS process, which uses a proprietary mass polymerization reactor configuration and devolatization system to produce high-quality, low-volatility content product. The properties of ABS can be widely varied by using different concentrations of butadiene rubber and acrylonitrile in the polymer.



Description: ABS production is accomplished by continuous copolymerization of styrene and acrylonitrile monomers with polybutadiene rubber (PBR) or styrene butadiene rubber (SBR) in the presence of organic peroxide, using multiple reactors in series. PBR or SBR is chopped (1) and fed to a slurry tank (2) with styrene monomer. Feed is then pumped into the ABS feed batch tank (3), where the rubber is completely dissolved. The concentrated rubber solution is diluted with fresh acrylonitrile, recovered recycle monomer and chain transfer agent according to product requirements. The combined ABS feed is preheated (4) prior to being fed to the polymerization reactors.

The polymerization section (5) uses a unique combination of plug flow and boiling stirred tank reactors operating in series. To initiate polymerization, organic peroxide is fed to the system. The reactor arrangement allows accurate control of the degree of rubber grafting, phase inversion, rubber particle size, extent of cross-linking, molecular weight and polymer morphology. Monomer conversion increases steadily through the reactor system to a final conversion of between 60%–75%.

Two options for devolatization (6) are offered: extrusion devolatilization or flash chamber devolatilization. Product from the last reactor is stripped of the unreacted monomers and byproducts in an extruder devolatilization system. The temperature gradient within the extruder is set to control the degree of flashing and recovery. Alternatively, the reactor product is stripped of volatiles in a multistage flash devolatilization system that operates under deep vacuum. Vapor from the devolatization steps are condensed in a series of exchangers (7). The recovered monomer and ethylbenzene mixture stream is recycled to the upfront ABS feed preparation section. Devolatilized polymer melt is then sent to a strand cut pelletizer system (8) to create polymer strands. After the cutting and cooling steps, the pellets are dried and then classified to remove

Continued ▼

ABS—Mass process, cont.

fines and over-sized pellets. The finished ABS pellets are then pneumatically conveyed to storage and packaging (9).

Products: A broad range of ABS products are available for license. Mass ABS products are well suited for low-gloss automotive, high-heat automotive, general-purpose and pipe applications. Cycolac* mass ABS resins provide an excellent balance of processability, impact, dimensional stability and high temperature resistance with a stable light base color. Mass ABS resins are available in a wide range of melt flow rates and impact strengths for both medium- to low-gloss general-purpose molding.

*Cycolac is a trade name of SABIC Innovative Plastics.

Commercial plants: SABIC operates two Mass ABS lines on the US Gulf Coast.

Key features:

- High polymer yields, typically greater than 99%
- A unique reactor design for grafting, phase inversion and accurate control of rubber particle size and distribution
- Reactors incorporate special features for effective control and removal of the exothermic heat of reaction
- Uses peroxide as an initiator and grafting agent, allowing for precise particle size control
- Customizable devolatilization processes based on utility cost considerations
- Produces medium- to low-gloss high-impact Mass ABS resins
- Produces a clean, stable base color ABS resin with low residual monomers that are ideal for coloring
- Limited polymer fouling results in turnaround frequency on the order of two years
- High safety and environmental performance in response to the more stringent regulations

Licensor: Technip Stone & Webster Process Technology CONTACT

Acetic acid

Application: To produce acetic acid by using the CT-ACETICA® process. 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 with 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 CT-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 its heterogeneous system, and, therefore, the system has much less corrosivity.

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

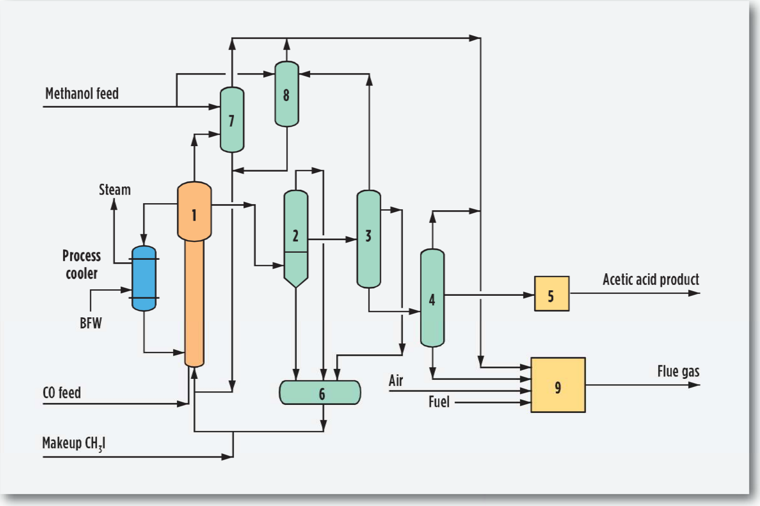
Vapor streams from the dehydration column overhead contacted with methanol in the low-pressure absorber (8). Unconverted CO, methane, and other light byproducts exiting in the vapor outlets of the high- and low-pressure absorbers and heavy byproducts from the finishing column are sent to the incinerator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

Economics: ISBL cost US$122 MM US Gulf @ 300,000 metric tons (MT)/year

Feed and utility consumption:

Methanol	0.537 MT/MT
Carbon monoxide	0.500 MT/MT
Power (@ CO supply 0 K/G)	129 kWh/MT
CW	122 m^3/MT
Steam @ 100 psig	1.6 MT/MT*

*Provided by steam generators on reactor and incinerator



Installations: Contract for the license and preparation of the basic design package was signed for a Brazilian client in October 2012.

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

"Chiyoda Acetic Acid Process ACETICA," *Handbook of Petrochemicals Production Processes,* Part 1, Chapter 1.1 (2005).

Licensor: Chiyoda Corporation 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).

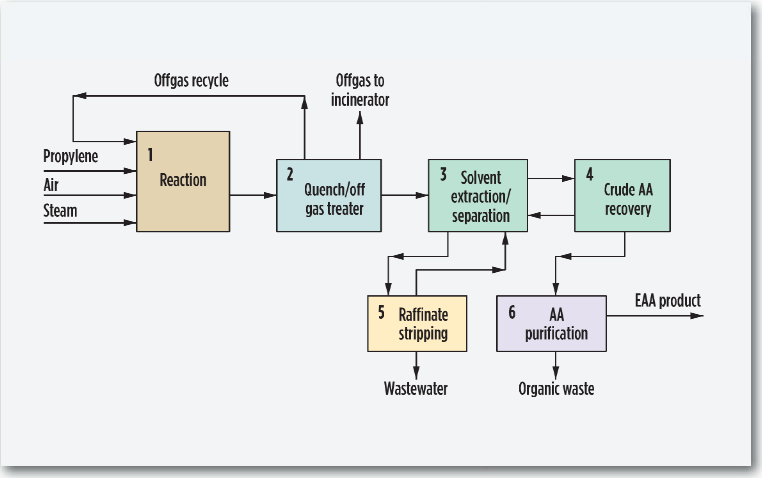
Description: The general flow diagram comprises six main sections: reaction, quench, solvent extraction, crude acrylic acid recovery, raffinate stripping and acrylic acid purification.

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. The 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 are 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. A part of the stripper bottom stream is recycled to the offgas treater; the remainder 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.

Economics: The Lurgi/Nippon Kayaku technology combines high-performance catalysts with highest acrylic acid yields and outstanding

Continued ▼

Acrylic acid, cont.

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 operated in China; startup took place in 2012.

Licensor: Air Liquide Global E&C Solutions Germany GmbH/
Nippon Kayaku Co., Ltd. CONTACT

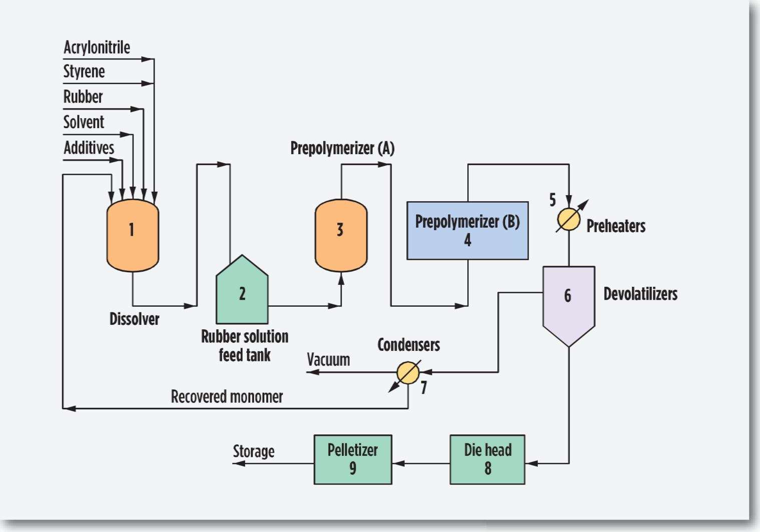
Acrylonitrile butadiene styrene (ABS) copolymer

Application: To produce a wide range of acrylonitrile butadiene styrene (ABS) copolymer with excellent impact strength, heat stability and process ability via the continuous bulk polymerization process using Mitsui Chemicals Inc. (MCI)/Toyo Engineering Corp. (TOYO) technology.

Description: Styrene monomer, acrylonitrile monomer, ground rubber chips and a small amount of additives are fed to the rubber dissolver (1). The rubber chips are completely dissolved in styrene and acrylonitrile. This rubber solution is sent to a rubber-solution-feed tank (2). The rubber solution from the tank is sent to the specially designed polymerizer (A) where the desired rubber morphology, which enables excellent impact strength and glosses, is established (3). The polymerization temperature of the reactor is carefully controlled at a constant level to keep certain conversion rates to obtain desired product properties. The heat of polymerization is easily removed by a specially designed heat-transfer system.

The polymerized solution is polymerized to the final stages in polymerizers (B) (4) and then transferred to the devolatilizers (6) after being preheated (5). Volatile components are recovered from the polymer solution by evaporation under vacuum to get molten polymer. The recovered volatile components are condensed (7) and recycled to the process. The molten polymer is pumped through a die head (8) and cut into pellets by a pelletizer (9).

The MCI/TOYO process is an environment-friendly process that releases very small amounts of waste water and waste gas to the environment, and its characteristic polymerization system enables excellent impact strength, heat stability and process ability in its products.



Economics: Basis: 50,000 mtpy ABS

Raw materials consumption per 1 metric ton of ABS, kg	1,009
Utilities consumption per 1 metric ton of ABS, US$	16

Installations: Toyo has licensed 42 polystyrene plants (GPPS/HIPS/SAN/ABS) with a total production capacity of 950,000 tpy.

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

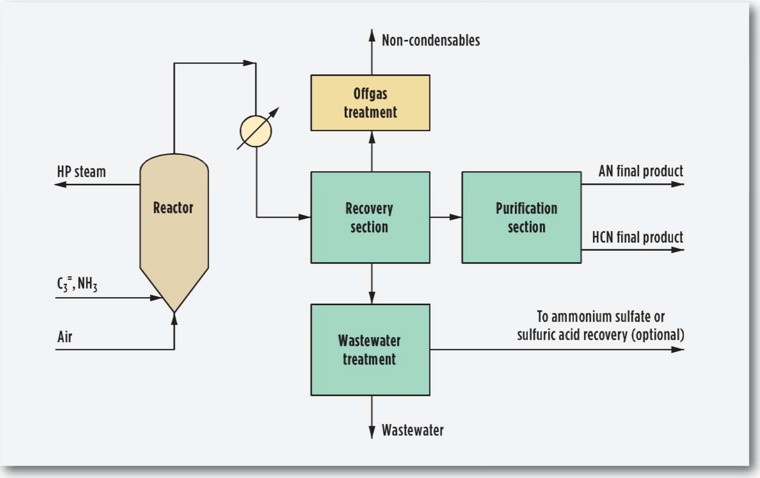
Description: The INEOS acrylonitrile technology uses its proven fluidized-bed reactor system. The feeds containing propylene, ammonia and air are introduced into the fluid-bed catalytic reactor, which operates at 5 psig–30 psig with a temperature range of 750°F–950°F (400°C–510°C). This exothermic reaction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

Continued ▼

Acrylonitrile, cont.

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

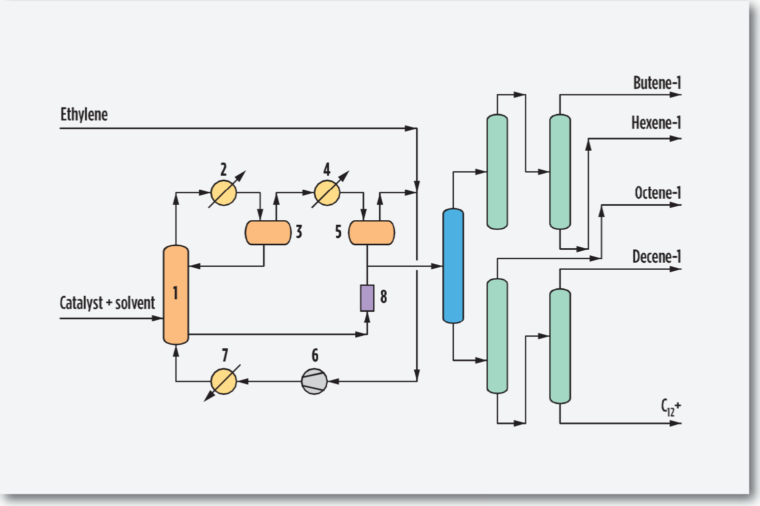
Alpha olefins

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

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.

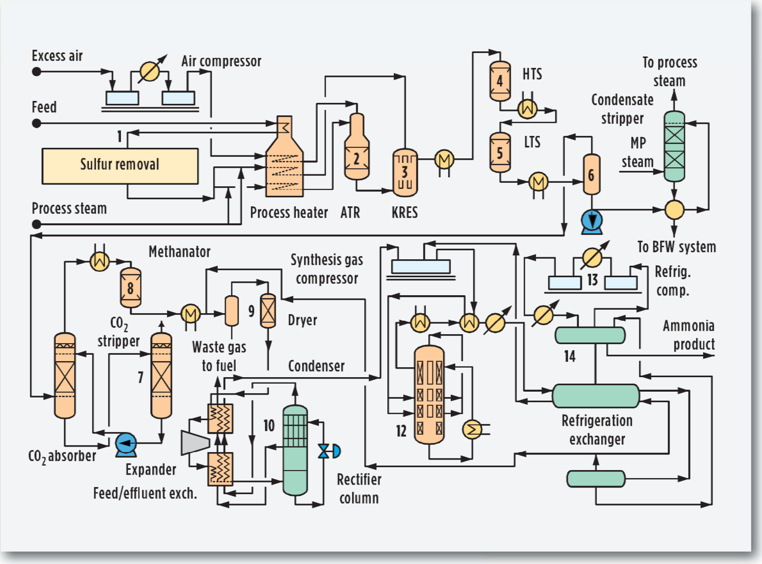
Description: The key steps in the KAAP*plus* process are reforming using the KBR reforming exchanger system (KRES), cryogenic purification of the synthesis gas and low-pressure ammonia synthesis using KAAP catalyst.

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 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 ATR 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.

The shell-side effluent from the reforming exchanger is cooled in a waste-heat boiler, where HP 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.

The shift reactor effluent is cooled and condensed water is separated (6). The effluent is then routed to the gas purification section. Carbon dioxide (CO_2) is removed from synthesis gas using a wet-CO_2 scrubbing system such as hot potassium carbonate or methyl diethanolamine (MDEA) (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 KAAPplus 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.

Continued ▼

Ammonia, KAAP*plus*, cont.

Commercial plants: More than 230 single-train plants of KBR design have been contracted worldwide. Over 30 of these plants use the KBR Purifier process for capacities up to 2,700 metric tpd. Seven plants use the KBR KAAP ammonia process. KBR has 20 large ammonia plants now in design or under construction.

Licensor: Kellogg Brown & Root, LLC CONTACT

Ammonia, KBR KAAP

Application: To produce ammonia from hydrocarbon feedstocks using a low-pressure advanced ammonia synthesis process

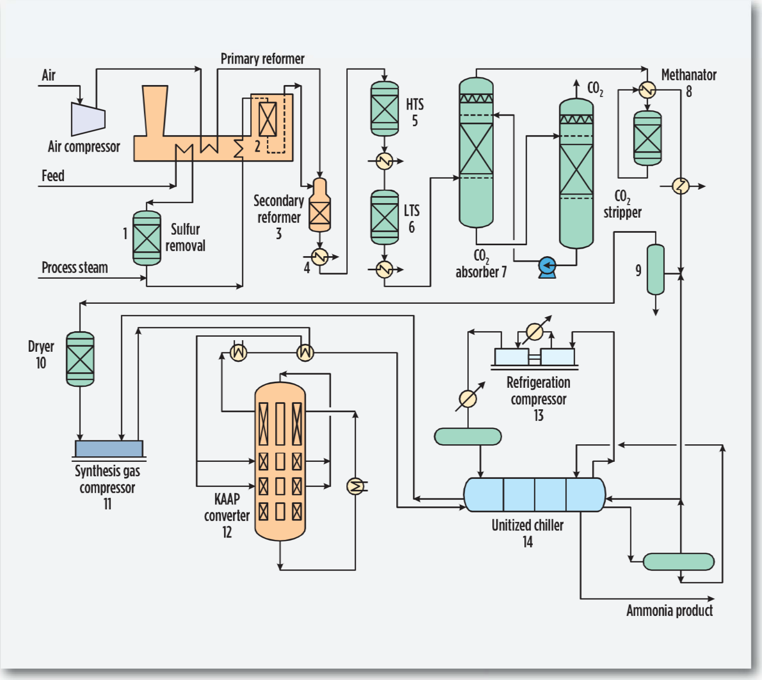
Description: The key steps in the KBR KAAP process are primary reforming, secondary reforming, and low-pressure ammonia synthesis using KAAP catalyst.

Following sulfur removal (1), the feed is reacted with steam in the primary reformer (2). Primary reformer effluent is reacted with air in the secondary reformer (3). An alternative to the above described conventional reforming is to use KBR's reforming exchanger system (KRES), as described in KBR's KAAP*plus* ammonia process.

The secondary reformer effluent is cooled in a waste-heat boiler (4), where high-pressure steam is generated, and then it flows to the CO shift converters containing two catalyst types: one (5) is a high-temperature catalyst, and the other (6) is a low-temperature catalyst.

The shift reactor effluent is cooled and condensed water is separated. The gas is then routed to the gas purification section. Carbon dioxide (CO_2) is removed from the synthesis gas using a CO_2 licensed process. Following CO_2 removal, the residual carbon oxides are converted to methane in the methanator (8). The methanator effluent is cooled, and water is separated (9) before the raw gas is dried (10).

The dried 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 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 from the effluent in the unitized chiller (14).



Commercial plants: More than 230 single-train plants of KBR design have been contracted worldwide. Over 30 of these plants use the KBR Purifier process for capacities up to 2,700 metric tpd. Seven plants use the KBR KAAP ammonia process. KBR has 20 large ammonia plants now in design or under construction.

Licensor: Kellogg Brown & Root, LLC CONTACT

Ammonia, KBR Purifier

Application: To produce ammonia from hydrocarbon feedstocks and air.

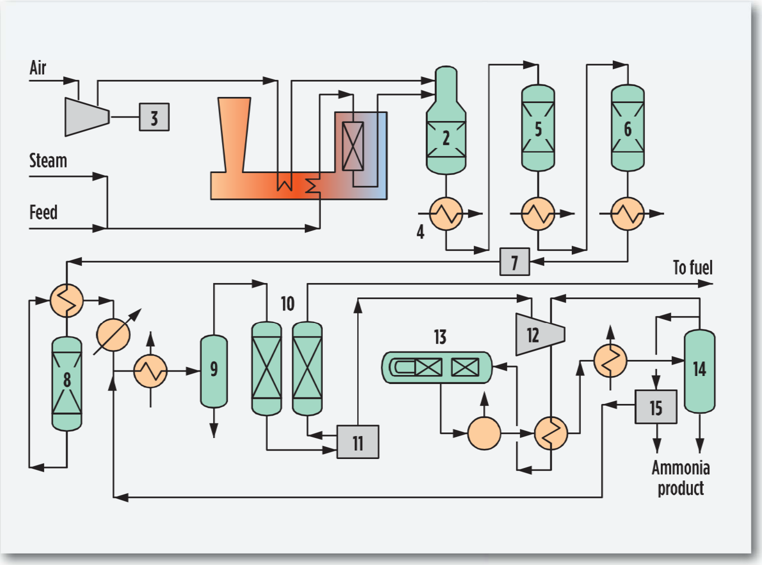
Description: The key features of the KBR Purifier process are mild primary reforming, secondary reforming with excess air, cryogenic purification of syngas and synthesis of ammonia over magnetite catalyst in a horizontal converter.

Desulfurized feed is reacted with steam in the primary reformer (1) with an exit temperature of about 700°C. The 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). The 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 (CO_2) removal (7) uses licensed processes. Following CO_2 removal, residual carbon oxides are converted to methane in the methanator (8). The methanator effluent is cooled, and water is separated (9) before the raw gas is dried (10).

The dried synthesis gas flows to the cryogenic purifier (11), where it is cooled by feed/effluent heat exchange and then 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 it 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). The converter effluent is cooled and then chilled by ammonia refrigeration. The 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 230 single-train plants of KBR design have been contracted worldwide. Over 30 of these plants use the KBR Purifier process for capacities up to 2,700 metric tpd. Seven plants use the KBR KAAP ammonia process. KBR has 20 large ammonia plants now in design or under construction.

Licensor: Kellogg Brown & Root, LLC CONTACT

Ammonia, KBR

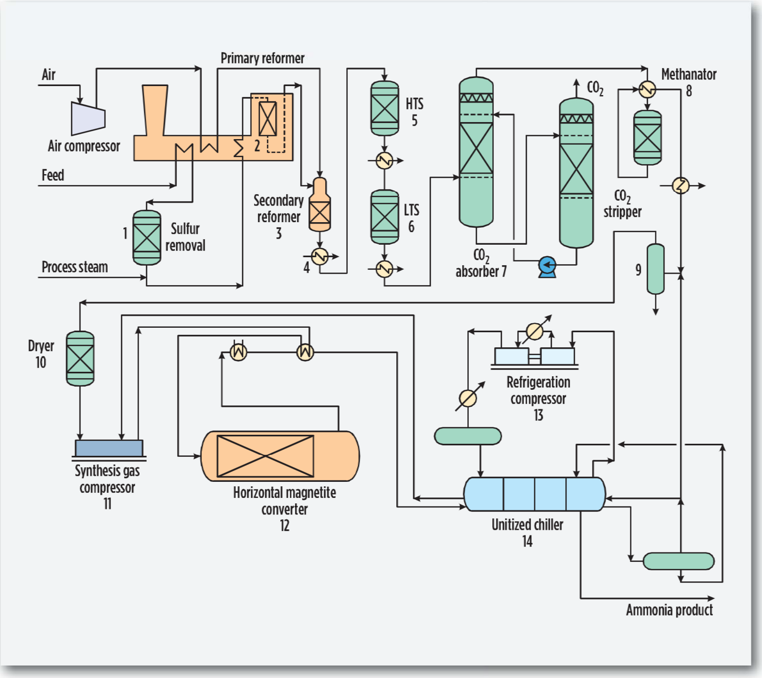
Application: To produce ammonia from hydrocarbon feedstocks and air.

Description: The key steps in the KBR ammonia process are primary reforming, secondary reforming and ammonia synthesis over magnetite catalyst in a horizontal converter.

Following sulfur removal (1), the feed is reacted with steam in the primary reformer (2). Primary reformer effluent is reacted with air in the secondary reformer (3). Secondary reformer effluent is cooled in a waste-heat boiler (4), where high-pressure steam is generated, and then it flows to the CO shift converters containing two catalyst types: one (5) is a high-temperature catalyst and the other (6) is a low-temperature catalyst.

The shift reactor effluent is cooled and condensed water is separated. The gas is then routed to the gas purification section. Carbon dioxide (CO_2) is removed from the synthesis gas using a licensed CO_2 removal process. Following CO_2 removal, residual carbon oxides are converted to methane in the methanator (8). The methanator effluent is cooled, and water is separated (9) before the raw gas is dried (10).

The dried synthesis gas is compressed in a single-case compressor and mixed with a recycle stream (11). The gas mixture is fed to the horizontal ammonia converter (12). Effluent vapors are cooled by ammonia refrigeration, (13) and unreacted gases are recycled. Anhydrous liquid ammonia is condensed and separated from the effluent in the unitized chiller (14).



Commercial plants: More than 230 single-train plants of KBR design have been contracted worldwide. Over 30 of these plants use the KBR Purifier process for capacities up to 2,700 metric tpd. Seven plants use the KBR KAAP ammonia process. KBR has 20 large ammonia plants now in design or under construction.

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.

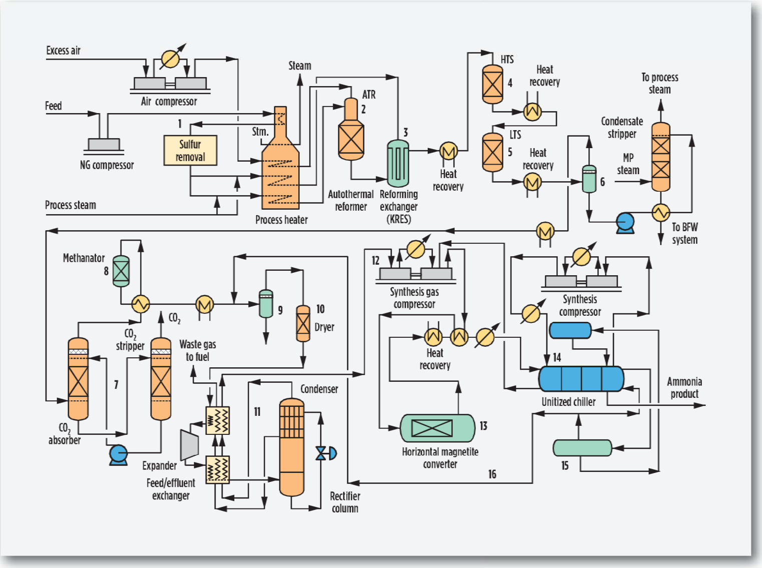
In the ATR, feed is partially combusted with excess air to supply the heat needed to reform the remaining hydrocarbon feed. The hot ATR effluent is fed to the shell side of the KRES reforming exchanger, where it combines with the reformed gas exiting the catalyst-packed tubes. The combined stream flows across the shell side of the reforming exchanger where it supplies heat to the reforming reaction inside the tubes.

The shell-side effluent from the reforming exchanger is cooled in a waste-heat boiler, where HP steam is generated, and it 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.

The shift-reactor effluent is cooled and condensed water is separated (6). The effluent is then routed to the gas purification section. Carbon dioxide (CO_2) is removed from synthesis gas using a wet-CO_2 scrubbing system such as hot potassium carbonate or methyl diethanolamine (MDEA) (7).

Following CO_2 removal, the 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



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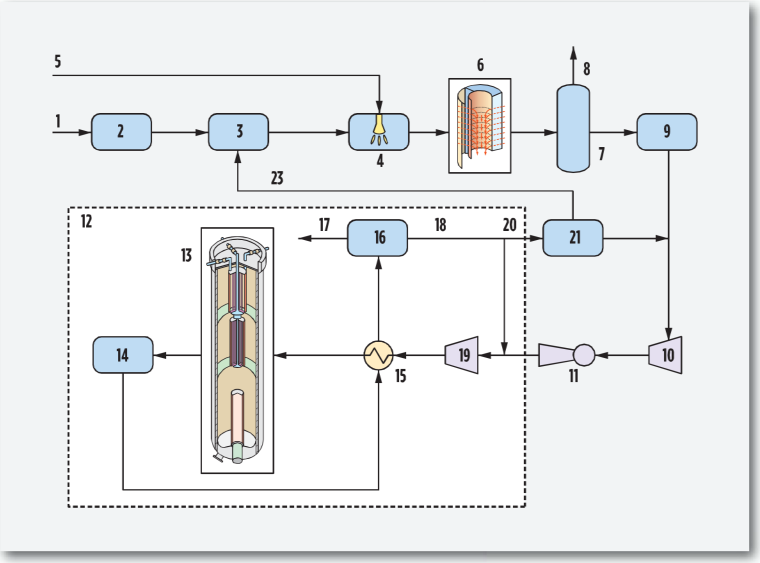
Ammonia, PURIFIER*plus,* cont.

(13). Converter effluent is cooled and then chilled by ammonia refrigeration in a unitized chiller (14). The ammonia product is separated (15) from the unreacted syngas, which is recycled back to the syngas compressor. A small purge is scrubbed with water (16) and recycled to the dryers.

Commercial plants: More than 230 single-train plants of KBR design have been contracted worldwide. Over 30 of these plants use the KBR Purifier process for capacities up to 2,700 metric tpd. Seven plants use the KBR KAAP ammonia process. KBR has 20 large ammonia plants now in design or under construction.

Licensor: Kellogg Brown & Root, LLC 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 (WHB) 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 WHB (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

Continued ▼

Ammonia, cont.

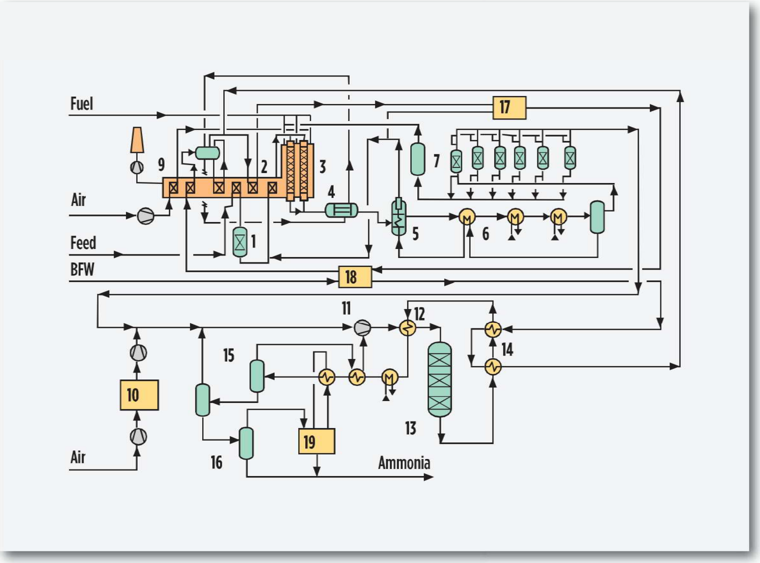
recovery of the purged hydrogen (22) back to the synthesis loop (12), while the inerts are recycled as fuel (23) back to the primary reformer (3).

Economics: Due 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: Casale has designed over 150 ammonia synthesis reactors.

Licensor: Ammonia Casale SA, Switzerland 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.

Continued ▼

Ammonia, cont.

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

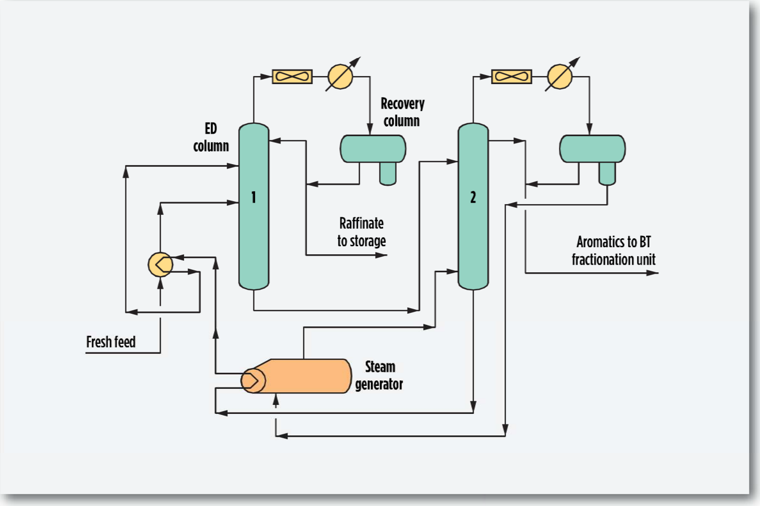
Aromatics extraction

Application: The UOP 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. Non-aromatics are separated from the top of this column and sent to storage. The ED column bottoms contain solvent and highly purified aromatics that are sent to the solvent recovery column (2). In this column, aromatics are separated from solvent under vacuum with steam stripping. The overhead aromatics product is sent to the BT fractionation section. Lean solvent is separated from the bottom of the column and recirculated back to the ED column.

Economics: The solvent used in the Sulfolane process exhibits higher selectivity and capacity for aromatics than any other commercial solvent. Using the Sulfalane process minimizes concern about trace nitrogen contamination that occurs with nitrogen-based solvents.

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 2013, UOP has licensed over 150 Sulfolane units throughout the world with 23 of these being ED Sulfolane units.



Licensor: UOP LLC, A Honeywell Company CONTACT

Aromatics extraction

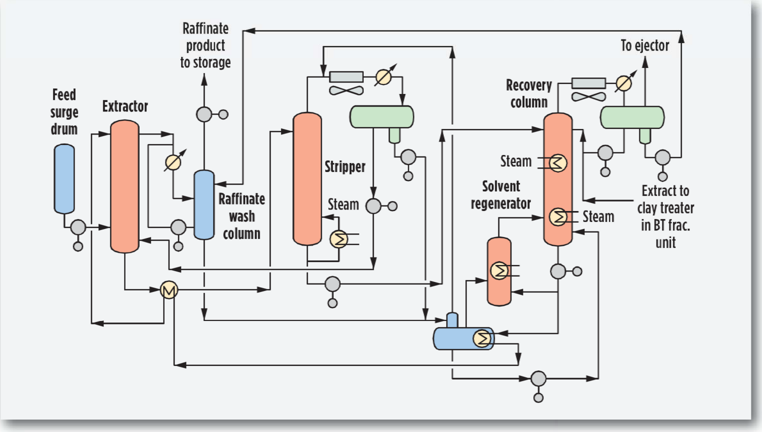
Application: The UOP Sulfolane process recovers high-purity C_6–C_9 aromatics from hydrocarbon mixtures, such as reformed petroleum naphtha (reformate), pyrolysis gasoline (pygas), or coke oven light oil (COLO), by combining extractive distillation with liquid-liquid extraction.

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.

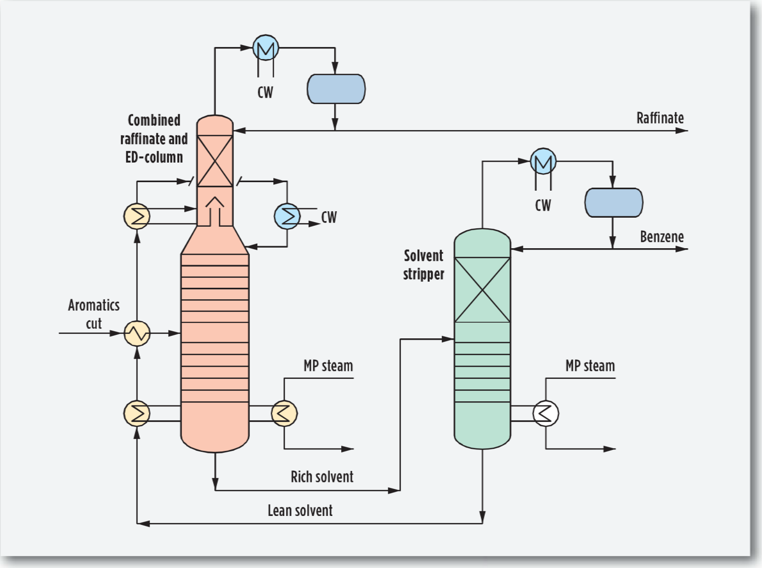


Economics: The purity and recovery performance of an aromatics extraction unit is largely a function of energy consumption. In general, higher solvent circulation rates result in better performance, but at the expense of higher energy consumption. The Sulfolane process demonstrates the lowest solvent-to-feed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

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 over 150 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 (MP) 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 MP steam is required.

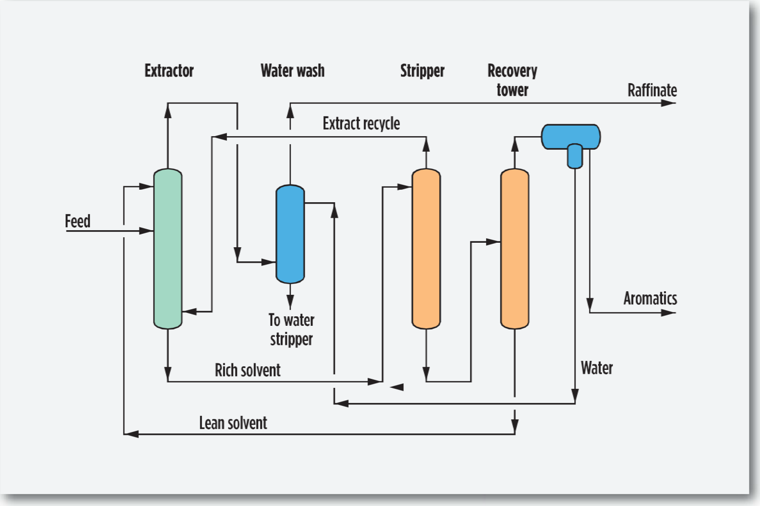
Utilities, e.g., per ton benzene

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 27 reference plants.

Licensor: Air Liquide Global E&C Solutions Germany GmbH 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.

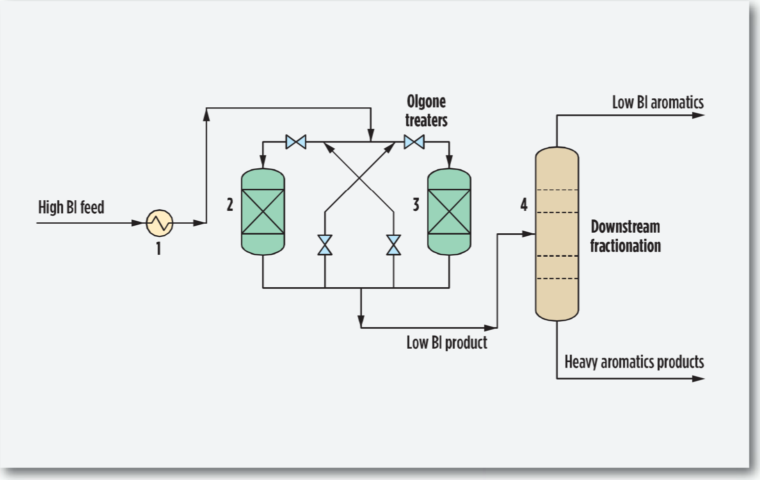
The solvent phase leaving the extractor contains aromatics and small amounts of non-aromatics. The latter are removed in the stripper (3) and recycled to the extraction column. The aromatic-enriched solvent is pumped from the stripper to the recovery tower (4) where the aromatics are vacuum distilled 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^{SM} process.

Description: The Olgone process 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 technology 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 the Olgone process 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 technology 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.

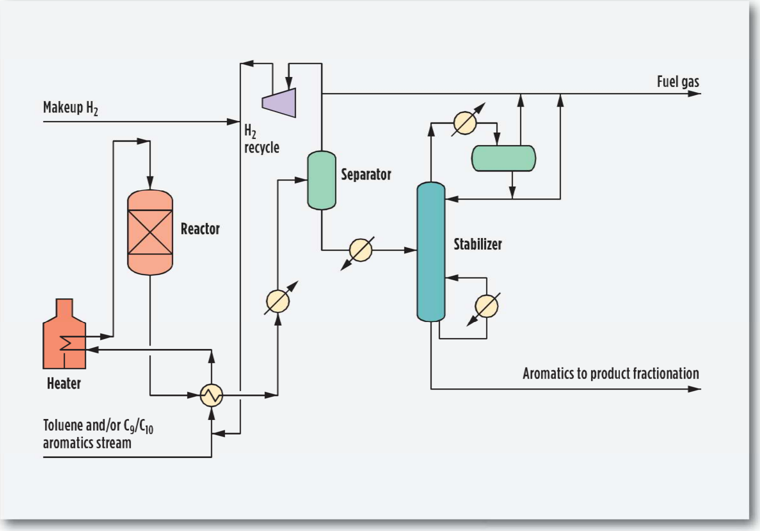
Licensor: ExxonMobil Chemical Technology Licensing LLC (retrofit applications)

Axens (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 (TransMax 501 from Clariant) and can accommodate varying ratios of feedstock, while maintaining high activity and selectivity. GT-TransAlk is especially well-suited for processing heavy aromatics (C_9–C_{10}^+) with a long run length, in order to maximize the production of xylenes from the aromatic feedstock. High-purity benzene is produced by simple distillation.

Description: The technology encompasses three main processing areas: splitter, reactor, and stabilizer sections. The overhead C_9/C_{10} aromatic product is the feed to the transalkylation reactor section. The aromatics product is mixed with toluene and hydrogen, vaporized, and fed to the reactor. The reactor gaseous product is primarily unreacted hydrogen, which is recycled to the reactor. The liquid product stream is subsequently stabilized to remove light components. The resulting aromatics are routed to product fractionation to produce the final benzene and xylene products. The reactor is charged with zeolite catalyst, which exhibits both long life and good flexibility to feed stream variations including substantial C_{10} aromatics. Depending on feed compositions and light components present, the xylene yield can vary from 25% to 32% and C_9 conversion from 53% to 67%.



Process advantages:

- 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 replacement for other transalkylation units or in grassroots 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) feed rate
Erected cost	$19 million (ISBL, 2014 US Gulf Coast basis)

Commercial plants: Three commercial licenses

Licensor: GTC Technology CONTACT

Benzene saturation

Application: GTC's process know-how can meet refiners' needs by providing a variety of cost-effective solutions, ranging from aromatics extraction to catalytic hydrogenation for benzene management in gasoline-bound streams. GTC's GT-BenZap^R process is suggested for refineries limited by economies of scale required for benzene extraction or for units located in remote areas away from benzene consumers.

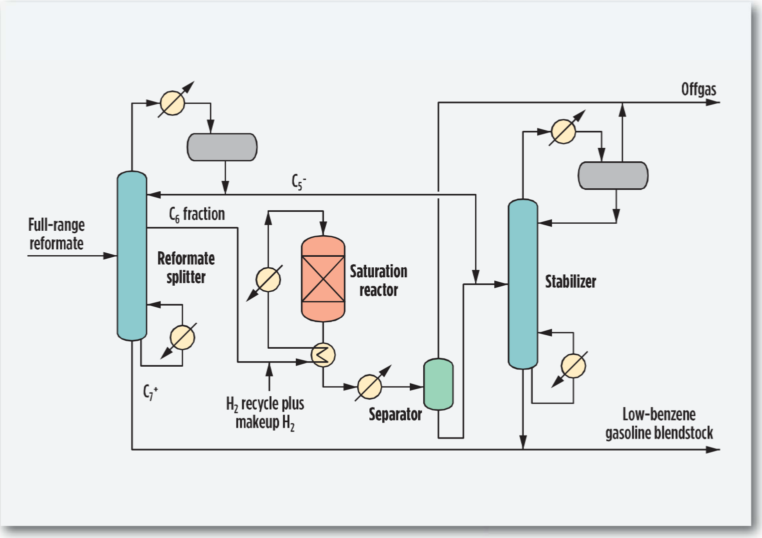
Description: GTC's GT-BenZap process features a reliable traditional design paired with a proven active hydrogenation catalyst. The process consists of hydrotreating a narrow-cut C_6 fraction, which is separated from the full-range reformate to saturate the benzene component into cyclohexane. The reformate 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 they form the full-range reformate, which is low in benzene. GTC also offers a modular construction option and the possibility to reuse existing equipment (Dividing Wall Column).

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	$13 million (ISBL, 2014 US Gulf Coast basis)

Commercial plants: Two licensed units

Licensor: GTC Technology CONTACT

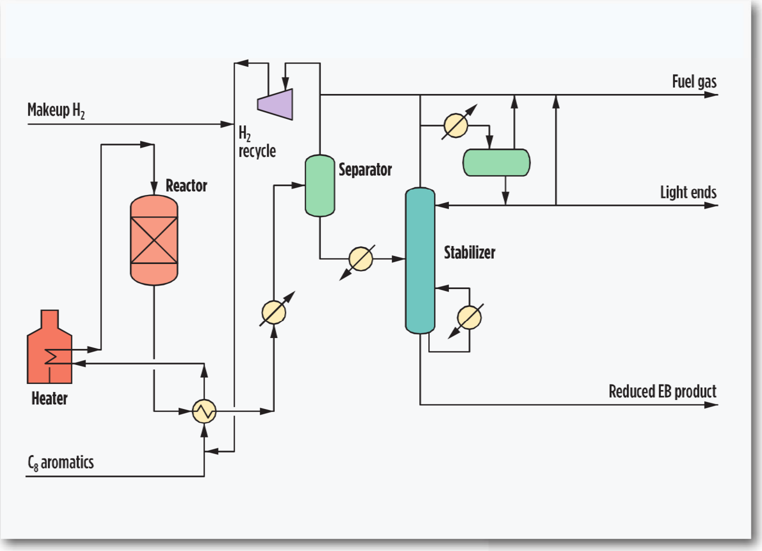
Benzene, ethylbenzene dealkylation

Application: The DX process was developed to convert ethylbenzene (EB) contained in the C_8 aromatic feedstocks to high-purity benzene plus ethane, and to 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: the reactor section and the product distillation section. In this process, a 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 dealkylated at very high conversion, and xylenes are isomerized to equilibrium.

The reactor effluent is cooled, and 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 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 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 feedstock and operation
- High EB conversion per pass can be nearly 100%
- DX products are isomerized to equilibrium composition of xylene, which relaxes the 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

Continued ▼

Benzene, ethylbenzene dealkylation, cont.

- Efficient heat integration scheme reduces energy consumption
- Turnkey package for high-purity benzene, toluene and paraxylene production available from licensor

Economics:

Basis	100,000 tpy (2,200 bpsd) feed rate
Erected cost	$10.6 million (ISBL, 2014 US Gulf Coast basis)

Commercial plants: Commercialized technology available for licensing

Licensor: GTC Technology CONTACT

Benzene

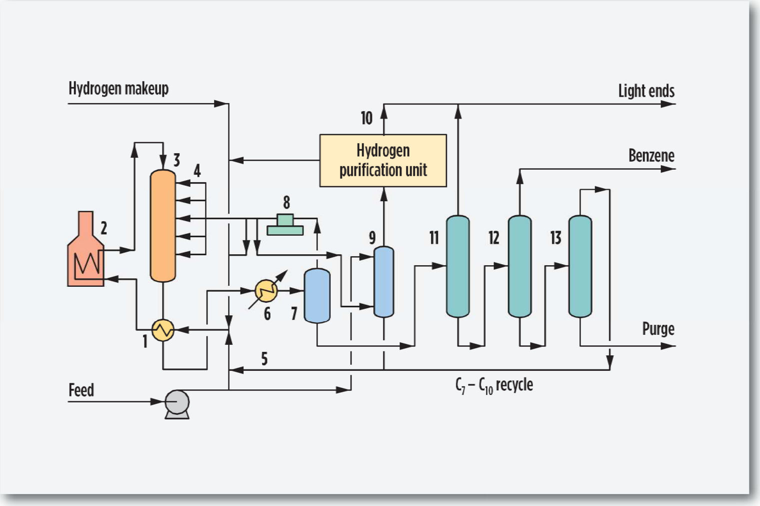
Application: Produce benzene via the hydrodealkylation of C_7–C_{11} aromatics.

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.

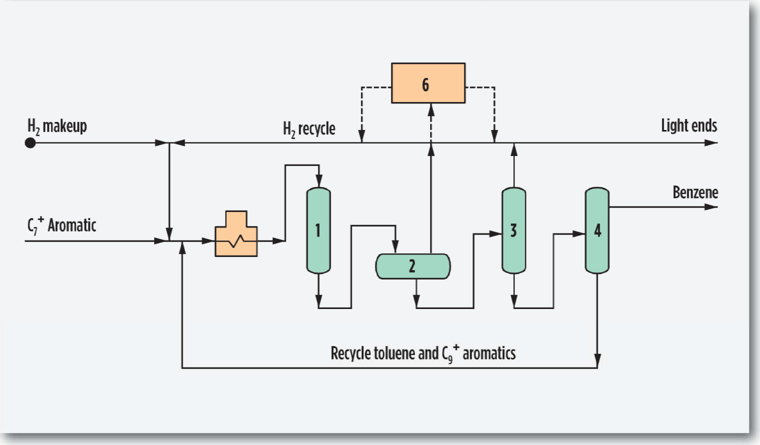


Yields: Benzene yields are close to the theoretical, owing to several techniques used such as proprietary reactor design, heavy aromatic (diphenyl) recycle and multi-point hydrogen quench.

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 from toluene and heavier aromatics. The process has been applied to pyrolysis gasoline (Pyrotol®), light coke-oven cases (Litol®) and toluene (Detol®).

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 purification of recycle hydrogen reduces the make-up hydrogen requirement.

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 are:

	Feed
Nonaromatics	3.2
Benzene	—
Toluene	47.3
C_8 aromatics	49.5
C_9^+ aromatics	—
Products, wt% of feed	
Benzene*	75.7

* 5.45°C minimum freeze point

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 31 hydrodealkylation plants have been licensed.

Licensor: CB&I CONTACT

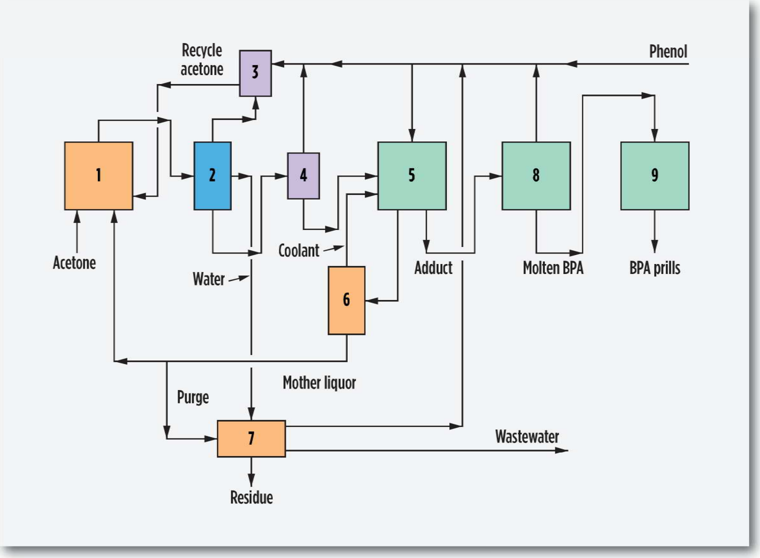
Bisphenol A

Application: The Badger BPA technology produces high-purity bisphenol A (BPA) product suitable for polycarbonate and epoxy resin applications. BPA 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 evaporative crystallization and recovery system (5) which produces adduct crystals of p,p BPA and phenol. Mother liquor from the purification system is distilled in column (6) to recover dissolved evaporative coolant. The distilled 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:

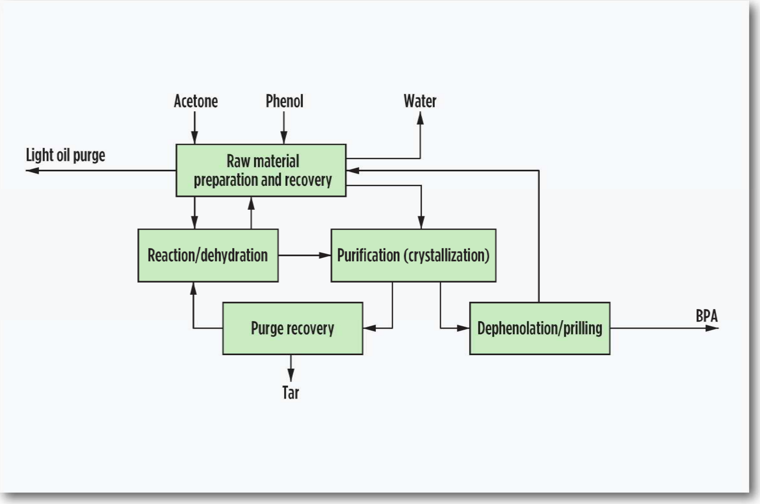
BPA w/w, wt%	99.95
Phenol, ppmw	15
Methanol color, APHA	5

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 Momentive Specialty Chemicals. Since that time, 10 other world-scale plants with a combined capacity of nearly 1.4 million metric tpy have been licensed to the Asia-Pacific and Middle East markets.

Licensor: Badger Licensing LLC CONTACT

Bisphenol A

Application: The Bisphenol A (BPA) process, owned by Mitsubishi Chemical Corp. (MCC) and offered by MCC and Kellogg Brown & Root (KBR) for license, produces the highest-quality BPA from phenol and acetone using an advanced, proprietary catalyst and an optimized purification section designed to incorporate MCC's many years of BPA operations experience.



Description: The phenol and acetone feed streams are treated in the raw material preparation and recovery section to remove impurities from the feed streams, while the water of reaction from the reaction/dehydration section is treated to maximize recovery of feed materials from the water effluent. In the reaction/dehydration section, phenol and acetone are reacted over MCC's proprietary catalyst to produce BPA and water of reaction. The reaction/dehydration section also separates water, along with unreacted acetone and small amounts of phenol, from the reactor effluent.

The dehydrated reactor effluent is then fed to the purification section. In the purification section, BPA/phenol adduct crystals are formed and separated from the mother liquor. Impurities and heavy byproducts remain in the mother liquor. Adduct crystals are sent forward, while the mother liquor is recycled to the BPA synthesis reaction. A purge is taken from the mother liquor to remove the impurities. The purge stream from the purification section is fed to the purge-recovery section, where heavy impurities are rejected from the process, and the recoverable materials are captured and recycled to the reaction/dehydration section to improve overall process yields. The adduct crystals from the purification section are fed to the dephenolation/prilling section, where the phenol component from the adduct crystals is removed. The resulting BPA stream is then fed to the prilling tower for the production of high purity BPA prills.

Process features: The advanced catalyst developed by MCC, utilizing a bound co catalyst, maximizes production of 4,4' BPA and minimizes byproduct formation, all without the use of a volatile, sulfur containing, free promoter. Elimination of the free promoter also reduces the equipment count by eliminating the need for the separation, purification, recycle and continuous makeup of the free promoter. MCC's long history and on going experience operating this technology has led to the design of crystallization and separation processes in the purification section that simplify operations to enhance process stability and onstream time, while delivering exceptional BPA purity. MCC's proprietary prilling technology produces product of superior consistency.

Commercial plants: MCC's BPA technology is currently in operation in nine plants, with startup of the first licensed plant in 1991.

Licensor: Kellogg Brown & Root, Inc. and Mitsubishi Chemical Corp.
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.

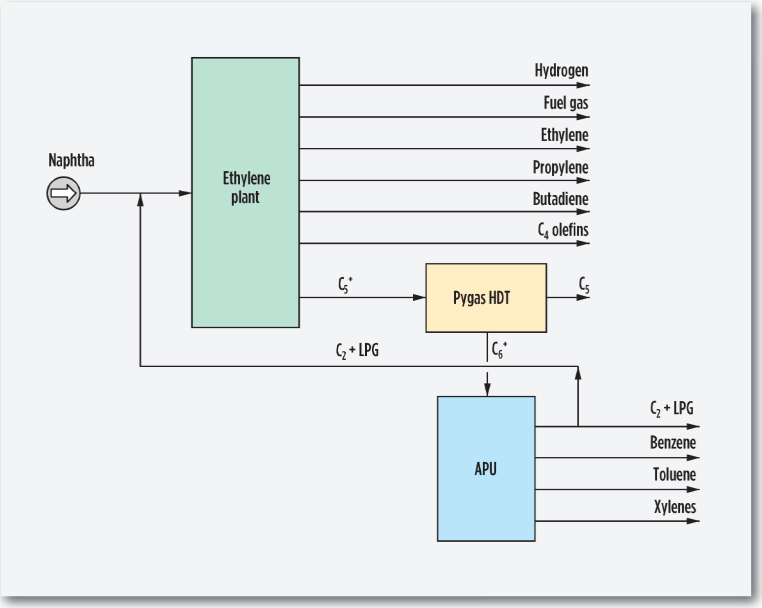
The reaction section product delivers after standard distillation high-purity individual BTX cuts, and there is no need for further extraction.

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%

Continued ▼

BTX aromatics and LPG, cont.

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
- 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 and SK Corp. CONTACT

BTX aromatics

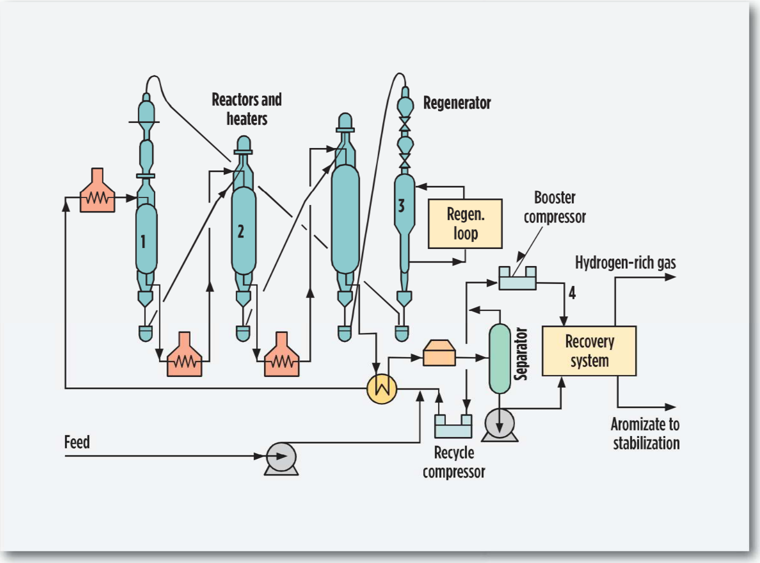
Application: To produce high yields of benzene, toluene, xylenes (BTX) and hydrogen from hydrotreated naphtha via the CCR Aromizing process coupled with RegenC continuous catalyst regeneration technology. Benzene and toluene cuts are fed directly to an aromatics extractive distillation unit. The xylenes 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 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: One hundred and ten 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.

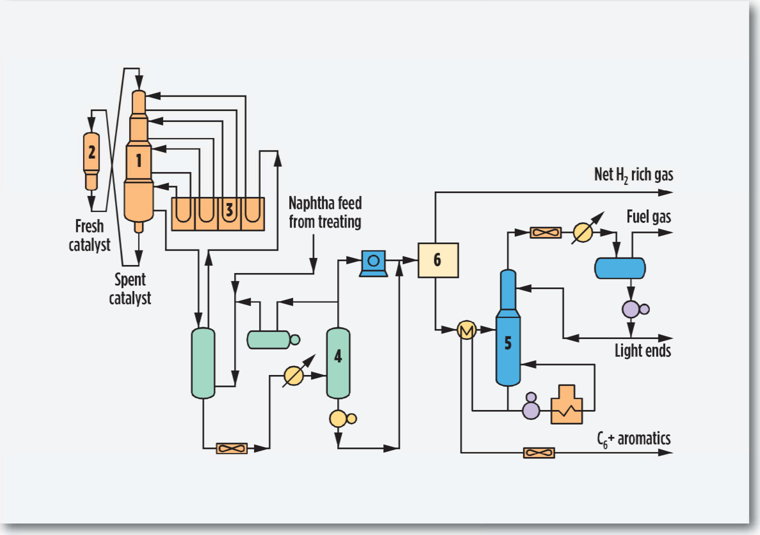
Reactor effluent is separated into liquid and vapor products (4). Liquid product is sent to a stabilizer (5) to remove light ends. Vapor from the separator is compressed and sent to a gas-recovery section (6) to separate 90%⁺-pure hydrogen byproduct. A fuel gas byproduct of LPG can also be produced. UOP's latest R-334 series catalyst maximizes aromatics yields.

Yields: Typical yields from lean Middle East naphtha:

H_2, wt%	3.9
C_5^+, wt%	88

Economics: Estimated ISBL investment per metric tpy of feed:

US$	65–80
Utilities per metric ton feedrate	
Electricity, kWh	100
Steam, HP, metric ton	0.13
Water, cooling m^3	5
Fuel, MMkcal	0.53



Commercial plants: There are 250 units in operation and over 40 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.

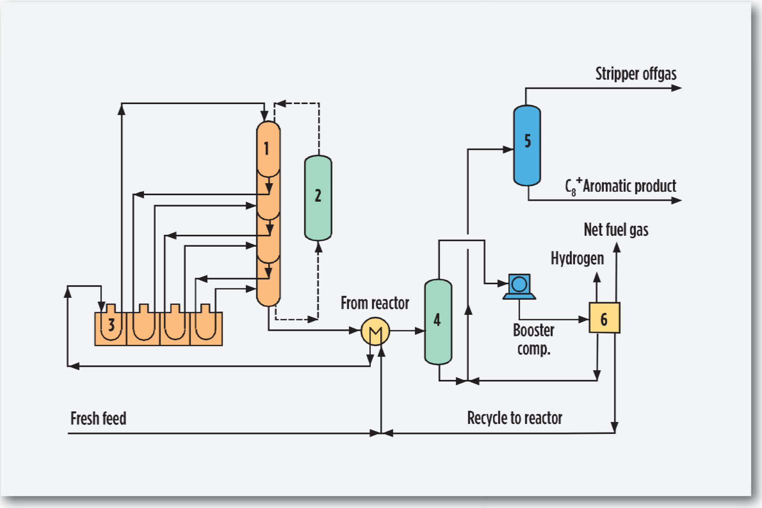
Yields: Total aromatics yields as a wt% of fresh feed is approximately 56%, but varies depending on feed composition. Hydrogen yield is approximately 5 wt% fresh feed. Typical product distribution is 25% benzene, 39% toluene, 24% C_8 aromatics and 12% C_9^+ aromatics.

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

Investment, US$ per metric ton of feed	250–350

Typical utility requirements, unit per metric ton of feed

Electricity, kWh	102
Steam, HP, 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. The second Cyclar unit was commissioned in 1999 and operated until 2013, processing 1.3 million metric tpy of mixed C_3/C_4 feedstock.

Licensor: UOP LLC, A Honeywell Company CONTACT

BTX extraction

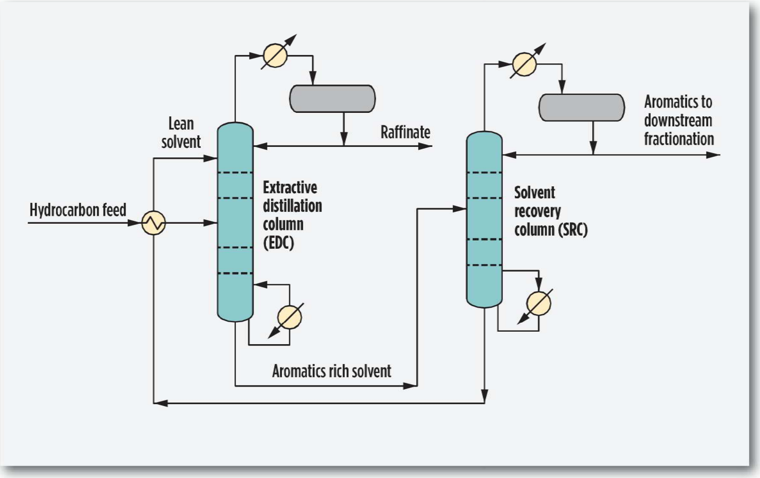
Application: GT-BTX® is an aromatics recovery technology that uses extractive distillation (ED) to purify benzene, toluene and xylene (BTX) from refinery or petrochemical aromatics streams such as catalytic reformate, pyrolysis gasoline (pygas) or coke oven light oil (COLO).

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 raffinate product and 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. A stripping stream 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 ED systems
- Energy integration reduces 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	$16 million (ISBL, 2014 US Gulf Coast basis)

Commercial plants: 27 commercial licenses of new and revamp units

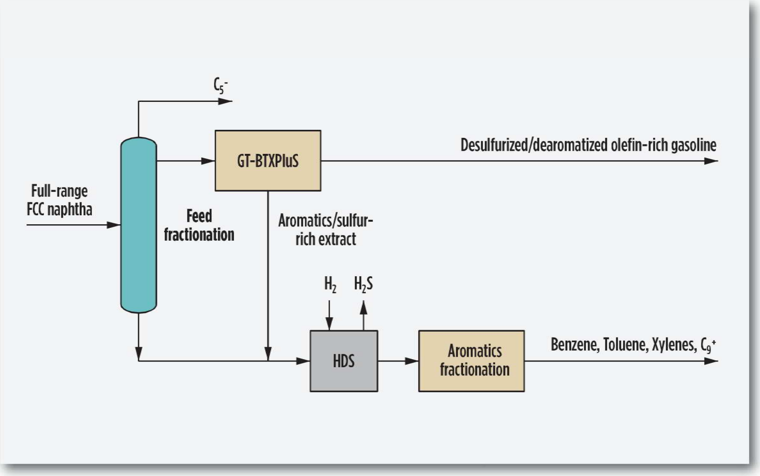
Licensor: GTC Technology CONTACT

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 change in octane value. An alternative use of GT-BTX PluS is to generate a large volume of aromatics to produce paraxylene without the requirement of a typical naphtha reformer unit. The aromatics recovery is especially attractive for use with feedstocks produced from high-severity FCC operations.

The process is optimally installed on the FCC mid-cut naphtha stream. GT-BTX PluS removes all thiophenes and some of the mercaptan species from the FCC gasoline feed. The olefin-rich raffinate can be sent directly to the gasoline pool for blending, or to a caustic treating unit to remove the mercaptan-type sulfur compounds before being sent to the gasoline. The desulfurized aromatics extract stream can be directly fed into petrochemical production units instead of recycling to the naphtha reformer. GT-BTX PluS provides an effective solution for meeting today's clean-gasoline requirements and gives refiners the ability to convert lower-value gasoline components into higher-value petrochemicals.

Description: The optimum feed is the mid-fraction of FCC gasoline from 70°C to 150°C. This material is fed to the GT-BTX PluS unit, which extracts the sulfur and aromatics from the hydrocarbon stream. The sulfur-containing 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 is free of olefins, hydrogen consumption and operating costs are greatly reduced. In contrast, conventional desulfurization schemes must process the majority of the gasoline through hydrotreating units to remove sulfur, which inevitably results in olefin saturation, octane downgrade and yield loss.



FCC gasoline 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 an aromatization unit to further increase BTX production.

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 columns 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.

Continued ▼

BTX recovery from FCC gasoline, cont.

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) feed rate
Erected cost	$32 million (ISBL including fractionation and HDT, 2014 US Gulf Coast basis)

Commercial plants: Four licensed units

Licensor: GTC Technology CONTACT

Butadiene from n-butane

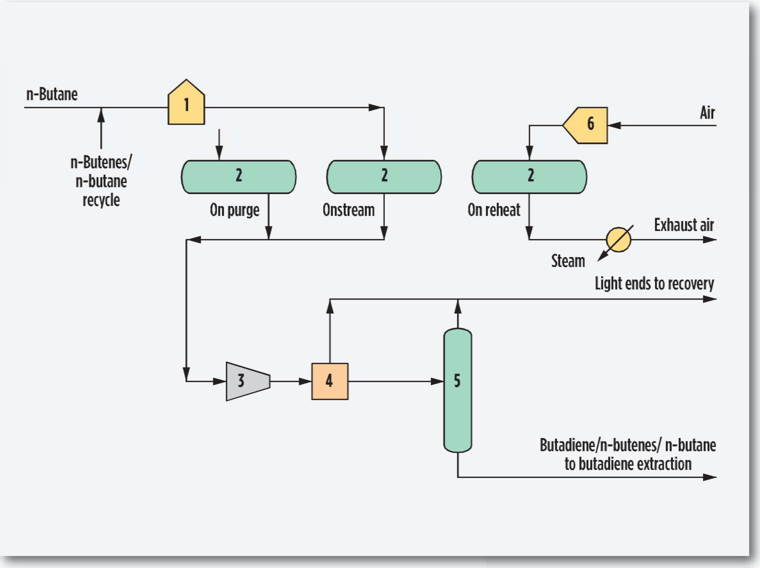
Application: Technology for dehydrogenation of n-butane to make butadiene. The CATADIENE® process uses specially formulated proprietary catalysts from Clariant.

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 switched to another reactor 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 Clariant 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 19 plants. Of these, three are currently in operation, producing 270,000 mtpy of butadiene.

Licensor: CB&I 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.

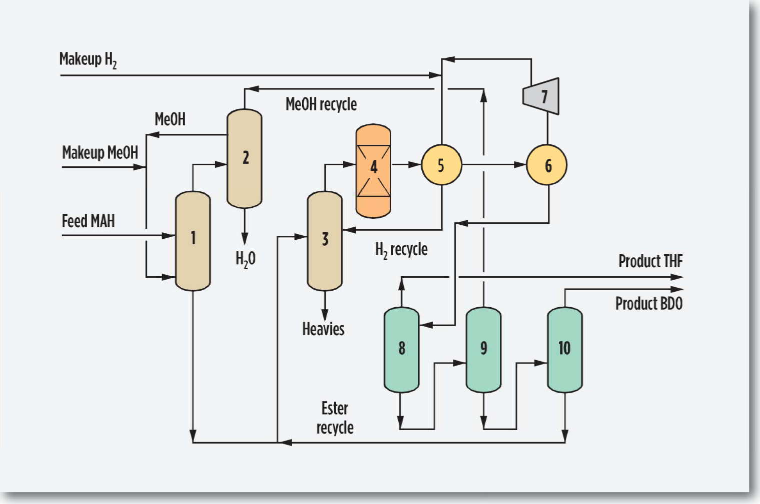
The ester is then fed directly to the low-pressure, vapor-phase hydrogenation system where it is vaporized into an excess of hydrogen in the vaporizer (3) and fed to a fixed-bed reactor (4), containing a copper catalyst. The reaction product is cooled (5) and condensed (6) with the hydrogen being recycled 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, 14 plants have been licensed with a total capacity of 800,000 tpy.

Licensor: Johnson Matthey Davy Technologies Ltd., 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 IFPEN/Axens in cooperation with SABIC.

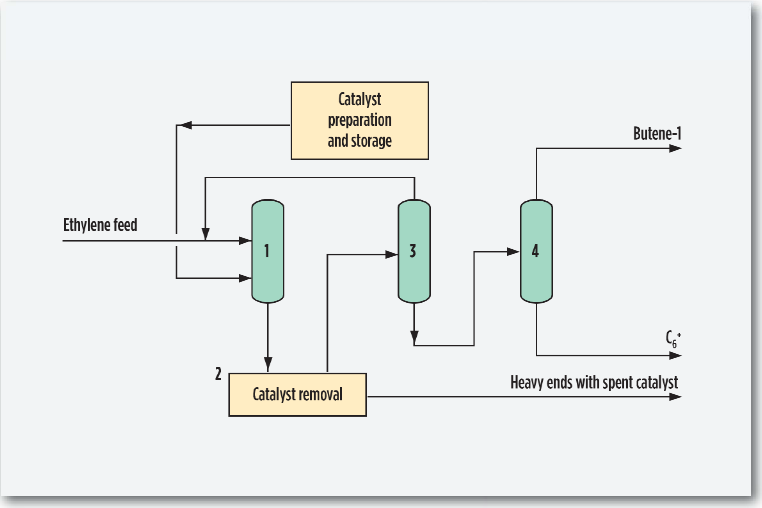
Description: Polymer-grade ethylene is oligomerized in a liquid-phase reactor (1) with a homogeneous liquid system that has high activity and selectivity.

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: Thirty-one AlphaButol units have been licensed producing 728,000 tpy. Eighteen units are in operation.

Licensor: Axens CONTACT

Butene-1

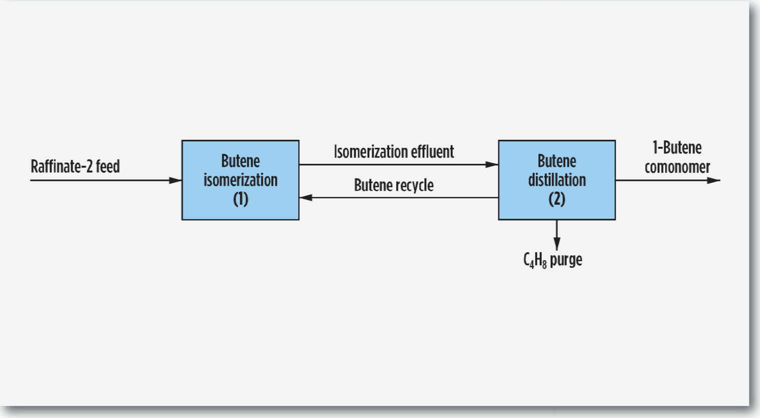
Application: To produce high-purity butene-1 from a mixed C_4 stream using CB&I's comonomer production technology (CPT). The feedstock can contain any amount of butene-1, butene-2 and butane.

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)

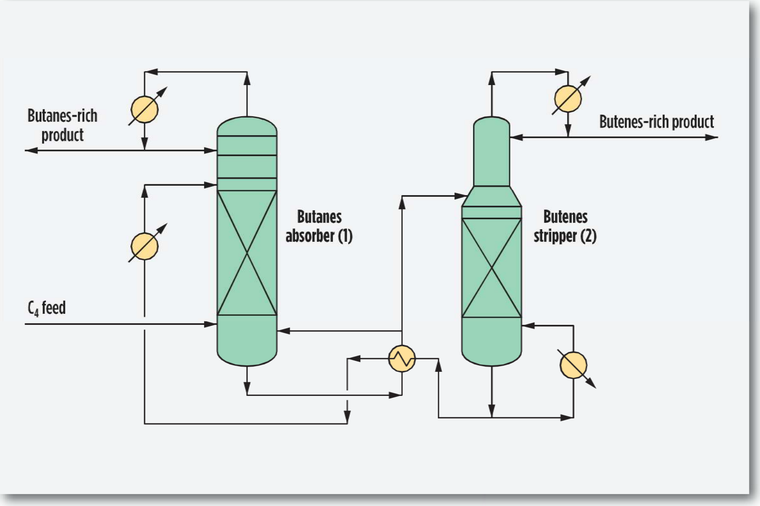
Steam + fuel, MMKcal	1.3
Water, cooling (10°C rise), m^3	190
Electricity, MWh	1.0

Commercial plants: The process has been demonstrated in a semi-commercial unit in Tianjin, China. The first CPT facility for butene-1 production started up in early 2014 and produces 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: CB&I 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 "on-purpose" 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: 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/CB&I 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.

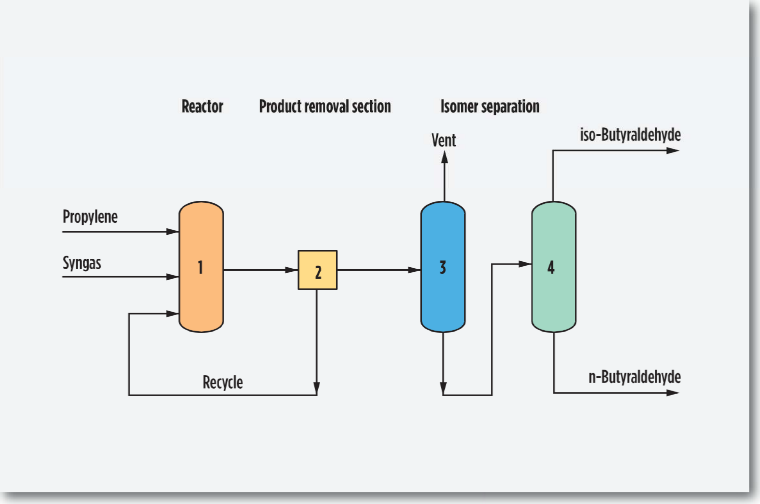
Description: The process reacts propylene with a 1:1 syngas at low pressure ($<$ 20/kg/cm^{2}g) in the presence of a rhodium catalyst complexed with a ligand (1). Depending on the desired selectivity, the hydroformylation reaction produces normal and iso–butyraldehyde ratios, which can be varied from 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: Forty-two projects worldwide since 1978.

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

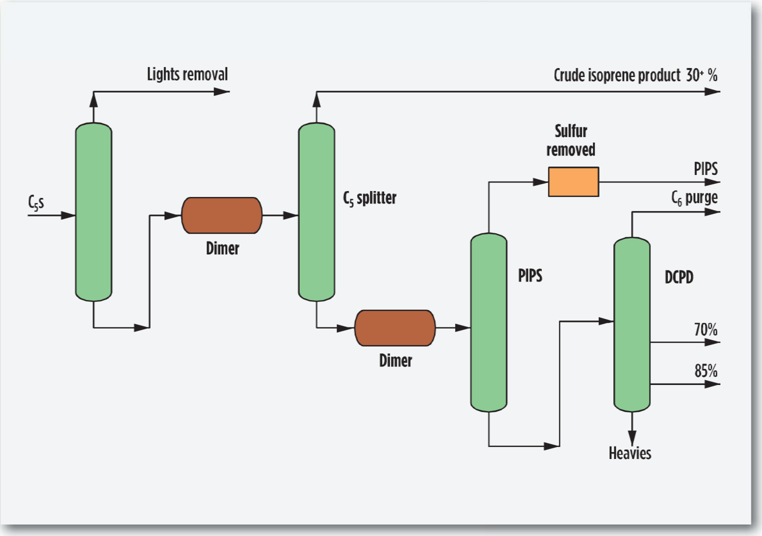
C_5 components recovery

Application: GTC offers GT-C_5℠, an optimized technology for producing valuable C_5 and C_{10} components that are suitable for producing hydrocarbon resins.

Description: The GT-C_5 process consists of five operating steps: 1) Fractionation to remove light boiling components; 2) Two-stage dimerization reaction for selective production of dicyclopentadiene (DCPD) and codimers; 3) Fractionation section to remove crude isoprene and similar boiling components; 4) Second-stage selective dimerization reaction to enhance the DCPD yield; 5) Fractionation section to produce piperylenes and DCPD suitable for hydrocarbon resin production.

Process advantages:

- Proprietary staged dimerization process to gain more flexibility
- Capable of producing DCPD stream loaded with co-dimers to minimize external purchase for hydrocarbon resin production
- Flexibility to operate the unit to maximize the isoprene recovery
- Optimum energy scheme to produce piperylene stream rich in components that are ideally suited for C_5 resin production
- Improved isoprene concentration in the crude isoprene stream
- Capability to produce up to 85% pure DCPD



Commercial plants: One licensed unit

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

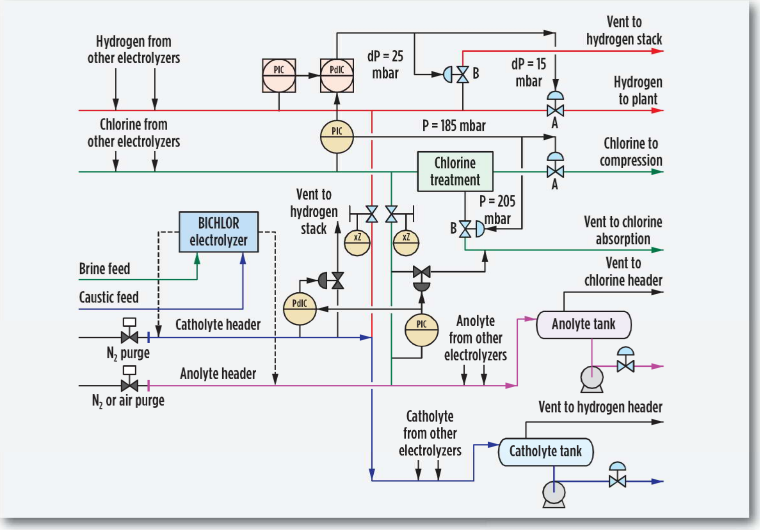
Low maintenance costs:
- Modular technology minimises down time and personnel
- Long life electrode coatings
- Electrodes can be re-coated "IN PAN"

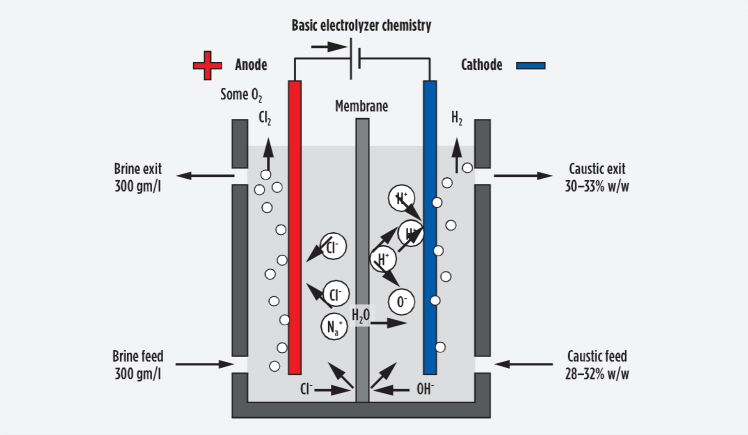
BICHLOR operating data:

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





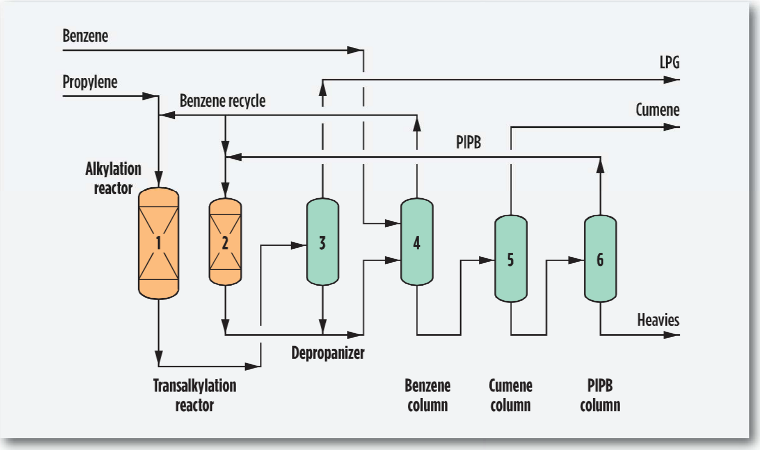
Cumene

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 22 operating plants with a combined capacity of nearly 8 million metric tpy. In addition, six grassroots plants and one SPA revamp are in the design or construction phase.

Licensor: Badger Licensing LLC CONTACT

Cumene

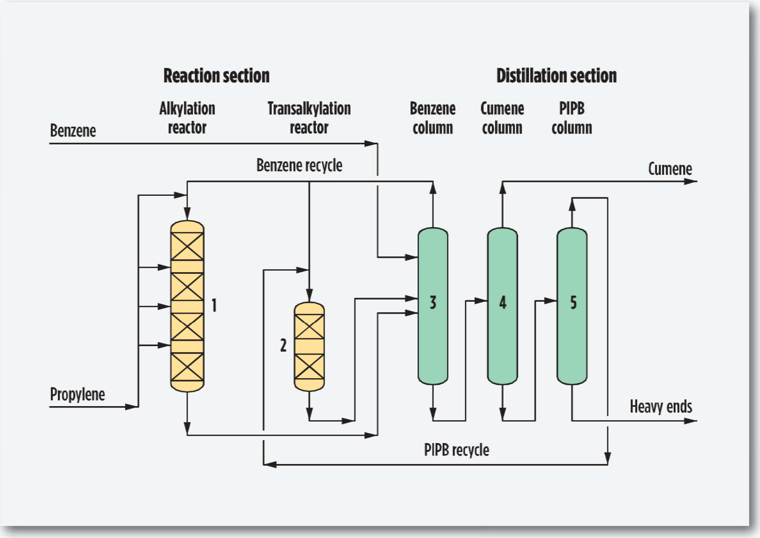
Application: The Versalis/CB&I process is used to produce high-purity cumene from propylene and benzene using a proprietary zeolite catalyst provided by Versalis. The process can handle a variety of propylene feedstocks, ranging from polymer grade to refinery grade.

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 effluents are 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 as a result of its unique zeolite catalyst. 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 ▼

Cumene, cont.

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 has been used in Versalis' 400,000 metric tpy cumene plant at Porto Torres, Sardinia. Another unit is currently under construction.

Licensor: CB&I CONTACT

Cumene

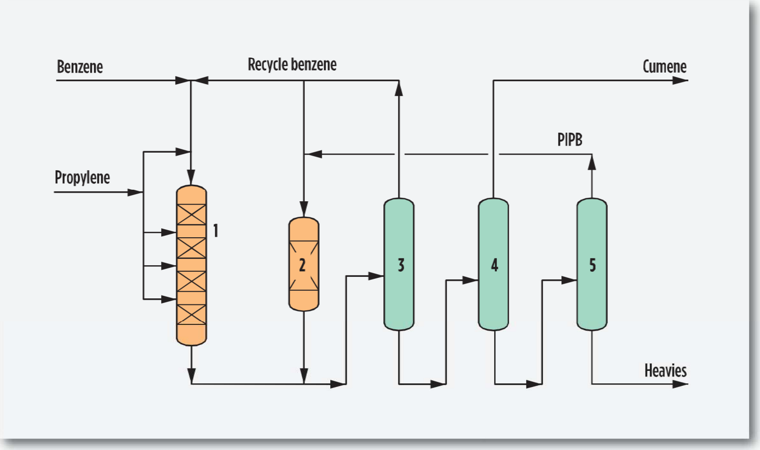
Application: The Q-Max process produces high-quality cumene (isopropylbenzene) by alkylating benzene with propylene (typically refinery, chemical or polymer grade) using zeolitic catalyst technology.

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 wt%–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 2013 US Gulf Coast



Investment, US$/tpy (270,000 tpy of cumene) 133 ± 50%

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: Twenty-two Q-Max projects have been licensed with a total cumene capacity of 6 million tpy.

Licensor: UOP LLC, A Honeywell Company CONTACT

Cyclohexane

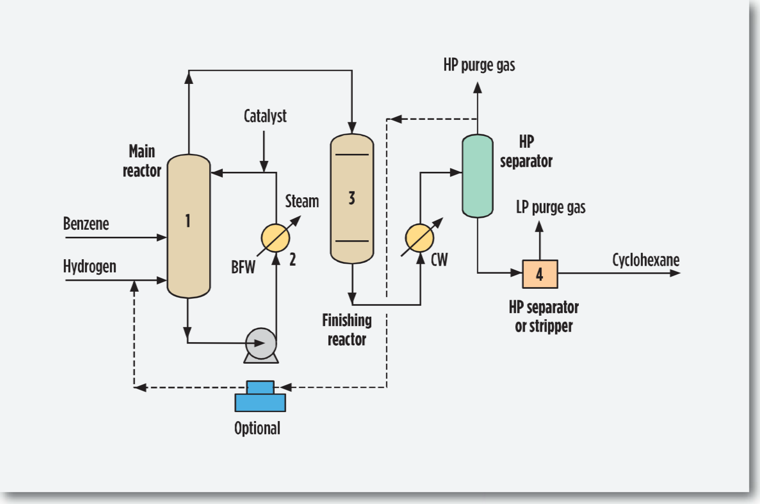
Application: Produce high-purity cyclohexane by liquid-phase catalytic hydrogenation of benzene.

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 pump-around 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

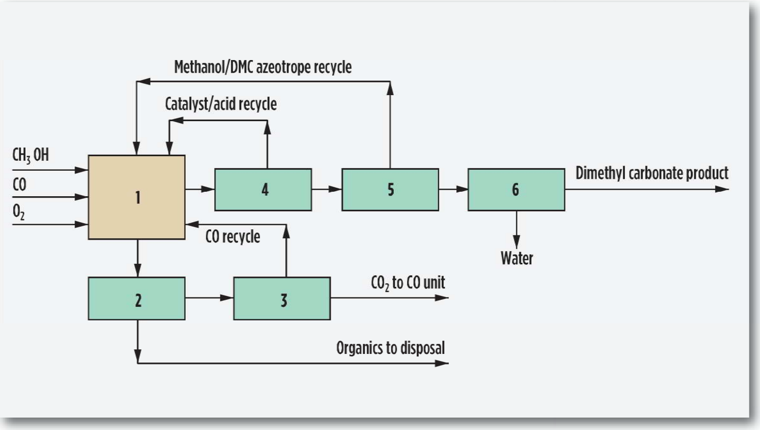
Dimethyl carbonate

Application: The Versalis/CB&I 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 CB&I also offers the Versalis/CB&I diphenyl carbonate (DPC) process, there are opportunities for energy integration as well.



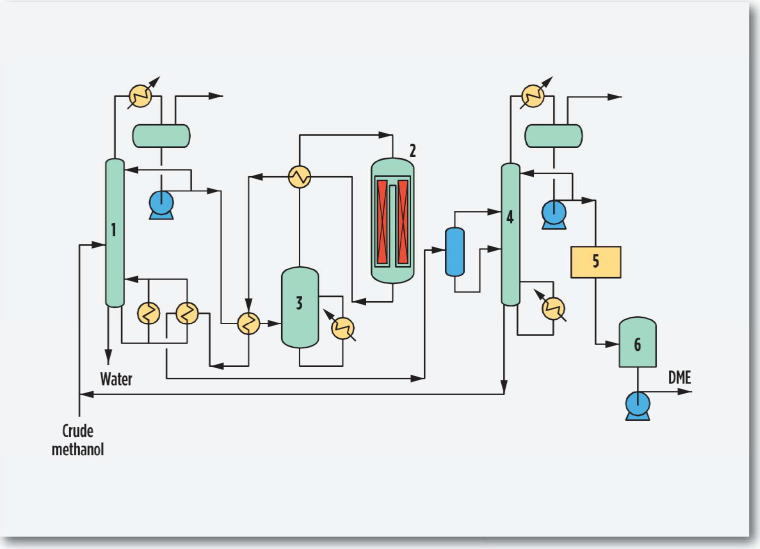
Typical yields and product quality:

	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: CB&I CONTACT

Dimethyl 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 1.0 MPaG–2.0 MPaG. The inlet temperature is 220°C–275°C, and the outlet is 300°C–375°C. Methanol one-pass conversion to DME is 70%–75% in the reactor. The reactor effluents—DME with byproduct water and unconverted methanol—are fed to a DME column (4) after heat recovery and cooling.

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

Economics: The methanol consumption for DME production is approximately 1.4 ton 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 was started up in 2006, with a third 210,000-tpy facility in 2007 and a fourth 140,000-tpy facility in 2008.

Licensor: Toyo Engineering Corp. (TOYO) CONTACT

Dimethylformamide

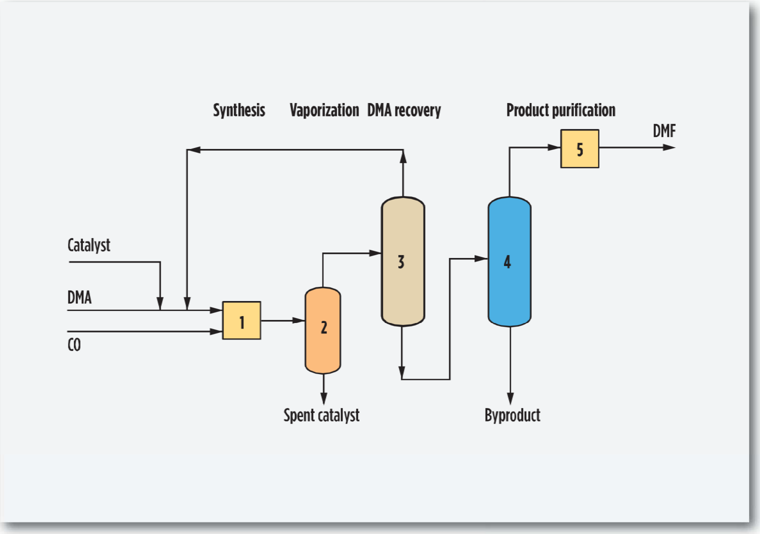
Application: To produce dimethylformamide (DMF) from dimethylamine (DMA) and carbon monoxide (CO).

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: Johnson Matthey Davy Technologies Ltd., UK CONTACT

Diphenyl carbonate

Application: The Versalis/CB&I 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.

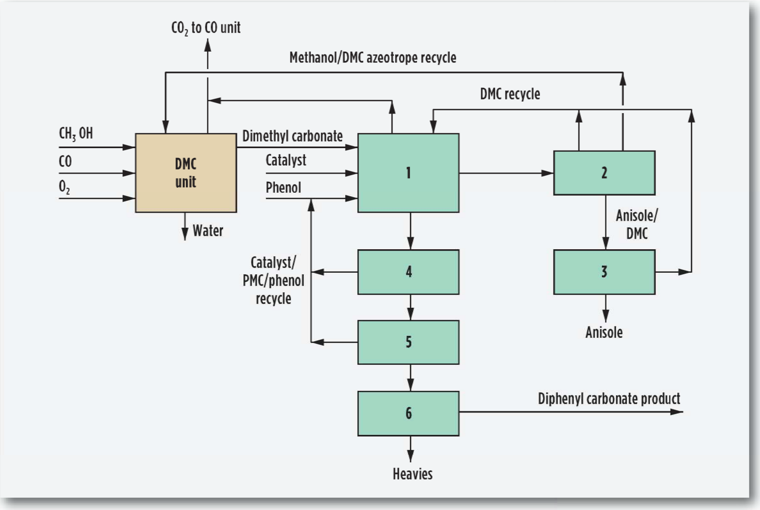
Phenol, DMC and catalyst are fed to the PMC reaction section (1) where a small amount of anisole and CO_2 are also produced. A "light" stream, containing mainly methanol, DMC and anisole, is fed to the azeotropic distillation section (2), from which a methanol-DMC azeotrope is recycled back to the DMC 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 CB&I also offers the Versalis/CB&I 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	0.89



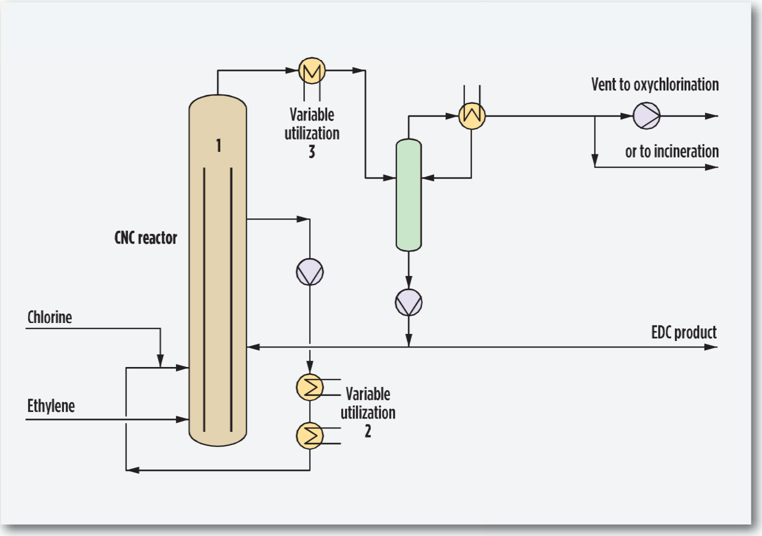
Main products	
Diphenyl carbonate	1.00
CO_2 to CO unit	0.13
Anisole (Methoxybenzene)	0.01

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 five different plants of various sizes. The largest plant capacity project using Versalis/CB&I DPC technology has 115,000 metric tpy of DPC capacity.

Licensor: CB&I CONTACT

Direct chlorination (DC)



Application: 1,2 dichloro ethane (EDC) is produced by an exothermic reaction from the feedstocks ethylene and chlorine in the Vinnolit Compact (C) Natural (N) Circulation (C) boiling reactor (CNC). EDC is used as feedstock for vinyl chloride monomer (VCM) production.

Description: Vinnolit's new high-temperature Direct Chlorination (DC) reactor provides an energy-efficient technology for the production of EDC. It is not necessary to purify the manufactured EDC for use as furnace feed EDC.

The liquid phase reaction of ethylene and chlorine releases 218 kJ/mol of produced EDC. In a simple carbon-steel CNC reactor (1), chlorine and ethylene are separately solved in EDC before the reaction takes place. Chlorine is dissolved in a small pre-cooled EDC stream that has been bled from the reactor. The heat can be utilized in a heat exchanger (2). In combination with the special Vinnolit catalyst, this method significantly minimizes byproduct formation.

Downstream of the reaction zone, the reactor content boils due to the lower static pressure, keeping the thermosyphon effect for circulation. The EDC vapor leaves the reactor at the top and enters a heat exchanger (3), which condenses the EDC vapor. The reaction heat is recovered by means of heating EDC distillation columns, by warm water production for PVC drying or by concentration of caustic solution in the chlorine plant.

Due to the high yields, the Vinnolit DC reactor can be operated without a tailgas reactor in:

a) Stand-alone mode, with vents fed to an incineration unit
b) As part of a complete VCM plant, where the vent gas stream can be fed to the oxychlorination reactor in order to recover the remaining ethylene quantities.

Important features:

- Low manufacturing costs: Carbon steel as main construction material together with high raw-material yields (99,9% for ethylene and 99,8% for chlorine) and a product quality that requires no further treatment ensure a highly competitive process with low production costs. The CNC reactor is simple, because no EDC washing, wastewater treatment or EDC distillation facility is necessary. A continuous catalyst makeup is not required.
- Energy saving: Vinnolit's DC process significantly reduces the steam consumption. The saving of steam equivalent is approx. 700 kg for each ton of produced EDC. The reaction heat can be used in the EDC distillation, PVC drying or caustic concentration unit.
- Low capital costs: A simple design with a minimized number of equipment results and mild steel as construction material results in low investment costs.

Continued ▼

Direct chlorination (DC), cont.

- No environmental effluents: The closed catalyst cycle, the vent gas recovery in the Oxychlorination unit and the produced EDC quality, which requires no further treatment, generate no liquid effluents.
- Operability and maintainability: A corrosion-inhibiting catalyst system, and simple equipment without major moving parts keep the maintenance costs low.

Economics:

Consumption figures in kg/1,000 kg of product	a) Stand-alone	b) Integrated in VCM plant
Ethylene	284,5	283,1
Chlorine	718,6	718,6
Yields in mass percent		
Ethylene	99,65	99,9
Chlorine	99,8	99,8
Utility consumption per 1,000 kg of product		
Steam consumption in kg	0	
Steam generation in kg	800	
Erection costs built on US Gulf Coast in 2013, excluding investments outside battery limit in US $	for 320,000 metric tpy EDC 20 million	

Installations: Since 1965, Vinnolit has licensed its modern Direct Chlorination process with an installed capacity of around 10 million metric tpy in plants worldwide.

Reference: R. A. Meyers (Ed.), *Handbook of Petrochemicals Production Processes,* pp 18.10–18.12, McGraw-Hill (2005)

Licensor: Vinnolit GmbH & Co. KG CONTACT

Ethyl acetate

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

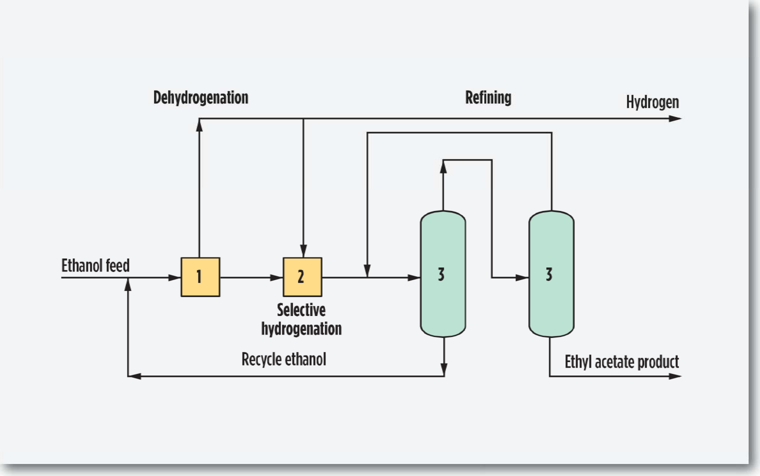
Description: Ethanol is heated and passed through a catalytic dehydrogenation reactor (1) where part of the ethanol is dehydrogenated to form ethyl acetate and hydrogen. The product is cooled in an integrated heat-exchanger system; hydrogen is separated from the crude product. The hydrogen is mainly exported. Crude product is passed through a second catalytic reactor (2) to allow "polishing" and remove minor byproducts such as carbonyls.

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

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

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

Feedstock	1.12 tons of ethanol
Product	45 kg of hydrogen



Commercial plants: The technology has been developed during the mid to late 1990s. The first commercial plant is a 50,000-tpy plant in South Africa, using synthetic ethanol. There are two additional commercial plants (50,000 tpy and 100,000 tpy) in China using fermentation ethanol.

Licensees: Three since 1998.

Licensor: Johnson Matthey Davy Technologies Ltd., UK CONTACT

Ethylbenzene

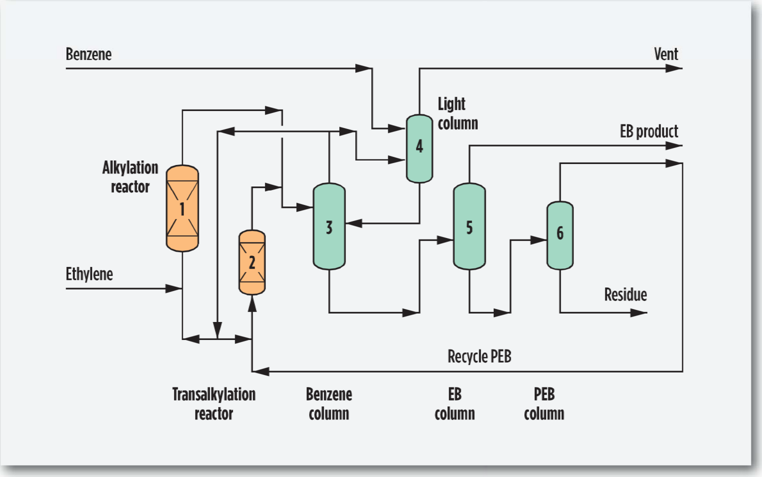
Application: To produce ethylbenzene (EB) from benzene and a polymer-grade ethylene or an ethylene/ethane feedstock using the Badger EBMax^{TM} process and proprietary ExxonMobil alkylation and transalkylation catalysts. The technology can be applied in the design of grassroots units, upgrading of existing vapor-phase or liquid-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 trade 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 over 50 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

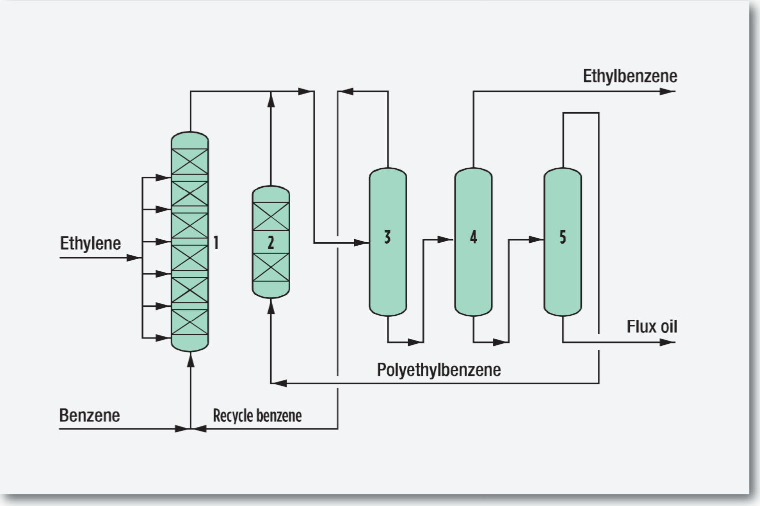
Application: State-of-the-art technology to produce high-purity ethylbenzene (EB) by liquid-phase alkylation of benzene with ethylene. The CB&I/UOP EB*One* process uses specially formulated, proprietary zeolite catalyst from UOP. The process can handle a range of ethylene feed compositions ranging from chemical grade (70% ethylene/30% ethane) to polymer grade (99.95+%).

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 up to a seven 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 EB*One* 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 to –5

Commercial plants: EB*One* technology has been selected for more than 45 projects worldwide, of which 25 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%.

Licensor: CB&I and UOP LLC CONTACT

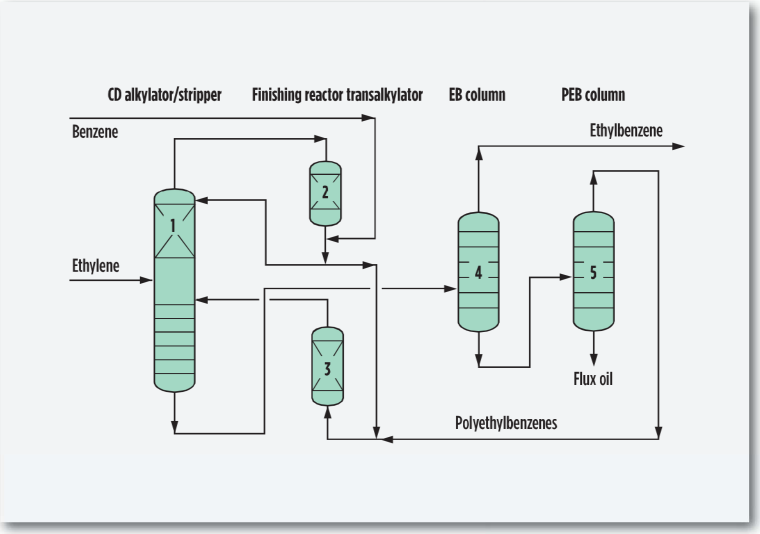
Ethylbenzene

Application: Advanced technology to produce high-purity ethylbenzene (EB) by alkylating benzene with ethylene using patented catalytic distillation (CD) technology. The CD 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 (PEB) and flux oil. The PEBs 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 from ethylene plants or FCC units containing as little as 10 mol% ethylene. Reactors can be designed for up to seven years of uninterrupted run-length. The process does not produce any hazardous effluent. Low operating temperatures allow using carbon steel for all equipment.

Yields and product quality: Both the alkylation and transalkylation reactions are highly selective—producing few byproducts. The EB product has 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: Three 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: CB&I 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.

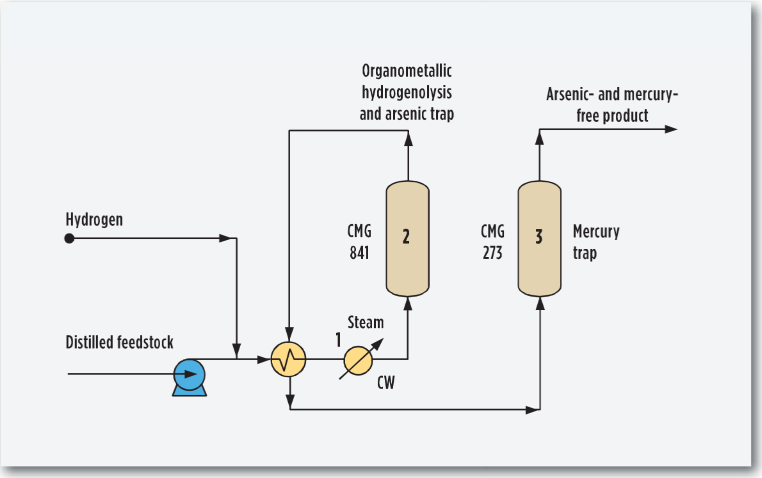
Description: Two RAM processes are available. In the presence of metallic mercury, a RAM I adsorber will be effective. In the presence of organometallic mercury and/or arsenic and/or lead, a two-stage process (called RAM II) will effectively purify the stream, whatever its endpoint.

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*

* 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: Sixteen RAM units have been licensed worldwide.

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

Licensor: Axens CONTACT

Ethylene glycol (EG)

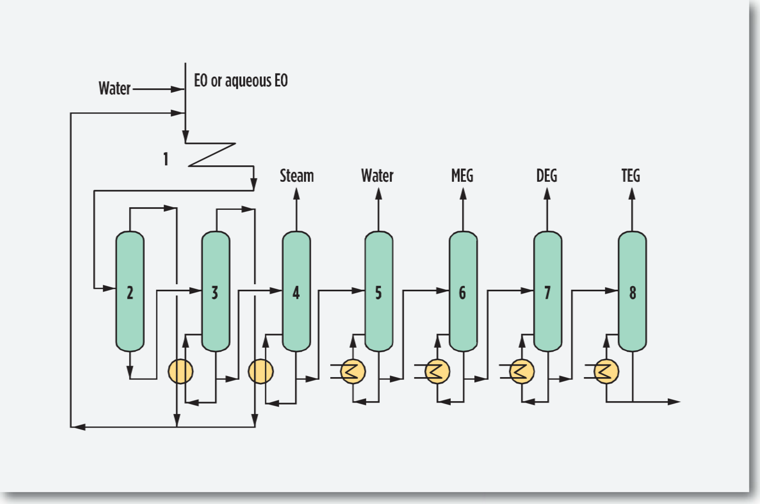
Application: To produce ethylene glycols—mono-ethylene glycol (MEG), di-ethylene glycol (DEG), and tri-ethylene glycol (TEG)—from ethylene oxide (EO).

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 MEG, with DEG and TEG as co-products in minor amounts. Excess water, required to achieve a high selectivity to MEG, is evaporated in a multistage 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 polyethylene terephthalate (PET) producers.



Installations: Since 1958, more than 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, mono (MEG)

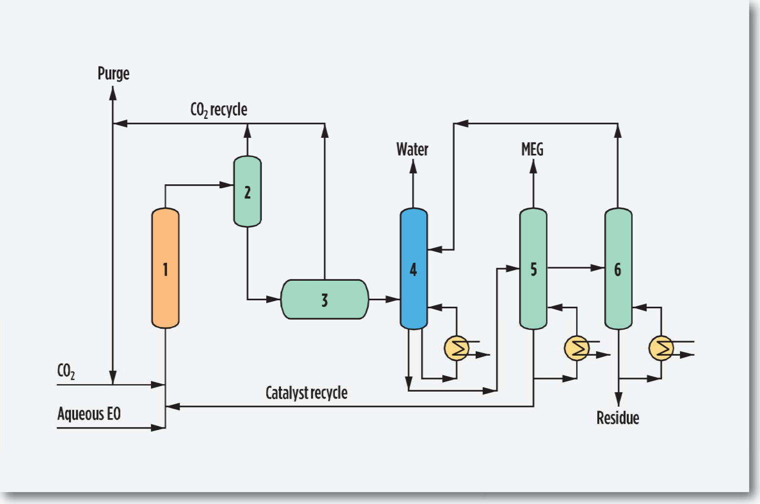
Application: To produce mono-ethylene glycol (MEG) from ethylene oxide (EO).

Description: EO in an aqueous solution is reacted with carbon dioxide (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.



Installations: Three commercial plants are currently in operation, the largest having a MEG capacity of 750,000 tpy in Singapore.

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

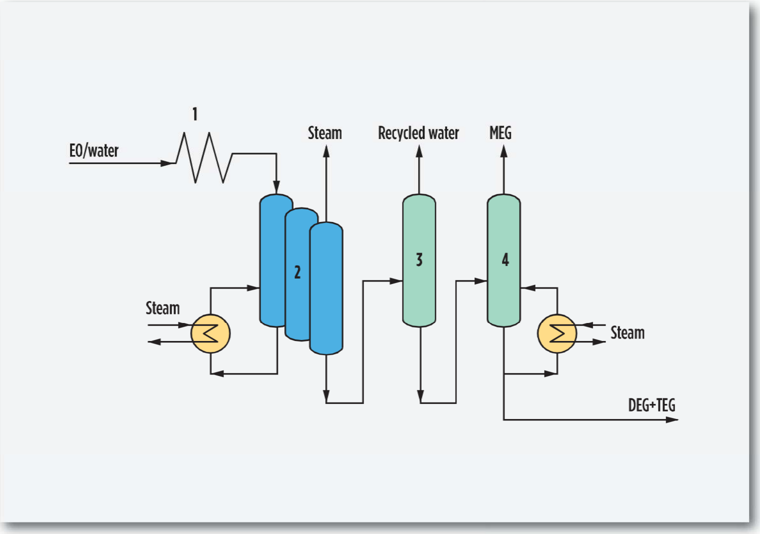
Ethylene glycol

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.

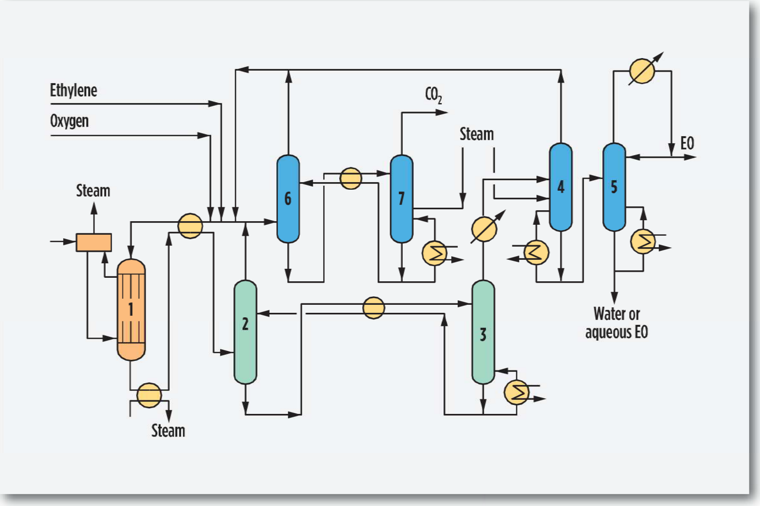
Economics: The conversion of EO to glycols is essentially complete. The reaction not only generates the desired MEG, but also produces DEG and TEG that can be recovered as coproducts. The production of more DEG and TEG may be desirable if the manufacturer has a specific use for these products or if market 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 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 reactor's shell side; the resulting high-pressure steam is used for heating purposes at various locations within the process.

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

EO reactor product-gas, after EO recovery, is mixed with fresh feed and returned to the EO reactor. Part of the recycle gas is passed through an activated carbonate solution (6, 7) to recover carbon dioxide (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.

Economics: 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.

Installations: Since 1958, more than 70 Shell-designed plants have been commissioned or are under construction.

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

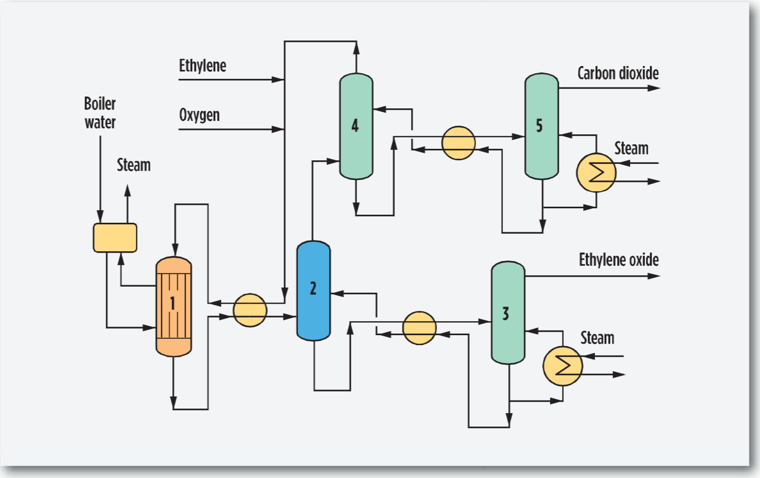
Ethylene oxide

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.

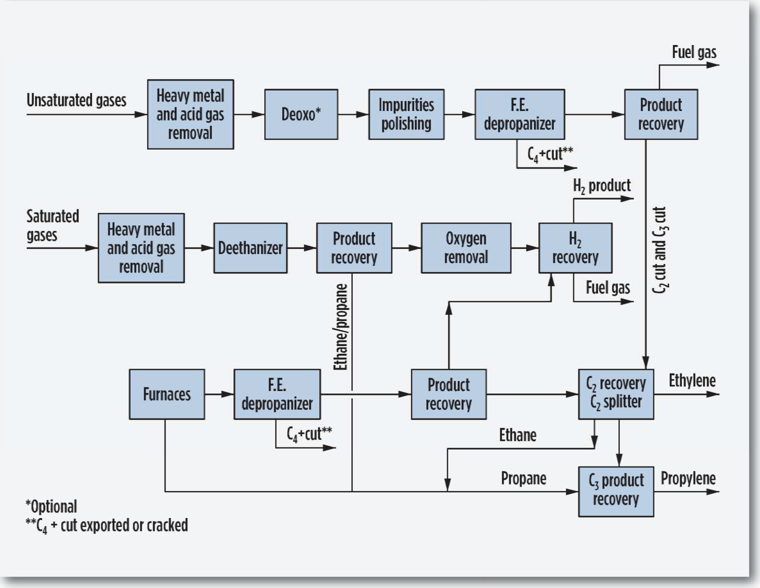
Licensor: Union Carbide Corp., a subsidiary of The Dow Chemical Co. CONTACT

Ethylene recovery from refinery offgas with contaminant removal

Application: Technip has developed an innovative technology that captures the petrochemical value versus fuel gas value of refinery offgas (ROG). Normally, contaminated fuel gas is used as fired fuel and burned within the refinery. ROG technology, which allows the production of valuable polymer-grade ethylene and propylene, can be classified in two categories:

- The unsaturated offgas coming from fluidized catalytic cracking (FCC), deep catalytic cracking (DCC) or coker units is rich in ethylene and propylene.
- The saturated offgas coming from other refining units is rich in ethane and propane; the recovered ethane and propane are then recovered and cracked to produce ethylene and propylene.

The ROG contains many light components (nitrogen, hydrogen and methane) and contaminants requiring dedicated treatment. An ROG unit provides a level of purity that allows either direct production of polymer grade or further processing in an ethylene plant recovery section.



*Optional
**C_4 + cut exported or cracked

Description: The ROG unit is broken down into sections including feed contaminant removal, and ethylene and propylene recovery. Feed contaminants including heavy metal, acid gases, oxygen, NO_x, arsine, mercury, ammonia, nitrites, COS, acetylene, chloride and water must be removed. The designer of the unit must be experienced with feedstock pretreatment since many trace components in the ROG can impact product quality, catalyst performance and operational safety.

The ROG unit can include an ethylene recovery section that produces either dilute ethylene or polymer-grade ethylene. Otherwise, the purified C_2 cut/C_3 cut is routed into the steam cracking plant for further purification and recovery. Depending on the capacity constraints of the steam cracking plant or the offgas quantity of nitrogen, hydrogen and methane, the ROG unit may include a cold box followed by a demethanizer and a C_2 splitter.

The ROG unit can be designed to remove contaminants such as acid gases, COS, RSH, NO_x, O_2, NH_3, HCN, AsH_3, Hg and H_2O. The most difficult contaminants to remove are oxygen and NO_x. Elimination of oxygen and NO_x is necessary to ensure safe operation of the subsequent processing steps of the ethylene plant. Oxygen and NO_x can promote the formation of potentially explosive deposits or potentially plug the cold box. Alternatively, the system must be designed to ensure that these

Continued ▼

Ethylene recovery from refinery offgas with contaminant removal, cont.

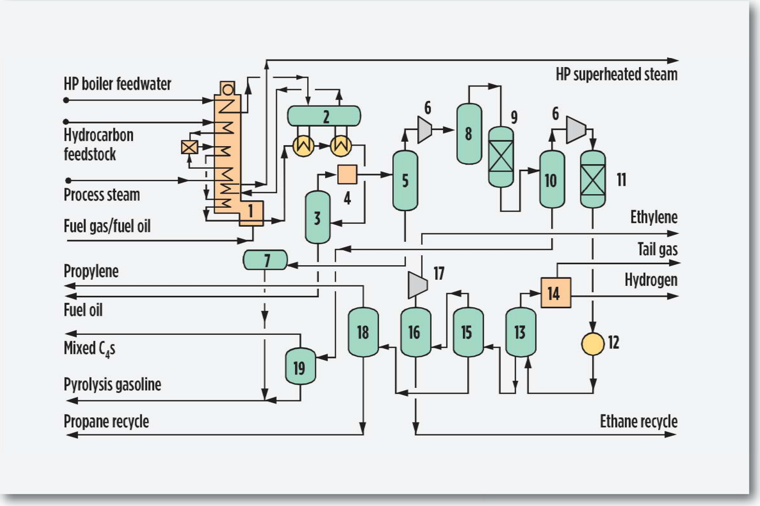
contaminants do not pose a problem, whether operationally or in terms of product specification.

Economics: ROG streams and, in particular, unsaturated gases from FCC, DCC and coker units contain a significant amount of ethylene and propylene. Normally, these streams are used as fuel gas in the refineries. Recovery of the olefins can be economical, with project payout duration often less than one year. Similarly, it is economical to treat the saturated gases with a relatively large amount of ethane and propane for further cracking and production of ethylene and propylene.

Commercial plants: Since 1997, when the first ROG unit started operation, more than 10 additional units have been put in operation. These units are either integrated with the steam cracker and producing dilute ethylene and/or propylene for further treatment in the ethylene plant, or are functioning as stand-alone ROG units producing polymer-grade ethylene and propylene. A recent cracker project for Reliance in India is the best example of ethylene production at world-scale capacity (1.4 MMtpy) using only refinery offgases as feedstock.

Licensor: Technip Stone & Webster Process Technology CONTACT

Ethylene, SCORE



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 engineering company, 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.

SCORE technology includes a portfolio of pyrolysis furnace designs that cover the broadest range of reaction times in the industry. This portfolio allows individual facilities to be designed for optimum value and return on investment. The SC-1 pyrolysis furnace design is unique to SCORE and 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 portfolio 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-

Continued ▼

Ethylene, SCORE, cont.

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 hydrogenated 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.

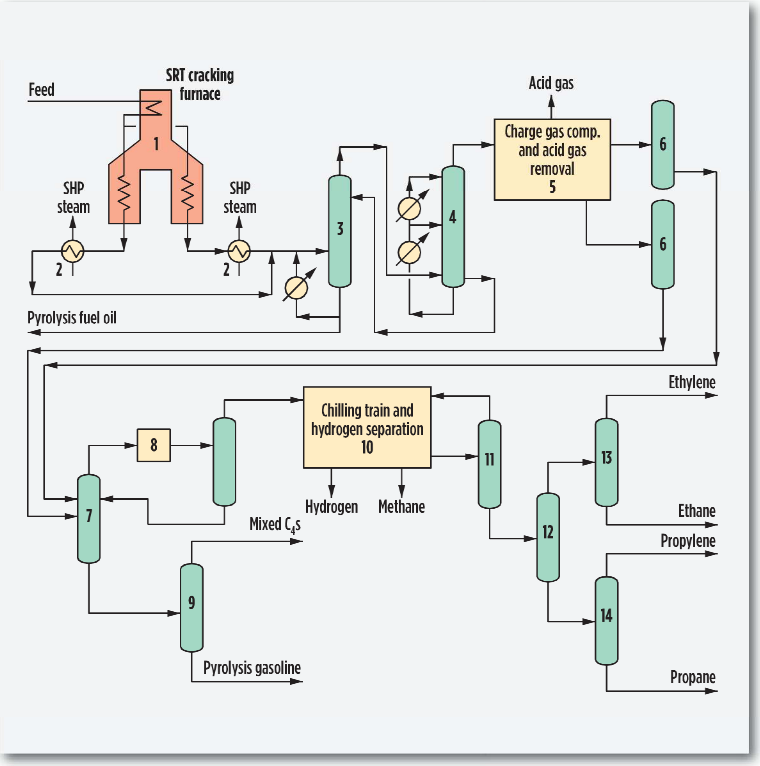
Yields: Ethylene yields to 84% for ethane, 38% for naphtha and 32% for gasoils may be achieved depending upon feedstock character and furnace design selected.

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

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, short-residence time (SRT) pyrolysis furnaces (1). This approach features extremely high olefin yields, long run-length 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). The compressed gas and condensed liquid are then dried (6) and chilled.

For propane and heavier feedstocks, the dried gas and liquid are depropanized (7). Acetylene and a portion of the methylacetylene and propadiene are hydrogenated in an acetylene converter (8) integrated into the depropanizer overhead system. The depropanizer bottoms is sent to a debutanizer (9) for separation into a raw C_4s stream and an aromatics-rich pyrolysis gasoline stream. Hydrogen is recovered in the chilling train (10), which feeds the demethanizer (11). The demethanizer operates at about 100 psia, providing increased energy efficiency. The bottoms from the demethanizer go to the deethanizer (12). The ethylene-ethane stream is fractionated (13) and polymer-grade ethylene is recovered. Ethane leaving the bottom of the ethylene fractionator is recycled and cracked to extinction. The propylene-propane stream from the deethanizer bottoms goes through trim hydrogenation to remove any remaining methylacetylene and propadiene, and then is fractionated (14) and polymer-grade propylene is recovered. Propane leaving the bottoms of the propylene fractionator is recycled and cracked to extinction.

Continued ▼

Ethylene, cont.

Refrigeration is provided by a single refrigeration system that replaces three separate systems, eliminating 15% of the equipment compared to a conventional flowsheet. For ethane cracking, the gasoline fractionator (3) is deleted. The depropanizer (7) becomes a deethanizer, and the deethanizer and ethylene fractionator in the back end (12 and 14) are also deleted. The debutanizer (9) is deleted and replaced by a depropylenizer to recover polymer-grade propylene from the deethanizer bottoms.

Metathesis can be applied to produce up to a third of the propylene product catalytically rather than by thermal cracking, thereby lowering energy consumption by 15%.

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

Commercial plants: Approximately 45% of the world's ethylene plants use CB&I's ethylene technology. Many existing units have been significantly expanded (above 150% of nameplate) using CB&I's MCET (maximum capacity expansion technology) approach.

Licensor: CB&I CONTACT

Ethylene—Cracking furnaces

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

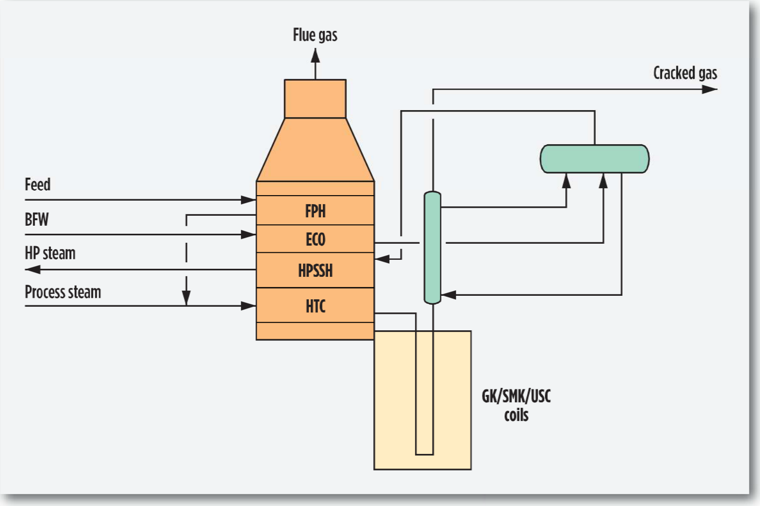
Feedstocks: Ethane, propane through liquid feeds up to heavy gasoil or up to 600°C EP.

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

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 to 880°C depending on feed quality and cracking severity. The recent proprietary coils are GK6® and USC®-U for liquids cracking and USC®-M and SMK™ coils for 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.

Cracking gases from the furnace coils pass through a transfer line exchanger (TLE) system, where heat is recovered to generate high-pressure steam. The primary TLEs are special shell and tube 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 very-high-pressure steam.

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



Performance data:

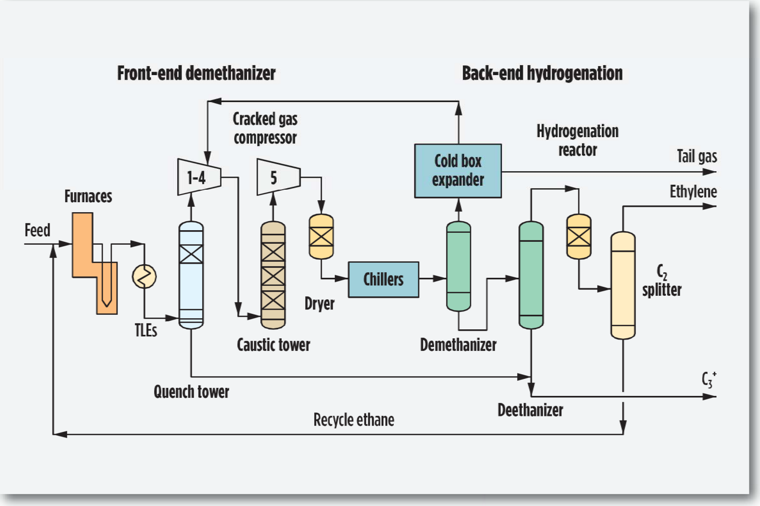
Ethane conversion, %	65–75
Naphtha cracking severity (P/E ratio)	0.4–0.75
Overall thermal efficiency, %	92–95
Coil residence time, sec	
GK6/USC-U	0.15–0.30
SMK/USC-M/USC-W	0.30–0.60

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

Commercial plants: Since 2000, Technip's furnace technology has been implemented in more than 160 gas cracking furnaces and more than 200 liquid cracking furnaces.

Licensor: Technip Stone & Webster Process Technology CONTACT

Ethylene—Steam cracking and product recovery (gaseous feedstocks)



Application: To produce polymer-grade ethylene by steam cracking of ethane (or in mixture with propane), the pyrolysis in cracking furnaces followed by progressive separation is used to minimize energy consumption.

Description: The technology is based on either Stone & Webster process technology or Technip technology using pyrolysis of ethane followed by progressive separation. This allows processing of hydrocarbons at low energy consumption with a particularly low environmental impact. This concept is applied either for front-end hydrogenation or back-end hydrogenation:

- Front-end hydrogenation corresponds to a front-end deethanizer, where the hydrogenation reactor is placed at the deethanizer overhead, or to a front-end depropanizer, where the hydrogenation reactor is placed at the depropanizer overhead.
- Back-end hydrogenation corresponds to a front-end demethanizer, where the hydrogenation reactor is placed at the tail-end C_2 cut.

Ethane is preheated (to recover heat) and then cracked by combining with steam in a tubular pyrolysis furnace at an outlet ranging between 1,500°F and 1,600°F. The furnace technology can be either SMK™ coils or USC®-M or W coils. Residence time in the pyrolysis section ranges from 0.30 seconds to 0.5 seconds. This design approach allows long run length (over 60 days), mechanical integrity and attractive economics.

The hydrocarbon mixture at the furnace outlet is quenched rapidly in the selective line exchangers (SLEs) or transfer line exchangers (TLEs) generating very-high-pressure steam. The cracked gas flows to a quench water tower for water recovery and removal of tars. The gas is then compressed to 450 psig and dried for further chilling. A caustic scrubber is placed at the compressor inter-stage to remove acid gases.

After chilling, a simple demethanizer at medium pressure allows removal of methane and recovery of the C_2 cut.

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

The C_2 splitter is operating as an open heat pump. The tower can be arranged as an open heat pump integrated with the ethylene refrigerant for front-end hydrogenation or as a closed heat pump with propylene refrigerant for the back-end hydrogenation scheme. The recovered polymer-grade ethylene polymer is sent either to downstream units or to storage.

The recovered ethane from the C_2 splitter is recycled to furnaces for further cracking.

Continued ▼

Ethylene—Steam cracking and product recovery (gaseous feedstocks), cont.

Cracking a mixed ethane/propane feed allows for production of polymer-grade propylene from a C_3 splitter. The residual propane is recycled to furnaces for cracking. The recovered C_4s and light gasoline are recovered in the debutanizer and exported with or without treatment.

Gas expansion (heat recovery) and external cascade using ethylene and propylene (or propane) systems supply the required refrigeration to achieve at least 99.6% ethylene recovery.

The main features are patented:

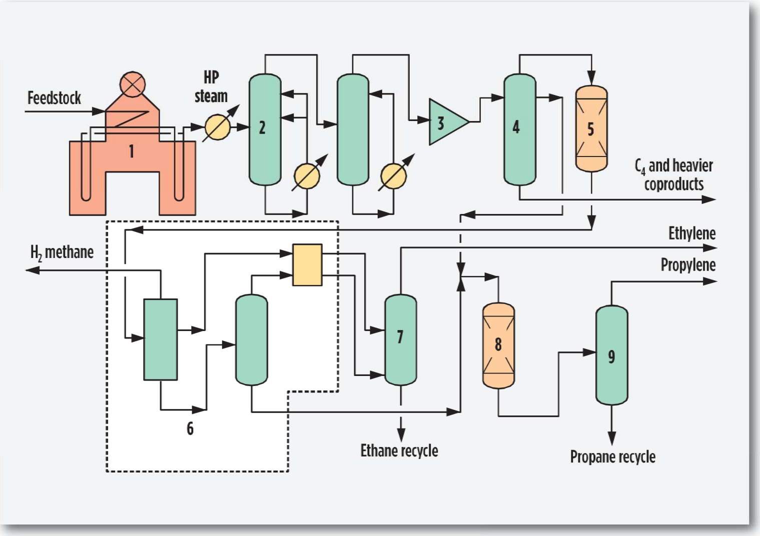
- Optimization of olefin yields and selection of furnaces
- Reduced external refrigeration in the separation sections
- Auto stable process, heat integration act as feed-forward system
- Simple process control

Economics: Ultimate range of ethylene yields vary from 83% to 78% depending on the selected ethane conversion. The specific energy consumption is in the range of 3,000 kcal/kg to 3,500 kcal/kg of ethylene produced.

Commercial plants: Since 2000, the technology has been applied in 11 ethylene plants using ethane as feedstock. The plants are located in the Middle East and North America, which represents more than 60% of the ethane cracking capacity awarded in recent years. Six of the 11 plants are based on very large capacities, between 1.0 million metric tons and 1.5 million metric tons per year.

Licensor: Technip Stone & Webster Process Technology CONTACT

Ethylene—Steam cracking and product recovery (liquid feedstocks)



Application: To produce polymer-grade ethylene, propylene and other valuable co-products by thermally cracking liquid feedstocks and efficiently purifying the products using state-of-the-art recovery systems. Key features include:

1. Cracking of liquid feeds in either USC® or GK® series proprietary Technip furnaces
2. Optional front-end or back-end C_2 hydrogenation system
3. Efficient recovery of olefins via a heat-integrated rectifier system (HRS). Optionally, the 100°C (–150°F) ethylene refrigeration level can be eliminated.
4. Enhanced reliability through use of low-fouling/high-capacity Ripple Trays™

Description: Fresh feed and recovered recycle streams are sent to the cracking furnaces (1). Cracking occurs at temperatures and resident time requirements specific to the feedstock and product requirements. Technip utilizes several radiant coil designs to reduce residence time and coil pressure drop and to maximize ethylene yield and lower operating cost.

Rapid quenching preserves olefin yield and simultaneously produces high-pressure steam, while lower-temperature heat is recovered for generation of dilution steam. Pyrolysis fuel oil and gasoline byproducts are recovered in the quench oil and quench water systems (2). Cracked gas is compressed (3) and treated with caustic to remove acid gases, and then dried prior to fractionation. For front-end C_2 hydrogenation schemes, C_3 and lighter components are separated from C_4 and heavier components in the low-fouling dual-pressure depropanizer (4) before acetylenes are hydrogenated in the acetylene hydrogenation reactor (5). The stream is then routed to the demethanizer chilling section (6) where methane and lighter components are separated from C_2 and heavier components using either HRS or Technip's patented cold section approach, which eliminates the –100°C (–150°F) ethylene refrigeration level. The demethanizer system includes a turbo-expander for energy efficiency and greater hydrogen recovery. The proprietary chilling section design offered by Technip minimizes refrigeration energy, lowering both capital and operating cost.

Ethylene is purified in the low-pressure C_2 splitter heat pump (7), which fractionates ethylene from ethane in a highly efficient manner. The C_2 overhead stream is routed directly to the integral C_2 refrigeration system, where polymer-grade ethylene is withdrawn. C_3s from the dual-pressure depropanizer system are combined and optionally further hydrogenated (8) before being directed to the propylene-propane fractionator

Continued ▼

Ethylene—Steam cracking and product recovery (liquid feedstocks), cont.

(9). The propylene-propane fractionator can be either a high-pressure system that is condensed by cooling water or a low-pressure system that utilizes a heat pump. C_4 and heavier co-products are further separated in a sequence of distillation steps.

Economics: Ultimate yields for ethylene in the range of 32% are achieved when cracking liquid feedstocks. The ethylene plants with USC and/or GK series furnaces, along with Technip's proprietary chilling section, are known for high-reliability, low-energy consumption, ease of operation and environmental compliance. The specific energy consumption is typically in the range of 4,500 kcal/kg to 5,500 kcal/kg of ethylene produced, depending on the feedstock quality and desired product slate.

Commercial plants: Since 2000, the technology has been applied in 12 grassroots facilities based on liquid feedstocks representing nearly 10 million metric tons of ethylene per year. Many of these facilities operate at well over 800,000 tpy.

Licensor: Technip Stone & Webster Process Technology CONTACT

Ethylene

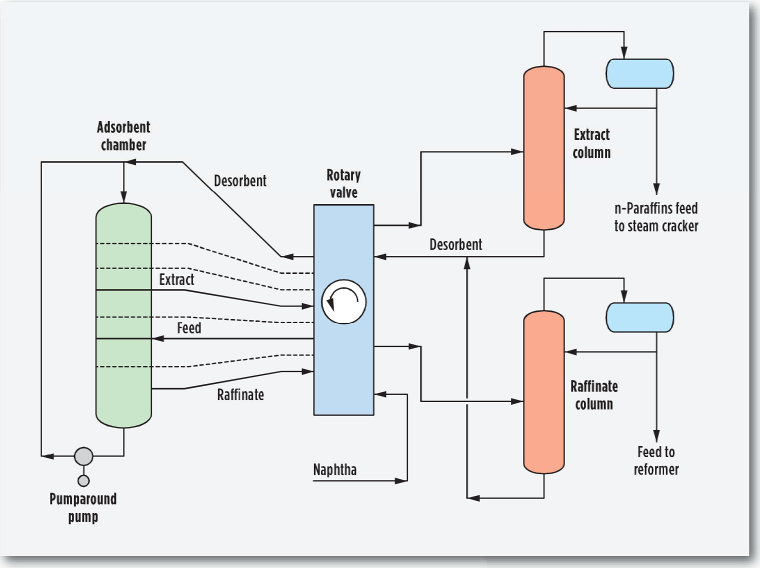
Application: The MaxEne process increases the ethylene yield from naphtha crackers by raising the concentration of normal paraffins (n-paraffins) in the naphtha-cracker feed. The MaxEne process is the newest application of UOP's Sorbex technology. The process uses adsorptive separation to separate C_5–C_{11} 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 components of the naphtha 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 up to 12% increase in aromatics 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 currently operating in China.

Licensor: UOP LLC, A Honeywell Company CONTACT

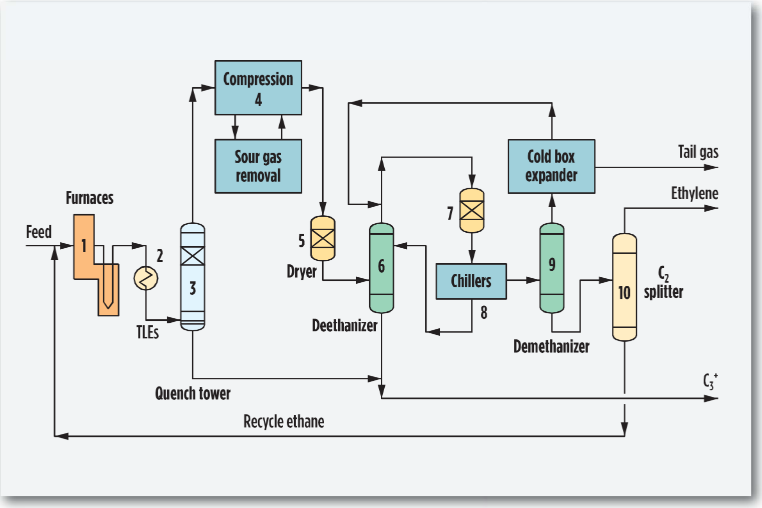
Ethylene: Ethane and E/P mix

Application: To produce polymer-grade ethylene by thermal cracking of ethane and E/P mixtures.

Description: Fresh feedstock and ethane recycle 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 high-pressure steam.

The cracked-gas stream is cooled and purified in the quench-water tower (3). The cracked gas from the quench tower is compressed (4) in a 4- or 5-stage compressor and dried in gas and liquid adsorbers (5). 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 and fed to the recovery section: front-end deethanizer (6), isothermal front-end C_2 hydrogenation (7), cold train (8), demethanizer (9) and the heatpumped low-pressure ethylene fractionatior (10), 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).

Economics: Ethylene yields are up to 85% for ethane at conversion of 60%–75%. The related specific energy consumption range is 3,500 kcal/kg ethylene. Typical installation costs for a world-scale ISBL ethane cracker are 800 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: Liquid feedstocks

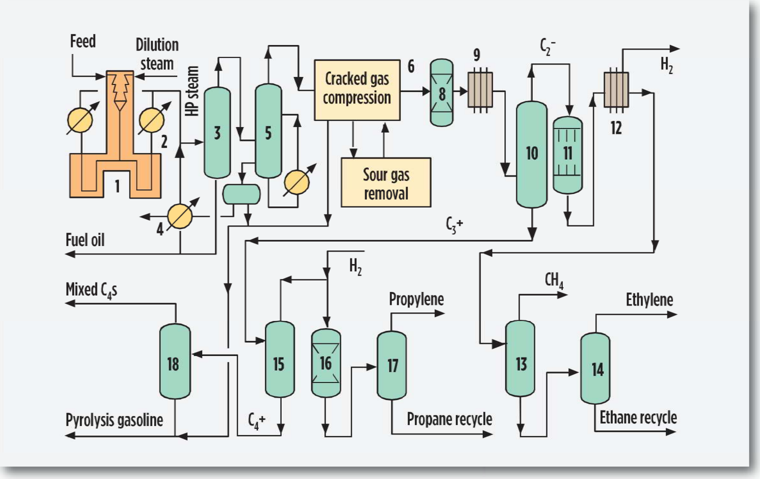
Application: To produce polymer-grade ethylene and propylene by thermal cracking of hydrocarbon fractions—from LPG through naphtha up to hydrocracker residue. Byproducts are a butadiene-rich C_4 stream, a C_6–C_8 gasoline stream rich in aromatics and fuel oil.

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 high-pressure 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) and 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% and 45% for gasoils, naphtha and LPG, 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, Tasnee (1.0 million metric tpy) in Saudi Arabia and Opal (1.1 million metric tpy) in India.

Licensor: Linde AG CONTACT

Ethylene: Value cracking

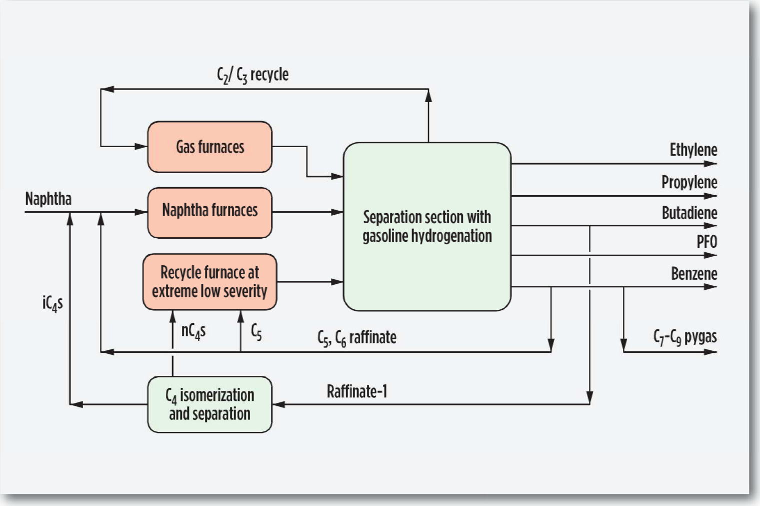
Application: To produce a maximum polymer-grade ethylene, propylene, butadiene and benzene by thermal cracking of hydrocarbon fractions, e.g., NGL, LPG, naphtha, AGO and hydrocracker residue.

Description: The process is similar to the scheme of steam crackers for liquid feedstocks. However, the scheme is tailored to maximize the value products by mild-cracking conditions and individual treatment of recycle streams.

The individual treatment includes separation, isomerization and hydrogenation steps. As an overall result, the output of ethylene in mild operation is similar to that of a severe cracking, but propylene and butadiene yields increase significantly. All product streams produced in this operation mode, except the PFO, are significantly higher in value as the feedstock. The patented scheme allows a maximum upgrade to valuable products and thus increases the revenue of the cracker operation significantly.

The proprietary scheme can be applied for new crackers, as well as for existing plants. The individual treatment of the recycle streams has to be adjusted to the product valuation scheme of the plant.

An increase in product revenues of a cracker is significant, and it increases cracker economics. Especially in integrated schemes of crackers and refineries, and for NGL and naphtha cracking, this scheme offers significant advantages.



Economics: Ethylene yields for a fixed amount of feedstock are the same as in severe operations, while propylene yields increase up to 55% and butadiene yields increase by 15%.

Licensor: Linde AG 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 IFPEN and based on selective ethylene homogeneous trimerization.

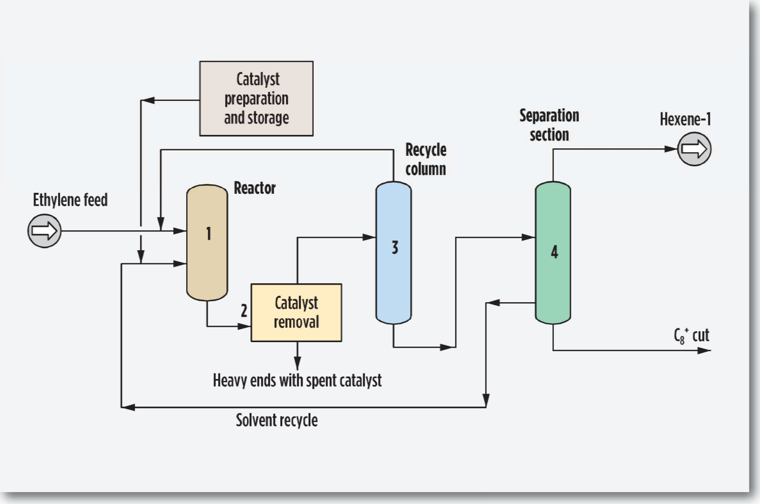
Description: Polymer-grade ethylene is oligomerized in a liquid-phase reactor (1) with a liquid homogeneous catalyst system that has high activity and selectivity.

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 first AlphaHexol unit was licensed in October 2011. The AlphaHexol process is strongly backed by extensive Axens industrial experience in homogeneous catalysis, in particular, the Alpha-Butol process for producing butene-1 for which 31 units have been licensed with a cumulated capacity of 728,000 tpy.

Licensor: Axens CONTACT

Hexene-1

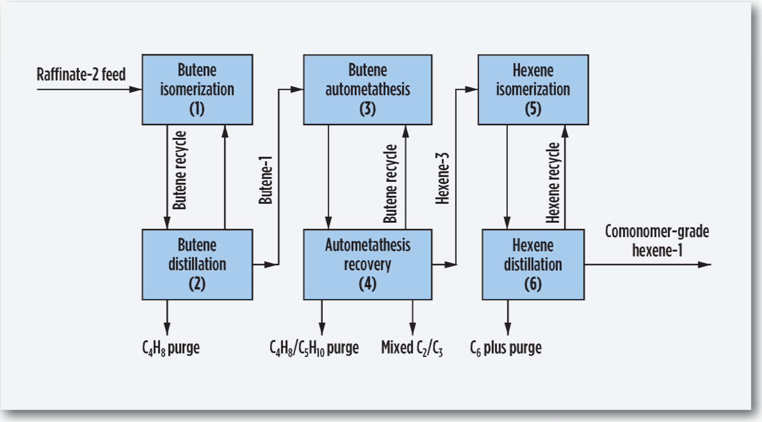
Application: To produce high-purity hexene-1 from a mixed C_4 stream using CB&I's comonomer production technology (CPT). The feedstock can contain any amount of butene-1, butene-2 and butane.

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.



Typical yields and product quality:

	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	
Hexene-1	99 wt% min.
Other C_6 olefins	1 wt% max.

Continued ▼

Hexene-1, cont.

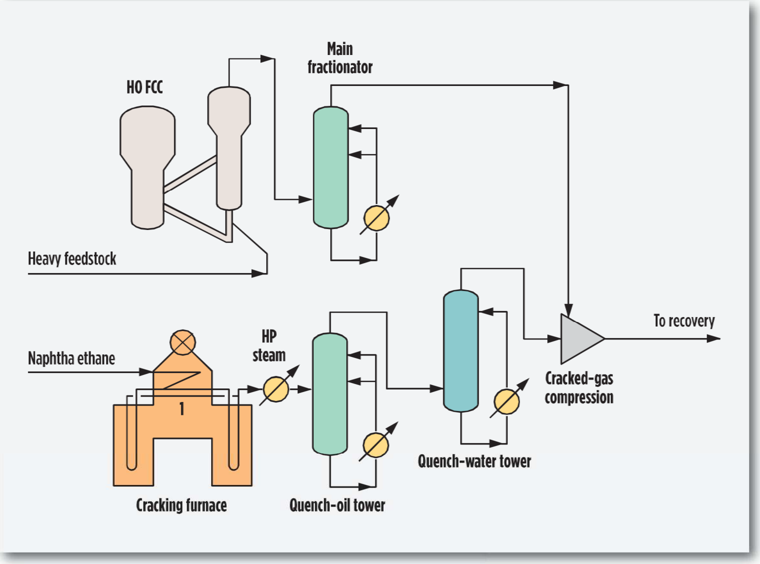
Economics: Typical utilities, per metric ton hexene-1 (80% butenes in feed)

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 started up in early 2014.

Licensor: CB&I CONTACT

High-olefins FCC and ethylene plant integration



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

Description: HOFCC technologies are FCC processes that convert heavy feedstocks, such as vacuum and atmospheric gasoils, to gasoline, diesel and light olefin products. The HOFCC reactor system is capable of producing 15 wt%–25 wt% propylene or 10 wt%–20 wt% ethylene. Steam cracking is commonly used with feedstocks varying from ethane to light gasoils. The high cracking temperatures of pyrolysis result in greater ethylene yield as compared to the HOFCC process. However, heavy gasoil feedstock would foul the cracking furnace too quickly to be economical. To process both heavy gasoil and light feeds, both systems are applied.

The HOFCC reactor effluent must first be processed in an FCC-style main fractionator. The main fractionator separates the heavy oil and light cycle oil from the overhead gas that is primarily light hydrocarbons and gasoline. The overhead of the main fractionator is processed through a wet-gas compressor before the light olefin LPG product is separated from gasoline and lighter gases. The ethylene-rich HOFCC offgas is treated before combining with the steam cracker effluent. The combined effluents are sent to compression and into a series of contaminant-removal beds and hydrogenation steps.

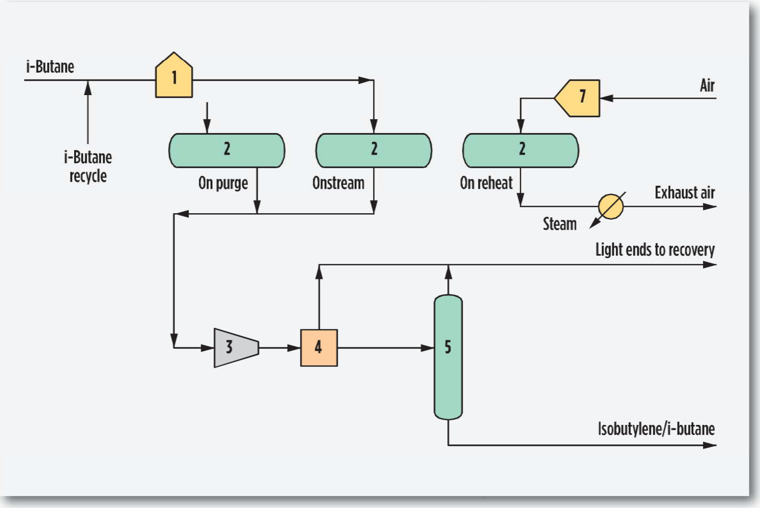
The heavy gasoil feedstock may contain contaminants that foul subsequent purification processes such as driers and hydrogenation reactors. Therefore, the HOFCC effluents need to be processed through contaminant-removal beds prior to entering the ethylene recovery unit. If both the steam cracker and HOFCC are processing contaminated feeds, many contaminant-removal processes can be shared to reduce capital costs.

This integrated technology is suitable for revamping ethylene plants or grassroots applications. The figure shows a maximum integration scheme for HOFCC and steam cracking. The level of integration is a function of contaminant levels, effluent gas composition, and other capital reduction considerations.

Installations: Technip has licensed a total of 20 HOFCC units. One is an integrated DCC and ethane cracker in operation in Saudi Arabia.

Licensor: Technip Stone & Webster Process Technology CONTACT

Isobutylene



Application: Technology for dehydrogenation of isobutane to make isobutylene. The CATOFIN® process uses specially formulated proprietary catalyst from Clariant.

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 switched to another reactor 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 Clariant 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 ▼

Isobutylene, cont.

Raw material and utilities, per mt of isobutylene	
Isobutane, mt	1.14
Power, kWh	39
Fuel, MWh	0.49

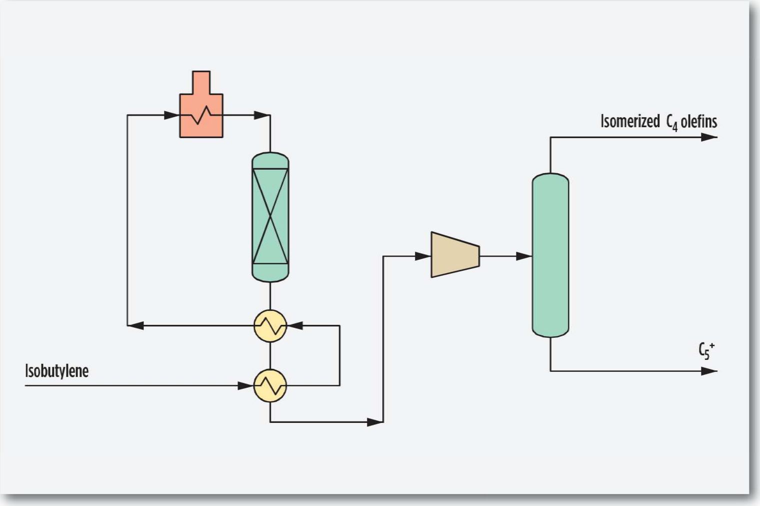
Commercial plants: Currently 12 CATOFIN dehydrogenation plants are on stream producing over 1.8 million mtpy of isobutylene and 2.3 million mtpy of propylene.

Licensor: CB&I 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 petrochemicals 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 a 300,000 tpy feed unit is US$25 MM.

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

Power, kWh	75
Fuel gas, 10^3 kcal	39
Steam, MP, kg	250
Water, cooling, m^3	23
Nitrogen, kg	30

Commercial plants: One unit licensed.

Licensor: CB&I CONTACT

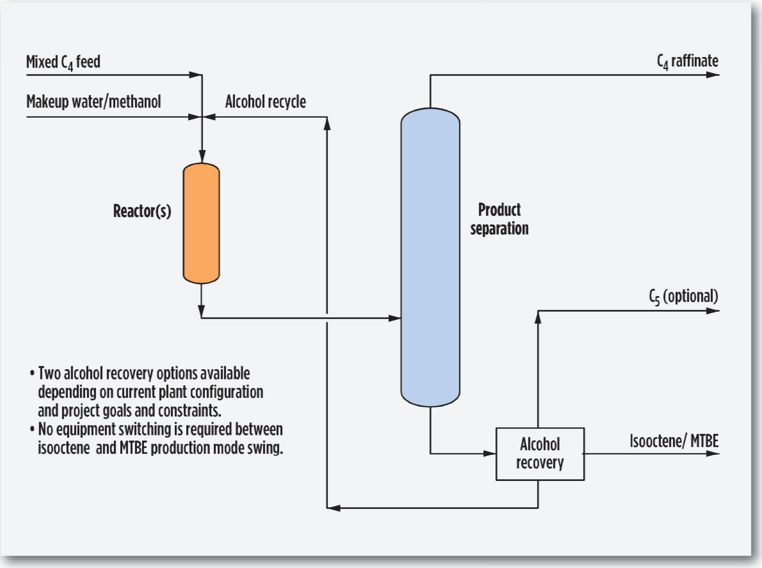
Isooctene/Isooctane

Application: Conversion of isobutylene contained in mixed-C_4 feeds to isooctane (2,2,4 tri-methyl pentane) to produce a high-quality gasoline blendstock. The full range of C_4 feeds can be processed—from refinery FCC, olefin-plant raffinate and isobutane dehydrogenation processes. The NExOCTANE process is specifically developed to minimize conversion costs of existing MTBE units and offers a cost-effective alternative to MTBE production.

Products: Isooctene and isooctane can be produced, depending on the refiner's gasoline pool. Flexibility to retain MTBE/ETBE production capability is also possible for a multipurpose swing plant. Typical product properties using C_4 feed from FCC are:

	Isooctene	Isooctane
RONC	101.1	99.1
MONC	85.7	96.3
(R+M)/2	93.4	97.7
Specific gravity	0.73	0.70
Vapor pressure, psia	1.8	1.8
Distillation ASTM D86		
T50, °F	221	216
T90, °F	238	234
EP, °F	380	390

Description: In the NExOCTANE process, reuse of existing equipment from the MTBE unit is maximized. The process consists of three sections. First, isobutylene is dimerized to isooctene in the reaction section. The dimerization reaction occurs in the liquid phase over a proprietary acidic ion-exchange resin catalyst. It uses simple liquid-phase fixed-bed reactors. The isooctene product is recovered in a distillation system that generally can utilize the existing fractionation equipment. Recovered isooctene product can be further hydrogenated to produce isooctane. A highly efficient trickle-bed hydrogenation technology is offered with the NExOCTANE process. This compact and cost-effective technology does not require recirculation of hydrogen. In the refinery, the NExOCTANE process fits as a replacement to MTBE production, thus associated refinery operations are mostly unaffected.



Process efficiency: The NExOCTANE process is optimized to minimize revamp costs but can also be designed for flexibility to multiple products (isooctene, isooctane, MTBE or ETBE) or to maximize product yield. Greater than 99% conversion of isobutylene with a selectivity of over 91% to isooctene can be achieved.

Continued ▼

Isooctene/Isooctane, cont.

Economics:

Investment cost for revamps depend on the existing MTBE plant design, capacity and feedstock composition.

Utilities, typical per bbl isooctene product

Steam, 150-psig, lb	700
Electricity, kWh	2.0
Water, cooling, ft^3	150

Installation: The NExOCTANE process has been in commercial operation since 2002. Present installed production capacity is over 37,000 bpd in both refinery and dehydrogenation applications. Recent projects include MTBE unit conversions at Valero's Corpus Christi refinery and the BP Carson refinery.

Reference: Hunszinger, et al. "Case History: Converting an MTBE Unit to Isooctane Operation," *Hydrocarbon Processing,* September 2003, pp. 57–62.

Halinen, et al., "Economic Evaluation of Production and Blending of Iso-octene and Iso-octane Produced by Isobutylene Dimerization," NPRA Annual Meeting, March 13–15, 2005, San Francisco.

Licensor: Kellogg Brown & Root LLC and Neste Jacobs OY CONTACT

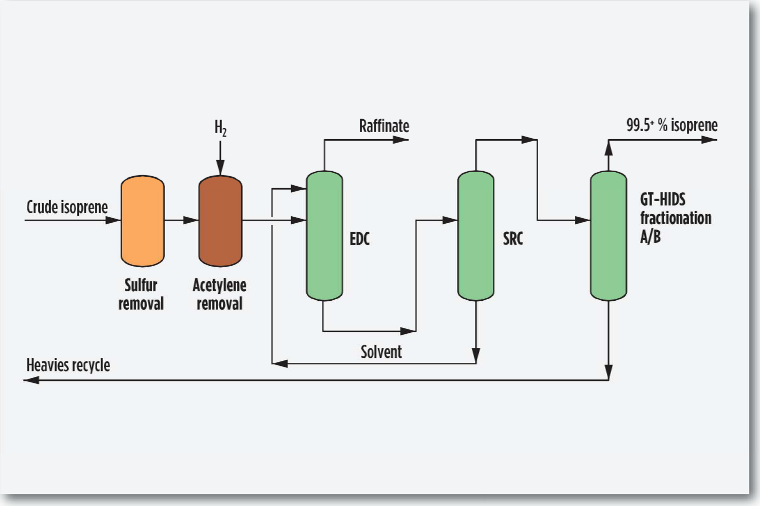
Isoprene

Application: GT-Isoprene℠ is a single-stage isoprene extraction technology using proprietary solvent. The technology uses less energy and equipment compared to competitive traditional extraction processes and uses corrosion-free environmentally friendly solvent unlike acetonitrile (ACN), dimethyl formamide (DMF), and n-methylpyrollidine (NMP).

Description: The GT-Isoprene process consists of a crude isoprene pretreatment section to remove sulfur, C_5 acetylene hydrogenation to selectively saturate the C_5 acetylenes, single-stage extractive distillation and a stripping section to produce an isoprene concentrate stream (up to 85%) and a super fractionation section to achieve SIS (styrene-isoprene-styrene block polymer) grade isoprene.

Process advantages:

- Single-stage extractive distillation
- Selective C_5 acetylene saturation and sulfur removal process produces gasoline blend quality raffinate
- Fewer number of stages and equipment in the purification section compared to traditional superfractionation
- Finishing section requires no hot or cold utility
- 50% less energy compared to conventional superfractionation
- Solvent has very low skin permeability and high stability, and poses no issues in the presence of water unlike DMF and ACN
- Improved extraction efficiency compared to traditional solvents
- GT-Isoprene uses GTC's proprietary solvent that has none of the water contamination or material corrosion issues that traditional solvents like DMF, ACN or NMP have. Fewer corrosion issues lead to reduced chemical consumption, lower energy consumption compared to DMF/ACN/NMP-based technologies and minimum solvent loss compared to DMF/ACN/NMP-based technologies. A polymer removal system increases the life and efficiency of the solvent.



Commercial plants: Commercialized technology available for license

Licensor: GTC Technology CONTACT

Linear alkylbenzene

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-Plus 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.

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

Licensor: UOP LLC, A Honeywell Company CONTACT

Low-pressure melamine 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.

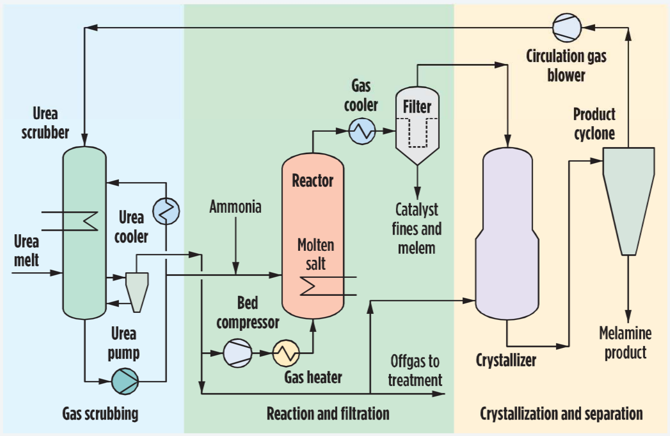
Urea melt is fed into the reactor and is atomized by spray nozzles with the aid of high-pressure ammonia. The reactor is a fluidized bed gas reactor using silica I aluminium oxide as catalyst. The reaction off gas, an ammonia (NH_3) and carbon dioxide (CO_2) mixture, is preheated and is used as fluidizing 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 is leaving the reactor together with gaseous melamine and the byproducts NH_3, CO_2, 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 gasfilter.

The filtered gas is further cooled down in the crystallizer to the desublimation temperature of the melamine-product. Cooling is performed using the offgas from the urea scrubber. The melamine is forming 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. Clean gas leaving the urea scrubber is partially used in the reactor as fluidizing gas and 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 drying unit. This results in lowest capital investment and operating cost.



Economics: Consumption per metric ton of melamine:

Urea melt:	3.15 tons, net value 1.5 tons
Ammonia:	0.18 tons
Catalyst:	3 kg
HP steam:	0.2 tons
Electrical power:	1,030 kWh
Natural gas:	13 GJ (ca. 384 Nm^3)
Water cooling:	26 tons

No quench water required (no waste water)

Continued ▼

Low-pressure melamine process, cont.

Commercial plants: A total capacity of 400,000 metric tpy has been licensed since 1993 within 18 plants. The latest plant with a capacity of 55,000 metric tpy was commissioned in May 2012 at Golden Elephant Industrial Zone, Hongze, Jiangsu, China. Another plant with a capacity of 50,000 metric tpy was commissioned in August 2012 in Stavropol, Russia.

Licensor: Edgein S&T Co. Ltd./Air Liquide Global E&C Solutions Germany GmbH CONTACT

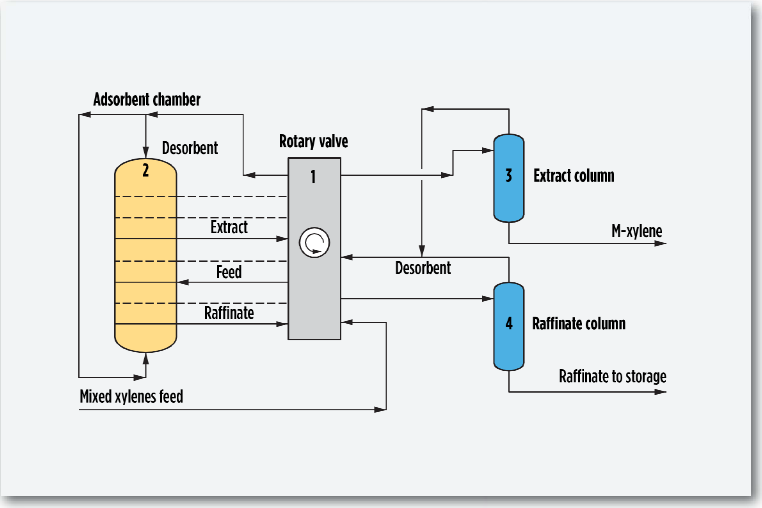
m-Xylene

Application: The UOP 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.



Commercial plants: Nine MX Sorbex units are currently in operation. These units represent an aggregate production of 590,000 metric tpy of *m*-xylene.

Licensor: UOP LLC, A Honeywell Company CONTACT

Maleic anhydride

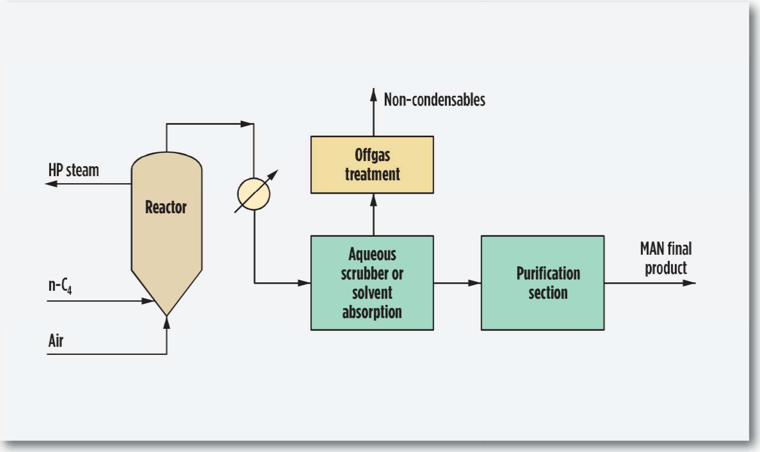
Application: INEOS is the recognized world leader in fluid-bed reactor technology for maleic anhydride production, which it licenses through INEOS Technologies. In addition to technology licensing, INEOS Technologies manufactures and markets the catalyst that is used in both the fixed-bed and fluid-bed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

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

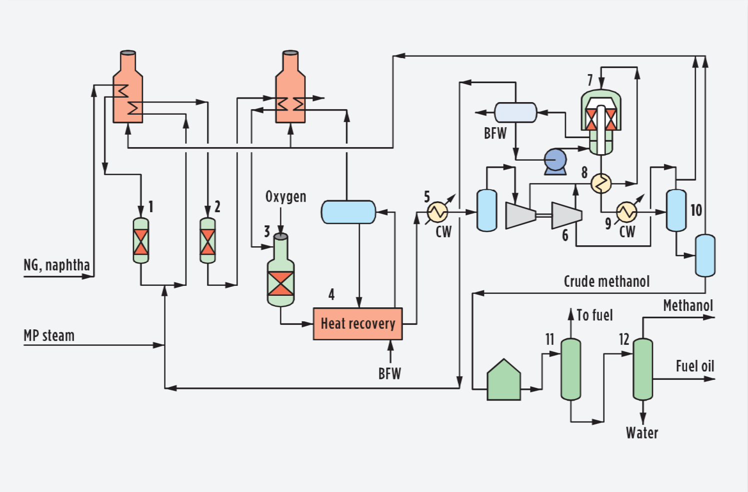
Methanol (autothermal reforming)

Application: To produce refined methanol from natural gas or naphtha-based synthesis gas using only a simple oxygen reformer followed by methanol synthesis with an MRF-Z® reactor.

Description: Steam-reforming section. In a natural-gas-based plant, the feedstock is first preheated by a direct heater, and sulfur compounds are removed in a desulfurizer (1). After steam is added, the feedstock-steam mixture is preheated similarly and a part of the feed is reformed adiabatically in a pre-reformer (2). The process steam is supplied from an MRF-Z reactor (7) and MP steam header. The pre-reformed gas is further preheated by direct heat sent to an oxygen-blown autothermal reformer to reform the residual methane almost completely. The high-temperature heat of the syngas obtained in the autothermal reformer is recovered for HP steam generation, the reboilers of the distillation section, and BFW heating (4). After final cooling (5), the syngas is compressed for makeup to the synloop.

Methanol synthesis section. The synthesis loop comprises a circulator combined with a compressor (6), an MRF-Z reactor (7), a feed/effluent heat exchanger (8), a methanol condenser (9) and an HP separator (10). The MRF-Z reactor is a reactor capable of producing 5,000 t/d to 6,000 t/d of methanol in a single-reactor vessel. The operation pressure is 5 MPa–10 MPa. The syngas enters the MRF-Z reactor at 220°C–240°C and normally leaves at 260°C–270°C.

The methanol synthesis catalyst to be purchased from one of the authorized catalyst vendors by TOYO is packed in the shell side of the reactor. Reaction heat is recovered and used to generate steam efficiently in the tube side. Reactor effluent gas is cooled to condense the crude methanol. The crude methanol is separated in an HP separator. The unreacted gas is circulated for further conversion. A purge is taken from the recycling gas used as fuels in the process's direct heaters.



Methanol purification section. The crude methanol is fed to a distillation system, which consists of a small light-ends stripper (11) and a methanol distillation column (12), for purification.

Economics: The autothermal reforming would be beneficial where extremely cheap oxygen is available via pipeline and the excess steam from the methanol plant can be exported.

Licensor: Toyo Engineering Corp. (TOYO) CONTACT

MRF-Z is a registered trademark of Toyo Engineering Corporation in Japan (Registered Number: 3172726)

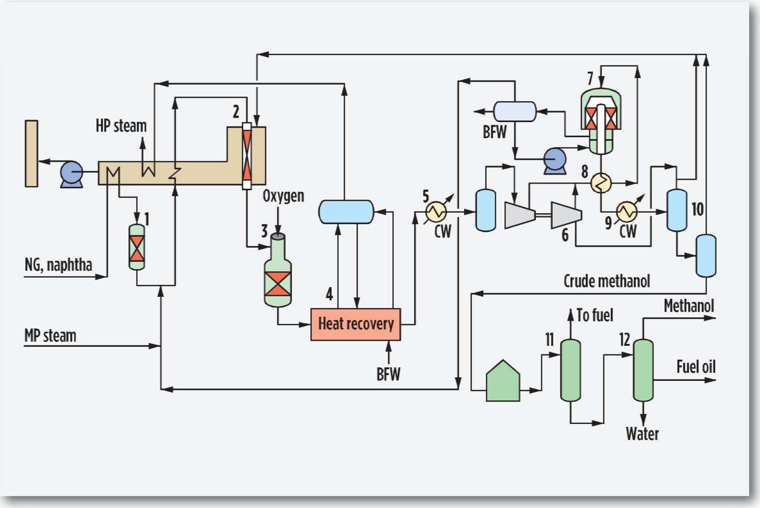
Methanol (combined reforming)

Application: To produce refined methanol from natural gas or naphtha-based synthesis gas, using a combination of a steam reformer and an oxygen reformer followed by methanol synthesis with an MRF-Z® reactor.

Description: Steam-reforming section. In a natural-gas-based plant, the feedstock is first preheated using the flue gas of a steam reformer (2), and sulfur compounds are removed in a desulfurizer (1). After steam is added, the feedstock-steam mixture is preheated similarly and sent into the catalyst tubes of a primary reformer for steam reforming. The process steam is supplied from an MRF-Z reactor (7) and a MP steam header. The primary-reformed gas is further conveyed to an oxygen-blown secondary reformer to reform the residual methane almost completely. The high-temperature heat of syngas obtained in the secondary reformer is recovered for HP steam generation, the reboilers of the distillation section, and BFW heating (4). After final cooling (5), the syngas is compressed for makeup to the synloop.

Methanol synthesis section. The synthesis loop comprises a circulator combined with a compressor (6), an MRF-Z reactor (7), a feed/effluent heat exchanger (8), a methanol condenser (9) and an HP separator (10). The MRF-Z reactor is a reactor capable of producing 5,000 t/d to 6,000 t/d of methanol in a single-reactor vessel. The operation pressure is 5 MPa–10 MPa. The syngas enters the MRF-Z reactor at 220°C–240°C and normally leaves at 260°C–270°C.

The methanol synthesis catalyst to be purchased from one of the authorized catalyst vendors by TOYO is packed in the shell side of the reactor. Reaction heat is recovered and used to generate steam efficiently in the tube side. Reactor effluent gas is cooled to condense the crude methanol. The crude methanol is separated in an HP separator. The unreacted gas is circulated for further conversion. A purge is taken from the recycling gas used as fuels in the primary reformer.



Methanol purification section. The crude methanol is fed to a distillation system, which consists of a small light-ends stripper (11) and a methanol distillation column (12), for purification.

Economics: In typical natural gas applications, approximately 30 GJ/ton-methanol, including utilities, is required. The combined reforming would normally be feasible for a plant capacity of more than 5,000 t/d.

Licensor: Toyo Engineering Corp. (TOYO) CONTACT

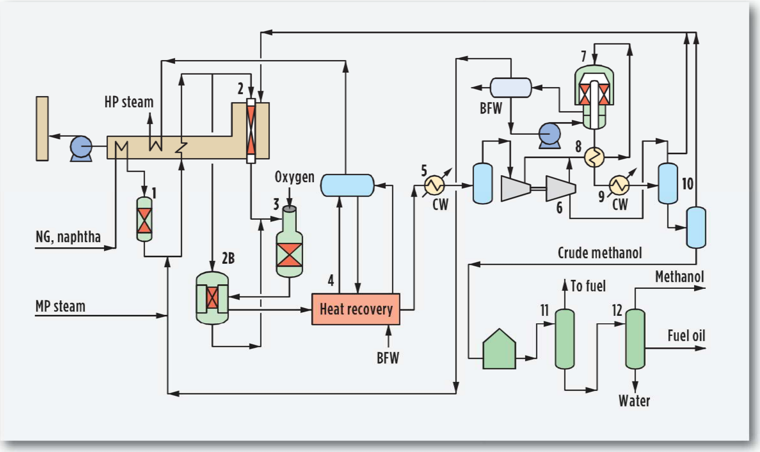
MRF-Z is a registered trademark of Toyo Engineering Corporation in Japan (Registered Number: 3172726)

Methanol (exchanger reformer combined)

Application: To produce refined methanol from natural gas or naphtha-based synthesis gas, using a combination of a conventional steam reformer, an exchanger reformer and an oxygen reformer followed by methanol synthesis with an MRF-Z® reactor suitable for an extremely large plant such as 10,000 t/d.

Description: Steam-reforming section. In a natural-gas-based plant, the feedstock is first preheated using the flue gas of a steam reformer (2), and sulfur compounds are removed in a desulfurizer (1). After steam is added, the feedstock-steam mixture is preheated similarly and sent into catalyst tubes of primary reformers installed in parallel for steam reforming, namely a conventional steam reformer (2A) and an exchanger reformer (2B). The process steam is supplied from an MRF-Z reactor (7) and MP steam header. The primary-reformed gases are mixed and further conveyed to an oxygen-blown secondary reformer to reform the residual methane almost completely. The high-temperature heat of the syngas obtained in the secondary reformer is recovered first for providing reaction heat in the exchanger reformer and next for HP steam generation, the reboilers of the distillation section, and BFW heating (4). After final cooling (5), the syngas is compressed for makeup to the synloop. The distribution of reforming duties of the conventional steam reformer and the exchanger reformer is subject to the economics of the individual project.

Methanol synthesis section. The synthesis loop comprises a circulator combined with a compressor (6), an MRF-Z reactor (7), a feed/effluent heat exchanger (8), a methanol condenser (9) and an HP separator (10). Two MRF-Z reactors are capable of producing 10,000 t/d of methanol. The operation pressure is 5 MPa–10 MPa. The syngas enters the MRF-Z reactor at 220°C–240°C and normally leaves at 260°C–270°C.



The methanol synthesis catalyst to be purchased from one of the authorized catalyst vendors by TOYO is packed in the shell side of the reactor. Reaction heat is recovered and used to generate steam efficiently in the tube side. Reactor effluent gas is cooled to condense the crude methanol. The crude methanol is separated in an HP separator. The unreacted gas is circulated for further conversion. A purge is taken from the recycling gas used as fuels in the primary reformer.

Methanol purification section. The crude methanol is fed to a distillation system, which consists of a small light-ends stripper (11) and a methanol distillation column (12), for purification.

Reference: US Patents 6100303, 7517373

Licensor: Toyo Engineering Corp. (TOYO) CONTACT

MRF-Z is a registered trademark of Toyo Engineering Corporation in Japan (Registered Number: 3172726)

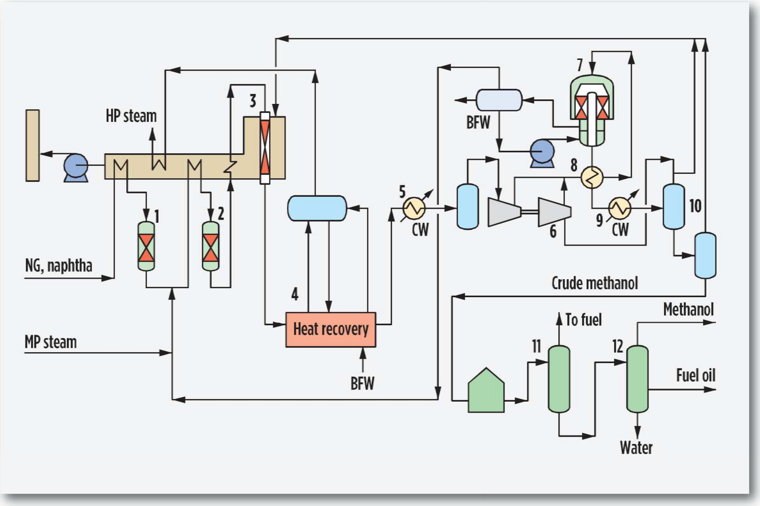
Methanol (steam reforming)

Application: To produce refined methanol from natural gas or naphtha-based synthesis gas, using Toyo Engineering Corp.'s (TOYO's) proprietary steam reformer and MRF-Z® reactor.

Description: Steam-reforming section. In a natural-gas-based plant, the feedstock is first preheated using the flue gas of a steam reformer (3), and sulfur compounds are removed in a desulfurizer (1). After steam is added, the feedstock-steam mixture is preheated similarly, and a part of the feed gas is reformed adiabatically in a pre-reformer (2) for reduced load of the steam reformer. The pre-reformed feedstock gas is preheated again and sent into catalyst tubes of the steam reformer as main reforming. The process steam is supplied from an MRF-Z reactor (7) and MP steam header. The high-temperature heat of syngas obtained in the steam reformer is recovered for HP steam generation, the reboilers of the distillation section, and BFW heating (4). After final cooling (5), the syngas is compressed for makeup to the synloop.

Methanol synthesis section. The synthesis loop comprises a circulator combined with a compressor (6), an MRF-Z reactor (7), a feed/effluent heat exchanger (8), a methanol condenser (9) and an HP separator (10). The MRF-Z reactor is a reactor capable of producing 5,000 t/d to 6,000 t/d of methanol in a single-reactor vessel. The operation pressure is 5 MPa–10 MPa. The syngas enters the MRF-Z reactor at 220°C–240°C and normally leaves at 260°C–270°C.

The methanol synthesis catalyst to be purchased from one of the authorized catalyst vendors by TOYO is packed in the shell side of the reactor. Reaction heat is recovered and used to efficiently generate steam in the tube side. Reactor effluent gas is cooled to condense the crude methanol. The crude methanol is separated in an HP separator. The unreacted gas is circulated for further conversion. A purge is taken from the recycling gas used as fuels in the steam reformer.



Methanol purification section. The crude methanol is fed to a distillation system, which consists of a small light-ends stripper (11) and a methanol distillation column (12) for purification.

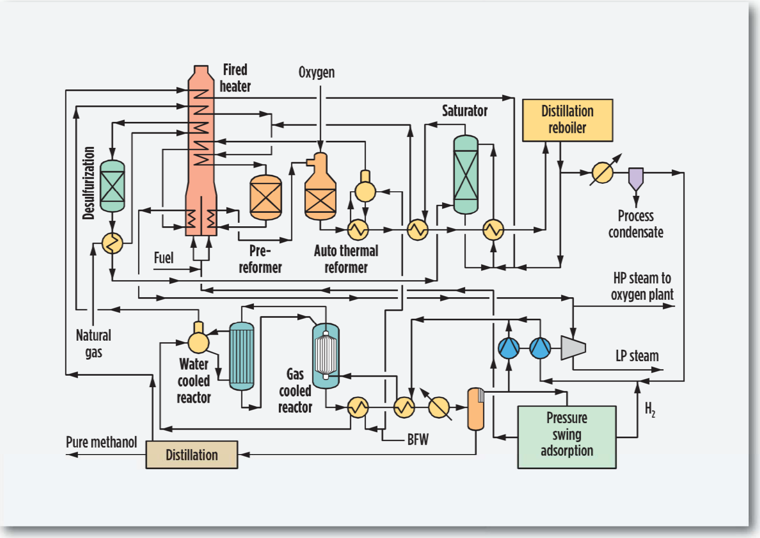
Economics: In typical natural gas applications, approximately 30 GJ/ton-methanol, including utilities, is required.

Commercial plants: Toyo has licensed 19 methanol plants, both in Japan and abroad. The MRF-Z reactor has been used in six plants.

Licensor: Toyo Engineering Corp. (TOYO) CONTACT

MRF-Z is a registered trademark of Toyo Engineering Corporation in Japan (Registered Number: 3172726).

Methanol



Application: To produce methanol in a single-train plant from natural gas or oil-associated gas with capacities up to 10,000 metric tpd (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

Continued ▼

Methanol, cont.

the tank farm, and the process water is preheated in the fired heater and used as makeup water for the saturator.

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$500 million–$800 million, depending on location.

Commercial plants: Fifty methanol plants have been licensed applying Lurgi's Low-Pressure methanol technology. Seven MegaMethanol licenses are in operation; several are in an engineering phase and under construction and a MegaMethanol license has been awarded with capacities up to 6,750 mtpd of methanol.

Licensor: Air Liquide Global E&C Solutions Germany GmbH CONTACT

Methanol

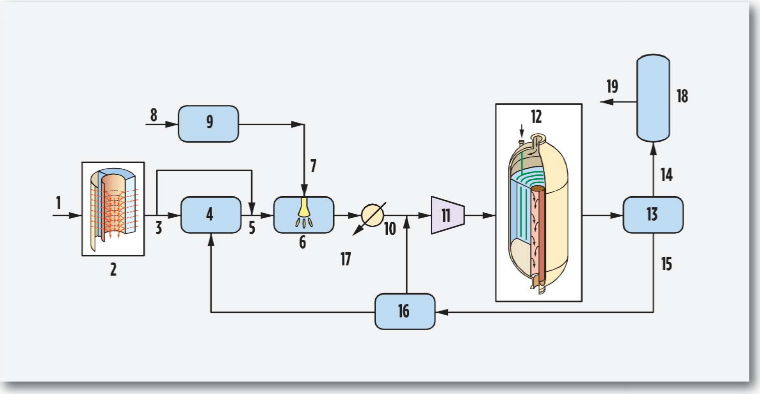
Application: To produce methanol from natural gas. The process is based on Casale's highly efficient equipment, including its:

- 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: Due 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

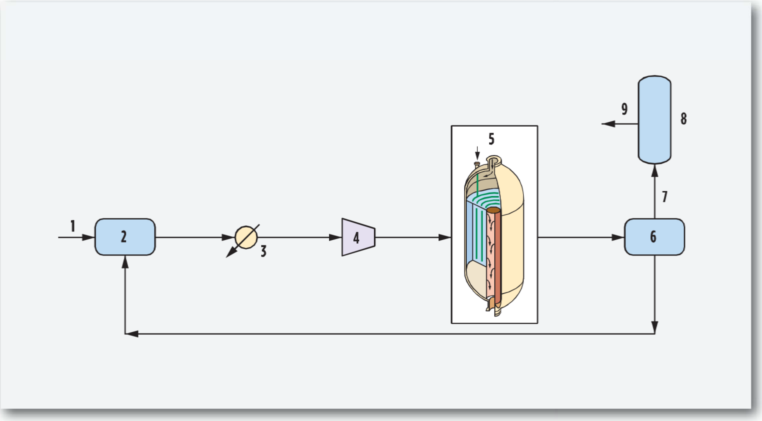
Methanol

Application: 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).

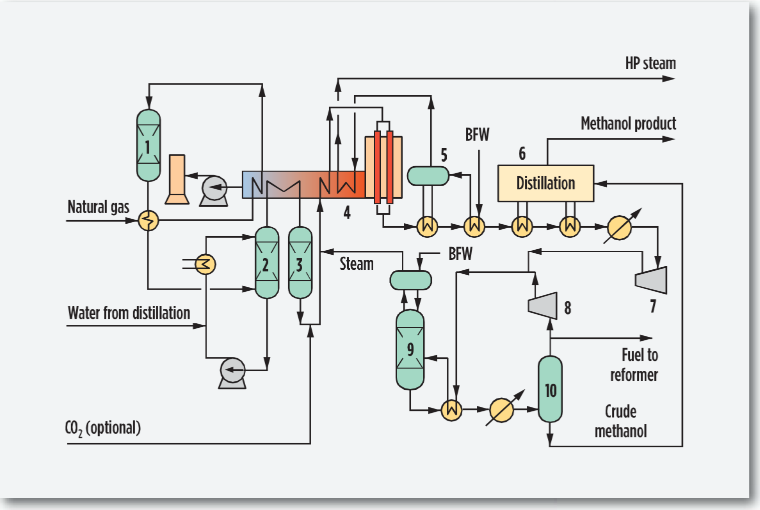


Economics: Thanks to the high efficiency of the process and equipment design, the total energy consumptions (evaluated as feeds + fuel + steam import from package boiler and steam export to urea) is about 7 Gcal/metric ton of produced methanol.

Installations: Casale has been involved in 41 projects since 1993. The company is constructing methanol plants with 7,000 metric tpd capacity.

Licensor: Methanol Casale SA, Switzerland CONTACT

Methanol



Application: The JM Davy–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-methane 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 (HP) steam (5), boiler feedwater preheat, and for reboil heat in the distillation system (6). The HP 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 ▼

Methanol, cont.

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: Eighty-one licensed plants with 11 current projects in design and construction, 7 of which are based on coal-derived syngas. Eight of the licensed plants are at capacities above 5,000 metric tpd.

Licensor: Johnson Matthey Davy Technologies Ltd. with Johnson Matthey Process Technology, both subsidiaries of Johnson Matthey Plc.
CONTACT

Methanol

Application: To produce high quality AA-grade methanol from hydrocarbon feedstocks using steam-reformer (SMR) process combined with O_2-oxygen supplying autothermal reformer (ATR) and integrated with low-pressure methanol synthesis with two stage distillations.

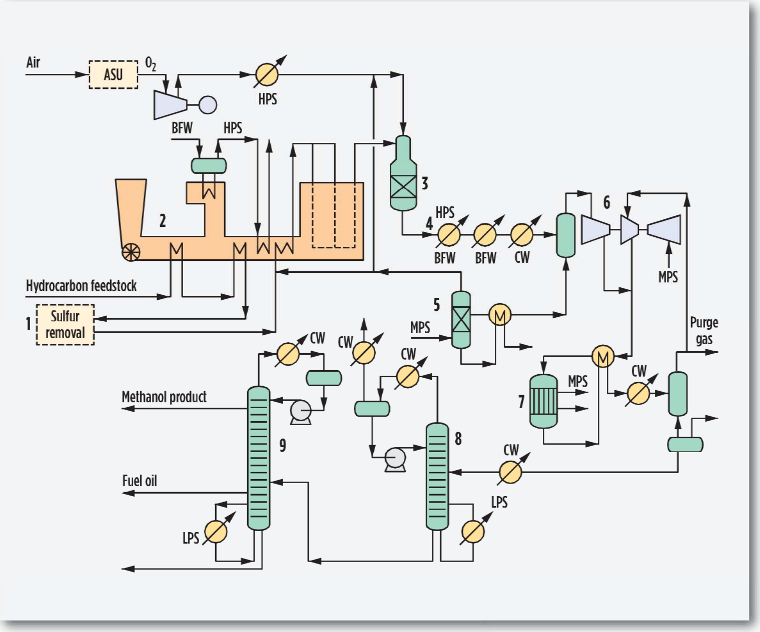
Description: The key features of the KBR low-pressure methanol process are the mild primary reforming, secondary reforming with oxygen blowing burner, synthesis of methanol at low pressure in an isothermal reactor and two- or three-column distillation.

Desulfurized (1) hydrocarbon feedstock is reacted with the steam in the primary reformer (2) with an exit temperature of about 780°C. Primary reformer effluent is reacted with oxygen (O_2) in the secondary reformer (3) with in exit temperature of about 950°C.

The secondary reformer exit gas is cooled by generating high-pressure steam (4) via a series of heat exchangers—boiler feedwater—and cooling water following separation of process condensate. The process condensate is stripped by medium-pressure steam (5) with vapor (top) feed as process steam to hydrocarbon feedstock and liquid (bottom) sent to treatment.

The cooled synthesis gas is compressed in syngas compressor (6), mixed with loop-recycle stream and fed to the water-cooled isothermal converter (7), thus generating medium-pressure steam. The converter effluent is cooled and sent for separation with liquid crude methanol fed to the distillation column and the recycle gas returned to the circulator compressor. A small purge gas is taken from the cycle gas to control inert levels within the synthesis loop.

The crude methanol is fed to light-end distillation column (8) to remove light hydrocarbons and effluents from the bottom and fed to the refining column (9) with methanol product taken from the top of the column, fusel oil from the middle, and process condensate from the bottom, which is sent to the water treatment plant.



Commercial plants: Four single-train methanol plants use the KBR methanol process, including a world-scale 2,500 metric tpd plant commissioned in 1988. Two large-capacity methanol plants are under design to revamp them from SMR front-end to SMR+O_2-ATR using KBR technology.

Licensor: Kellogg Brown & Root, LLC 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.

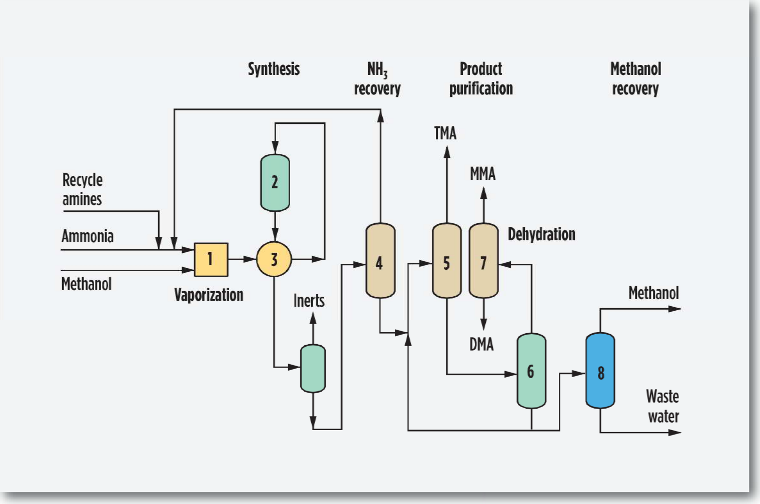
Methanol recovery (8) improves efficiency and extends catalyst life by allowing greater methanol slip exit from the converter. Addition of a methanol-recovery column to existing plants can help to increase production rates.

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

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: Johnson Matthey Davy Technologies Ltd., UK CONTACT

Mixed xylenes

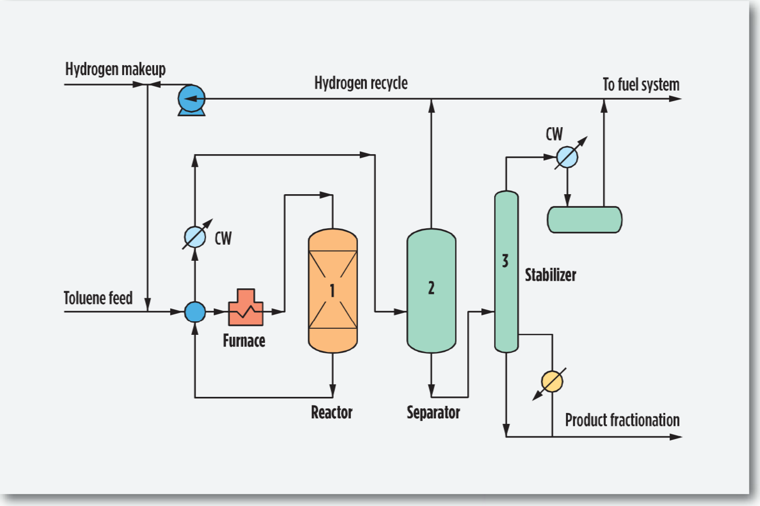
Application: To selectively convert toluene to mixed xylene and high-purity benzene using ExxonMobil Chemical's Toluene DisProportionation 3rd Generation (MTDP-3^{SM}) process.

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: The MTDP-3 process 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. 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)
Axens (grassroots applications) CONTACT

Mixed xylenes

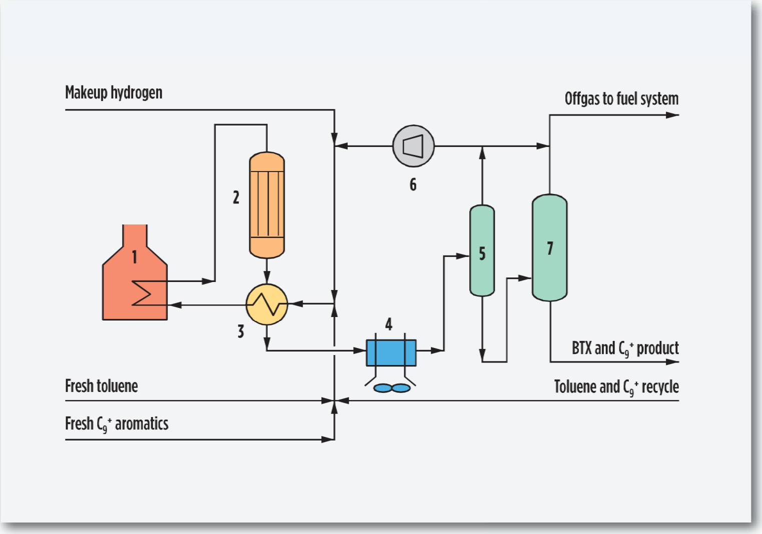
Application: To convert C_9^+ heavy aromatics, alone or in conjunction with toluene or benzene co-feed, primarily to mixed xylenes using ExxonMobil Chemical's TransPlus NG^{SM} process.

Description: Fresh feeds, 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 NG 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 NG technology to process feeds rich in C_9^+ aromatics enhances the product slate toward xylenes. Owing to its unique high activity 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 using the prior generation TransPlus^{SM} process technology was started up in Taiwan in 1997. The first commercial unit running the TransPlus NG process was started up in 2010. There are 10 TransPlus and 7 TransPlus NG references.

Licensor: ExxonMobil Chemical Technology Licensing LLC (retrofit applications)

Axens (grassroots applications) CONTACT

Mixed xylenes

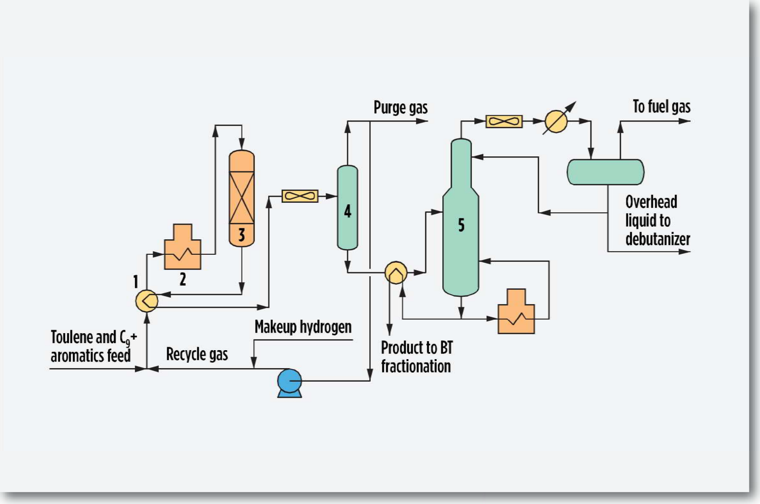
Application: The UOP Tatoray process produces mixed xylenes and petrochemical grade benzene by disproportionation of toluene and transalklyation of toluene and C_9^+ aromatics.

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 wt%–60 wt%. The Tatoray process provides an ideal way to produce additional mixed xylenes from toluene and heavy aromatics.

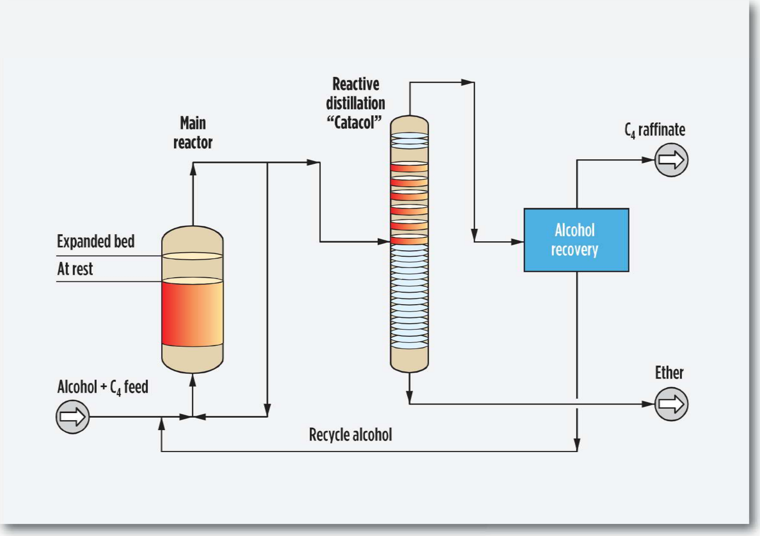
Economics: The process is designed to function at a high level of conversion per pass. High conversion minimizes the size of the BT columns, and the size of Tatoray process unit, as well as the utility consumption of all of these units.



Commercial plants: UOP has licensed a total of 65 Tatoray units; 47 of these units are in operation and the remainder are in various stages of construction.

Licensor: UOP LLC, A Honeywell Company 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 removed 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 IFPEN 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.

Continued ▼

MTBE/ETBE and TAME/TAEE: Etherification technologies, cont.

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

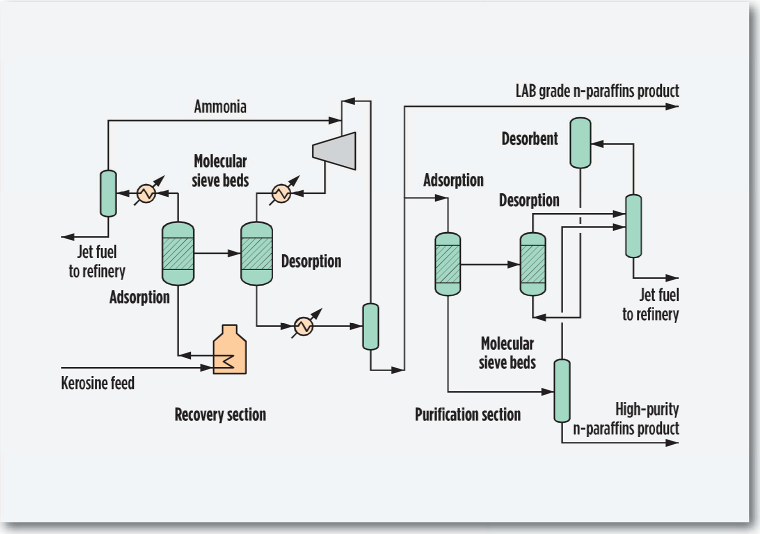
	MTBE	ETBE	TAME	TAEE
C_4 cut feedstock, tpy	329,000	275,000	369,000	355,000
Investment, US$ million	12	10	13	13
Utilities per ton of ether				
Electrical power, kWh	18	14	20	20
Steam, tons	1	0.9	1.2	1.2
Water, cooling m^3	65	57	73	70

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: Fifty-four etherification units have been licensed.

Licensor: Axens 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-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

Continued ▼

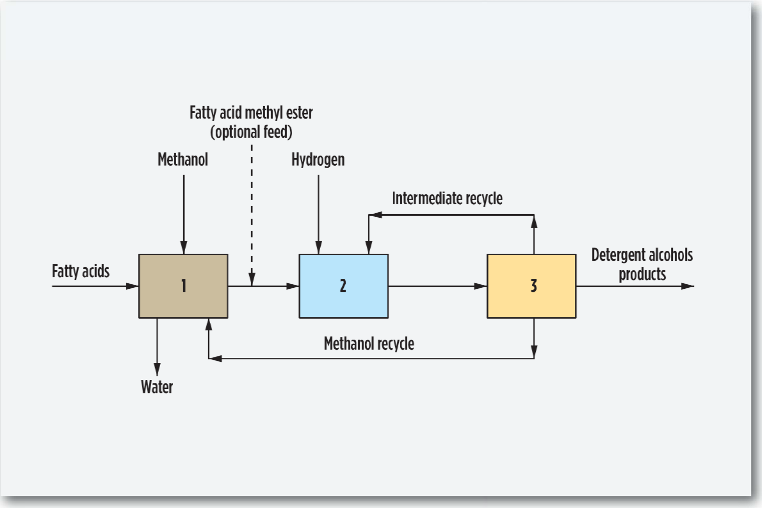
n-Paraffin, cont.

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

Natural detergent alcohols



Application: To produce natural detergent alcohols from fatty acids using esterification, hydrogenolysis and refining. Methyl ester can optionally be fed directly to the plant.

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.

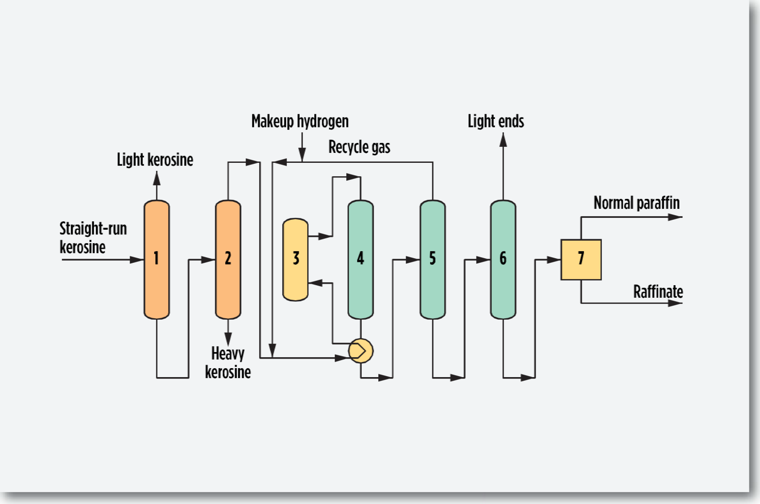
Commercial plants: The first commercial scale plant (30,000 metric tpy) to use the Davy process was started up in the Philippines in 1998. A further project for a 50,000-metric tpy plant was licensed and designed. This plant was moved to Indonesia and expanded by a further 20,000 metric tpy. In 2005/2006, 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. In 2010–2013, a further five plants were licensed, now mostly in operation with production capacities ranging from 80,000 tpy–150,000 tpy.

Reference: Brochure, “Lions share of NDA plants,” JM Davy, www.davyprotech.com

Licensees: Eleven licensees since 1998.

Licensor: Johnson Matthey Davy Technologies Ltd., 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%–40% normal paraffin content. Product purity is typically greater than 99 wt%.

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

Licensor: UOP LLC, A Honeywell Company 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.

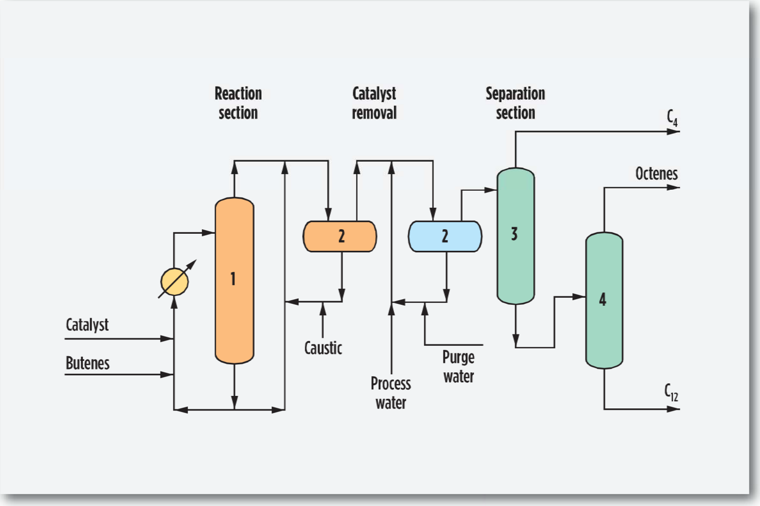
Yields: Nearly 80% conversion of n-butenes can be attained and selectivities toward octenes are about 85%. The typical C_8 product is a mixture having a minimum of 98.5% octene isomers with the following distribution:

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-seven 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—Deep catalytic cracking

Application: Selective conversion of gasoil and paraffinic residual feedstock in the presence of catalyst to produce high yields of light olefins including propylene, ethylene and butylene as well as high-octane gasoline and distillate.

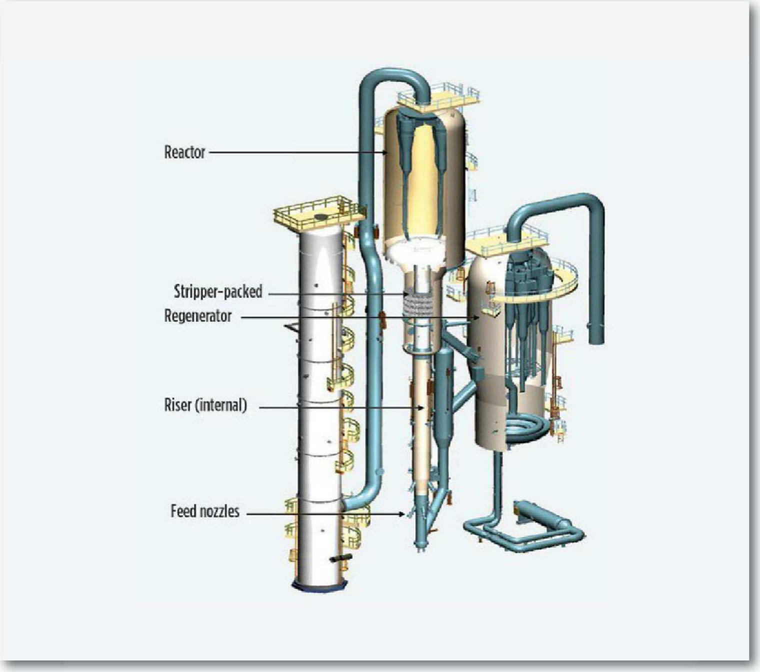
Description: Deep catalytic cracking (DCC) is a fluidized process for selectively cracking a wide variety of feedstock to light olefins. Propylene yields over 24 wt% are achievable with paraffinic feeds. DCC uses a conventional reactor/regenerator design with a catalyst that has physical properties similar to traditional fluidized catalytic cracker (FCC) catalyst. The DCC unit may be operated in two operational modes: maximum propylene (Type I) or maximum iso-olefins (Type II).

Each operational mode utilizes unique catalyst and reaction conditions. Type I DCC utilizes both riser and bed cracking at severe reactor conditions to maximize light olefins production. Type II DCC considers only riser cracking at milder conditions, similar to a conventional FCC unit. The configuration for the reactor and regenerator is shown in the schematic.

The overall DCC flow scheme is similar to that of a conventional FCC. However, innovations in the areas of catalyst development, process variable selection, severity and gas plant design enable the DCC to produce significantly more olefins than through an FCC application.

The technology is suitable for revamps as well as grassroots applications. Integrating DCC technology into an existing plant as either a grassroots unit or revamp can offer an attractive opportunity to produce large quantities of light olefins from low-value feedstock.

In a market requiring increased propylene to ethylene ratios, use of a catalytic cracking process in addition to traditional thermal cracking processes should be considered, due to the fundamental differences in the reaction mechanisms involved. The benefits associated with DCC over the steam cracking process for propylene production are a direct consequence of the relative cost differences between DCC heavy feeds and the steam cracker's light feeds. By integrating a DCC with a steam cracker, it is possible to capture the production benefits of each and to achieve cost savings in capital and operating expenses.



Economics: Typical yields from the DCC process and the conventional FCC process are given below. Production yields will vary based on the quality of feed and availability of internal and external unit recycles.

Continued ▼

Olefins—Deep catalytic cracking, cont.

Products, wt% of fresh feed	**DCC Type I**	**DCC Type II**	**FCC**
Ethylene	5.1	2.3	0.9
Propylene	20.5	14.3	6.8
Butylene	14.3	14.6	11.0
in which $iC_4^=$	5.4	6.1	3.3
Amylene	—	9.8	8.5
in which $iC_5^=$	—	6.5	4.3

Installation: A total of 17 DCC units have been licensed.

Reference: Dharia, D., et al., “Increase light olefins production,” *Hydrocarbon Processing,* April 2004, pp. 61–66.

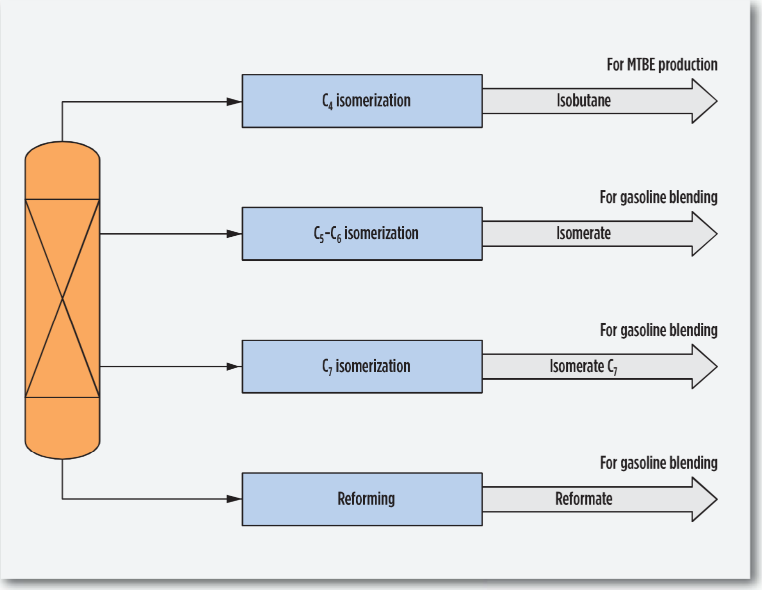
Licensor: Technip Stone & Webster Process Technology and Research Institute of Petroleum Processing, Sinopec. CONTACT

Paraffin isomerization

Application: The Isomalk℠ technologies are based on the use of mixed metal oxide (non-chlorinated) catalysts that operate at low-temperatures, allowing refiners to enjoy the high conversions to the key iso-components, while maintaining prolonged catalyst service lifetimes, simple operation and resistance to process impurities. This includes Isomalk-2℠ for C_5–C_6 isomerization, Isomalk-3℠ for C_4 isomerization, and Isomalk-4℠—a unique offering for C_7 paraffin isomerization.

Description: Isomalk-2 is a low-temperature isomerization technology that has been applied in grassroots applications, revamps of semi-regenerative reforming units, and replacement of other isomerization technologies. This flexible process utilizes a robust platinum-containing mixed-metal oxide SI-2™ catalyst that works effectively at the low temperatures of 120°C–140°C (250°F–285°F), while delivering great stability against the influence of catalytic poisons. Isomalk-2 is a competitive alternative to the three most commonly used light gasoline isomerization processes: zeolite, chlorinated aluminum oxide and sulfated zirconium oxide catalysts, applicable to a simple replacement of these catalyst types. This technology has been commercialized in all possible modes of configuration. By applying the full recycle configuration, an isomerate with a 92.5 RON value has been achieved in a world-scale reference unit.

Isomalk-3 is a low-temperature C_4 isomerization technology based on a use of mixed-metal oxide SI-3™ catalyst with high selectivity to i-butane. Operating at the temperature of 150°C–170°C—the yield and OPEX are optimized. Isomalk-3 has a catalyst lifetime of over 10 years with no need for chlorine injection, offgas caustic scrubbing. The water, sulfur and nitrogen specifications for the feed are significantly relaxed. As with the other catalysts from the Isomalk family, operation is simple and robust.



Isomalk-4 is a low-temperature isomerization technology for processing C_7 paraffins derived from hydrotreated straight run naphtha and raffinate from aromatics recovery units.In a conventional refinery, C_7 paraffins are sent to the C_5–C_6 isomerization unit and the reformer. For both of these units, this is an X-factor type feed that reduces the overall yield of the liquid products, along with the RON of the gasoline, and forms unwanted amounts of benzene. GTC's innovative process allows the isomerization of the C_7's to achieve a low-RVP gasoline component with 84–86 RON, and to improve the operation of the other naphtha processing units. By applying Isomalk-4, the C_7 paraffins in the raffinate stream, coming from the GT-BTX aromatics extraction unit, produce a high-octane blend stock and free additional C_5/C_6 feed to the isom unit and a rich C_8^+ naphthenes feed for the reformer.

Continued ▼

Paraffin isomerization, cont.

Process advantages:

Isomalk-2

- No need for corrosive chlorine promoters to achieve high levels of activity; no need for a caustic treatment section; no perchloroethylene (PCE) injection equipment
- Superior stability against catalytic poisons and, most importantly, water; no feed dryers; optimized startup, turnaround, shutdown procedures
- High conversion to the key isoparaffins requiring low energy consumption
- No process wastes, no ecological risks
- Flexible application for grassroots projects or revamps
- Accumulated technical expertise available through engineering packages and follow-up services

Isomalk-3

- No need for corrosive chlorine promoters to achieve high levels of activity; no need for a caustic treatment section; no PCE injection equipment
- Superior stability against catalytic poisons and, most importantly, water; no feed dryers; optimized startup, turnaround, shutdown procedures
- High conversion to isobutane requiring low energy consumption and chemical consumption
- One-reactor configuration, with fewer equipment pieces than competitor processes
- No process wastes; no ecological risks

Isomalk-4

- Optimum use of all molecules in the straight-run naphtha
- Best performance of isomerization and reforming unit
- Octane boost of C_7 paraffins to 84–86 RON

Commercial plants: Over 20 licensed units

Licensor: GTC Technology CONTACT

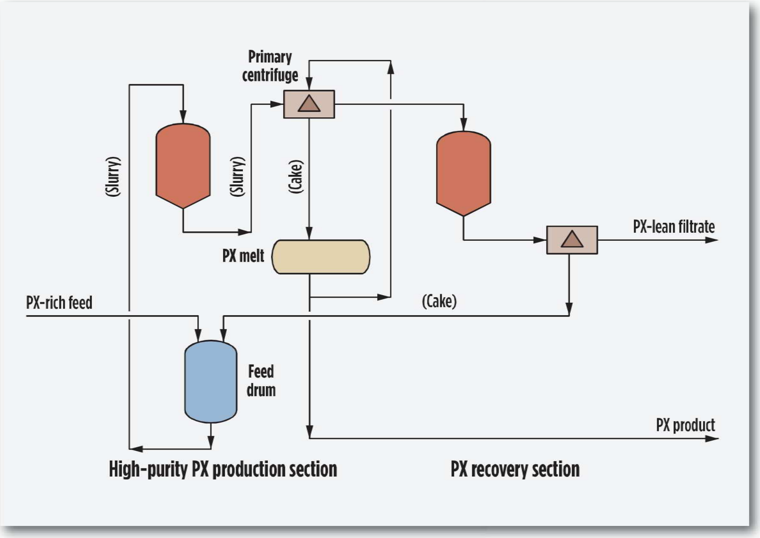
Paraxylene, crystallization

Application: CrystPX℠ is a modern suspension crystallization technology for production of paraxylene (PX), offered through alliance with LyondellBasell. This process separates PX by slurry phase crystallization and separation of the PX crystals from the remaining liquid. CrystPX technology is applicable with high- or low-concentration PX feedstocks, and is a lower-cost alternative to adsorption methods for PX production. GTC takes advantage of recent advances in crystallization techniques and improvements in equipment to create this attractive method for PX recovery and purification.

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

When paraxylene 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. This simplicity of equipment promotes low maintenance costs, easy incremental expansions, and controlled flexibility. High-purity paraxylene is produced in the front section of the process at warm temperatures, taking advantage of the high concentration of paraxylene already in the feed. At the back end of the process, high paraxylene recovery is obtained 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 paraxylene purity and recovery (99.8+ wt% purity at up to 95% recovery)
- Crystallization equipment is simple and operationally trouble free
- Compact design requires small plot size and lowest capital investment
- Operation is flexible to meet market requirements for paraxylene purity

Continued ▼

Paraxylene, crystallization, cont.

- System is easily amendable to future requirements for incremental capacity increases
- Feed concentration of paraxylene is used efficiently
- Technology is flexible to process a range of feed concentrations (75 wt%–95 wt% paraxylene) in a one-stage refrigeration system
- Design variations are used to recover paraxylene efficiently from equilibrium feedstocks (~22% PX) in a progressive crystallization system, more cost effective than adsorption-based systems.
- Dividing wall distillation (GT-DWC^{SM}) and Advanced Thermal Coupling Systems (GT-ATCS^{SM}) provide even more energy-efficient operation.

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

ISBL investment cost (2014)	$37 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 US, LLC, in alliance with LyondellBasell. CONTACT

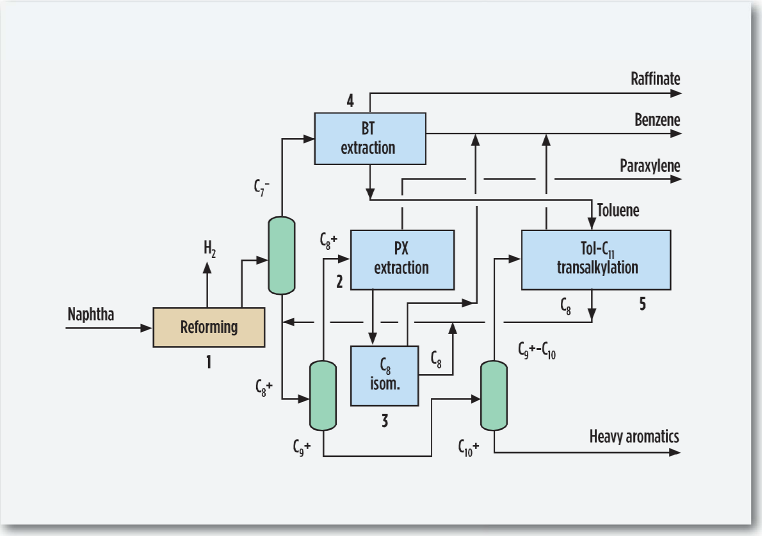
Paraxylene

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 capacities above one million 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 PX single-train complex from naphtha to PX, featuring Aromizing, Eluxyl, XyMax and TransPlus units.



Commercial plants: Twenty ParamaX integrated plants have been licensed, accounting for more than 20 million tpy of PX. Twelve ParamaX integrated plants are in operation. Twenty five Eluxyl units have been licensed 15 Eluxyl Unit are in commercial operation with single-line capacity ranging from 180,000 metric tpy to 1,000,000 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

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

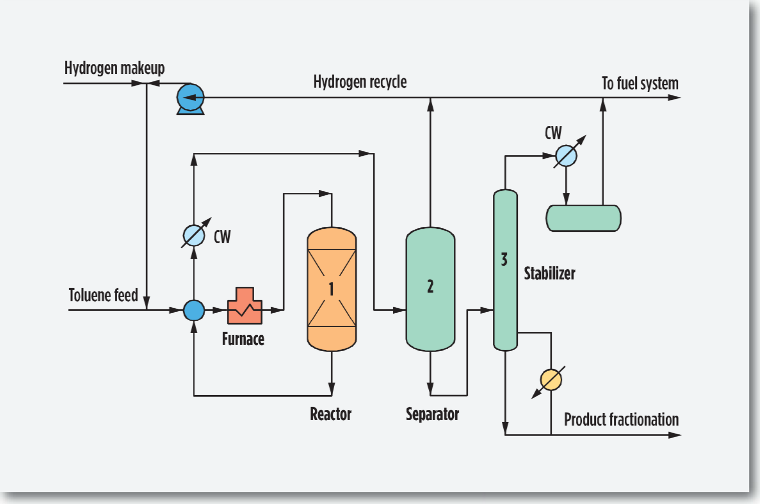
Paraxylene

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

Description: Dry toluene feed and hydrogen-rich recycle gas are pumped through feed/effluent exchangers and the charge heater and into the reactor (1). Selective toluene disproportionation (STDP) occurs in the vapor phase to produce the PX-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 permanently selectivated by ex-situ pretreatment during catalyst manufacture. PxMax technology provides significantly higher selectivity and longer operating cycles than other STDP technologies. Operating costs associated with downstream recovery are also reduced by the high paraxylene purity from the process.

Operating conditions: The PxMax process operates at lower start-of-cycle temperature 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 two MSTDP units (predecessor technology to PxMax) and 12 PxMax units currently in operation. The first two units running the PxMax process started up in 1996 and 1997 at Chalmette Refining's Louisiana refinery and Mobil Chemical's Beaumont, Texas, plant, respectively.

Licensor: ExxonMobil Chemical Technology Licensing LLC (retrofit applications)

Axens (grassroots applications) CONTACT

Paraxylene

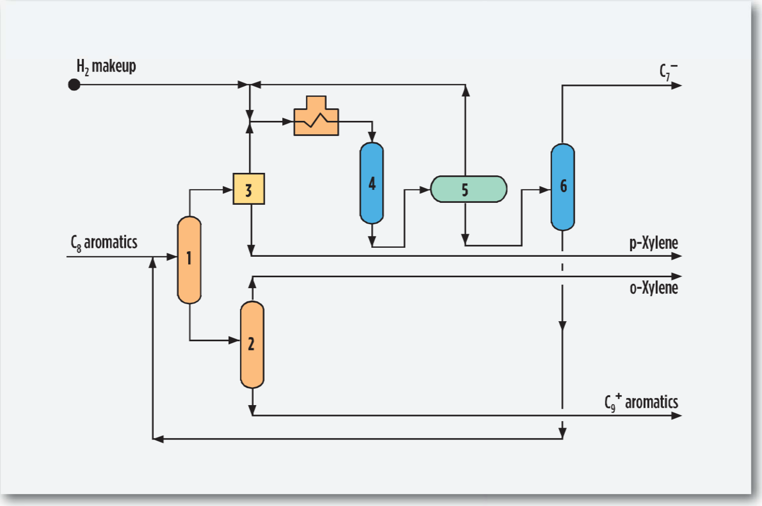
Application: To produce a desired xylene isomer (or isomers) from a mixture of C_8 aromatics using the UOP Isomar and Parex processes.

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

Commercial plants: Since 1971, UOP has licensed 101 Parex units and 81 Isomar units.

Licensor: UOP LLC, A Honeywell Company CONTACT

Paraxylene

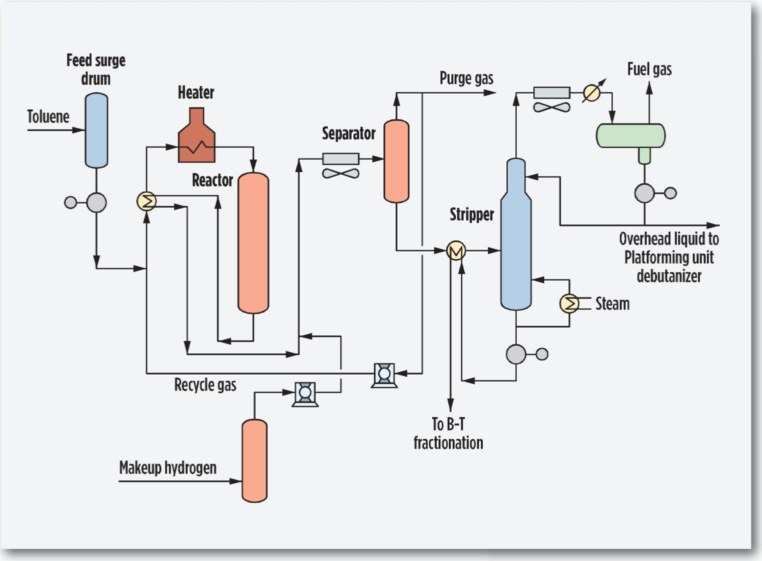
Application: The UOP PX-Plus Process converts toluene to paraxylene and benzene. The paraxylene concentrate is directed to a single-stage crystallizer or the Parex process for further purification.

Description: In the PX-Plus unit, fresh toluene feed is first combined with hydrogen-rich recycle gas, preheated by an exchanger with the hot reactor effluent and vaporized. It is then raised to the reaction temperature in a fired heater. The PX-Plus reactor is typically a down-flow design. The reactants exit through the feed-effluent exchanger, are condensed and sent to the product (gas-liquid) separator, where recycle hydrogen is removed. The separator liquid is sent to the stripper column, where light byproducts are removed in the overhead. The stripper bottoms stream is sent to benzene-toluene fractionation. High-purity benzene is recovered by the overhead, and unconverted toluene is recovered and recycled to the reactor.

The paraxylene concentrate may be fed directly to a single-stage crystallizer, or it can be sent to the Parex unit via the xylene column along with fresh feed mixed xylenes and recycle isomerate.

Yields:

Toluene conversion per pass	30%
Paraxylene concentrate in xylene	90%
Benzene xylenes, mol%	1.32
Light ends, wt%	< 2
Benzene quality	High



Commercial plants: Three PX-Plus units have been brought online with feeds ranging from 650, 000 metric tpy to 1.6 million metric tpy. The first unit came onstream in 2003.

Licensor: UOP LLC, A Honeywell Company CONTACT

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.

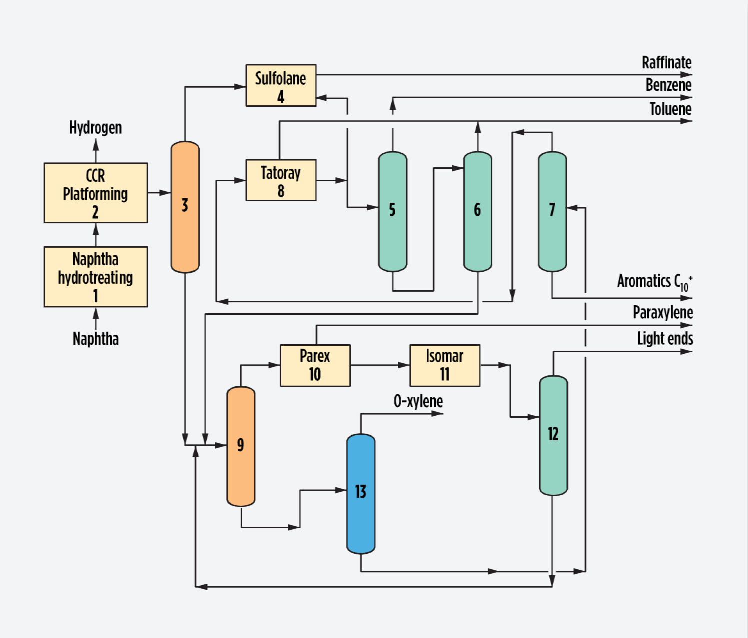
The naphtha feed is first sent to a UOP naphtha hydrotreating unit (1) to remove sulfur and nitrogen compounds and then sent to a UOP CCR Platforming unit (2) to reform paraffins and naphthenes to aromatics.

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 and 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.

The C_8^+ fraction from the bottom of the reformate splitter is charged to a xylene splitter column (9). 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.



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 300

Continued ▼

Paraxylene, cont.

CCR Platforming units, 150 Sulfolane units, 101 Parex units, 81 Isomar units and 65 Tatoray units.

UOP has designed 101 integrated aromatics complexes, which produce both benzene and paraxylene. These complexes range in paraxylene production capacity from 21,000 tpy to 1.7 million metric tpy.

Licensor: UOP LLC, A Honeywell Company CONTACT

Phenol

Application: The Versalis/CB&I 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.

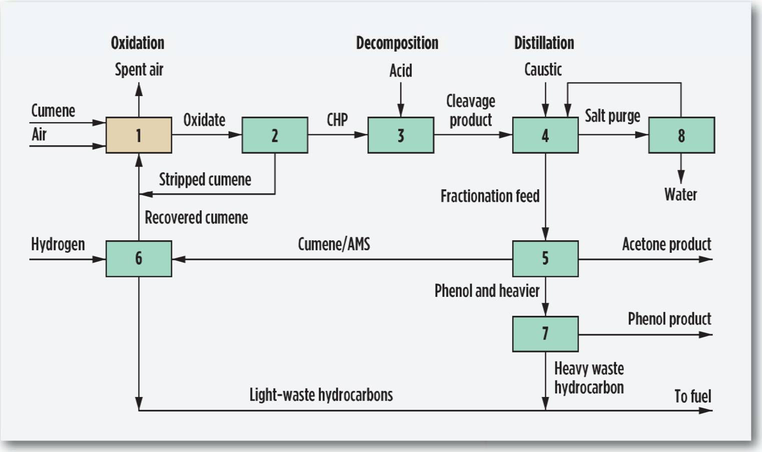
Fresh and recycle cumene is oxidized with air to produce CHP in a series of oxidizers (1) having a unique internal design that improves selectivity and enhances safety. Oxidate is then concentrated in two evaporation stages (2) and fed to a two-stage cleavage section (3) in which CHP is decomposed to 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 byproducts 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. Versalis' 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 (mt) of phenol product is 1.308 mt. Phenol purity is higher than 99.99 wt% with less than 10 ppm of carbonyl impurities.

Economics: Typical utilities, per mt of phenol

High- and medium-pressure steam, mt	2.3
Power, kWh	150

Commercial Plants: The process is used in Versalis' phenol plants at Mantova and Porto Torres, Italy. Three licenses have been granted.

Licensor: CB&I CONTACT

Phenol

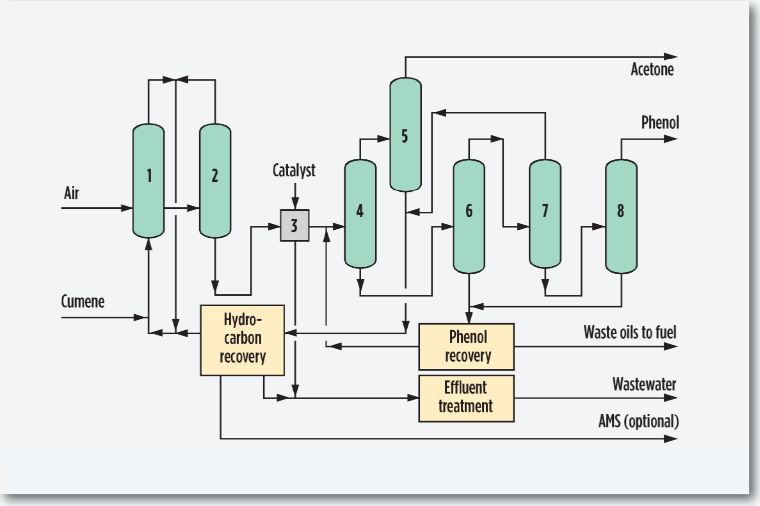
Application: A high-yield process to produce high-purity phenol and acetone from cumene with optional byproduct recovery of alpha methylstyrene (AMS) and acetophenone (AP).

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 50 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 26 producers, and the technology is well-proven commercially at over 300,000 metric tpy for single-train operations. In the last five years, KBR was awarded four grassroots phenol plants including two in China, one in Korea, and one in Saudi Arabia. More than 50% of the world's licensed phenol capacity is produced via the KBR process.

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

Licensor: Kellogg Brown & Root LLC CONTACT

Phenol

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

Description: Key process steps:

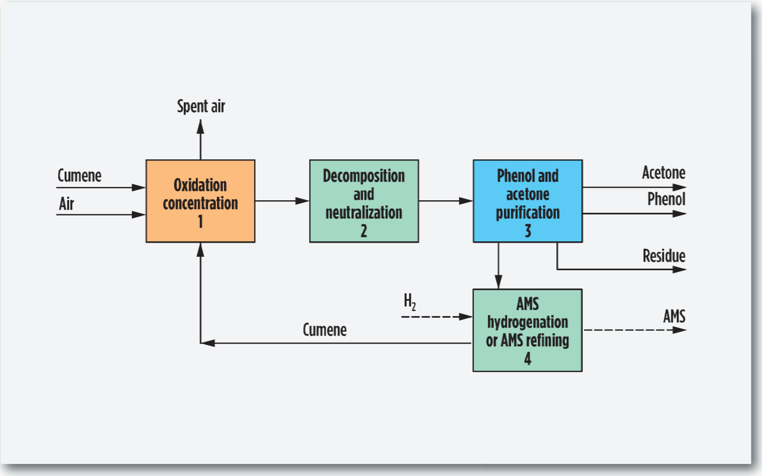
Oxidation and concentration (1): Cumene is oxidized to cumene hydroperoxide (CHP). A small amount of dimethylphenylcarbinol (DMPC) is also formed, but low-pressure and low-temperature oxidation results in very high selectivity of CHP. CHP is then concentrated and unreacted cumene is recycled back to 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 UOP Phenol process features low feedstock consumption (1.30 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 UOP Phenol process easier to operate.



Economics: Basis: ISBL 2013 US Gulf Coast

Investment, US$/tpy (200,000 tpy of phenol)	1,010 ± 50%
Raw materials and utilities, per metric ton of phenol	
Cumene, tons	1.30
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.

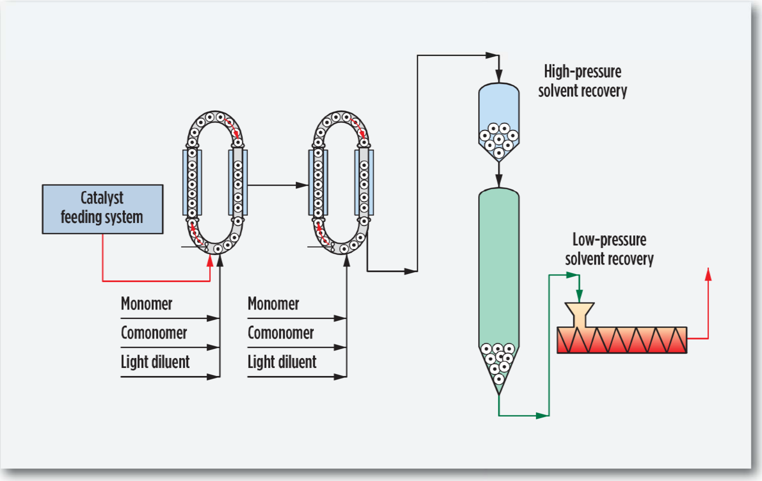
Licensor: UOP LLC, A Honeywell Company CONTACT

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 (JV) in 2002 and acquired by BP when they bought out Solvay's share of their JV 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 (Ti)-based and chromium (Cr)-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 Cr catalyst, using monomodal and bimodal configuration with market leading products such PE100.

Continued ▼

Polyethylene, cont.

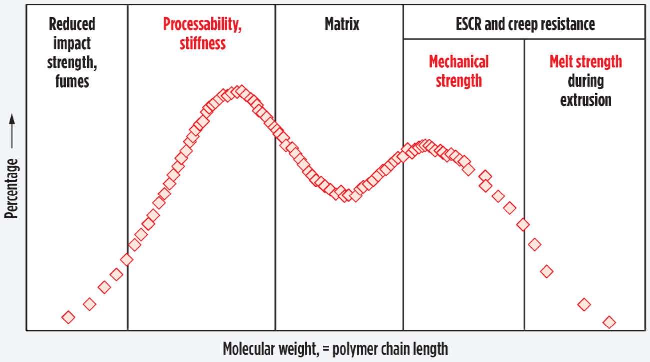
High added-value products, in addition to the lowest investment and operational costs allow INNOVENE S technology to make a winning MDPE/HDPE business.

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

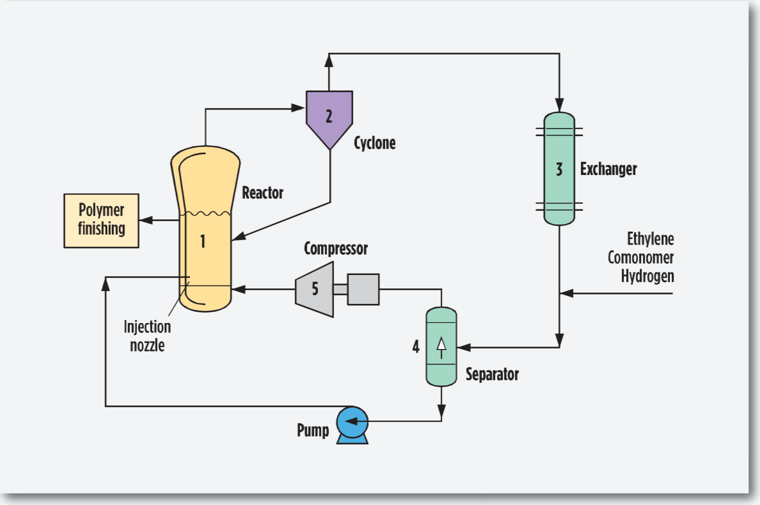
Product advantages:

- Broad MDPE and HDPE product range based
- Monomodal and biomodal capability
- Cr 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 Innovene G (gas phase) process produces linear-low-density polyethylene (LLDPE) and high-density polyethylene (HDPE) using Ziegler-Natta, chromium (Cr) or metallocene catalysts.

Description: Ziegler-Natta and metallocene catalysts are directly injected into the reactor from storage where as Cr 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 injec-

Continued ▼

Polyethylene, cont.

tion 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

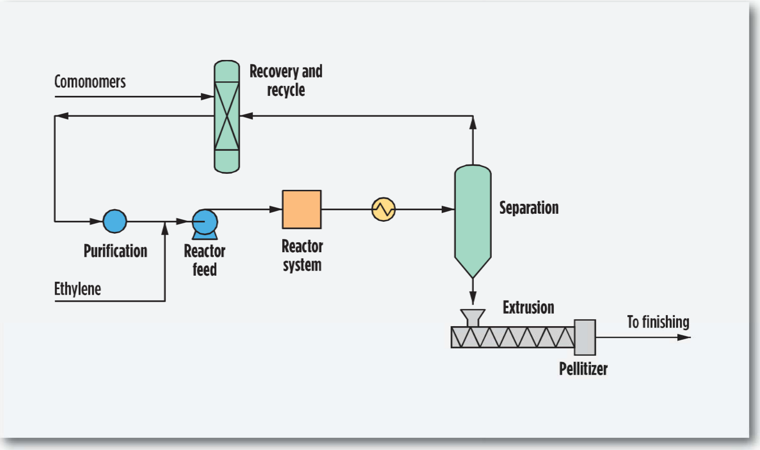
Application: The SCLAIRTECH[1] technology process produces the full range of linear polyethylene (PE) products, including linear-low-density, medium-density and high-density grades with narrow to broad molecular weight distribution. It is the most efficient PE swing process that allows for economical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

Description: Ethylene and comonomer are dissolved in solvent and 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: The SCLAIRTECH process can produce PE products with a density range of 0.905 kg/m^3 to 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, and 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, as well as 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.

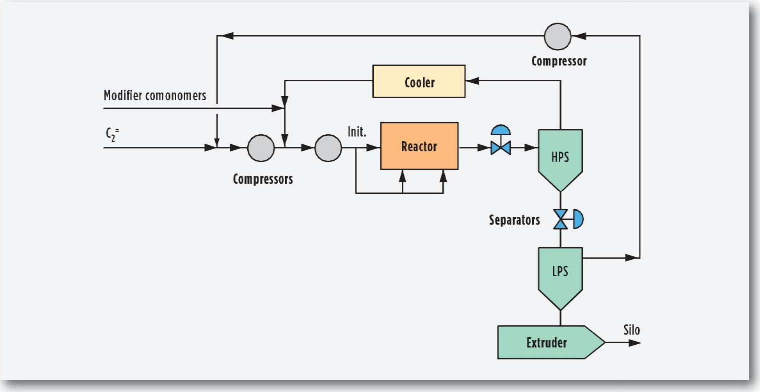
Polyethylene—LDPE

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 200,000 tpy–450,000 tpy, as well as stirred autoclave reactors with capacity up to 150,000 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 to greater than 30 wt%.

Economics: Raw materials and utilities, per metric ton of pelletized polymer (450,000 tpy tubular):

Ethylene, ton/ton	1.007
Electricity, kWh	700
Steam, ton/ton	0.1
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 1.8 million tpy. Homopolymers and a variety of copolymers are produced. Since 1996, ExxonMobil's LDPE process has been licensed to 14 licensees with a total installed capacity (either in operation or under construction) of approximately 3.1 million tpy.

Licensor: ExxonMobil Chemical Technology Licensing LLC CONTACT

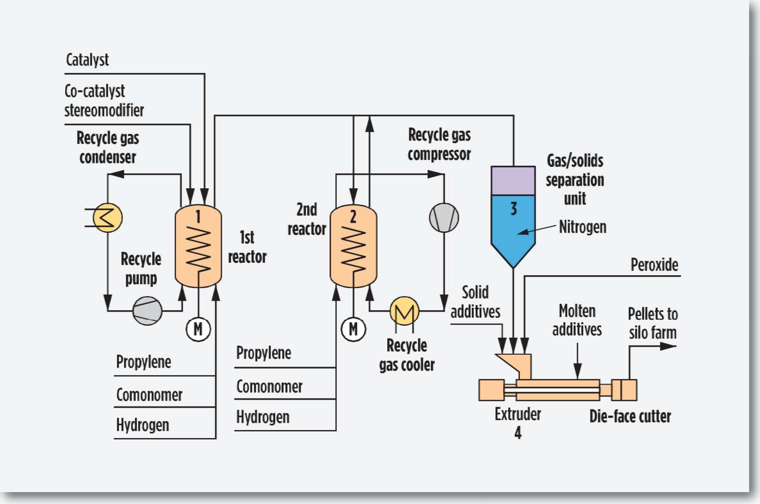
Polypropylene

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 PP 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.

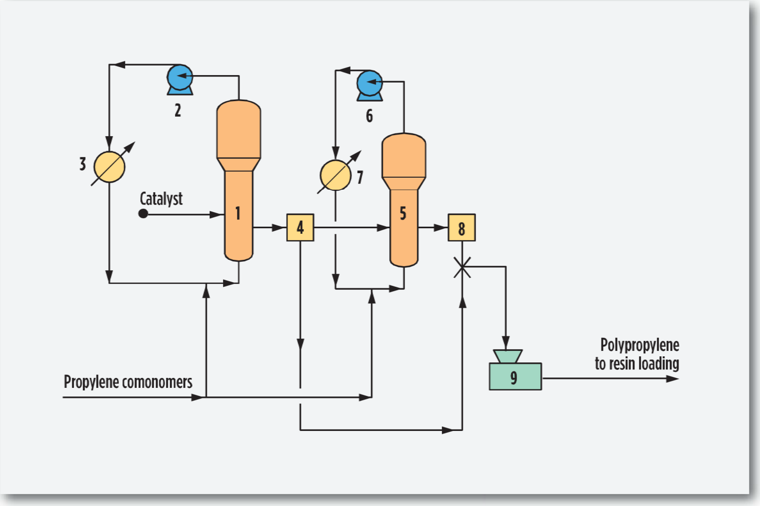


Commercial plants: The capacities range from 60,000 to 450,000 metric tpy for single lines. Over 50 production lines are in operation, engineering or under construction. The total licensed capacity worldwide for the Novolen process is in excess of 8 million tons.

Licensor: CB&I 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). A

Continued ▼

Polypropylene, cont.

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: Forty-eight reaction lines are in operation, and 15 reactor lines are under design and construction with capacities ranging from 80,000 tpy to 650,000 tpy. About 17% of the global polypropylene production is based on the Unipol process.

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

CONTACT

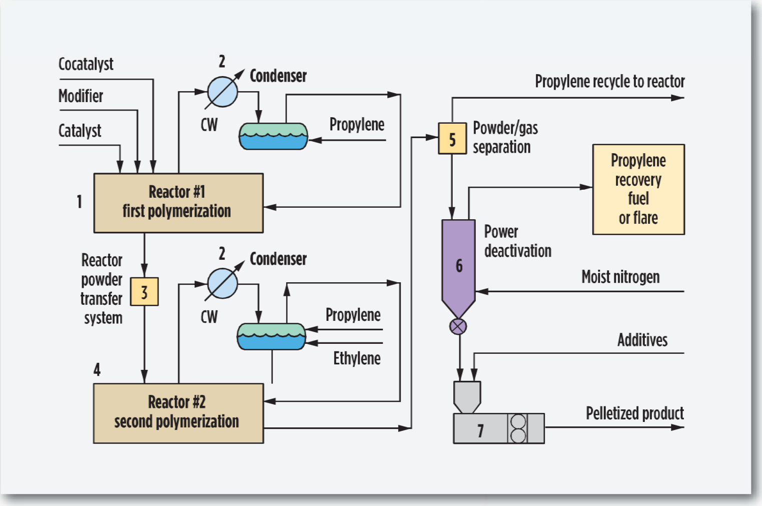
Polypropylene

Application: To produce polypropylene (PP) homopolymer, random copolymer and impact copolymer using the Innovene PP gas-phase process with proprietary 5th 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 into the stirred reactor 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.

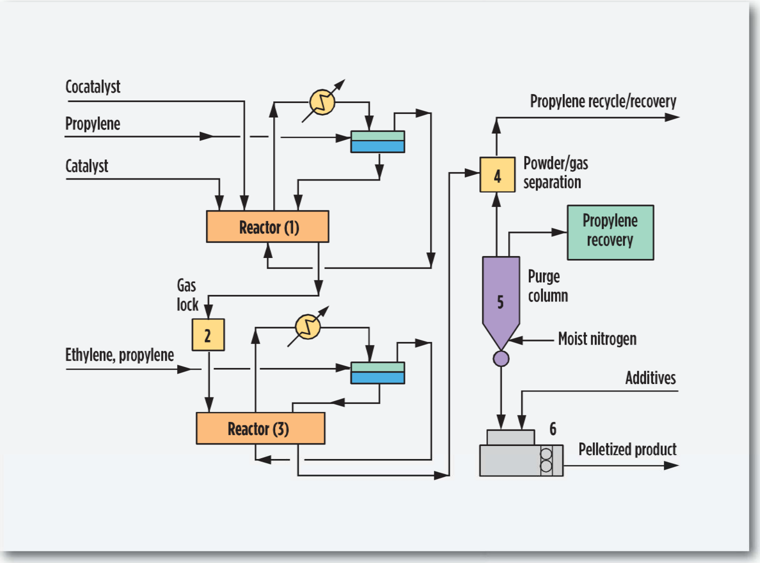


Products: A wide range of polypropylene products (homopolymer, random copolymer and impact copolymer) can be produced to serve many applications, including injection molding, blow molding, thermoforming, film, extrusion, sheet and fiber. Impact copolymer produced using this process exhibits a superior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

Commercial plants: Thirty-nine plants are either in operation or in design/construction worldwide with capacities ranging from 65,000 to 600,000 metric tpy.

Licensor: INEOS Technologies CONTACT

Polypropylene



Application: A process to produce homopolymer polypropylene, ethylene-propylene random copolymer, impact copolymer and reactor-made TPO. Japan Polypropylene Corp. (JPP) HORIZONE Technology (formerly known as Chisso Gas Phase Technology) utilizes horizontal plug-flow reactors.

Description: The process features horizontal agitated reactors and utilizes high-performance catalyst specifically developed by the licensor. The catalyst has controlled morphology, very high activity, and very high stereoregularity. Therefore, this catalyst and the process are advantageous to produce impact copolymer and reactor-made TPO without fouling troubles. The process also provides low energy consumption, superior ethylene-propylene impact copolymer properties, minimum transition material, high polymer throughput and a high operating factor. Each process step has been simplified; consequently, the technology offers low initial capital investment and reduced manufacturing cost, while providing product uniformity, excellent quality control and a wide range of polymer design, especially for copolymer products. Catalyst and monomer propylene are fed to the first reactor (1) with hydrogen as the molecular weight regulator. In the reactor, propylene is continuously polymerized under low pressure condition forming polypropylene powder. Removal of the polymerization heat is carried out by evaporation of liquid monomer. Liquid propylene is sprayed onto the agitated powder bed and evaporated gas is condensed at the condenser and recycled to the reactor. The powder is sent to the second reactor (3) through the gas-lock system (2). In the second reactor, polymerization is carried out similarly to the first reactor. For impact copolymer production, ethylene is fed as a monomer. In the horizontal reactor, the flow pattern of powder is close to plug-flow, so the residence time distribution is narrower than the back-mixed reactor. It minimizes the transition material and prevents short-passing of catalyst particle which gives significant influence on the product quality. The powder is released periodically to a powder/gas separation system (4). The separated monomer is recovered and recycled at the recovery system. The powder is sent to the purge column (5), where moist nitrogen deactivates the catalyst and removes remaining monomer. The residual monomer purged with nitrogen is concentrated by the Propylene Recovery Unit (PRU) system and recovered. The powder is converted into a variety of pelletized resins (6) tailored for specific market applications.

Continued ▼

Polypropylene, cont.

Economics: Typical unit consumption

(Unit/ton–PP pellet)	Homopolymer	Impact copolymer
Propylene and ethylene, kg	1,005	1,005
Electricity, kWh	293	337
Steam, kg	150	254
Cooling water, ton	84	112
Nitrogen, Nm^3	27	31

Installations: After 2000, 12 polypropylene plants are in operation or under construction in Japan, China, Taiwan and the US, with capacities ranging from 65,000 tpy to 300,000 tpy. JPP offers process designs with capacities up to 400,000 tpy for single train.

Licensor: Japan Polypropylene Corp. (JPP) CONTACT

Polystyrene, expandable

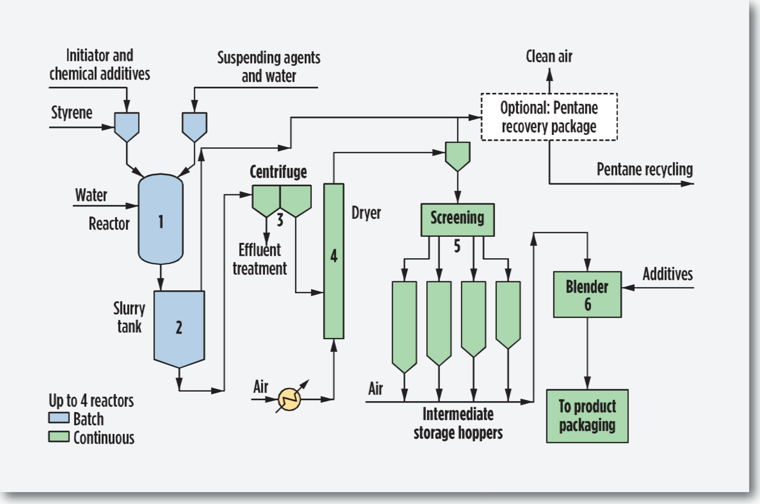
Application: For the production of regular and flame-retardant expandable polystyrene, INEOS offers the "one-step" suspension process.

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:

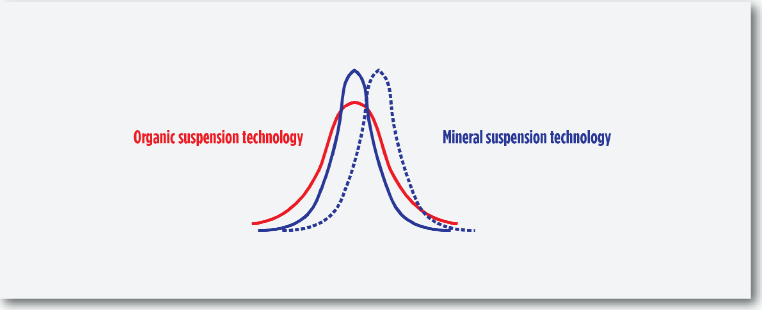
- Regular and flame-retardant grades available
- Narrow-bead size distribution thanks to the mineral suspension system
- High reactor productivity/high capacity design (up to 100,000 metric tpy on a single line)
- Proven and easy to operate technology
- Optional volatile organic compound (VOC) recovery system
- The process includes batch reactions automatically controlled followed by a fully continuous downstream section
- Continuous low residence time coating process.

Continued ▼

Polystyrene, expandable, cont.

Market advantages:

- Outstanding raw material and utility yields
- Consistent high-quality products widely accepted in the market-place
- 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)

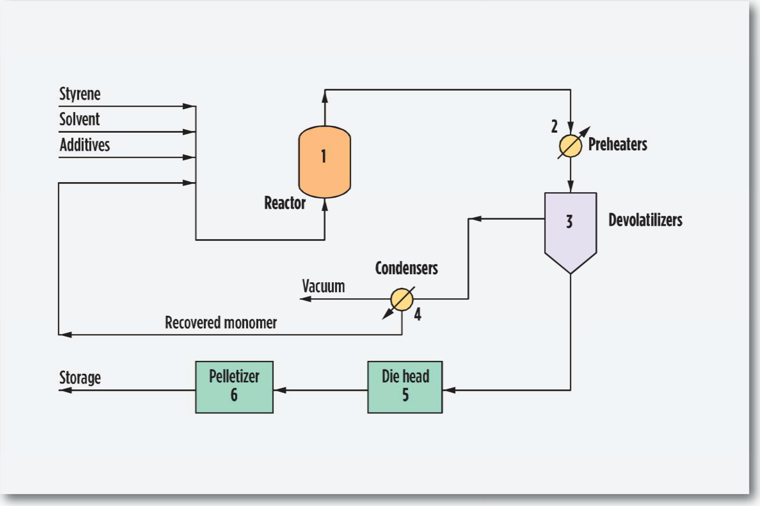
Application: To produce a wide range of general-purpose polystyrene (GPPS) with excellent high clarity and suitable properties to process PS foam via direct injection extrusion by the continuous bulk polymerization process using Toyo Engineering Corp. (TOYO)/Mitsui Chemicals, Inc. (MCI) technology.

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

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

Economics: Basis: 50,000 mtpy GPPS

Raw materials consumption per 1 metric ton of GPPS, kg	1,009
Utilities consumption per 1 metric ton of GPPS, US$	10.5



Installations: Toyo has licensed 42 polystyrene plants (GPPS/HIPS/SAN/ABS) with a total production capacity of 950,000 tpy.

Licensor: Toyo Engineering Corp. (TOYO)/Mitsui Chemicals, Inc. (MCI)
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. (MCI) technology. The process has a swing production feature and is also capable of producing general-purpose polystyrene (GPPS).

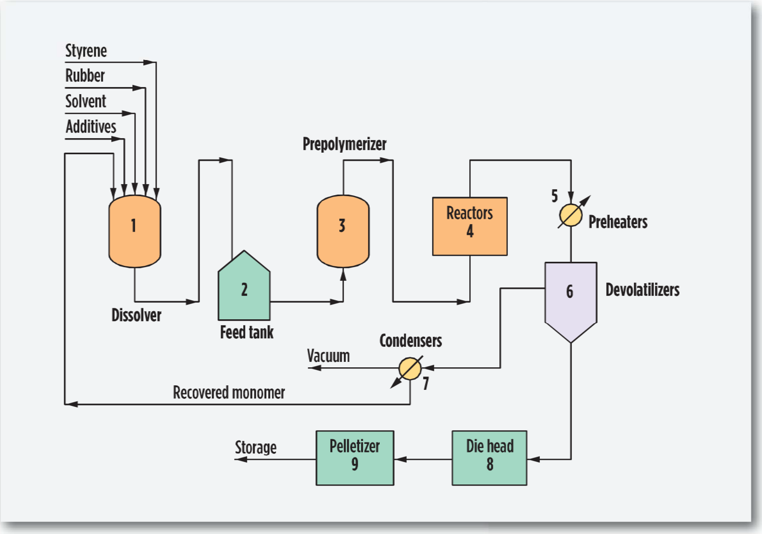
Description: Styrene monomer, ground rubber chips, and a small amount of additives are fed to the rubber dissolver (1). The rubber chips completely dissolved in styrene. This rubber solution is sent to a rubber-solution-feed tank (2). The rubber solution from the tank is sent to the prepolymerizer (3)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

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

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

Economics: Basis: 50,000-metric tpy HIPS unit

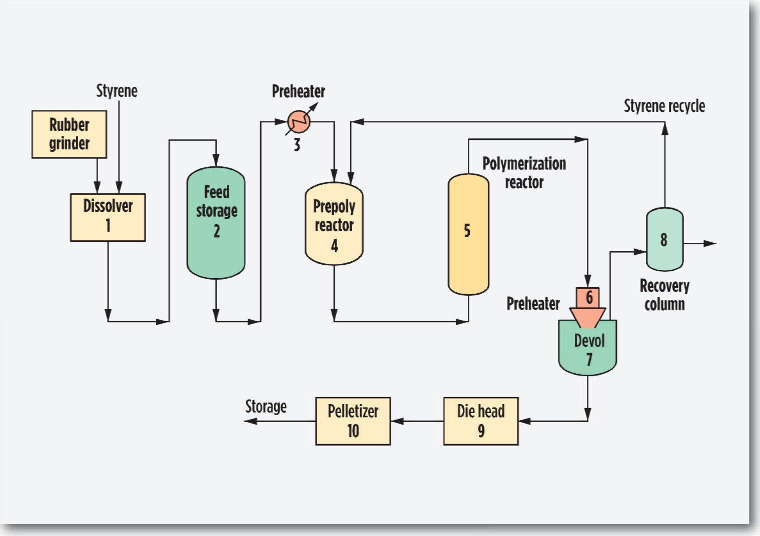
Raw materials consumption per 1 metric ton of HIPS, kg	1,009
Utilities consumption per 1 metric ton of HIPS, US$	8



Installations: Toyo has licensed 42 polystyrene plants (GPPS/HIPS/SAN/ABS) with a total production capacity of 950,000 tpy.

Licensor: Toyo Engineering Corp. (TOYO)/Mitsui Chemicals, Inc. (MCI)
CONTACT

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.

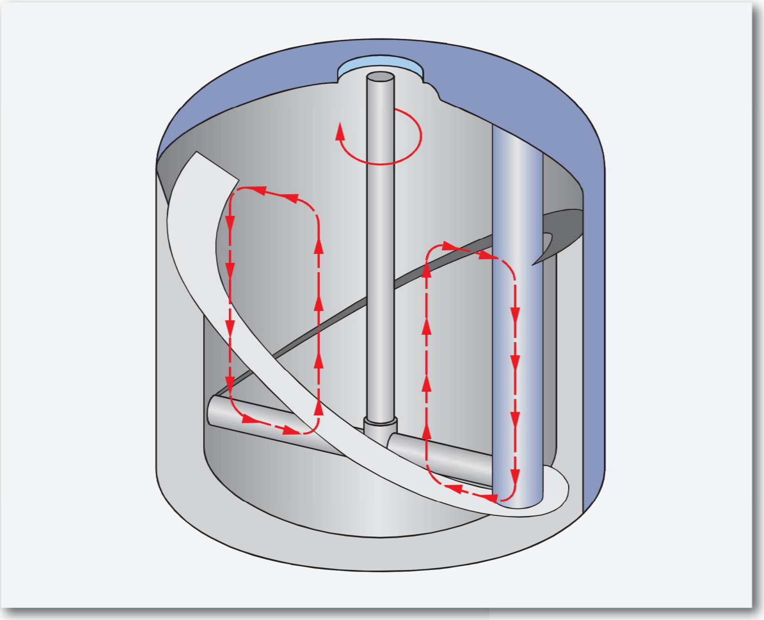
Continued ▼

Polystyrene, cont.

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:
  - Enhanced polymer/rubber grafting
  - 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—GPPS and HIPS

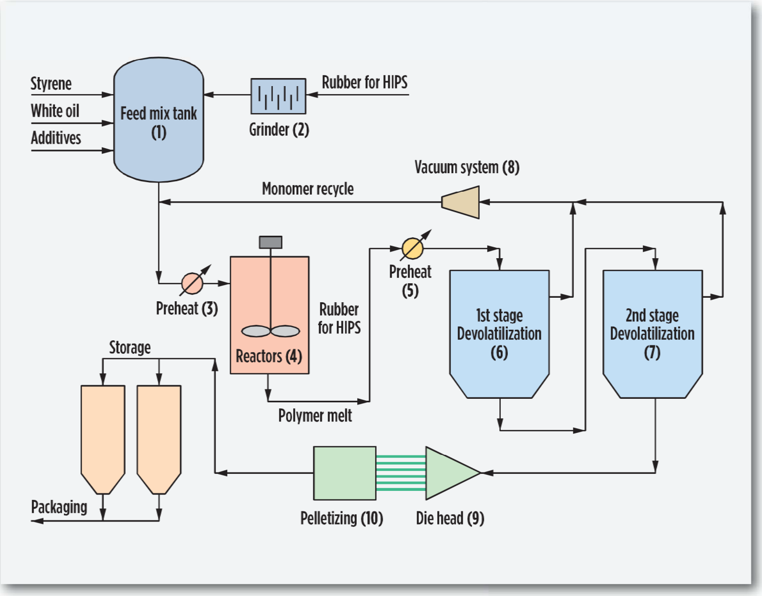
Application: Polystyrene (PS) is used in the electronics, appliances, building, food service, construction and transportation industries. Total's PS technology is based on a mass continuous process that uses a proprietary polymerization reactor and devolatization system to produce a wide range of high-quality, low-volatility content, general-purpose polystyrene (GPPS) and/or high-impact polystyrene (HIPS).

Description: For GPPS, styrene monomer, additives and white oil are sent to a feed mix tank (1). For HIPS, polybutadiene rubber bales are first ground (2) and then dissolved in styrene monomer (SM).

The HIPS or GPPS feed solution and recycle streams are preheated (3) upstream of the polymerization reactors (4). The reactor configuration, based on the combination of continuous stirred-tank reactor (CSTR) and plug-flow reactors (PFRs), depends on the product slate and plant capacity. Polymerization may be initiated chemically or thermally and occurs step-wise in multiple reactors. With the reactors arranged in series, residence time, initiator and chemical concentrations, reactor temperature profiles are accurately controlled to maintain the optimum conversion rate and the product's physical properties.

Devolatilization is accomplished in a two-stage deep-vacuum system. Polymer melt from the last reactor is preheated (5) upstream of the first devolatilizing (6) step, where unreacted SM and ethylbenzene solvent are stripped. The second devolatilizer (7) operates at very low absolute pressure, reducing residual SM to values as low as 150 ppm, exceeding European food-grade requirements. Devolatilization equipment is designed for trouble-free operations and to minimize residence times at high temperatures, avoiding product degradation.

A vacuum system (8) is utilized to cool vapors from the reactors and devolatilization systems. Vapors are condensed in water-cooled exchangers, collected in a surge drum and recycled to the reactor system.



Devolatilized polymer melt is then sent to a strand die head (9) to create polymer strands. After the cooling and cutting steps (10), the pellets are dried and then classified to remove fines and oversized pellets. The finished PS pellets are then pneumatically conveyed to storage and packaging.

Economics: The technology features high product yields and low energy consumption. Typical raw material and utilities based on 1 metric ton of GPPS are:

Continued ▼

Polystyrene—GPPS and HIPS, cont.

Styrene monomer, kg	976
White oil, kg	30
Electric power, kWh	115
Fuel, kcal	120,000

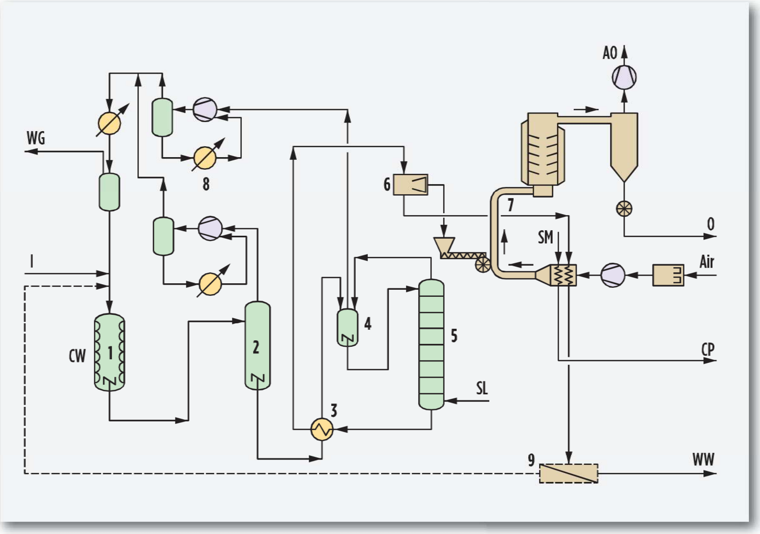
Products: The technology gives licensees access to a broad range of recognized high-quality PS products with a low-cost capital investment. The basic offering covers major PS applications such as packaging, electronics, home appliances and insulation. The product slate can also include specialty grades presenting enhanced performances such as low-molecular-weight and high-molecular-weight GPPS or HIPS presenting environmental stress crack resistance (ESCR) properties and high gloss.

Commercial plants: The technology is currently operated in approximately 50 commercial PS production units with capacities ranging from 10,000 tpy to 230,000 tpy. The units are located in 20 countries, with an aggregate installed capacity of 2.9 million metric tpy. Total is the second largest global producer of PS, operating seven plant sites with a combined capacity of nearly 1.5 metric tpy including the largest single mass polystyrene production unit in the world (230,000 metric tpy) located in Carville, Louisiana, in the US.

Key features:
- High polymer yields, typically greater than 99%
- High efficiency heat transfer system, allowing accurate temperature control
- Mechanically simple and reliable reactor and devolatization systems
- Simple process scheme and control, requiring fewer operators
- Process scheme produces finished product with low residual aromatics content
- Low maintenance as a result of optimized process design and operations control
- High safety and environmental performances in response to more stringent regulations

Licensor: Technip Stone & Webster Process Technology CONTACT

Polyvinyl chloride, suspension



Application: In Vinnolit's suspension PVC process, vinyl chloride monomer is polymerized to polyvinyl chloride by radical polymerization in aqueous suspension. The process comprises supply for VCM, DM water and auxiliary chemical solutions, reaction, removal and recovery of unconverted VCM and drying.

Description: The polymerization reaction is carried out in a proprietary reactor (1) that is characterized by the arrangement of cooling half pipes on the inner shell of the reactor. In the strongly exothermal VCM polymerization, the minimum reaction time, and thus the reactor's productivity is determined by the cooling capacity of the reactor. A considerable increase of the heat-transfer coefficient is achieved for the Vinnolit reactor by a reduction of the wall thickness for heat conduction and an increase of the heat-transfer area by the half pipes. Cooling water (CW) is used for heat removal. Before start of charging, the internal wall of the empty and flushed reactor is coated with commercially available antifouling agent. Together with the sophisticated reactor design and proven auxiliary chemicals, operating times of half a year and more are achieved without need for opening the reactor.

DM water, auxiliary chemicals, VCM and initiators are supplied from battery limit as input stream (I). VCM is charged simultaneously with hot DM water under computer control. So, at the end of charging, the desired polymerization temperature is achieved and the polymerization is started by the addition of initiators.

At a conversion around 80%–90%, the reaction is stopped and the slurry is transferred from the discontinuous reactor to the blowdown vessel (2) as interface to the continuously operated downstream units. The unconverted VCM evaporates and is guided without gasholder directly to the recovery unit (8). The PVC itself is stripped with steam (SL) in a predegassing vessel (4) and the proprietary stripping tower (5) to a residual VCM content below 1 ppm. The heat content of the degassed slurry is utilized (3) for the heat-up of the VCM-containing slurry. The compressed recovered VCM is after condensation is again used as polymerization raw material. Noncondensable impurities are sent as waste gas (WG) for external combustion.

After separation of the wet PVC from the process water in decantation centrifuges (6), the PVC is dried under gentle conditions in a combination of a flash dryer with a proprietary cyclone dryer (7). Ambient drying air (AIR) is heatedup by steam (SM), and the condensate (CP) can be used outside the unit. Fuel gas is also possible as a source for drying heat. The cyclone dryer provides the residence time of several minutes required for removal of the water from the pores after the surface water has been evaporated in the flash dryer. This combination is easy to oper-

Continued ▼

Polyvinyl chloride, suspension, cont.

ate and requires low maintenance work. After separation, the humid drying off-air (AO) goes back to atmosphere and the dry PVC product (O) is conveyed to the product storage.

As an additional option for the production, the replacement of around 50% of the DM water by recycled process water is now possible for pipe grade. A modern membrane apparatus (9) is used to guarantee the required cleanliness of the recycled process water. The (remaining) water from the centrifuge (6) is as wastewater (WW) sent for biological wastewater treatment.

Economics:

- Raw material consumption 1,001 kg VCM per t of PVC
- Reactor size up to 162 m^3
- Long reactor operating times without opening due to effective suppression of wall fouling
- Commercially available auxiliary chemicals
- Short non-reaction time due to charging heated DM water simultaneously with the VCM
- For energy saving reasons, the suspension stream to the degassing column is preheated with the already degassed slurry from the degassing column.
- Residual VCM in PVC below 1 ppm
- 1.5 m^3 DM water/ft PVC for pipe grade possible with optional wastewater recycling
- Steam consumption approximately 800 kg/t PVC
- Electric power approximately 170 kWh/t PVC
- Integration of parts of the Vinnolit process into existing plants during revamps is possible and proven
- Technical assistance from experienced PVC manufacturer also after startup of a project

Installations: Five licensed units, more than 30 licensed cyclone dryers (also for other products than PVC)

Reference: R. A. Meyers (Editor), *Handbook of Petrochemicals Production Processes,* pp 18.21–18.35, McGraw-Hill (2005).

Licensor: Vinnolit GmbH & Co. KG CONTACT

Propylene and ethylene

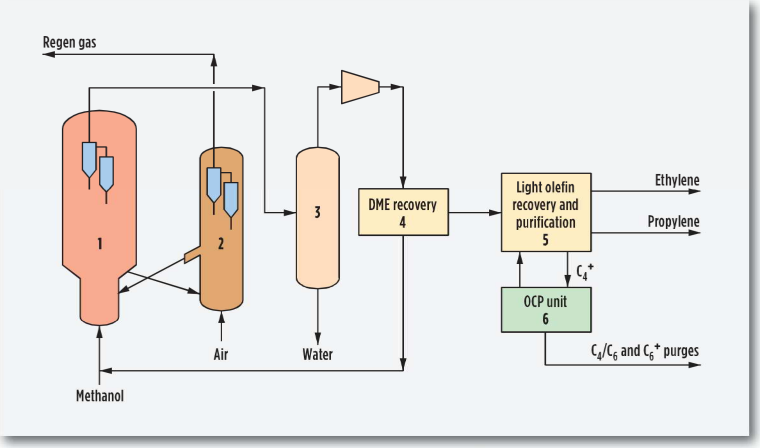
Application: The UOP/HYDRO Methanol-to-Olefins (MTO) Process produces ethylene and propylene from methanol derived from alternative, low-cost raw materials such as natural gas, coal, petroleum coke or biomass.

Description: Methanol is converted to ethylene, propylene and several byproducts when contacted with proprietary MTO-100 catalyst at elevated temperature and pressure in a fluidized-bed reactor (1). Due to a small amount of coke formation, a small fraction of catalyst is continuously passed through a catalyst regeneration unit (2) to maintain optimal activity.

Catalyst is retained in the reactor and catalyst regenerator using a series of cyclones. The reaction products leave the reactor and are processed through a series of separation units. First, the main byproduct, water, is removed (3). Next, a small amount of dimethylether (DME) reaction intermediate is recovered (4) and recycled to the reactor inlet. The remaining reaction products are sent to a light olefin recovery and purification section (5) where adsorption and cryogenic distillation units are used to produce polymer-grade ethylene and propylene.

Byproduct C_4^+ olefins can either be recovered as separate valuable products, or they can be processed through a Total Petrochemicals/UOP Olefin Cracking Process (OCP) unit (6) where they are converted to additional propylene and ethylene. The combination of MTO and OCP, which is referred to as Advanced MTO, provides carbon yields to ethylene and propylene of approximately 90%.

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: When cost advantaged feedstocks are available, the MTO process gives financial returns that are significantly more attractive than naphtha steam crackers producing the same amount of light olefin product. MTO projects often include the upstream process units to convert raw materials into synthesis gas and then to methanol, as well as downstream units to produce olefin derivatives. The total project capital costs for MTO (including upstream and downstream process units) very significantly and depend on the raw materials to be utilized and the types of olefin derivative products being produced.

Commercial plants: The first commercial scale (300,000 metric tpy of light olefins) MTO unit came on stream in Nanjing, China during late 2013. This unit has an integrated Total Petrochemicals/UOP Olefin Cracking Process unit. Additional MTO units have been licensed and are planned to come on stream in 2014 and 2015.

Licensor: UOP LLC, A Honeywell Company CONTACT

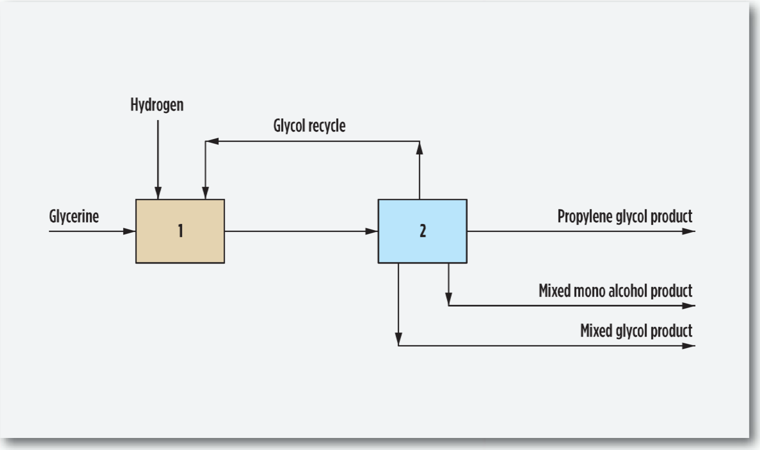
Propylene glycol

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: Johnson Matthey Davy Technologies Ltd., UK CONTACT

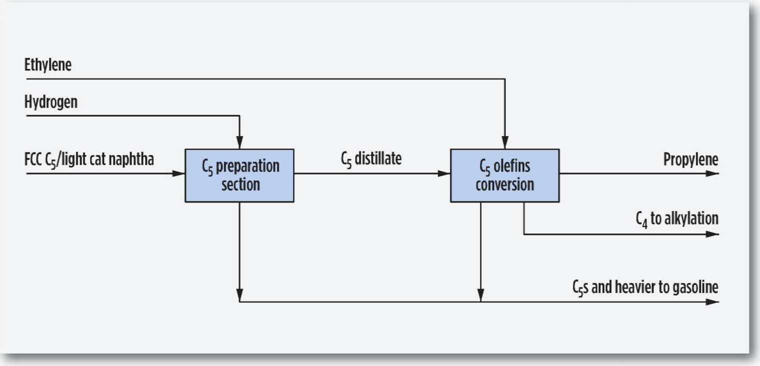
Propylene production from refinery C_5s via metathesis

Application: To produce polymer-grade propylene from refinery-based C_5s using metathesis technology.

Description: FCC C_5s contain 30%–40% C_5 olefins. All of these olefins can be isomerized to 2-pentene and isopentene, which take part in metathesis with ethylene. Metathesis of one mole of 2-pentene and two moles of ethylene gives three moles of propylene. Also, metathesis of isopentene and ethylene produces propylene and isobutene. The FCC C_5 feed is first processed in the C_5 preparation section, which includes integrated selective hydrogenation and a catalytic distillation unit to hydrogenate the dienes, and to separate pentenes and pentanes from cyclopentene, cyclopentane and heavier compounds. The catalytic column also selectively hydrogenates, isomerizes pentenes and removes sulfur compounds. The bottoms product containing the cyclo-C_5s and heavier compounds are cooled and sent to battery limits for blending into the gasoline pool. Net overhead distillate containing the pentenes flows to the metathesis unit.

The metathesis unit consists of a feed purification section, a reaction section and a recovery section. In the feed purification section, pentene feed is purified in fixed-bed treaters that remove potential metathesis catalyst poisons such as oxygenates, sulfur compounds, nitriles, and water. Treated feed flows directly from the online treater to the metathesis reaction section. In the reaction section, 2-pentenes and 2-methyl-2-butene react with ethylene to produce propylene and normal isobutenes. The n-butenes also react with ethylene to produce additional propylene.

The recovery section includes three towers. The first separates unreacted ethylene for recycle to the OCT or metathesis reactor. The second produces a polymer-grade propylene overhead product, C_4/C_5, as a side draw for recycle to the reactor of unconverted butenes and pentenes, and a bottoms C_4^+ stream. This bottoms stream is processed in the third tower, which separates the C_4 components from the C_5^+. The overhead C_4s byproduct, primarily isobutene, can be used as feed to an alkylation unit. The bottoms C_5^+ byproduct contains primarily the pentanes in the feed plus some unreacted n-pentenes and isopentenes, and any C_6^+ components formed in the reactor. The bottoms is cooled and sent to the battery limits for blending directly into the gasoline pool.



Yields and product quality:

Typical yields

Feed	mt/mt of propylene
C_5 feed	2.19
Ethylene	0.48
Hydrogen	0.002
Main products	
Polymer-grade propylene	1.00
C_4s to alkylation	0.22
C_5s and heavier	1.42
Vents	0.03

Continued ▼

Propylene production from refinery C_5s via metathesis, cont.

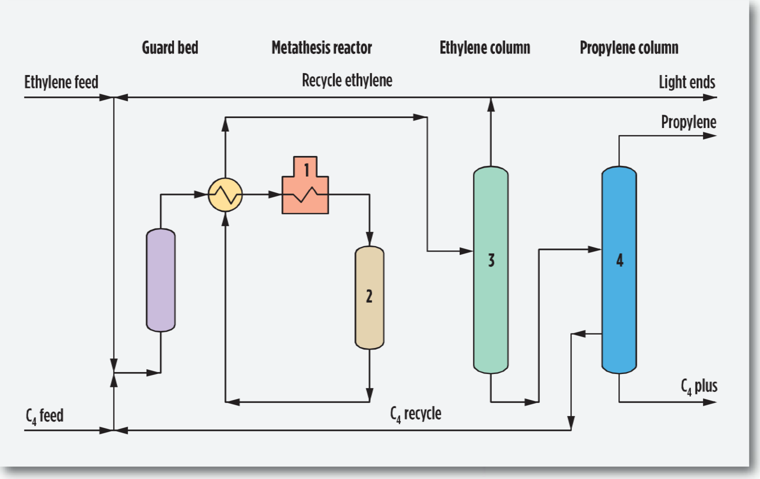
Typical product quality	
Propylene	99.9 mol% min.

Typical average utilities, per mt of propylene	
Fuel gas (fired), MMKcal	0.61
Electricity, kWh	40
Steam, mt	3.30
Steam for refrigeration compressor, mt	0.57

Commercial plants: As of 2013, there are four licensed units of C_4/C_5 metathesis, and one of the licensed C_4/C_5 metathesis units is expected to be in commercial operation by the fourth quarter of 2015.

Licensor: CB&I 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 the majority of C_4s are recycled to the reactor and some C_4s are 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 and refrigeration—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	mt/mt Propylene
Feed	
Raffinate (66% n-butenes)	1.22
Polymer-grade ethylene	0.33
Main products	
Polymer-grade propylene	1.00
C_4^+ byproduct	0.55
Typical product quality	
Propylene	99.9 mol% min.

Continued ▼

Propylene via metathesis, cont.

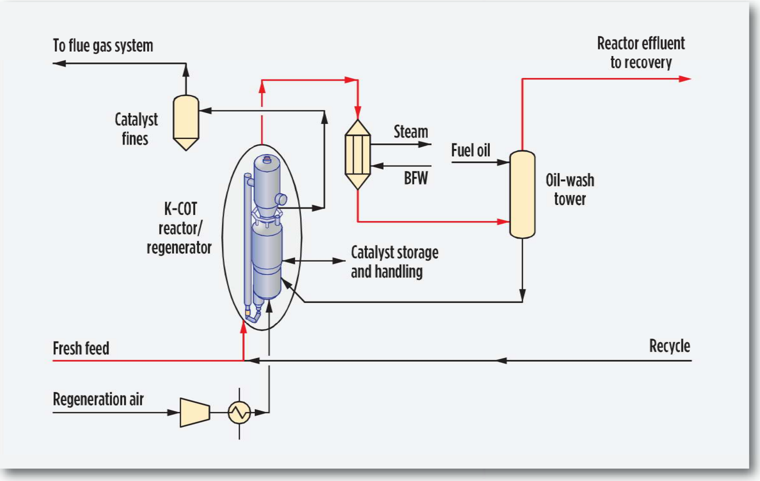
Economics: Typical average utilities, per mt propylene

Fuel gas (fired), MMKcal	0.25
Electricity, kWh	22
Steam, mt	1.3
Refrigeration @ –25°C, MMKcal/h	0.18

Commercial plants: The OCT process has been licensed in 47 plants, 24 of which are currently operating and producing almost 5 million metric tpy of propylene. By 2017, total worldwide propylene capacity via OCT is expected to reach almost 9 million metric tpy.

Licensor: CB&I CONTACT

Propylene, K-COT



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. It can also be used as 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 K-COT process is a proprietary technology patented, which uses a fluidized catalytic reactor system with a proprietary catalyst to convert low-value feedstocks to predominantly propylene and ethylene products. The process is very robust; thus, no feed pretreatment is generally 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 full flexibility in the amounts of paraffins in the feeds to K-COT and the ability to recycle unconverted feed to extinction.

The cooled reactor effluent can be processed for the ultimate production of polymer-grade olefins. Several design options are available, including fully dedicated recovery facilities; recovery in a nearby, existing ethylene plant recovery section to minimize capital investment; or processing in a partial recovery unit to recover recycle streams and concentrate olefin-rich streams for further processing in nearby plants. 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 from olefin-rich streams are shown in FIG. 2.

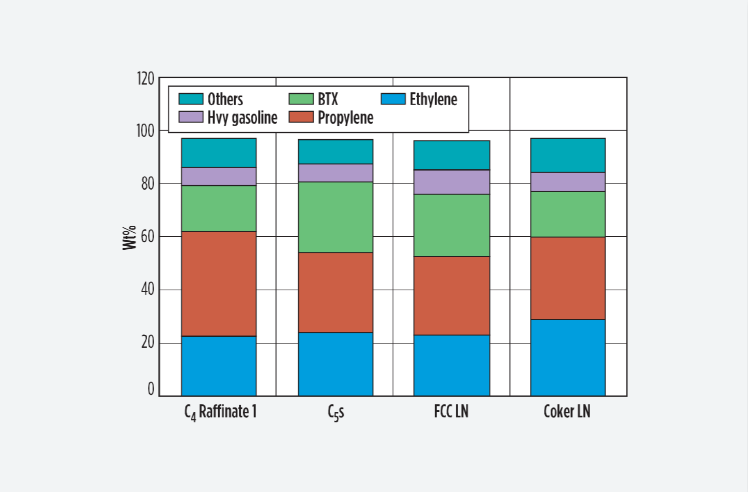
Light olefins yields from straight-run naphtha feeds are greater than in a steam cracker, and the P/E ratio is about 1:1 as opposed to 0.5. FIG. 2 is a comparison of steam cracker and K-COT ultimate yields for a typical naphtha.

Continued ▼

Propylene, K-COT, cont.

Commercial plants: The first licensee with a propylene production capacity of 250,000 metric tpy is Sasol Technology; this plant has been in operation since December 2006. For a period of time, a commercial demonstration unit with a capacity of 40,000 metric tpy operated on a variety of naphtha streams particularly light straight run, FRN and FCC naphtha at SK's facilities in Ulsan, South Korea. Three additional units have been licensed.

Licensor: Kellogg Brown & Root LLC CONTACT



Propylene

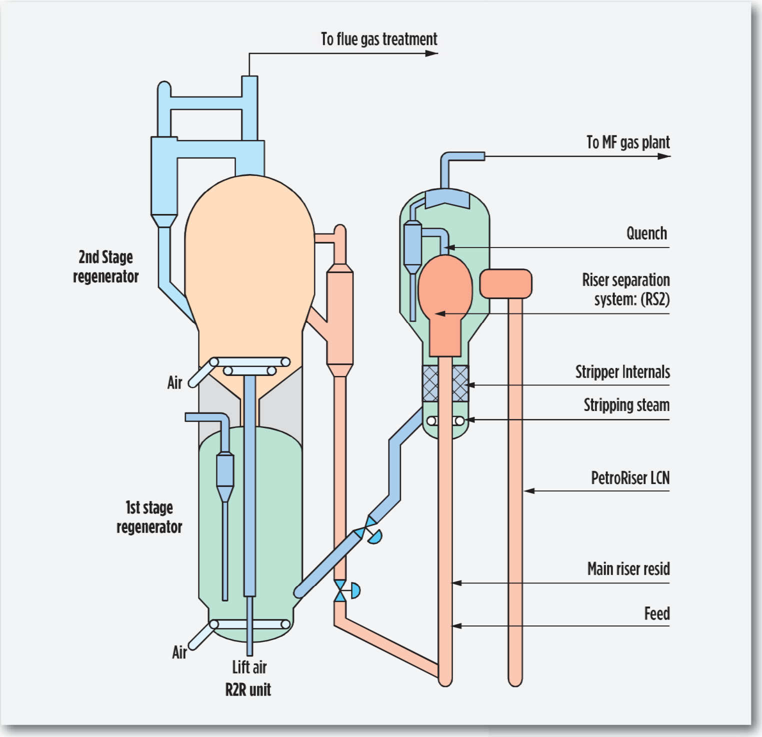
Application: When the process objective is maximum propylene production, specific technology features must be added to the fluid catalytic cracking (FCC)/resid FCC (RFCC) unit. The challenge is particularly great when the feedstock contains residue.

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: 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.

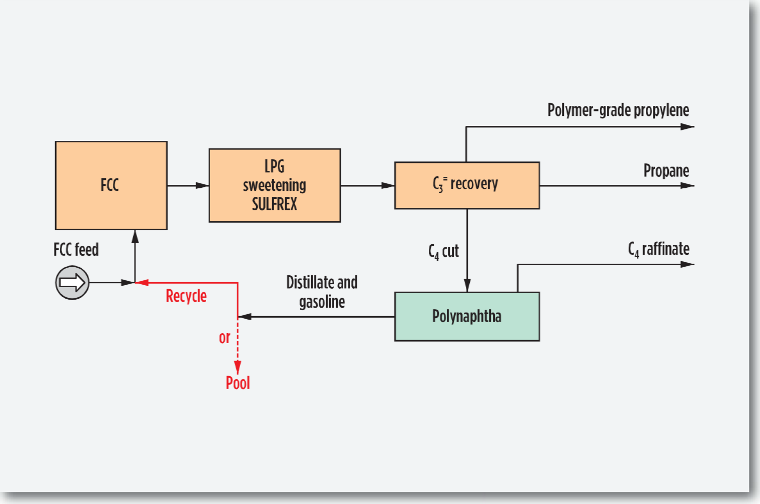
Description: FlexEne relies on the integration of an FCC and an oligomerization unit called Polynaphtha to process light FCC olefins and to deliver good molecules back to the FCC and to provide product flexibility required by the marketplace.

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/IFPEN 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: Seven FlexEne units have been licensed for new R2R/Polynaphtha projects.

Licensor: Axens CONTACT

Propylene

Application: Technology for dehydrogenation of propane to make high-purity propylene. The CATOFIN® process uses specially formulated proprietary catalyst from Clariant.

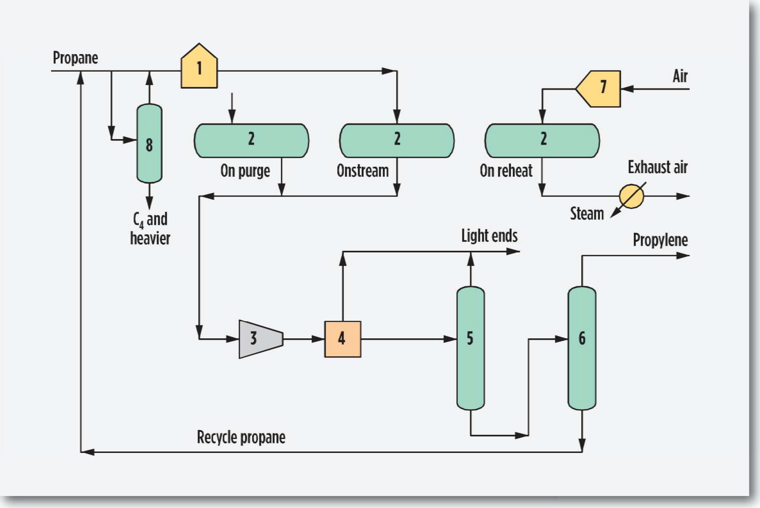
Description: The CATOFIN reaction system consists of parallel fixed-bed reactors and a regeneration air system. The reactors are cycled through a sequence consisting of reaction, regeneration and evacuation/purge steps. Multiple reactors are used so that the reactor feed/product system and regeneration 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 switched to another reactor 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 Clariant 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 1.15 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 (exceeding 850,000 metric tpy propylene) minimizes the investment cost/mt of product.

Continued ▼

Propylene, cont.

Raw material and utilities, per mt of propylene	
Propane, mt	1.15
Power, kWh	50
Fuel, MWh	1.2

Commercial plants: Ten CATOFIN dehydrogenation plants are onstream producing over 2,000,000 metric tpy of isobutylene and 2.5 million metric tpy of propylene. The plants have successfully met their guarantees and continue to operate well above design capacity.

Licensor: CB&I 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.

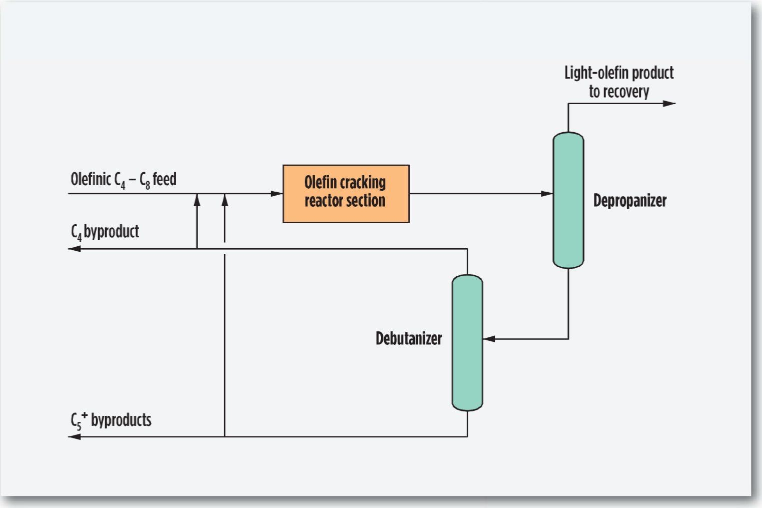
Description: The Olefin Cracking Process was jointly developed by Total Petrochemicals (formerly ATOFINA) and UOP to convert low-value C_4 to C_8 olefins to propylene and ethylene. The process features fixed-bed reactors operating at temperatures between 500°C and 600°C and pressures between 1 and 5 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: The first commercial scale OCP unit, which is integrated with a UOP/Hydro Methanol-to-Olefins (MTO) process unit, came onstream in 2013. Additional units have been licensed and are planned to be commercial operation in 2014 and 2015.

Licensor: UOP LLC, A Honeywell Company CONTACT

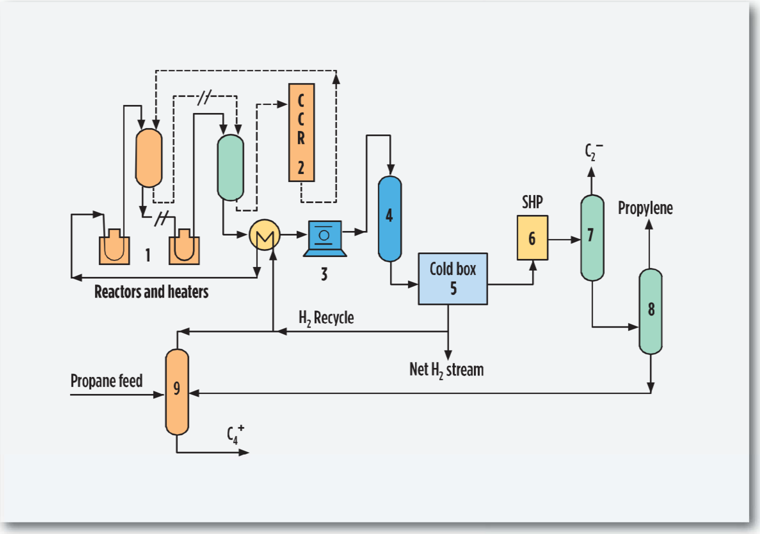
Propylene

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 converted to additional propylene. The propylene stream goes to a deethanizer (7) where light-ends are removed prior to recovery of the high-purity propylene in 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 of up to 87 wt% of fresh feed. Hydrogen yield is about 3.5 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 $400 million/tpy.



Commercial plants: Fourteen Oleflex units are in operation to produce propylene and isobutylene. Nine of these units produce propylene. These units represent 2.9 million metric tpy of propylene production. Fourteen additional Oleflex units for propylene production are in design or under construction.

Licensor: UOP LLC, A Honeywell Company CONTACT

Purified terephthalic acid (PTA)

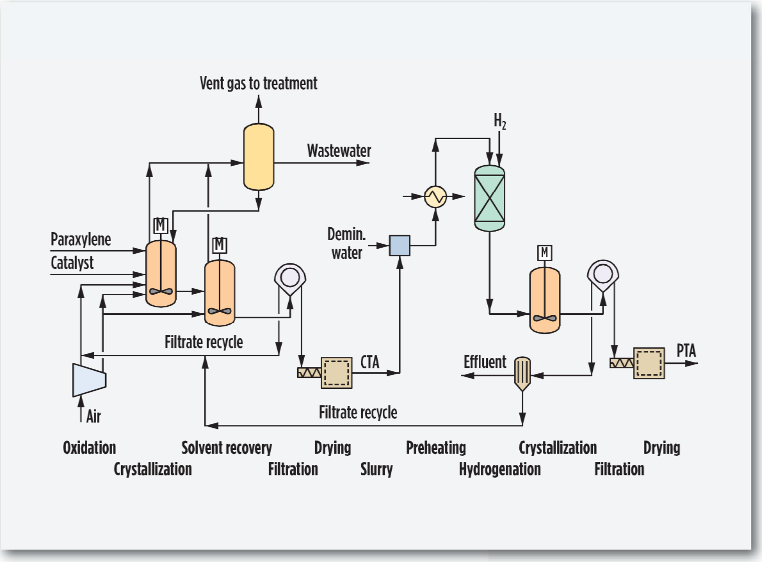
Application: The production of purified terephthalic acid (PTA) for use across all downstream polyester products. The process offered by The Dow Chemical Co. (Dow) and Johnson Matthey Davy Technologies Ltd. (JM Davy) has undergone a substantial upgrade to meet the high hurdles for investment, quality and environmental protection essential for success in this industry. The result is COMPRESS PTA.

Description: Following a PTA joint licensing agreement in 2008, JM Davy 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 JM Davy 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 ▼

Purified terephthalic acid (PTA), cont.

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 Johnson Matthey Davy Technologies Ltd. CONTACT

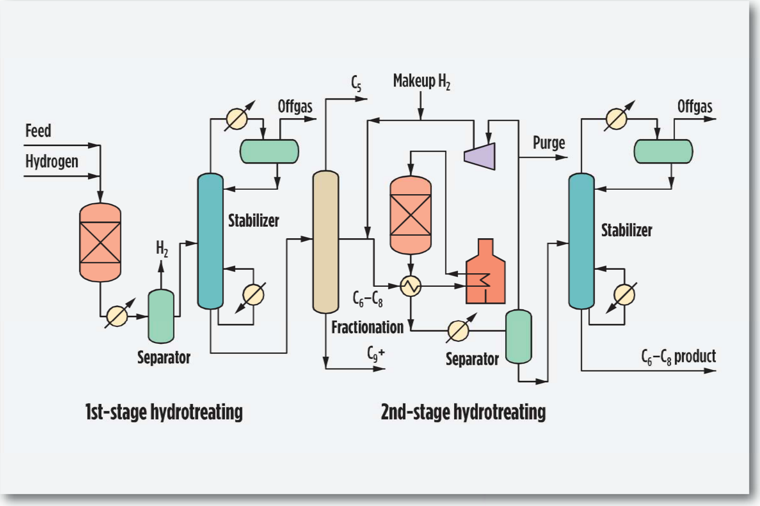
Pygas hydrotreating

Application: GTC Technology offers an optimized technology for two-stage pyrolysis gasoline (pygas) hydrotreating (HDT), where diolefins, 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 pygas.

Description: In GTC's pyrolysis hydrotreating technology process, the hydrotreating unit consists of three sections:

1. First-stage hydrotreating section to convert diolefins to olefins, and styrene to ethylbenzene
2. Second-stage hydrotreating section to saturate the olefins and desulfurize the pygas
3. Fractionation section to stabilize the hydrotreated streams and to recover the C_6–C_8 heart cut for further processing.

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 HDT reactor where most diolefins 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 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 BTX, this C_5^+ stream is sent to a fractionation section to obtain a C_6–C_8 heart 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

Continued ▼

Pygas hydrotreating, cont.

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 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 the 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 available from licensor

Economics:

Basis	500,000 tpy (11,000 bpsd) feed rate
Erected cost	$28 million (ISBL, 2014 US Gulf Coast basis)

Commercial plants: Commercialized technology available for license

Licensor: GTC Technology CONTACT

Styrene acrylonitrile (SAN) copolymer

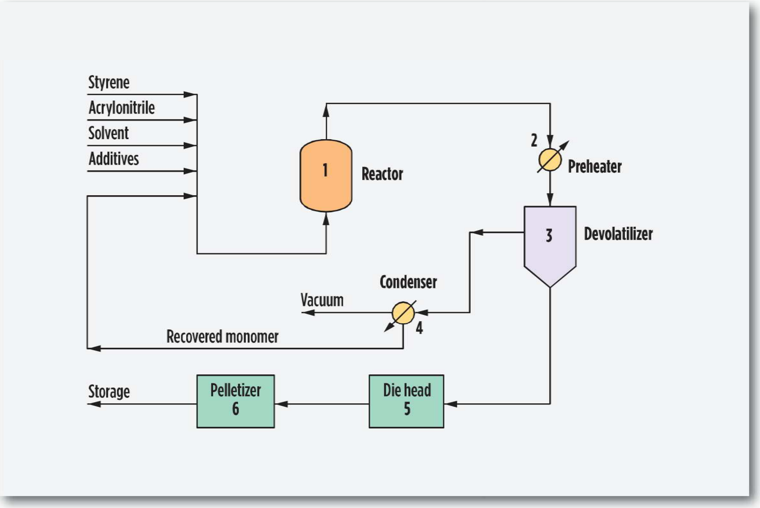
Application: To produce a wide range of styrene acrylonitrile (SAN) copolymer with excellent chemical resistance, heat resistance and suitable property for compounding with ABS via the continuous bulk polymerization process using Toyo Engineering Corp. (TOYO) technology.

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 head (5) and cut into pellets by a pelletizer (6).

Economics: Basis: 50,000 metric tpy SAN

Raw materials consumption per 1 metric ton of SAN, kg	1,009
Utilities consumption per 1 metric ton of SAN, US$	18



Installations: Toyo has licensed 42 polystyrene plants (GPPS/HIPS/SAN/ABS) with a total production capacity of 950,000 tpy.

Licensor: Toyo Engineering Corp. (TOYO) CONTACT

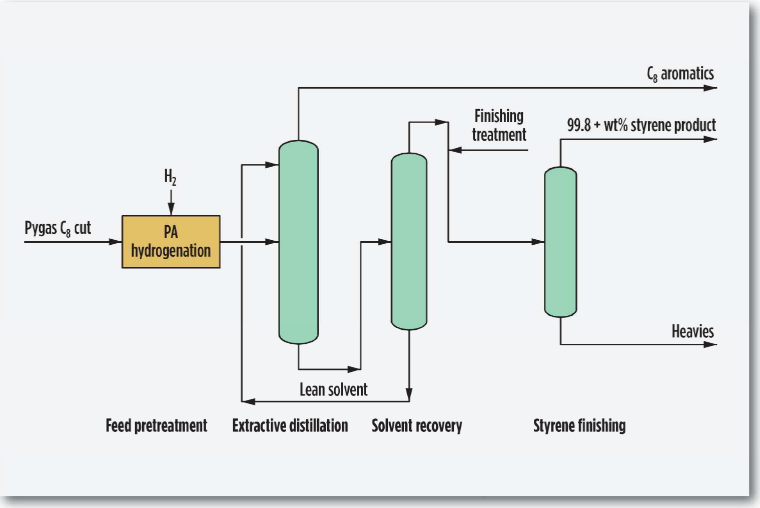
Styrene recovery from pygas

Application: GT-Styrene® is an extractive distillation process that directly recovers styrene from the raw pyrolysis gasoline (pygas) derived from the steam cracking of naphtha, gasoils, and natural gas liquids (NGL). The styrene, produced at high purities and suitable for polymerization, is a less costly alternative to conventional styrene production routes. If desired, the mixed xylenes can also be extracted from the pygas, raising their value as a chemical feedstock. The GT-Styrene process is economically attractive to steam cracker operators that produce greater than 500 KMTA of ethylene from liquids feedstock.

Description: Raw pyrolysis gasoline is prefractionated into a heartcut C_8 stream. The resulting styrene concentrate is fed to an extractive distillation column (EDC) 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 (SRC), which recycles the lean solvent back to the EDC and recovers the styrene overhead. A final purification step produces high-purity styrene product meeting the ASTM specifications. The EDC 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 pygas.

Process advantages:

- Produces polymer-grade styrene at 99.8% 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
- Optimizes solvent system and design to provide economical operating costs



Economics:

Basis	25,000 tpy styrene recovery
Erected cost	$21 million (ISBL, 2014 US Gulf Coast basis)

Commercial plants: Three commercial plants

Licensor: GTC Technology CONTACT

Styrene

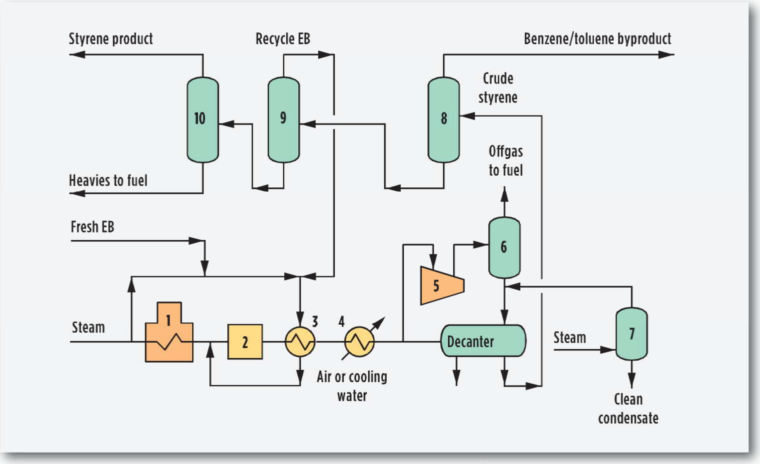
Application: Process to manufacture styrene monomer (SM) by dehydrogenating ethylbenzene (EB) to styrene. Feedstock EB is produced by alkylating benzene with ethylene using the EBMax^{TM} process.

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 about 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 Technip.

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	1.056
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

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

Styrene

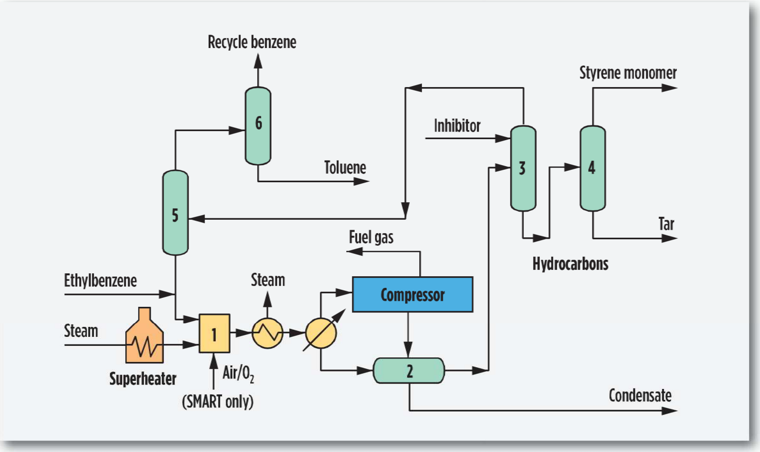
Application: To produce polymer-grade styrene monomer (SM) by dehydrogenating ethylbenzene (EB) using the Lummus/UOP "Classic" styrene process or the CB&I/UOP SMART process (for revamps involving plant capacity expansion).

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, mt/mt SM	1.055
Utilities, US$/mt SM	29

Commercial plants: Currently, 35 operating plants incorporate the CB&I/UOP Classic styrene technology. The largest single train plant in operation has a capacity of 815,000 metric tpy SM. Eight 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: CB&I and UOP LLC, A Honeywell Company CONTACT

Substitute natural gas (SNG)

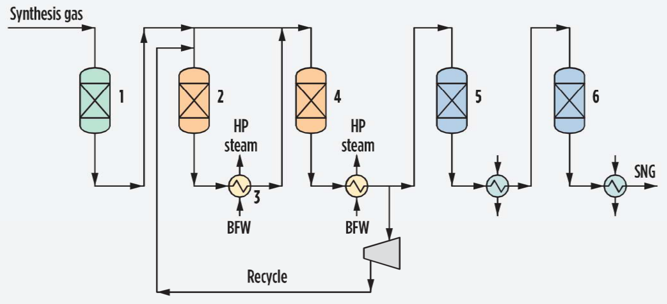
Application: To produce substitute natural gas (SNG) from synthesis gas produced by gasification of any suitable carbonaceous feedstock or other syngas such as coke oven gas, using shift and methanation reactions.

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 or non-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.

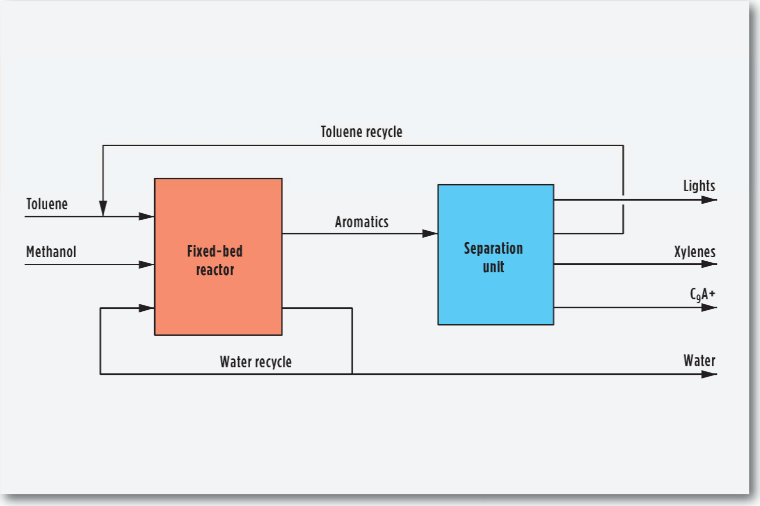
Licensor: Johnson Matthey Davy Technologies Ltd., UK CONTACT

Toluene alkylation

Application: Toluene alkylation, also known as toluene methylation, is an effective and economical solution to maximize PX yields by adding methyl groups from low-cost methanol to the aromatic ring. Current toluene-based PX technologies revolve around rearrangement of the alkyl groups through various methods. Benzene is the typical byproduct due to the imbalance of the methyl group. By adding a methyl group to the aromatic ring, the toluene methylation process favors xylene production over benzene.

Description: GTC's GT-TolAlk^{SM} yields xylenes for PX manufacturing while eliminating benzene production. The feedstock consists of methanol and toluene, which are processed in the toluene methylation reaction section, where toluene is alkylated to mixed xylene. The reactor effluent is processed in the fractionation section to produce mixed xylene product. Unconverted toluene is separated and recycled back to the reaction section. C_9^+ aromatics fraction is also produced and separated, and is available as feedstock to the transalkylation unit.

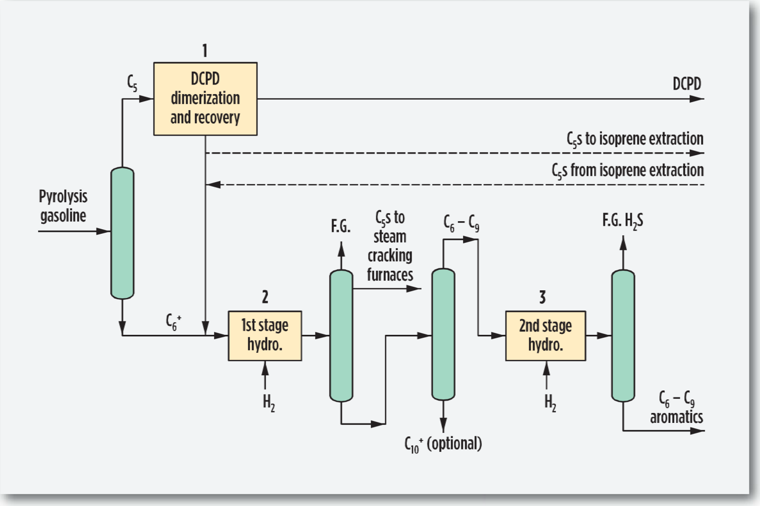
Process advantages:
- Simple fixed-bed, low-pressure process
- No hydrogen is needed
- High production capacity
- Effective addition of methyl group to aromatic ring
- Very low EB
- No benzene byproduct



Commercial plants: Commercial licensing available

Licensor: GTC Technology 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:

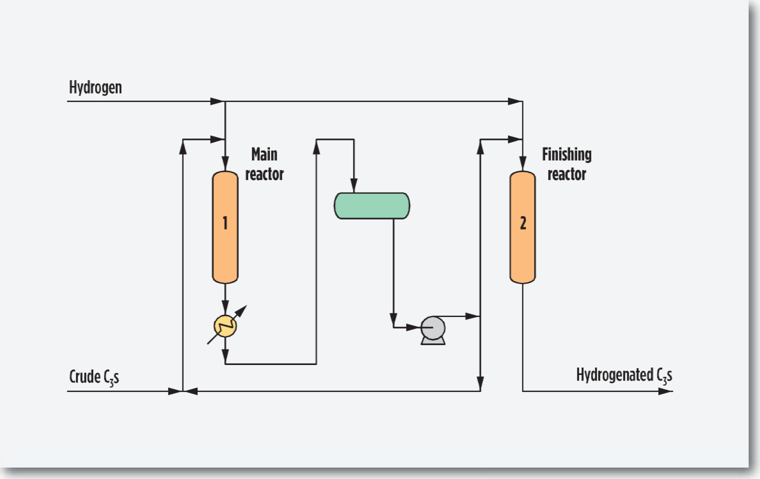
Investment, US$/ metric ton of feed	50
Utilities & catalysts, US$/ metric ton	10

Reference: Debuisschert, Q., "Innovation in Selective Hydrogenation Latest Technologies" 8th Asian Petrochemicals Strategy and Technology Conference, May 2010, Kuala Lumpur.

Commercial plants: One hundred and five grassroots and 29 revamps first-stage pygas hydrogenation units have been licensed. Seventy one grassroots and 20 revamps 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 (ppm) 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: One hundred and twenty C_3 hydrogenation units have been licensed (107 grassroots and 13 revamps).

Licensor: Axens CONTACT

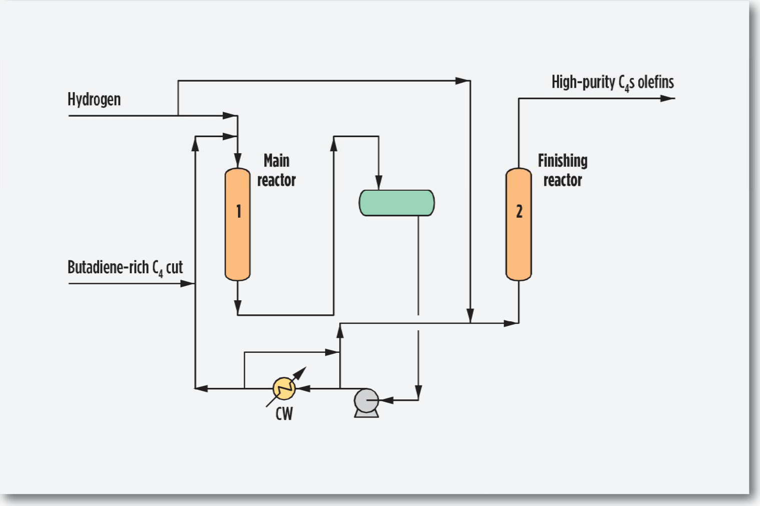
Upgrading steam cracker C_4 cuts

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 C_4 cuts, cont.

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 200 C_4 hydrogenation units have been licensed for this process applications.

A total of 54 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.

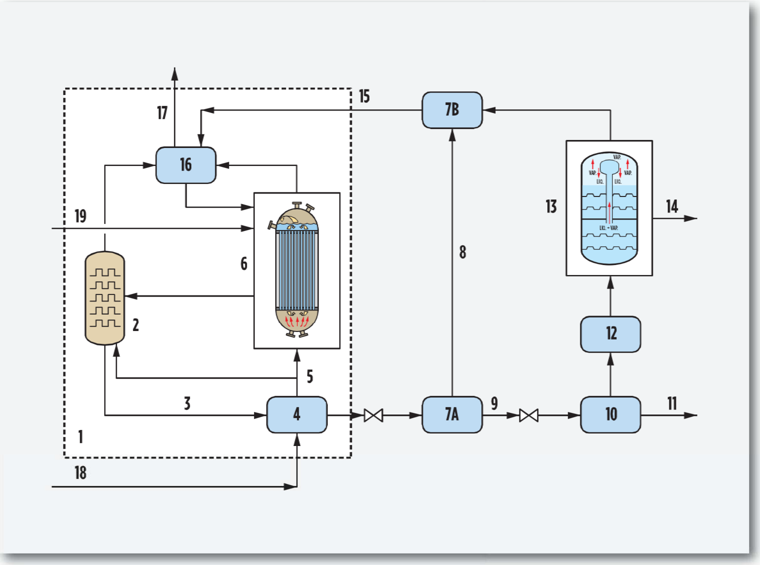
Description: Urea is formed from CO_2 (18) and NH_3 (19) in the HP loop (1) in a reactor (2) fitted with Casale-Dente high-efficiency trays. The urea solution (3) from the reactor (2), which still contains unreacted NH_3 and CO_2, is first treated in a stripper (4), operating at the same pressure as 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

Continued ▼

Urea, cont.

consumption (22 bar, superheated) of 750 kg/metric tons and almost stoichiometric raw material consumption.

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 (NH_3) and carbon dioxide (CO_2) using an ammonia-stripping process.

Description: NH_3 and 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.

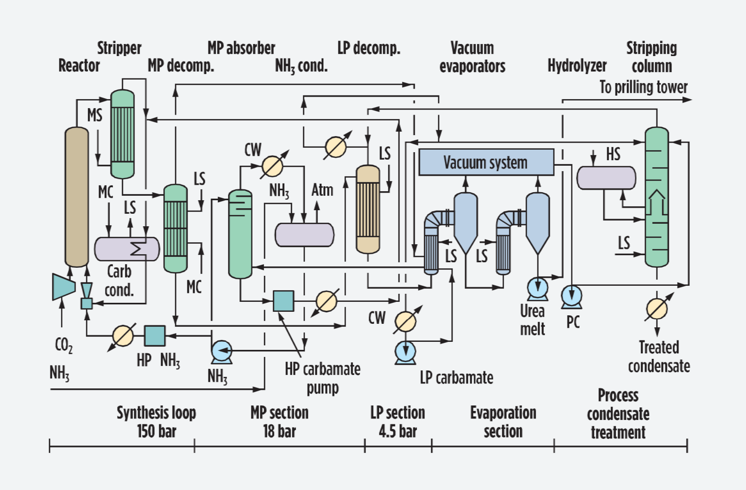
The plant is completely free from pollution problems. All vents are efficiently treated or flared so that they are discharged to atmosphere practically free of ammonia and/or urea. Process wastewater is hydrolyzed within the plant to achieve boiler feedwater specification and to recover NH_3 and CO_2.

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	733
Steam, 110 bar, 510°C, kg	730*
Electric power, kWh	21
Water, cooling, m^3	80
Condensate, kg	1,045

* Includes steam to the CO_2 compressor turbine, as well as all utilities for effluent treatment



Commercial plants: One hundred and thirty plants have been licensed, with capacity up to 4,000 tpd on a single line. Next-generation plants are under development to attain 5,000 tpd production capacity.

Licensor: Saipem CONTACT

Urea

Application: To produce urea from ammonia (NH_3) and carbon dioxide (CO_2) using Toyo Engineering Corp.'s (TOYO's) proprietary urea synthesis technology ACES21®.

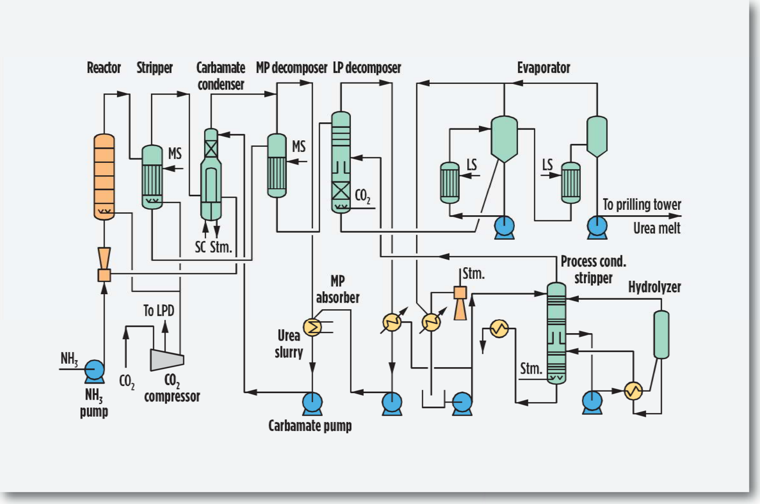
Description: The ACES21 synthesis section consists of a reactor, a stripper and a carbamate condenser. Ammonia and carbon dioxide react at 155 bar to synthesize urea and carbamate. The reactor conversion rate is very high under the N/C ratio of 3.7 with a temperature of 182°C–185°C. Unconverted materials in the synthesis solution are efficiently separated by CO_2 stripping. The gas from the stripper is fed to a vertical submerged carbamate condenser (VSCC) using a high-pressure (HP) ejector for internal synthesis recycle. Major synthesis equipment is located on the ground level. The milder operating conditions and using duplex alloy stainless steel prevent corrosion problems.

The urea solution from the 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 treated to hydrolyze urea to ammonia and carbon dioxide so as to be re-utilized as boiler feed water.

Economics: Integrated with the granulation process, ACES21 is advantageous in low investment cost and low energy consumption for urea production. Raw materials and utilities consumptions per metric ton of granular urea are:

Ammonia, (100%) kg	563
Carbon dioxide (100%), kg	731
Steam, 110 bar, 510°C	690*
Electric power, kWh	
Synthesis	20
Granulation	24
Water cooling, m^3	75

* Includes steam for CO_2 compressor turbine and steam for process condensate treatment

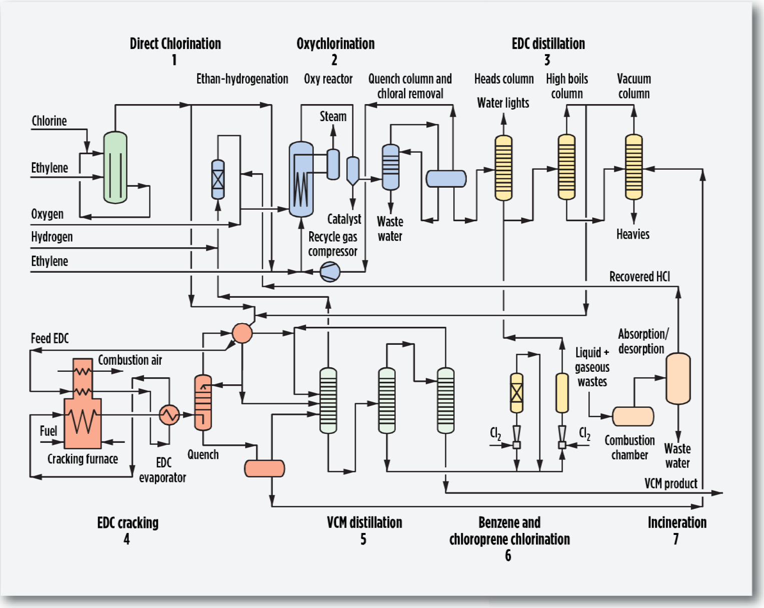


Commercial plants: More than 100 synthesis plants, including a 4,000-mtpd plant in single train, have been designed and constructed based on TOYO technologies.

Licensor: Toyo Engineering Corp. (TOYO) CONTACT

ACES21 is a registered trademark of Toyo Engineering Corporation in Japan (Registered Number: 4309123).

Vinyl chloride monomer (VCM)



Application: Vinyl chloride monomer (VCM) is produced by an endothermic reaction from 1,2 dichloro ethane (EDC). VCM is mainly used as feedstock for polyvinyl chloride (PVC) production.

Description: A balanced vinyl chloride monomer plant consists of the following process units:

- Direct chlorination
- Oxychlorination
- EDC distillation
- EDC cracking
- VCM distillation
- Chloroprene and benzene chlorination

The production process of vinyl chloride monomer (VCM) from ethylene and chlorine is based on two different routes.

In the Direct Chlorination process (1) (see separate description), as well as in the Oxychlorination process, EDC is produced. Both reactions proceed exothermally.

Due to the better quality, EDC produced by direct chlorination can be used directly for cracking, whereas EDC from the Oxychlorination (2) process has to pass a purification stage (EDC distillation) before cracking. The EDC distillation (3) unit consists of three distillation columns. In the first column, the heads column, water and low-boiling byproducts are drawn off at the top of the column. The bottom product of the heads column is combined with the unconverted recycled EDC from the cracking furnace and fed to the high-boil column, where high-boiling byproducts are separated as bottom product. The high-boil column overhead product is pumped to the furnace feed EDC tank and the bottom product is transferred to the vacuum column for further concentration of the high-boiling byproducts. To minimize the reboiler fouling, this column is operated under vacuum. The overhead product of the vacuum column is used as feed EDC, while the bottom product with a high boil content of > 95% is fed to the byproduct incineration unit.

In the EDC cracking (4) unit, EDC is thermally cracked, giving VCM and HCl. VCM, HCl products and the unconverted EDC are separated from each other in the VCM distillation (5) unit. In the first distillation column, the HCl column, the overhead product HCl is fed to the Oxychlorination unit as raw material. The bottom product, a mixture of EDC and VCM, is separated in the VCM column. Traces of HCl remaining in the

Continued ▼

Vinyl chloride monomer (VCM), cont.

product VCM are removed in the VCM stripper and recycled to the HCl column. The final product VCM is sent to the VCM storage for shipment or for further use in a PVC plant. The low-boiling byproducts in the unconverted EDC (coming from the bottom of the VCM column) are chlorinated in the benzene and chloropren chlorination (6) to high-boiling byproducts, which are then removed in the EDC distillation unit.

Water obtained from this process is treated in appropriate water purification plants. Gaseous and liquid byproducts are fed to the incineration process (7) to recover HCl.

The recovered HCl is reused either for the production of hydrochloric acid or in the Oxychlorination process. This leads to a complete usage of the input chlorine.

Important features:

- Reliability: Oxychlorination: A stable temperature control combined with an excellent heat transfer and a uniform temperature profile (no hot spots) in the fluidized bed assures an onstream time > 99% per year. A specially designed raw-material gas distributor allows for operation spans of more than two years without maintenance. Vinnolit oxychlorination reactors are made of carbon steel and have been in operation for more than 40 years. Compared to the competitive processes, the increased heat-transfer area allows for a higher steam temperature and steam pressure in the cooling coils, which gives a much wider safety margin to the critical surface temperature with the danger of hydrochloric acid dewpoint corrosion occurring. All common Oxychlorination catalysts that are available on the market can be used.
- Safety: Oxychlorination: The oxygen is mixed with anhydrous hydrochloride outside the reactor and is fed into the fluidized bed independently of the ethylene. The oxygen concentration in the recycle stream is approximately 0.5% by volume, which is far outside of the explosion range.
- Flexibility: Oxychlorination: A turn down ratio as low as 20% capacity utilization can be achieved. The load of the oxychlorination reactor can be increased from 20% to 100% within 30 minutes and vice versa. In addition, the feasibility of an immediate startup after a shutdown makes operation very easy.
- Low manufacturing costs: Oxychlorination: The unlimited catalyst life time, the low catalyst losses due to the highly efficient cyclone system (less than 20 g catalyst per ton of produced EDC), the high raw-material yields (98% ethylene, 99% anhydrous hydrochloride, and 93% oxygen) and the possibility to use inexpensive oxygen from PSA units ensure a highly economic process. EDC cracking: The long cracking furnace operating cycles between cleaning shutdowns of up to two years, the high raw-material yield (99.5% EDC) and the possibility to adapt the heat recovery to the customer requirements assure low production costs.
- Energy saving: EDC cracking: Recovery of primary and secondary energy by using the energy from the cracking gas for external EDC evaporation and steam generation. With minimized electrical power consumption for refrigeration at the top of the HCl column by operation at energy and yield optimized cracker operation pressure, recycle EDC chlorination requires no steam.

Continued ▼

Vinyl chloride monomer (VCM), cont.

Economics:

	Direct Chlorination[1]		VCM plant[2] incl. DC and OC
Consumption figures in kg/1,000 kg of product	**a) Stand-alone**	**b) Integrated in VCM plant**	
Ethylene	284,5	283,1	456
Chlorine	718,6	718,6	584
Hydrochloride	—	—	—
Oxygen	—	—	139
Yields in mass percent			
Ethylene	99,65	99,9	98,5
Chlorine	99,8	99,8	98,5
Hydrochloride	—	—	—
Oxygen	—	—	92,4
Utility consumption per 1,000 kg of product			
Electrical power in kWh	10	15	100
Steam consumption in kg	0		0
Steam generation in kg	800		0
Cooling water in m^3 (10°C temperature difference)	25		130
Fuel gas in MJ	2720		
Catalyst consumption in g	only for initial filling		16[3]
Erection costs built on US Gulf Coast in 2013, excluding investments outside battery limit in US $	for 320,000 metric tpy EDC 15 million		for 400,000 metric tpy VCM 160 million[4]

[1] All figures are based on EDC

[2] All figures are based on VCM

[3] Oxychlorination catalyst consumption based on VCM

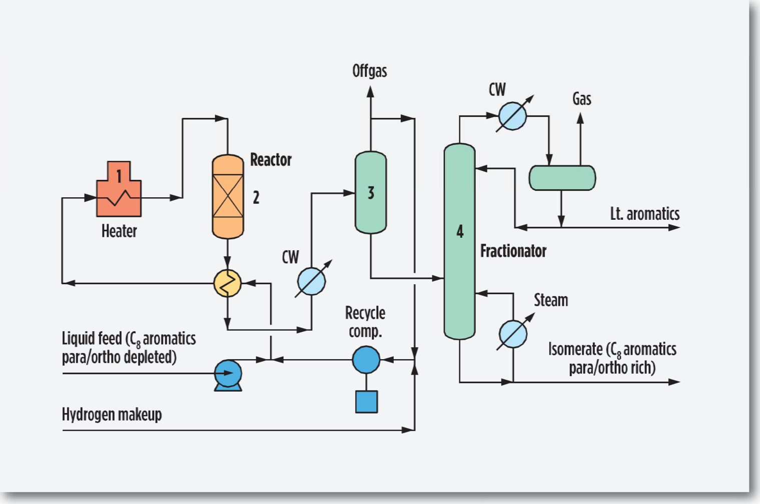
[4] Costs include Direct Chlorination and Oxychlorination units

Installations: Since 1965, Vinnolit has licensed its modern EDC/VCM process with an installed capacity of around 14 million metric tpy EDC and 6.2 million metric tpy VCM in plants worldwide.

Reference: R. A. Meyers (Ed.), *Handbook of Petrochemicals Production Processes,* pp 18.12–18.21, McGraw-Hill (2005).

Licensor: Vinnolit GmbH & Co. KG CONTACT

Xylene isomerization



Application: To selectively isomerize a paraxylene (PX)-depleted C_8 aromatics mixture to greater than equilibrium PX concentration using ExxonMobil Chemical's XyMax-2^{SM} and Enhanced MHAI^{SM} processes. Simultaneously, ethylbenzene (EB) and non-aromatics in the feed are converted to benzene and light paraffins, respectively. Conversion of EB is typically 60%–85%.

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 Enhanced MHAI (EMHAI^{SM}), provides higher selectivity and lower operating costs compared to isomerization processes used in the past. The EMHAI technology offers increased operating flexibility in terms of greater range of EB conversion and a lower temperature requirement. The second technology, referred to as XyMax-2, 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-2 and EMHAI units operate with a high space velocity and a low hydrogen-to-hydrocarbon ratio, which results in increased debottlenecking potential and decreased utility costs. By converting a high portion of EB in the feed, these technologies can provide significant savings in associated PX recovery facilities. Both technologies offer very long operating cycles.

Commercial plants: Advanced MHAI^{SM}, a predecessor process, was first commercialized in 1999, and its most recent upgrade, EMHAI, was commercialized in 2009. There are five reference plants for AMHAI and two for EMHAI. The first commercial unit using XyMax-2 technology was brought onstream in 2007. There are four reference plants utilizing XyMax-2 technology and 16 references for its predecessor XyMax^{SM} technology.

Licensor: ExxonMobil Chemical Technology Licensing LLC (retrofit applications)

Axens (grassroots applications) CONTACT

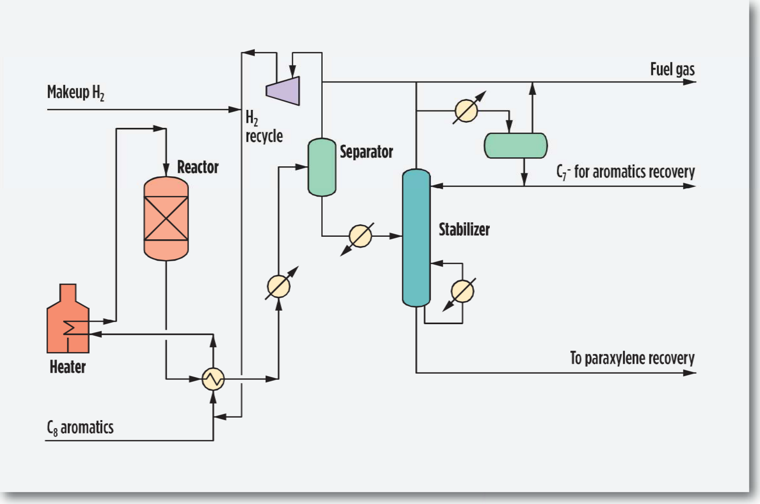
Xylene isomerization

Application: GTC's GT-IsomPX℠ xylene isomerization technology is available in two versions: ethylbenzene (EB) isomerization and EB dealkylation. Both versions gain high EB conversion rates while producing equilibrium mixed xylenes—metaxylene (MX), orthoxylene (OX) and paraxylene (PX). Catalysts that exhibit superior physical activity and and stability (such as ISOXYL by Clariant) are the key to this technology. Both the technology and catalysts are used commercially in several applications.

Description: For an EB dealkylation type of isomerization, the technology encompasses two main processing areas: a reactor section and a product distillation section. In this process, a PX-depleted feed stream is first mixed with hydrogen. The mixed stream is then heated against reactor effluent and through a process furnace. The heated mixture is fed into an isomerization reaction unit, where MX, OX and PX are isomerized to equilibrium and EB is dealkylated 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 reaction
- EB dealkylation to benzene or isomerization to xylenes. With the EB-dealkylation catalyst, the byproduct benzene is produced at high purity by simple distillation.
- Low H_2/HC, high WHSV, low xylenes loss
- Long cycle length
- Efficient heat integration scheme reduces energy consumption
- Turnkey package for high-purity benzene, toluene and paraxylene production available

Economics:

Basis	4 million tpy (88,000 bpsd) feed rate
Erected cost	$31 million (ISBL, 2014 US Gulf Coast basis)

Commercial plants: Two commercial licenses

Licensor: GTC Technology CONTACT

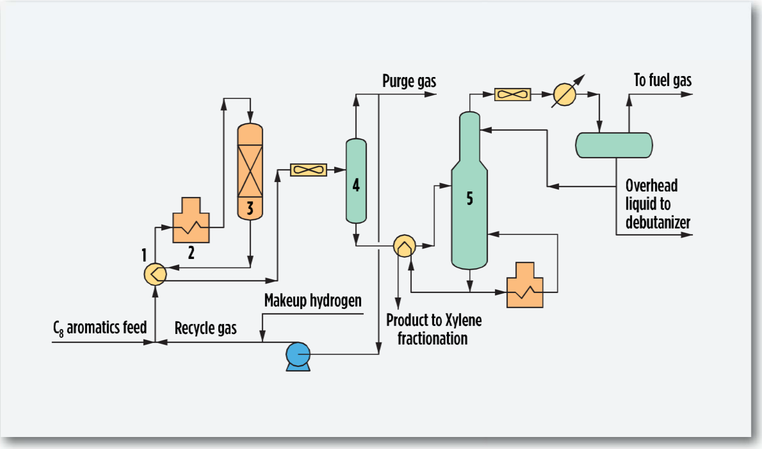
Xylene isomerization

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 EB into additional xylenes; and EB dealkylation catalysts, which convert EB 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.



Yields: The EB isomerization reaction is an equilibrium limited to approximately 30 wt% EB conversion per pass, while the EB dealkylation reaction is not equilibrium limited, allowing up to 90 wt% EB conversion per pass. An existing facility designed for EB isomerization catalyst can be revamped with an EB dealkylation catalyst, as a means of increasing paraxylene production. However, this additional capacity comes at the expense of lower paraxylene yield per unit of mixed xylene feed, since EB is being converted to benzene instead of additional xylenes.

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 81 Isomar units.

Licensor: UOP LLC, A Honeywell Company CONTACT

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