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Hydrocarbon Processing's 2011 Refining Processes Handbook reflects the dynamic advancements now available in licensed process technologies, catalysts and equipment. The refining industry is under tremendous pressure to process "cleaner" transportation fuels with varying specifications for a global market.

Refiners must balance capital investment and operating strategies that provide the optimum profitability for their organization. Accordingly, refining organizations will apply leading-edge technology in conjunction with "best practices" for refining fuels and petrochemical feedstocks from crude oil.

HP's process handbooks are inclusive catalogs of established and emerging refining technologies that can be applied to existing and grassroots facilities. Economic stresses drive efforts to conserve energy consumption, minimize waste, improve product qualities, and, most important, increase yields and throughput.

In further expansion, the process entries presented an expanded description of the licensed technology including a process flow diagram, product description, economic information and other vital information. Specific processing operations to be emphasized include alkylation, biofuels, coking, (crude) distillation, catalytic cracking (fluid and resid), gasification, hydrocracking, hydrotreating, hydrogen, isomerization, desulfurization, lube treating, visbreaking, etc. To maintain as complete a listing as possible, the 2011 Refining Processes Handbook is available on CD-ROM and at our website for paid subscribers. Additional copies may be ordered from our website.

Photo: Sinopec RIPP's Clean Gasoline and Propylene (CGP) technology was applied in this 2.8 million tpy grassroots FCC unit in Hainan province, China. Photo courtesy of Shaw Group.



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

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

Axens is a fully-owned subsidiary of IFP.

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BASF Refinery Catalysts is a global industry leader in Fluid Catalytic Cracking (FCC) catalysts with an unparalleled commitment to the delivery of cutting-edge technology and services to the refining industry. As part of BASF—The Chemical Company, BASF Refinery Catalysts is leveraging its leading development platforms, global research infrastructure and passionate pursuit of innovation to develop novel, proprietary technologies to help customers meet the challenges of the market.

BASF Refinery Catalysts offers the highest degree of product flexibility in terms of surface area, zeolite/matrix ratio, metal traps, and particle size distribution. Our FCC catalysts offer not just a wide range of cost-effective solutions to meet our customers' specific needs but also the ability to deliver value through tailored products and services.

The award-winning Distributed Matrix Structures (DMS) and Proximal Stable Matrix & Zeolite (Prox-SMZ) technology platforms, plus our newly developed Multi-Stage Reaction Catalysts (MSRC) manufacturing platform form the foundation of our innovative products. Further information is available on the internet at www.catalysts.basf.com/innovation.

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KBR

TECHNOLOGY

Technology specializes in developing and licensing energy-efficient and cost-effective process technologies that enhance the technical and economic positions of global oil and gas and petrochemical companies. With thousands of successful projects worldwide, KBR combines its technology expertise with full engineering, procurement and construction services to help clients maximize the value of their assets.

KBR offers a breadth of technology licenses and process equipment for: Ammonia and Fertilizer, Synthesis Gas/Syngas; Olefins; Coal Gasification; Refining; Carbon Capture and Storage/CO₂ Sequestration; Hydrogen; and Organic Chemicals.

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- Improved margins, safety and reliability through licensor developed operator training simulators
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Slurry-phase hydrocracking—possible solution to refining margins

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The Linde Group is a world-leading gases and engineering company. The Gases Division offers a wide range of compressed and liquefied gases as well as chemicals and is the partner of choice across a huge variety of industries. Linde gases are used in the energy sector, steel production, chemical processing, environmental protection and welding, as well as in food processing, glass production and electronics. The company is also investing in the expansion of its fast-growing Healthcare business, i. e. medical gases, and is a leading global player in the development of environmentally friendly hydrogen technologies.

Linde's Engineering Division is successful throughout the world, with its focus on promising market segments such as olefin plants, natural gas plants and air separation plants, as well as hydrogen and synthesis gas plants. In contrast to virtually all competitors, the company can rely on its own extensive process engineering know-how in the planning, project development and construction of turnkey industrial plants. Linde plants are used in a wide variety of fields: in the petrochemical and chemical industries, in refineries and fertiliser plants, to recover air gases, to produce hydrogen and synthesis gases, to treat natural gas and in the pharmaceutical industry.

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Lurgi is a leading technology company operating worldwide in the fields of process engineering and plant contracting for the refining and petrochemicals markets. Its technological leadership is based on proprietary technologies and exclusively licensed technologies which aim to convert all carbon energy resources (oil, coal, natural gas, biomass...) in clean products. Lurgi is a subsidiary of the Air Liquide Group.

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Merichem Company ("Merichem") is a global partner serving the oil and gas industries with focused technology, chemical, and service solutions. Merichem provides the Oil and Gas industry with critical proprietary impurity removal processes to increase the guality of Refinery Products and Gas streams. Merichem beneficially re-uses spent caustics and other byproducts produced by oil refining and petrochemical plants around the globe. We are also one of the leading suppliers of naphthenic acid and its derivatives in the world. Merichem Process Technologies has been providing key proprietary refinery product improvement technologies, many based on the FIBER FILM® technology for over 35 years. Merichem Gas Technologies provide proprietary solutions for the removal of H2S and other impurities from a wide range of gas applications. Merichem Caustic Services is the group that provides the beneficial reuse option for Refinery Caustics including the production of naphthenic acids. Merichem Company has been involved with refinery caustics for over almost all of its history.

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Uhde

Uhde has a workforce of more than 4,500 employees worldwide and is a company in the Plant Technology business area of the ThyssenKrupp Group. The company's activities focus on the engineering and construction of chemical and other industrial plants in the following fields: fertilisers; electrolysis; gas technologies; oil, coal, and residue gasification; refining technologies; organic intermediates, polymers and synthetic fibres; and also coke plant and high-pressure technologies. We also provide our customers with professional services and comprehensive solutions in all areas of industrial plant operation. Details are available at www.uhde.eu.

Processes

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UOP A Honeywell Company

For nearly a century, Honeywell' UOP has been a leading international supplier and technology licensor for the oil refining, petrochemicals, gas processing, biofuels and major manufacturing industries. As a respected pioneer, the company is responsible for developing and implementing some of the most useful, original technologies in the world. Today more than 60 percent of the world's gasoline and 85 percent of biodegradable detergents are made using UOP technology. UOP currently holds more than 2,500 active patents as a result of its dedicated research and development commitment and provides sales, service and technical support from its offices across North America, South America, Europe, Asia and the Middle East.

UOP is positioned globally to help our customers achieve long-term growth by responding to their needs, being highly competitive in all of our markets and finding solutions to address today's energy challenges. Innovation is the driving force behind our growth. For more information, go to www.uop.com.

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Maximize assets. Drive results. Hydroprocessing technology innovations

Maximizing diesel in existing assets

Operations skills for the 21st century

Reforming solutions for improved profits in an up-down world

UOP FCC design advancements to reduce energy consumption and \mbox{CO}_2 emissions

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Acid-gas treating

Application: Rectisol is a gas purification process for removing of carbon dioxide (CO_2) down to mol% and/or vppm levels and hydrogen sulfide/carbonyl sulfide (H_2S/COS) down to 0.1 vppm) from a feed gas downstream of a gasifier—e.g., GE-Texaco, Shell, ConocoPhillips, ECUST and others.

Description: The Rectisol process uses methanol as a wash solvent. The methanol has many benefits, globally available and a low-cost washing agent. Furthermore, methanol is chemically and thermally stable and will not change its behavior and structure over a long service life.

The Rectisol wash unit (RWU) operates under favorable at temperatures below 0°C. To lower feedgas temperatures, it is cooled against the cold-product streams, before entering the absorber tower. At the absorber tower, CO_2 and H_2S/COS are removed. The CO_2 content in the purified gas is adjusted to a specific requirement, which can be from 5 vppm to 5 mole %. Sulfur components including H_2S and COS can be removed below 0.1 vppm. The Rectisol process does not need a COS hydrolysis for total COS removal.

By an intermediate flash, co-absorbed products such as hydrogen (H_2) and carbon monoxide (CO) are recovered, thus increasing the product recovery rate.

To reduce the required energy demand for the CO_2 compressor, the CO_2 product is recovered in two different pressure steps (medium pressure and lower pressure). The CO_2 product is essentially sulfur (H₂S and COS) and water free. The CO_2 products can be used for enhanced oil recovery (EOR) and/or sequestration or as pure CO_2 for other processes.

The benefits of the RWU are that no additional downstream COS hydrolysis and/or sulfur treatment is required. Since the CO_2 product is water free, the compressor material can be designed from carbon steel instead of stainless material. Depending on the allowable CO_2 level in



the treated gas, nearly 99% of the CO_2 from the feed gas can be concentrated in the two CO_2 product streams.

In the regeneration column, the loaded methanol is fully regenerated. In the H_2S fraction, the sulfur components are concentrated in a sulfur-enriched stream suitable for downstream sulfur recovery units. Even for low-sulfur containing feed gas streams, the Rectisol wash can economically produce a high-sulfur enriched H_2S fraction. After cooling, the methanol is used in the absorber tower to wash out CO_2 and H_2S/COS .

The water, contained in the feed gas is withdrawn from the process in the methanol/water separation. The amount of water purged from the process is driven by water concentration in the feed gas (water saturation at battery limit).

Acid-gas treating, continued

Economics:

Feed gas	From different gasification types (GE Texaco, Shell, Conoco Phillips, ECUST, etc.)
Treated gas	Adjusted in CO ₂ content (5 vppm to 5 mol%) H ₂ S + COS < 0.1 vppm (w/o additional downstream treatment)
CO ₂ capture rate	Up to 99%
CO ₂ product	For EOR and/or Sequestration Substantially free of H ₂ S and COS w/o COS hydrolysis water free w/o additional drying
H_2S fraction	Suitable for downstream sulfur recovery unit; also for low-sulfur containing feed gases

Installations: Nearly 65 Rectisol wash units are engineered by Linde worldwide. Most of the plants are located in China. But there are also references in the US, Africa and Europe.

Licensor: Linde AG CONTACT
Alkylate, butanes to alkylate

Application: With the conversion of butanes to high-value motor fuel alkylate using the CDA/kyPlus process, NGL producers now have another route to upgrade butanes to gasoline blend stock. By using isobutylene as the sole olefin source, the CDA/kyPlus technology allows for the profitable conversion of isobutylene and isobutane into high-value motor fuel alkylate.

Description: The patented CDAlkyPlus process is a low-temperature sulfuric acid-catalyzed alkylation process coupled with a simple olefin pretreatment step. This combination provides significant benefits over direct alkylation of isobutylene as well as other isobutylene upgrading processes such is isooctene production. Because isobutane and isobutylene are incorporated together to produce a high-value alkylate product, the CDAlkyPlus process produces two times the volume of gasoline blendstock compared with isooctene production. This process is ideal for use downstream of an isobutane dehydrogentation process. The whole dehydrogenation unit product, a roughly 50/50 blend of isobutane and isobutylene, is fed directly to the CDAlkyPlus process.

This technology also provides a unique opportunity for revamping an existing dehydrogenation unit-based methyl tertiary butyl ether (MTBE) plant to produce alkylate. Much of the existing MTBE equipment can be used in the CD*AlkyPlus* process, thus reducing capital requirements. For these retrofit cases, the isobutane recycle around the dehydrogenation unit is essentially eliminated. This means the n-butane capacity of the complex can be doubled without expanding the existing dehydrogenation unit.

Process advantages: The benefits of CDAlkyPlus process:

Compared to direct alkylation of isobutylene

- Lower acid consumption
- Compressor horsepower requirements reduced by 50%



- Lower utilities
- No caustic waste streams
- Higher octane alkylate product
- Lower vapor pressure product.

Compared to iso-octene product alternative

• Twice the product volume.

Licensor: Lummus Technology, a CB&I company CONTACT

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Alkylation

Application: To combine propylene, butylenes and amylenes with isobutane in the presence of strong sulfuric acid to produce high-octane branched chain hydrocarbons using the STRATCO Effluent Refrigeration Alkylation process.

Products: Branched chain hydrocarbons for use in high-octane motor fuel and aviation gasoline.

Description: Plants are designed to process a mixture of propylene, butylenes and amylenes. Olefins and isobutane-rich streams along with a recycle stream of H₂SO₄ are charged to the STRATCO Contactor reactor (1). The liquid contents of the Contactor reactor are circulated at high velocities and an extremely large amount of interfacial area is exposed between the reacting hydrocarbons and the acid catalyst from the acid settler (2). The entire volume of the liquid in the Contactor reactor is maintained at a uniform temperature, less than 1°F between any two points within the reaction mass. Contactor reactor products pass through a flash drum (3) and deisobutanizer (4). The refrigeration section consists of a compressor (5) and depropanizer (6).

The overhead from the deisobutanizer (4) and effluent refrigerant recycle (6) constitutes the total isobutane recycle to the reaction zone. This total quantity of isobutane and all other hydrocarbons is maintained in the liquid phase throughout the Contactor reactor, thereby serving to promote the alkylation reaction. Onsite acid regeneration technology is also available.

Product quality: The total debutanized alkylate has RON of 92 to 96 clear and MON of 90 to 94 clear. When processing straight butylenes, the debutanized total alkylate has RON as high as 98 clear. Endpoint of the total alkylate from straight butylene feeds is less than 390°F, and less than 420°F for mixed feeds containing amylenes in most cases.



Economics (basis: butylene feed):

Investment (basis: 10,000-bpsd unit), \$ per bpsd4,500Utilities, typical per bbl alkylate:
Electricity, kWh13.5Steam, 150 psig, lb180Water, cooling (20°F rise), 10³ gal1.85Acid, lb15Caustic, lb0.1

Installation: Over 850,000 bpsd licensed capacity.

Reference: *Hydrocarbon Processing,* Vol. 64, No. 9, September 1985, pp. 67–71.

Licensor: DuPont CONTACT

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Alkylation

Application: The AlkyClean process converts light olefins into alkylate by reacting the olefins with isobutane over a true solid acid catalyst. AlkyClean's unique catalyst, reactor design and process scheme allow operation at low external isobutane-to-olefin ratios while maintaining excellent product quality.

Products: Alkylate is a high-octane, low-Rvp gasoline component used for blending in all grades of gasoline.

Description: The light olefin feed is combined with the isobutane makeup and recycle and sent to the alkylation reactors which convert the olefins into alkylate using a solid acid catalyst (1). The AlkyClean process uses a true solid acid catalyst to produce alkylate, eliminating the safety and environmental hazards associated with liquid acid technologies. Simultaneously, reactors are undergoing a mild liquid-phase regeneration using isobutane and hydrogen and, periodically, a reactor undergoes a higher temperature vapor phase hydrogen strip (2). The reactor and mild regeneration effluent is sent to the product-fractionation section, which produces n-butane and alkylate products, while also recycling isobutane and recovering hydrogen used in regeneration for reuse in other refinery hydroprocessing units (3). The AlkyClean process does not produce any acid soluble oils (ASO) or require post treatment of the reactor effluent or final products.

Product: The C_5^+ alkylate has a RON of 93–98 depending on processing conditions and feed composition.

Economics:

Investment (2007 USGC basis 10,000-bpsd unit) \$/bpsd	5,200
Utility and catalyst costs, \$/gal (2007)	0.10



Installation: Demonstration unit at Neste Oil's Porvoo, Finland Refinery.

Reference: "The AlkyClean process: New technology eliminates liquid acids," NPRA 2006 Annual Meeting, March 19–21, 2006.

D'Amico, V., J. Gieseman, E. von Broekhoven, E. van Rooijen and H. Nousiainen, "Consider new methods to debottleneck clean alkylate production," *Hydrocarbon Processing*, February 2006, pp. 65–70.

Licensors: Lummus Technology, a CB&I company, Albemarle Catalysts and Neste Oil **CONTACT**

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Alkylation

Application: The RHT-Alkylation process is an improved method to react C_3-C_5 olefins with isobutane using the classical sulfuric acid alkylation process. This process uses a unique mixing device—eductor(s)—that provides low-temperature (25°F–30°F) operations at isothermal conditions. This eductor mixing device is more cost-effective than other devices being used or proposed. It is maintenance free and does not require replacement every two to three years. This mixing device can be a retrofit replacement for existing contactors. In addition, the auto refrigeration vapor can be condensed by enhancing pressure and then easily absorbed in hydrocarbon liquid, without revamping the compressor.

Description: In the RHT-Alkylation, C_3-C_5 feed from FCC or any other source including steam cracker, etc., with isobutane make-up, recycle isobutene, and recovered hydrocarbons from the depropanizer bottom and refrigeration vapors are collected in a surge drum—the C_4 system (5). The mixture is pumped to the reactor (1) to the eductor suction port. The motive fluid is sent to the eductor nozzle from the bottom of reactor, which is essentially sulfuric acid, through pumps to mix the reactants with the sulfuric-acid catalyst.

The mixing is vigorous to move the reaction to completion. The makeup acid and acid-soluble oil (ASO) is removed from the pump discharge. The process has provisions to install a static mixer at the pump discharge. Some feed can be injected here to provide higher OSV, which is required for C_3 alkylation. Reactor effluent is withdrawn from the reactor as a side draw and is sent to acid/ hydrocarbon coalescer (2) where most of the acid is removed and recycled to the reactor (1). The coalescers are being used by conventional process to reduce the acid in the hydrocarbon phase to 7–15 wppm. The enhanced coalescer design RHT can reduce the sulfuric acid content in the hydrocarbon phase to negligible levels (below <1 wppm).



After the coalescer, the hydrocarbon phase is heated and flashed increasing the alkylate concentration in the hydrocarbon, which is sent through the finishing coalescer (4) where essentially all of the remaining acid is removed.

The hydrocarbon is sent to distillation column(s) (7), to separate alkylate product and isobutane, which is recycled. The butane is sent to offsites or can be converted back to isobutane for processing units requirements. The auto refrigeration occurs in the reactor at temperatures 25–30°F. The isothermal condition lowers acid consumption and yields higher octane product due to improved selectivity of 2,4,4 trimethylpentane.

Alkylation, continued

The auto-refrigeration vapor is first enhanced by the ejector and then absorbed in a heavy liquid—alkylate, which provides a low-cost option and then condensed. Some liquid is sent to depropanizer (6); propane and light ends are removed. The bottoms are recycled to C_4 system and sent to the reactor.

The major advances of RHT process are threefold: eductor mixing device, advance coalescer system to remove acid from hydrocarbon (dry system), and C_4 autorefrigeration vapors recovery by absorption, making compressor redundant.

Economics: For a US Gulf Coast unit 1Q 2006 with a capacity of 10,000 bpd alkylate unit

CAPEX ISBL, MM USD	29.5
Power, kWh	2,800
Water, cooling, m ³ /h	1,750
Steam, kg/h	25,600
FCC Feed (about 15% isobutelene in C_4	mixed stream)

Product properties: Octane (R+M)/2:94.8-95.4

Commercial units: Technology is ready for commercialization.

References:

US patent 5,095168. US Patent 4,130593. Kranz, K., "Alkylation Chemistry," Stratco, Inc., 2001. Branzaru, J., "Introduction to Sulfuric Acid Alkylation," Stratco, Inc., 2001. Nelson, *Handbook of Refining*.

Meyers, R. A., Handbook of Refining, McGraw Hill, New York, 1997.

Licensor: Refining Hydrocarbon Technologies LLC CONTACT

Alkylation

Application: The UOP Indirect Alkylation (InAlk) process uses solid catalysts to convert light olefins (mainly C_4 but also C_3 and C_5) to alkylate.

Description: The InAlk process makes premium alkylate using a combination of commercially proven technologies. Iso-butene reacts with itself or with other C_3-C_5 olefins via polymerization. The resulting mixture of higher molecular weight iso-olefins may then be hydrogenated to form a high-octane paraffinic gasoline blendstock that is similar to alkylate, but usually higher in octane, or it may be left as an olefinic high-octane gasoline blending component.

Either resin or solid phosphoric acid (SPA) catalysts are used to polymerize the olefins. Resin catalyst primarily converts iso-butene. SPA catalyst also converts n-butenes. The saturation section uses either a base-metal or noble-metal catalyst.

Feed: A wide variety of feeds can be processed in the InAlk process. Typical feeds include FCC-derived light olefins, steam-cracker olefins and iC_4 dehydrogenation olefins.

Installation: The InAlk process is an extension of UOP's catalytic condensation and olefin saturation technologies. UOP has licensed and designed more than 400 catalytic condensation units for the production of polygasoline and petrochemical olefins and more than 200 hydrogenation units of various types. A total of 12 InAlk units have been licensed



by UOP. Of those units, six are operating, two are in design and construction. The remaining four licensed units either have been shutdown and/or were never built. Of the 12 units licensed to date, seven were licensed to convert MTBE units to the InAlk technology.

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Alkylation

Application: The UOP ReVAP process when used with the HF alkylation technology reduces aerosol formation in the event of an HF release, while maintaining unit operability and product quality. The UOP ReVAP process is a passive mitigation system that will reduce aerosol from any leak that occurs while the additive is in the system.

Description: The additive stripper sends acid, water and light-acid soluble oils overhead and on to the acid regenerator. Heavy acid soluble oils and the concentrated HF-additive complex are sent to the additive stripper bottoms separator. From this separator the polymer is sent to neutralization, and the HF-additive complex is recycled to the reactor section. The acid regenerator removes water and light-acid soluble oils from the additive stripper overhead stream. The water is in the form of a constant boiling mixture (CBM) of water and HF.

There is no expected increase in the need for operator manpower. Maintenance requirements are similar to equipment currently in standard operation in an HF alkylation unit in similar service.

Installation: Eleven units have been licensed at present. Four are in operation.



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Alkylation

Application: The UOP Alky Plus Alkylation Process improves gasoline quality by adding clean-burning, mid-boiling-range isoparaffins and reducing gasoline pool vapor pressure and olefin content by conversion of C_3-C_5 olefin components to alkylate.

Description: The alkylation reaction catalytically combines C_3-C_5 olefins with isobutane to produce motor-fuel alkylate. Alkylation takes place in the presence of a modified HF catalyst, the UOP Revap process, under conditions selected to maximize alkylate yield and quality.

UOP offers a gravity flow design configuration to obtain good mixing without the need for a catalyst circulation pump. The forced circulation design reduces acid inventory and reaction vessel elevations.

Acid regeneration occurs in a small acid regenerator, location on plot, which reduced acid consumption and eliminating spent acid disposal.

Feed: Alkylation feedstocks are typically treated to remove sulfur and water. In cases where MTBE and TAME raffinates are still being processed, an oxygenate removal unit (ORU) may be desirable.

Selective hydrogenation of butylene feedstock can further reduce acid regeneration requirements, catalyst (acid) consumption and even increase alkylate octane by isomerizing 1-butene to 2-butene.

Efficiency: HF Alkylation remains the most economically viable method for the production of alkylate. The acid consumption rate for HF Alkylation is less than 1/100th the rate for sulfuric alkylation units. Unlike sulfuric alkylation units, the Alky Plus Alkylation Process does not require refrigeration equipment to maintain a low reactor temperature.



Installations: Since 1942, UOP has licensed 216 alkylation units.

Alkylation, low-temperature acid catalyzed

Application: The patented CD*Alky* process is an advanced sulfuric acidcatalyzed alkylation process for the production of motor fuel alkylate.

Description: The CDA/ky low-temperature sulfuric acid alkylation technology reacts light olefin streams from refinery sources such as fluid catalytic cracking units or from steam-cracking units with isoparaffins to produce motor fuel alkylate. Central to the CDA/ky process is a novel scalable contactor/reactor design. The CDA/ky process is available for license to the petroleum refining and petrochemical industries.

The process flow diagram shows the basic configuration to process a mixed- C_4 olefin feed and produce a high-octane motor fuel alkylate, without the need for a reactor effluent alkaline water wash. The CDA/ky process yields a higher quality product while consuming significantly less acid than conventional sulfuric acid-based technologies. The flow scheme is also less complex than conventional designs, which reduces capital and operating costs.

Conventional sulfuric acid alkylation units use mechanical mixing in their contactors, which are characterized by their high acid consumption. In addition, they are unable to take full benefit of operating at very low temperature, which substantially improves alkylate quality and reduces acid consumption. This scalable, vertical reactor also reduces capital costs and plot space requirements. This process has also eliminated the need for reactor effluent alkaline water wash, thus reducing caustic waste. In addition, this dry fractionation section reduces the potential for downstream corrosion and thereby reducing overall maintenance costs.

Advantages: The benefits of the CDAlky process:

- Lower acid consumption
- Lower utilities
- Reduced operating cost



- Reduced environmental exposure
- Higher octane product
- Lower CAPEX—simpler flowsheet with fewer pieces of equipment
- Highly flexible operation range—maximum absolute product octane or maximum octane barrels
 - Lower maintenance—no mechanical agitator or complex seals
 - Less corrosion due to dry system
 - No caustic waste stream.

Licensor: Lummus Technology, a CB&I company CONTACT

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Amine treating

Applications: Bechtel Hydrocarbon Technology Solutions, Inc. (BHTS) offers the complete suite of sulfur block technologies including Amine treating. So called "activated amines" are frequently used for tight specifications or reduced capex. BHTS will compare the performance of generic amines and activated amines to optimize opex and capex for our clients.

Hydrogen sulfide (H_2S ,) carbon dioxide (CO_2) and carbonyl sulfide (COS) are removed from fuel gas headers, hydrotreaters (DHT, NHT, etc.), cokers, and LPG. Depending upon the specific service, amines utilized include MEA, DEA, DGA, DIPA, MDEA and proprietary activated amines.

Products: Bechtel's amine treating units can reduce contaminant acid gases to the standard US fuel gas specification of 160 ppmv H_2S or lower if desired. Specialty amines are commonly used to reach concentrations to as low as 10 ppmv.

Description: The gases frequently encountered are saturated with hydrocarbons, so a sour KO drum (1) is used to remove entrained liquid droplets. The stream then enters the amine absorber (2) where the gas flows counter-current to the amine stream. The amine will pick up contaminants such as H_2S , CO_2 , and COS and remove them from the process gas. To reduce carry-over losses and opex, the sweetened process gas then flows through a Sweet KO drum (3) to recover entrained droplets of amine. The sweetened gas is then returned to the refinery.

The amine containing the acid gases, called rich amine, flows to the regeneration area. The stream is first flashed from header pressure to \sim 5 psig (or flare header pressure) in the rich-amine flash drum (4). This drum serves three purposes:

• Remove entrained hydrocarbon droplets

• Allow phase separation from hydrocarbons that vaporize at the lower pressure



• Provide operational surge capacity. Flashed vapors can be either flared or sent to a wet gas compressor for recovery. Recovered hydrocarbon liquids are typically sent to the refinery slop-oil system.

The rich-amine pumps (5) send the stream to a filtration system (not shown for simplicity) where particulates are removed to 10 microns or less. This helps keep the downstream equipment free of particulates, which can cause erosion, fouling, and loss of performance. Any remaining dissolved hydrocarbons are then removed with activated carbon. An after-filter will catch any migrating carbon fines and then the rich amine flows through a lean/rich-heat exchanger (6) for energy conservation and then to the regenerator (also called a stripper, 7). There the acid gases are stripped from the amine. The gases flow through an over-

Continued ▼

Amine treating, continued

head condenser (8) where the stream is cooled and reflux (primarily sour water) is generated. The overhead accumulator (9) separates the reflux from the acid gas, which is sent to the sulfur recovery unit (SRU) or Claus unit. The reflux pumps (10) then send the sour reflux back to the Regenerator. Vapors in the tower are generated by adding heat in the regenerator reboiler (11), typically by using the refinery's existing low pressure steam system.

From the bottom of the tower, the lean amine flows through the lean/rich exchanger to pre-heat the incoming feed. The lean-amine pumps (12) move the amine through the lean-amine coolers (13), which can be a combination of air and water cooled exchangers, and back to the absorber.

Water balance in the amine system is very important for meeting specifications and is maintained by either purging some of the reflux stream to the sour water header (for eventual processing in the sour water stripper) or made up by adding demineralized water to the regenerator overhead stream. Adding makeup water here has the added benefit of acting as an ammonia wash on the acid-gas stream before it enters the SRU.

Economics:

Investment: (basis 425 gpm, 2010 US Gulf Coast)	
\$ per gpm	22,000
Utilities, typical per gal of feed:	
Fuel, absorbed, 10 ³ Btu	_
Electricity, kWh	0.0098
Steam, LP, lb/gallon of amine	1.2
Water, cooling (25°F), gal	5.8

Installations: This process has been used in literally thousands of units to produce low-sulfur content and low-CO₂ content process streams around the world.

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT

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Aromatics

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

Process description: The technology encompasses three main processing areas: splitter, reactor and stabilizer sections. The heavy-aromatics stream (C_9^+ feed) is fed to the splitter. The overhead C_9/C_{10} aromatic product is the feed to the transalkylation reactor section. The splitter bottoms are exchanged with other streams for heat recovery before leaving the system.

The aromatic product is mixed with toluene and hydrogen, vaporized and fed to the reactor. The reactor gaseous product is primarily unreacted hydrogen, which is recycled to the reactor. The liquid product stream is subsequently stabilized to remove 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 to other transalkylation units, or in grass roots designs

• Decreased hydrogen consumption due to low cracking rates

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

Economics: Feedrate 1,000 thousand tpy (22,000 bpsd); erected cost \$18 MM (ISBL, 2007 US Gulf Coast Basis).

Installation: Three commercial licenses.

Licensor: GTC Technology US, LLC CONTACT

Aromatics extractive distillation

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

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

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

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

Uhde's new single-column morphylane extractive distillation process uses a single-column configuration, which integrates the ED column and the stripper column of the conventional design. It represents a superior process option in terms of investment and operating cost.

Economics:

Pygas feedstock:

Production yield	Benzene	Benzene/toluene
Benzene	99.95%	99.95%
Toluene	_	99.98%
Quality		
Benzene	30 wt ppm NA*	80 wt ppm NA*
Toluene	-	600 wt ppm NA*



Consumption

Steam475 kg/t ED feed680 kg/t ED feed**Reformate feedstock with low-aromatics content (20 wt%):

Quality	Benzene
Benzene	10 wt ppm NA*
Consumption	
Steam	320 kg/t ED feed
*Maximum content of	nonaromatics **Including benzene/toluene splitter

Installation: More than 55 Morphylane plants (total capacity of more than 11 MMtpy). The first single-column Morphylane unit went onstream in 2004.

Aromatics extractive distillation, continued

References: Diehl, T., B. Kolbe and H. Gehrke, "Uhde Morphylane Extractive Distillation—Where do we stand?" ERTC Petrochemical Conference, October 3–5, 2005, Prague.

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

Licensor: Uhde GmbH CONTACT

Aromatics recovery

Application: GT-BTX is an aromatics recovery technology that uses extractive distillation to remove benzene, toluene, and xylene (BTX) from refinery or petrochemical aromatics streams such as catalytic reformate or pyrolysis gasoline. With lower capital and operating costs, simplicity of operation, and range of feedstock and solvent performance, extractive distillation is superior to conventional liquid-liquid extraction processes. Flexibility of design allows use for grassroots aromatics recovery units, debottlenecking or expansion of conventional extraction systems.

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

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

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



Process advantages:

- Lower capital cost compared to conventional liquid-liquid extraction or other extractive distillation systems
- Energy integration options to further reduce operating costs
- Higher product purity and aromatic recovery
- Recovers aromatics from full-range BTX feedstock
- Distillation-based operation provides better control and simplified operation
- Proprietary formulation of commercially available solvent exhibits high selectivity and capacity
- Low solvent circulation rates
- Insignificant fouling due to elimination of liquid-liquid contactors
- Fewer hydrocarbon emission sources for environmental benefits.

Continued ▼

Aromatics recovery, continued

Economics:New unitFeedrate12,000 bdp reformate or pygasISBL capital cost\$15 MM

Installations: Twenty-eight.

Licensor: GTC Technology US, LLC CONTACT

Asphaltene pelletization

Application: The AQUAFORM unit is designed for pelletizing heavy hydrocarbons including asphaltenes from ROSE solvent deasphalting process.

Description: AQUAFORM has been designed for easy integration with the KBR ROSE solvent deasphalting unit. Asphaltenes from the ROSE asphaltene product drum are pumped through an exchanger to the AQUAFORM pelletizing vessel. A rotating head inside the vessel produces small droplets of asphaltene, which are quenched in a water bath. The pellets are removed on screen separators and then transferred to storage using conveyer systems. The water is filtered, cooled and returned to the pelletizing vessel.

The unit is constructed of carbon steel metallurgy and operates at moderate temperatures and at near atmospheric pressure. An asphaltene pelletizing vessel is designed for up to 1,000 tpd of asphaltene feed. Pellet size can be controlled by adjusting key operating conditions.

Properties of pellets: The pellets have ~ 30% higher heating value than petroleum coke. The crush strength is high thus allowing for storage in silos.

Process applications: The asphaltene pellets can be stored at ambient conditions and can be transported using bulk transporters. The pellets are suitable for use in cement plants and steel mills. The higher heating



value of the pellets as compared to coke can help in the debottlenecking of cement and steel mills. The pellets can be melted again after transportation for gasification and cracking in cokers.

Licensor: KBR CONTACT

Benzene saturation

Application: GTC Technology's GT-BenZap is a benzene saturation technology that allows refiners to achieve the upcoming benzene limit required by EPA's regulations under Mobile Sources Air Toxics Phase 2 (MSAT2). Benzene saturation is applied when the logistics of benzene recovery and production are unfavorable, or where the economy of scale for benzene production is not sufficient.

Description: GT-BenZap process features a reliable traditional design paired with a proven nickel-based catalyst. The process consists of hydrotreating a narrow-cut C₆ 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 C₆ heart cut is separated as a side-draw fraction, while the C₇⁺ cut and the C₅⁻ light fraction are removed as bottom and top products of the column.

The C₆ olefins present in the C₆ cut are also hydrogenated to paraffins, while the C₅⁻ olefins removed at the top of the splitter are not, thus preserving the octane number. The hydrogenated C₆ fraction from the reactor outlet is sent to a stabilizer column where the remaining hydrogen and lights are removed overhead. The C₅⁻ cut, produced from the splitter overhead, is recombined with the hydrogenated C₆ 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 C₇⁺ cut from the splitter column and together form the full-range reformate, which is low in benzene. GTC also offers a modular construction option and the possibility to reuse existing equipment.

Process advantages:

- Simple and reliable technology; low operating costs
- An economical alternative to platinum-based systems
- \bullet Ability to reduce the benzene in the reformate stream by over 99.9%
 - Minimized impact to hydrogen balance and octane loss.



Installation: Three commercial licenses.

Licensor: GTC Technology US, LLC CONTACT

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Biodiesel

Application: Consumption of primary energy has risen substantially in recent years, and greenhouse gases (GHG) emissions have increased by a substantial amount. To counter this trend, there is a global strong emphasis on regenerative energy such as biofuels to effectively reduce or avoid such emissions.

Description: The Lurgi biodiesel process is centered on the transesterification of different raw materials to methyl ester using methanol in the presence of a catalyst. In principle, most edible oils and fats—both vegetable and animal sources—can be transesterified if suitably prepared.

Transesterification is based on the chemical reaction of triglycerides with methanol to methyl ester and glycerine in the presence of an alkaline catalyst. The reaction occurs in two mixer-settler units. The actual conversion occurs in the mixers. The separation of methyl ester as the light phase and glycerine water as the heavy phase occurs in the settlers due to the insolubility of both products and the difference in density. Byproduct components are removed from the methyl ester in the downstream washing stage, which operates in a counter-current mode. After a final drying step under vacuum, the biodiesel is ready for use.

Any residual methanol contained in the glycerine water is removed in a rectification column. In this unit operation, the methanol has a purity, which is suitable for recycling back to process. For further refinement of the glycerine water, optional steps are available such as chemical treatment, evaporation, distillation and bleaching to either deliver crude glycerine at approximately 80% concentration or pharmaceutical-grade glycerine at > 99.7% purity.

Economics: The (approximate) consumption figures—without glycerine distillation and bleaching—stated below are valid for the production of one ton of rapeseed methyl ester at continuous operation and nominal capacity.



Steam, kg	320
Water, cooling ($\Delta t = 10^{\circ}$ C), m ³	25
Electrical energy, kWh	12
Methanol, kg	96
Catalyst (Na-methylate 100%), kg	5
Hydrochloric acid (37%), kg	10
Caustic soda (50%), kg	1.5
Nitrogen, Nm ³	1

Installation: Lurgi has been building biodiesel plants for 20 years. Only in the last five years, Lurgi has contracted more than 40 plants for the production of biodiesel with capacities ranging from 30,000 to 250,000 tpy.

Licensors: Lurgi GmbH CONTACT

HYDROCARBON PROCESSING®

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Biodiesel

Application: The RHT- Biodiesel process is optimized to produce biodiesel from palm oil, rape-seed oil, vegetable and animal products that contain fatty acids with even number of carbon atom (12 to 22). The lack of sulfur in the biodiesel enables complying with many international fuel specifications.

The biodiesel is comparable to petroleum-based diesel. Triglycerides are reacted with methanol, ethanol or higher alcohols to yield biodiesel within the acceptable boiling range. Methanol is most commonly used for the biodiesel production since it is the most cost-effective of alcohols, and it can provide better economics for the biodiesel producers. Biodiesel is produced by reacting vegetable oils and animal fats (triglycerides) with methanol in the presence of highly alkaline heterogeneous catalyst at moderate pressure and temperature. **Pretreatment may be required if the vegetable oil has a high free-fatty acids content to optimize methyl esters yield. If free fatty acids are present in the feed, first step is esterfication of the free-fatty acid with methanol. However if the free-fatty acids concentrations are low, then this step can be deleted.**

The triglycerides and methanol are converted by transesterification reaction to yield methyl esters of the oils and fats, and glycerine is produced as a byproduct. The glycerine is separated from the methyl esters (biodiesel) by phase separation via gravity settling. The methyl esters and glycerine are purified to meet the product specifications.

Description: In the simplified process flow diagram (1), the feed—vegetable oil or animal fats—is pumped from storage and is mixed with methanol in the required molar ratio vegetable/methanol at moderate operating pressure. The feed is heated to the reaction temperature and is sent to esterification reactor. Free-fatty acids are pretreated if the concentration exceeds 3% percent of the feed. The reactor contains an acid catalyst for this reaction and can remove 99.9 % of free-fatty acids from



the vegetable oils. (**Note:** the pretreatment is only required when the feed contains free-fatty acids; otherwise, this step can be omitted.

The effluent from the first reactor (if free-fatty acids are present) or the heated feed is sent to the transesterfication reactor, where 3 moles

Biodiesel, continued

of methanol react with the triglyceride to produce 3 moles of methyl ester oil (biodiesel) and one mole of glycerine. The transesterification reactor uses a highly alkaline heterogeneous catalyst and provides essentially 100% conversion. The transesterification reactor effluent is sent to gravity separator/settler. The biodiesel product is taken from the top of the separator, and is water washed. The washed biodiesel product is taken from the top of the drum. Water washing removes excess methanol from the reaction products, which is recovered by normal distillation; the pure methanol is recycled back to the reactor. The bottoms from the separator/settler are sent to the purification unit to remove impurities and residual methanol, which is recycled back. Pure glycerine product is sent to storage.

Fig. 2 is an alternate flow scheme; a spare transesterification reactor is added to remove glycerine from the reactor to sustain reaction rates. Once the reaction rates are reduced the reactor is switched and washed with hot solvent to remove residual glycerine and biodiesel. This extra reactor patented mode of operation provides higher reactions rates and onstream capability while enhancing yield and productivity. Glycerine purity can exceed 99.8% after distillation.

Reaction chemistry: Transesterification reactions:

Triglycerides + 3 Methanol ---- Methyl Ester of the oil (biodiesel) + Glycerol

Comparision of the Diesel/Biodiesel Properties

Fuel Property	Diesel	Biodiesel
Fuel standard	ASTM D 975	ASTM P S 121
Fuel composition	C ₁₀ –C ₂₁ HC	C ₁₂ –C ₂₂ FAME
Lower heating value, Btu/gal	131	117
Kinemetic Vis @ 40°C	1.3-4.1	1.9–6
SG at 60°F	0.85	0.88
Water, wppm	161	500
Carbon	87	77
Hydrogen	13	12
Oxygen	0	11
Sulfur, wppm	15–500	0
Bp, °F	380–650	370–340
Flash Pt, °F	140–175	210-140

Economics: The normal utilities for continuous biodiesel unit based on heterogeneous catalyst for tph of biodiesel capacity are listed. This does not include the glycerine purification utilities. The capital cost for the ISBL Biodiesel plant on Gulf coast site basis based on 1Q 2006 is provided below.

CAPEX ISBL plant: USD/ton Biodiesel	235–265
Steam, lb/h	368
Water, cooling gpm	64
Power, kWh	9

Licensor: Refining Hydrocarbon Technologies LLC CONTACT

Biofuel, Green diesel

Application: The UOP/Eni Ecofining process for the production of Green Diesel fuel is UOP's solution to meeting the increasing demand for a sustainable high-quality renewable diesel using conventional hydroprocessing technology already widely used in refineries.

Description: The Ecofining process deoxygenates and then hydrogenates triglycerides and/or free fatty-acid feedstocks such as vegetable oils and animal fats. The resulting paraffins are then isomerized to create a high-quality hydrocarbon known as Green Diesel. If desired, the Ecofining process can also be designed to produce a slipstream of a paraffinic Green Jet Fuel stream in addition to the Green Diesel product.

A thermochemical process, the Ecofining process produces green diesel fuel that is indistinguishable from traditional diesel fuel. It can be used as a direct replacement fuel or as a valuable blendstock to enhance the quality of the existing diesel pool. Blending of high-quality green diesel will allow the use of lower quality diesel range refinery product streams, ultimately reducing the cost of biofuel compliance and increasing the overall diesel pool.

Designed for feedstock flexibility, the Ecofining process works with a wide range of pretreated biofeedstocks—from vegetable oils and animal fats to second generation, non-food-based options such as jatropha and algal oils.

The diesel yield and hydrogen consumption vary slightly according to the feed-stock source and the required product cloud point. The hydrogen consumption may also vary between different feeds.

Experience: UOP introduced Ecofining in early 2007 as the first commercial offering from its Renewable Energy & Chemicals business group dedicated to introducing new technology for processing renewable energy sources in existing or new petroleum refineries worldwide. The Ecofining process is an extension of UOP's leading portfolio of hydroprocessing and isomerization technologies.



Installation: Valero has joined forces with Darling International for the construction of the first Ecofining unit at its facility near St. Charles, Louisiana. The facility, which will convert waste animal fats into Green Diesel, will start-up by the end of 2012.

Biofuel, Green jet fuel

Application: The UOP Renewable Jet process produces Green Jet Fuel from sustainable natural sources that meets all specifications for flight with no modifications to the aircraft or engine and can reduce emissions by as much as 85% compared to petroleum-based fuels.

Description: Based upon the UOP/Eni Ecofining process for the production of Green Diesel, the Renewable Jet process is designed to maximize the yield of biofuel or bio-synthetic paraffinic Kerosine (bio-SPK) to 50 to 70% by volume. This is achieved by optimizing the catalytic processes of deoxygenation, isomerization and selective cracking of hydrocarbons present in the natural oils and fats. The product is a high-quality, ultralow-sulfur jet fuel.

Co-products in the process are diesel and naphtha-range materials. The process can be adjusted to produce a specific freeze point, or, alternatively, be operated in a maximum diesel mode.

The process is also feedstock flexible, allowing for a variety of natural oils and fats.

Experience: UOP has actively participated in the fuel approval process in both commercial and military applications.



Butene-1 recovery

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

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

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

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

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

Utilities:

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



Installation: Four units have been licensed by Saipem.

Licensor: Saipem CONTACT

Carboxylic acid recovery

Application: The GT-CAR recovery process combines GTC's liquid-liquid extraction technology with distillation to recover and concentrate carboxylic acids from wastewater. Using a high-boiling solvent enables the process to attain the lowest energy use of any commercially available process with minimal capital costs. The recovered acids have sufficient purity to be sold as glacial grade or recycled back to the process. The biological oxygen demand (BOD) of the resulting wastewater stream is greatly reduced. The process is economical for any aqueous stream generated in the production of dimethyl terephthalate (DMT), acetic acid, pulp/paper, furfural and other processes.

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

Advantages:

• Up to 98% of the acids can be recovered

• Acid concentrations as low as 0.5%+ can be economically recovered

- Low capital investment results in typical ROI up to 40%
- Modular systems approach enables minimal disruption of plant operation and shorter project schedule



• Use of high-boiling solvent yields high-acetic recovery and substantial energy savings

• Solvent is easily separated from water, giving a solvent-free

- (< 20 ppm) wastewater exit stream
 - Acetic acid product purity allows for recycle or resale
- High acid recovery provides environmental benefits, unloading the biological treatment system

Installation: Two licensed units.

Licensor: GTC Technology US, LLC CONTACT

Catalytic dewaxing

Application: Use ExxonMobil's Research & Engineering's (EMRE's) Selective Catalytic Dewaxing (MSDW) process to make high VI lube base stock.

Products: High VI / low-aromatics lube base oils (light neutral through bright stocks). Byproducts include fuel gas, naphtha and low-pour diesel.

Description: EMRE's MSDW is targeted for hydrocracked or severely hydrotreated stocks. The improved selectivity of MSDW for the highly isoparaffinic-lube components results in higher lube yields and VIs. The process uses multiple catalyst systems with multiple reactors. Internals are proprietary (the Spider Vortex Quench Zone technology is used). Feed and recycle gases are preheated and contact the catalyst in a down-flow-fixed-bed reactor.

Reactor effluent is cooled, and the remaining aromatics are saturated in a post-treat reactor. The process can be integrated into a lube hydrocracker or lube hydrotreater. Post-fractionation is targeted for client needs.

Operating conditions:

Temperatures, °F	550–800
Hydrogen partial pressures, psig	500–2,500
LHSV	0.4-3.0
Conversion depends on feed wax content Pour point reduction as needed.	

Yields:

	Light neutral	Heavy neutral
Lube yield, wt%	94.5	96.5
C ₁ –C ₄ , wt%	1.5	1.0
C ₅ –400°F, wt%	2.7	1.8
400°F–Lube, wt%	1.5	1.0
H ₂ cons, scf/bbl	100–300	100–300



Installation: Twenty-one units are operating and three are in design.

Licensor: ExxonMobil Research and Engineering Co. CONTACT

Catalytic reforming

Application: Upgrade various types of naphtha to produce high-octane reformate, BTX and LPG.

Description: Two different designs are offered. One design is conventional where the catalyst is regenerated in place at the end of each cycle. Operating normally in a pressure range of 12 to 25 kg/cm² (170 to 350 psig) and with low pressure drop in the hydrogen loop, the product is 90 to 100 RONC. With their higher selectivity, trimetallic catalysts RG582 and RG682 make an excellent catalyst replacement for semi-regenerative reformers.

The second, the advanced Octanizing process, uses continuous catalyst regeneration allowing operating pressures as low as 3.5 kg/ cm^2 (50 psig). This is made possible by smooth-flowing moving bed reactors (1–3) which use a highly stable and selective catalyst suitable for continuous regeneration (4). Main features of Axens' regenerative technology are:

- Side-by-side reactor arrangement, which is very easy to erect and consequently leads to low investment cost.
- The RegenC-2 catalyst regeneration system featuring the dry burn loop, completely restores the catalyst activity while maintaining its specific area for more than 600 cycles.

Finally, with the new CR 601 (gasoline mode) and AR 701 (aromatics production) catalysts specifically developed for ultra-low operating pressure and the very effective catalyst regeneration system, refiners operating Octanizing or Aromizing processes can obtain the highest hydrogen, C_5 + and aromatics yields over the entire catalyst life.

Yields: Typical for a 90°C to 170°C (176°F to 338°F) cut from light Arabian feedstock:

	Conventional	Octanizing/Aromizing
Oper. press., kg/cm ²	10–15	3–7



Yield, wt% of feed:		
Hydrogen	2.8	3–4
C ₅ +	83	88–95
RONC	100	100-105
MONC	89	89–92

Installation: Of 150 units licensed, 100 units are designed with continuous regeneration technology capability.

Reference: "Fixed Bed Reformer Revamp Solutions for Gasoline Pool Improvement," *Petroleum Technology Quarterly,* Summer 2000.

"Increase reformer performance through catalytic solutions," Seventh ERTC, November 2002, Paris.

Catalytic reforming, continued

"Squeezing the most out of fixed-bed reactors," *Hart Show Special,* NPRA 2003 Annual.

"Octanizing reformer options to optimize existing assets," NPRA Annual Meeting, March 15–17, 2005, San Francisco.

"Octanizing reformer options," *Petroleum Technology Quarterly,* Spring, 2006.

Boitiaux, J. P., et al., "New developments accelerating catalyst research," *Hydrocarbon Processing*, September 2006, pp. 33–40.

Licensor: Axens CONTACT

Catalytic reforming

Application: The UOP CCR Platforming process is used throughout the world in the petroleum and petrochemical industries. It produces feed for an aromatics complex or a high-octane gasoline blending product and a significant amount of hydrogen.

Description: Hydrotreated naphtha feed is combined with recycle hydrogen gas and heat exchanged against reactor effluent. The combined feed is then raised to reaction temperature in the charge heater and sent to the reactor section.

Radial-flow reactors are arranged in a vertical stack. The predominant reactions are endothermic; so an interheater is used between each reactor to reheat the charge to reaction temperature. The effluent from the last reactor is heat exchanged against combined feed, cooled and split into vapor and liquid products in a separator. The vapor phase is hydrogen-rich. A portion of the gas is compressed and recycled back to the reactors. The net hydrogen-rich gas is compressed and charged together with the separator liquid phase to the product recovery section. This section is engineered to provide optimum performance.

Catalyst flows vertically by gravity down the reactor stack. Over time, coke builds up on the catalyst at reaction conditions. Partially deactivated catalyst is continually withdrawn from the bottom of the reactor stack and transferred to the CCR regenerator.

Installation: UOP commercialized the CCR Platforming process in 1971 and now has licensed more than 280 units.



Efficiency/product quality: Commercial onstream efficiencies of more than 97% are routinely achieved in CCR Platforming units.

Claus sulfur recovery units

Applications: Bechtel Hydrocarbon Technology Solutions, Inc. (BHTS) offers the complete suite of sulfur block technologies including Claus sulfur recovery units (SRUs), SRU tail-gas units, amine treating units and sour-water stripping (SWS) units.

Environmental regulations limit sulfur compounds in refining products, natural gas and discharge streams from refineries and natural gas processing plants. The Claus SRU converts the sulfur species, primarily hydrogen sulfide (H_2S), removed from the various refinery hydrocarbons stream or natural gas and converts it to elemental sulfur.

Permutations include handling of ammonia (NH₃) with H₂S from a SWS, indirect reheat with high-pressure steam generated within the SRU, low-level oxygen (O₂) enrichment (up to 28% O₂ equivalent), high-level oxygen enrichment (up to 50% O₂ equivalent), sub-dewpoint operation, processing of very lean acid gas (less than 15% H₂S) and many others.

Products: BHTS's Claus units produce liquid sulfur that meets all industrial standards for color, ash and contaminants. We also offer degassing, that is, the removal of H_2S (and other dissolved gases) to meet the specifications that are required by most sulfur solidification units. The resulting carrier stream can be sent to incineration or back to the front of the Claus unit.

Description: The SRU receives feed from the amine regeneration unit (ARU) and the SWS and converts the H_2S into liquid sulfur. The unit also destroys the NH_3 and hydrocarbons in the feed and converts them into nitrogen, water vapor, carbon monoxide and carbon dioxide. The amine-acid gas and the SWS acid gas feeds are partially combusted in the thermal reactor (1) and some sulfur is produced. The process gas is cooled in the high-pressure waste-heat boiler (2) and then in the LP steam generating sulfur condenser (3).



Sulfur is condensed and removed in the sulfur condenser. The remaining process gas is then sent through three catalytic reactor stages where additional sulfur is produced. Each catalytic stage consists of a reheat exchanger (4), a catalytic reactor (5) and a sulfur condenser (6). The sulfur produced in the catalytic reactor is condensed and removed in the sulfur condenser. The sulfur product flows into a sulfur storage pit (7) or tank and is then pumped to truck or rail car loading for transport.

Depending on the local environmental regulations, the effluent (SRU tail gas) from the SRU is sent to the tail-gas treating unit for additional processing or to a thermal oxidizer for combustion and discharge.

Claus sulfur recovery units, continued

Economics:

Investment: (basis 100 long tpd SRU, 2010 US \$ per long ton	5 Gulf Coast) 81,000
Utilities, typical per long ton feed:	
Fuel, absorbed, 10 ³ Btu	_
Electricity, kWh	75
HP BFW, Ib	6,500
Steam HP (export), lb	5,500
LP BFW, lb	1,200
Steam LP (export), lb	1,000

Installations: The Claus process has been used in literally thousands of units to produce millions of tons per year of essentially pure sulfur.

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT

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Claus tail-gas treating

Applications: Bechtel Hydrocarbon Technology Solutions, Inc. (BHTS) offers the complete suite of sulfur block technologies including Claus sulfur recovery units (SRUs), SRU tail-gas units, amine-treating units and sour-water stripping (SWS) units.

BHTS offers a hydrogenation-amine tail gas unit designed to meet the local environmental regulations. This technology has been around for decades and has been used on hundreds of SRU tail-gas streams to reduce the sulfur emissions from the sulfur complex to environmentally acceptable levels. This mature technology has been modified several times since its introduction, and the most popular permutations are offered by BHTS. These permutations include the use of special lowtemperature catalyst, medium-pressure (MP) steam from the SRU for the catalytic reactor feed heater instead of a fired heater-reducing gas generator (if an external source of hydrogen is available), and specialty amines to improve energy efficiency and to reduce sulfur emissions.

Many US states (and the US EPA) allow venting a 10 ppmv hydrogen sulfide (H₂S) stream directly to the atmosphere. This is especially advantageous if carbonyl sulfide (COS) presence is low and incineration can be avoided. Depending upon the specific service and emissions requirements, BHTS will select generic MDEA or a proprietary activated amine. So called "specialty amines" are frequently used for tight specifications or reduced capex. BHTS will compare the performance of generic amines and activated amines to optimize opex and capex for our clients.

Products: BHTS's Claus tail-gas units (TGUs) can reduce H_2S concentrations to as low as 10 ppmv. This ability boosts overall sulfur block recovery to $99.9^+\%$ of the incoming sulfur.

Description: Because the stream in question is essentially a low-sulfur concentration stream that must be cleaned up, an amine system is used. The resulting acid gas is routed to the SRU header as a "recycle stream."



Before treating in the amine section of the unit, however, the sulfurbearing compounds that are non- H_2S (such as SO_2 , sulfur vapor and COS) must first be converted to H_2S . In other refinery units, this is done via hydrotreating (heating the gas and reacting with hydrogen over a catalyst,) and it is done here as well.

The Claus tail gas is combined with hydrogen (PSA hydrogen is best) and the resulting mixture is heated in the tail-gas feed heater (1). The heated stream is then sent to the catalytic reactor (2), where the sulfur species in the feed gas are converted to H_2S . A significant amount of heat is generated by these reactions, and it must be removed before

Claus tail-gas treating, continued

treating with an amine. For this purpose low-pressure (LP) steam is typically generated in the waste-heat exchanger (3).

The contact condenser or quench tower (4) further cools the gas to the appropriate amine operating temperature. Gas flows from beneath the bottom tray counter currently to cooled water. The overhead gas is sent to the amine absorber (7) in the amine section of the TGU, where the H_2S and some carbon dioxide (CO_2) are absorbed. The rich amine from the absorber is stripped of the H_2S and CO_2 in the stripper-regenerator (8). Because the only difference between a tail-gas amine regeneration system and a main amine regeneration system is the absence of a rich-amine flash drum, please refer to the BHTS entry on amine treating for a more detailed description of the amine system.

The quench-water pumps (5) send water from the bottom of the tower to a filtration circuit (not shown for simplicity) and then to the quench-water coolers (6) for removing the heat of condensation from the stream. After this cooling, which can be a combination of air cooling and water cooling, the stream is returned to the quench tower.

Recall that the Claus reaction generates one mole of water for every mole of sulfur created. This water is removed in the quench tower via a small purge from the quench-water pumps. Because the purge is condensed in the presence of H_2S and CO_2 , it is both sour and acidic, so it is sent to the sour-water header for processing.

Economics:

Investment: (basis 100 Long tpd SRU, 2010 US Gulf Coast)		
\$ per long ton SRU feed	130,000	
Utilities, typical per long ton SRU feed:		
Electricity, kWh	21	
Steam MP (600 psig), lb	470	
Steam LP (50 psig), lb	2,300	
Water, cooling (25°F), gal	14,000	
Hydrogen, SCF	4,200	

Installations: This process has been used in literally hundreds of units to produce low and ultra-low sulfur content discharge streams around the world.

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT

Clean gasoline and propylene (CGP)

Application: Upgrade of conventional high-severity fluid catalytic cracking (FCC) to increase propylene yield while improving quality of FCC gasoline, i.e., with more iso-paraffins and less olefins, sulfur and benzene.

Products: High-octane clean gasoline, propylene, isobutane-rich LPG and distillate

Description: FCC units have become the second largest contributor (about 30%) of global propylene supplies. The CGP technology can be applied for upgrading conventional FCC to increase propylene yield and produce cleaner gasoline.

The process scheme and operation of CGP is similar to conventional FCC units, but with some unique characteristics:

• A two-zone riser, with the two zones operated at different conditions, provides favorable environments for the desired reactions.

• A stream of recycled catalyst is injected into the second zone to control the riser temperature profile and increases catalyst-to-oil ratio.

• Proprietary catalysts promote hydrogen-transfer reactions for conversion of the gasoline olefins into iso-paraffins and aromatics while cracking some of the olefins into propylene.

The two riser zones are connected in series with a larger diameter Zone 2 on top of Zone 1, which has a smaller diameter. Similar to a conventional FCC riser, Zone 1 is operated at high temperature and short residence time. However Zone 2 is operated at lower temperature and longer residence time for promoting hydrogen-transfer reactions. Such configuration provides much better control of the desired reactions than a single-diameter riser that is commonly used in conventional FCC.

In a CGP riser, the primary cracking reactions are carried out in Zone 1, while the secondary reactions (hydrogen transfer, isomerization and alkylation) are favorably promoted in Zone 2 to convert gasoline olefins to iso-paraffins and aromatics, without addition of external hydrogen.



Most of the propylene is produced in Zone 1 of the riser. There is also a net increase of propylene yield in Zone 2, where the gasoline olefins are selectively cracked into propylene by increased catalyst-to-oil ratio. It is the combination of catalyst formulation and specific operating conditions that produces the higher yield of propylene, and higher quality gasoline than high-severity FCC.

CGP offers advantages over conventional FCC:

- Produces cleaner gasoline
 - o Reduces olefins (20%–50%), sulfur and benzene (20%–40%)
 - o Improves octane number
- Produces higher yield of propylene and LPG
- Increases isobutane (up to 40%) in LPG
- Produces less dry gas and slurry.

Clean gasoline and propylene (CGP), continued

CGP technology is applicable for either existing or grassroots FCC units through modifications to a unit's riser reactor section. The expansion of the existing light ends recovery section may be needed.

Product s (wt% of fresh feed)	FCC	CGP
Dry Gas	3.7	3.5
LPG	19.1	27.4
Gasoline	40.7	38.2
Total liquid yield	81.7	81.9
Propylene yield	6.3	9.5
Gasoline properties		
Olefins, vol%	41.1	13.4
Sulfur	Base	77% of Base
RON	91.6	93.5

Installations: A total of 18 CGP units have been installed (15 revamps of FCC and three grassroots) with capacities ranging from 0.5 to 3.0 million tpy.

Reference: Long, J. et al., "New generation of fluid catalytic cracking processes for production of clean gasoline and propylene," unpublished, *Hydrocarbon Processing,* September 2011.

Licensor: Shaw and Sinopec RIPP CONTACT

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Coking

Application: The Bechtel ThruPlus delayed coking process is a thermalcracking process used to upgrade petroleum residuum to liquid and gas streams yielding solid petroleum coke. The unit can handle a wide variety of feedstocks, including vacuum tower bottoms, bitumen, solvent deasphalter pitch, slurry oil, thermal and pyrolysis tar, and hydrocracker bottoms. The process can also process waste streams from the refinery such as tank bottoms or API separator sludge.

Description: Fresh feed to the unit is sent to the fractionator (1) bottom where it is combined with natural recycle to comprise the feed to the coker furnace (2). The coker furnace heats the combined stream to cracking temperatures (900°F–950°F). Residence time in the furnace tubes is limited, and coking of the feed is thereby "delayed" until it reaches the online coke drum (3), where the reactions are completed. Coke accumulates in the coke drum and hot gases exit the top of the drum and flow to the fractionator, where they are separated into heavy and light coker gasoils, while lighter gases leave the top of the fractionator. These gases are partially condensed in the fractionator overhead system (4), before being sent to the gas plant, (5) which separates the overhead into naph-tha, LPG and offgas.

Delayed coking is a batch-continuous process, with flow through the furnace continuous, and when the online coke drum is filled with coke to a predetermined level, it is switched into an empty, pre-warmed coke drum. The full coke drum is cooled and decoked using high-pressure water, and then pre-warmed again. A closed blowdown system is available to recover all water and hydrocarbon liquid and vapor from the offline drum during these operating steps.

Competitive advantages:

• Distillate recycle technology to maximize light coker gasoil (diesel) production

• Demonstrated best coke-drum life in the industry



- Cost-effective furnace design with maximum furnace run lengths
- Demonstrated seven-year unit run between turnarounds.

Economics:

Jtilities, typical per bbl feed:	
Fuel, (absorbed) 10 ³ Btu	120
Electricity, kWh	3.4
Steam Export, lb	5
Water, cooling, (25°F rise) gal	50

Installations: Since 1981, 42 grassroots and revamp unit licenses have been sold.

References: Handbook of Petroleum Refining Processes, Third Ed., Mc-Graw-Hill, pp. 12.3 – 12.31.

"Delayed Coking Advances," *Petroleum Technology Quarterly,* Q4 2005.

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT

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Coking

Application: The coking process involves cracking of heavy residual oils into more valuable gasoil, distillate, naphtha and LPG products. Coke is also produced. Normal feeds include vacuum bottoms, atmospheric bottoms, asphaltenes from ROSE and other types of solvent deasphalting units, bitumen and other heavy oils, thermal and pyrolsis tars, decant oils, visbreaker and thermal tars.

Description: Delayed coking is a semi-batch thermal cracking process. The process is comprised of coker heaters, coke drums, fractionation, vapor recovery unit, hydraulic decoking, coke handling and blowdown systems. Feed is normally routed via coker fractionator to remove light fractions. Feed plus recycle from the fractionator are brought to coking temperature in a specially designed heater and then sent to the coke drum. The feed cracks into lighter fractions and coke in the coke drum. Cracked material exiting from the overhead is guenched and sent to the fractionator.

After the coke level in the drum has reached the maximum accepted level, the feed is directed to the second drum. The drum with coke is cooled, then cut with high-pressure water jets and removed to coke handling area. The drum is then heated and put back in service when the second drum fills up with coke.

Process applications: Process applications: The solution to obtaining anode-grade coke from traditional crudes lies in alternative low-sulfur, low-metals content feed options to the coker unit. The resin product from the three product ROSE process is a relatively low-metal, low-sulfur residuum that is high in asphaltene free CCR. Due to these characteristics, resin is very good for producing higher-guality coke, and an excellent feedstock for the production of anode-grade coke.

Clarified slurry oil (CSO) from the FCCU may not have the superior guality required for producing high-value distillate products; it can still be blended with the ROSE resin to be used as feedstock for anode-grade



coke production. An optimum feed to the delayed coker to produce anode-grade coke would be a blend of the resin from the ROSE process, the CSO from the FCCU and the required amount of vacuum residue to compensate for any quality giveaway. This provides the refiner with the ability to insulate the coke grade from fluctuations in the feed and always produce anode coke, irrespective of the crude quality.

Process development: KBR operates a large one bpd coker pilot plant at its Technology Center in Houston. The pilot plant is used for process development and for running coker pilot tests for clients.

Experience: KBR has provided process technology for more than 15 cokers. The most recent design is for a bitumen vacuum resid coker.

Licensor: KBR CONTACT

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Coking

Application: Conversion of atmospheric and vacuum residues, hydrotreated and hydrocracked resids, asphalt, pyrolysis tar, decant oil, visbroken or coal tar pitch, solvent-refined and Athabasca bitumen.

Description: Feedstock is introduced (after heat exchange) to the bottom of the coker fractionator (1) where it mixes with condensed recycle. The mixture is pumped to one of two coke drums (3) through the coker heater (2) where the desired coking temperature is achieved. Steam or boiler feedwater is injected into the heater tubes to prevent coking in the furnace tubes. Coke drum overhead vapors flow to the fractionator (1) where they are separated into an overhead stream containing the wet gas, LPG and naphtha and two gasoil sidestreams.

The overhead stream is sent to a vapor recovery unit (4) where the individual light product streams are separated. The coke that forms in one of at least two (parallel connected) drums is then removed using high-pressure water. The plant also includes a blow-down system for recovery of all vent gas and slop streams, coke handling and a water recovery system.

Operating conditions:

Heater outlet temperature, °F	900–950
Coke drum pressure, psig	15–90
Recycle ratio, vol/vol feed, %	0–100

Yields:

Feedstock	Middle East vac. residue	Vacuum residue of hydrotreated bottoms	Athabasca bitumen
Gravity, °API	7.4	1.3	2.5
Sulfur, wt%	4.2	2.3	5.7
Conradson			
carbon, wt%	20.0	27.6	23.0



Products, wt%			
Gas + LPG	7.9	9.0	9.2
Naphtha	12.6	11.1	12.5
Gas oils	50.8	44.0	46.0
Coke	28.7	35.9	32.5

Economics:

Investment (basis: 20,000 bpsd straight-run vacuum residue feed, US Gulf Coast 2008, fuel-grade coke, includes vapor recovery), US\$ per bpsd (typical) 8,000

Coking, continued

Economics (continued):

Utilities, typical/bbl of feed:	
Fuel, 10 ³ Btu	123
Electricity, kWh	3.6
Steam (exported), lb	1
Water, cooling, gal	58
Boiler feedwater, lbs	38
Condensate (exported), lbs	24

Installation: More than 60 units.

Reference: Sieli, G. M., A. Faegh and S. Shimoda, "The impact of delayed coker operating conditions on refinery operations," ERTC Coking & Gasification Conference, April 16–18, 2007.

Licensor: Lummus Technology, a CB&I company CONTACT

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Coking

Application: Upgrade residues to lighter hydrocarbon fractions using the Selective Yield Delayed Coking (SYDEC) process.

Description: Charge is fed directly to the fractionator (1) where it combines with recycle and is pumped to the coker heater. The mixture is heated to coking temperature, causing partial vaporization and mild cracking. The vapor-liquid mix enters a coke drum (2 or 3) for further cracking. Drum overhead enters the fractionator (1) to be separated into gas, naphtha, and light and heavy gas oils. Gas and naphtha enter the vapor recovery unit (VRU)(4). There are at least two coking drums, one coking while the other is decoked using high-pressure water jets. The coking unit also includes a coke handling, coke cutting, water recovered in the VRU.

Operating conditions: Typical ranges are:

Heater outlet temperature, °F	900–950
Coke drum pressure, psig	15–100
Recycle ratio, equiv. fresh feed	0–1.0

Increased coking temperature decreases coke production; increases liquid yield and gas oil end point. Increasing pressure and/or recycle ratio increases gas and coke make, decreases liquid yield and gas oil end point.

Yields:

Operation:			
Products, wt%	Max dist.	Anode coke	Needle coke
Gas	8.7	8.4	9.8
Naphtha	14.0	21.6	8.4
Gas oil	48.3	43.8	41.6
Coke	29.3	26.2	40.2



Installations: Currently, 52 delayed cokers are installed worldwide with a total installed capacity over 2.5 million bpsd

References: *Handbook of Petroleum Refining Processes,* Third Ed., McGraw-Hill, pp. 12.33–12.89.

"Delayed coking revamps," Hydrocarbon Processing, September 2004.

"Residue upgrading with SYDEC Delayed Coking: Benefits and Economics," AIChE Spring National Meeting, April 23–27, 2006, Orlando.

"Upgrade refinery residuals into value-added products," *Hydrocarbon Processing*, June 2006.

Licensor: UOP, A Honeywell Company/Foster Wheeler USA Corp. **CONTACT**

Crude distillation

Application: Separates and recovers the relatively lighter fractions (e.g., naphtha, kerosine, diesel and cracking stock) from a fresh crude oil charge. The vacuum flasher processes the crude distillation bottoms to produce an increased yield of liquid distillates and a heavy residual material.

Description: The charge is preheated (1), desalted (2) and directed to a preheat train (3) where it recovers heat from product and reflux streams. The typical crude fired heater (4) inlet temperature is on the order of 550°F, while the outlet temperature is on the order of 675°F to 725°F. Heater effluent then enters a crude distillation column (5) where light naphtha is drawn off the tower overhead (6); heavy naphtha, kerosine, diesel and cracking stock are sidestream drawoffs. External reflux for the tower is provided by pumparound streams (7–10). The atmospheric residue is charged to a fired heater (11) where the typical outlet temperature is on the order of 725°F.

From the heater outlet, the stream is fed into a vacuum tower (12), where the distillate is condensed in two sections and withdrawn as two sidestreams. The two sidestreams are combined to form cracking feed-stock. An asphalt base stock is pumped from the bottom of the tower. Two circulating reflux streams serve as heat removal media for the tower.

Yields: Typical for Merey crude oil:

Crude unit products	wt%	°API	Pour, °F
Overhead & naphtha	6.2	58.0	
Kerosine	4.5	41.4	-85
Diesel	18.0	30.0	-10
Gas oil	3.9	24.0	20
Lt. vac. gasoil	2.6	23.4	35
Hvy. vac. gasoil	10.9	19.5	85
Vac. bottoms	53.9	5.8	(<u>120</u>)*
Total	100.0	8.7	85

*Softening point, °F

Note: Crude unit feed is 2.19 wt% sulfur. Vacuum unit feed is 2.91 wt% sulfur.



Economics:

Investment (basis: 100,000–50,000 bpsd,	
4th Q 2010, US Gulf), \$ per bpsd	1,700-2,200
Utility requirements, typical per bbl fresh fee	ed
Steam, lb	24
Fuel (liberated), 10 ³ Btu	(80–120)
Power, kWh	0.6
Water, cooling, gal	300–400

Installation: Foster Wheeler has designed and constructed crude units having a total crude capacity in excess of 15 MMbpsd.

Reference: Encyclopedia of Chemical Processing and Design, Marcel-Dekker, 1997, pp. 230–249.

Licensor: Foster Wheeler USA Corp CONTACT

Crude distillation

Application: The D2000 process is progressive distillation to minimize the total energy consumption required to separate crude oils or condensates into hydrocarbon cuts, which number and properties are optimized to fit with sophisticated refining schemes and future regulations. This process is applied normally for new topping units or new integrated topping/vacuum units but the concept can be used for debottlenecking purpose.

Products: This process is particularly suitable when more than two naphtha cuts are to be produced. Typically the process is optimized to produce three naphtha cuts or more, one or two kerosine cuts, two atmospheric gas oil cuts, one vacuum gas oil cut, two vacuum distillates cuts, and one vacuum residue.

Description: The crude is preheated and desalted (1). It is fed to a first dry reboiled pre-flash tower (2) and then to a wet pre-flash tower (3). The overhead products of the two pre-flash towers are then fractionated as required in a gas plant and rectification towers (4).

The topped crude typically reduced by $2/_3$ of the total naphtha cut is then heated in a conventional heater and conventional topping column (5). If necessary the reduced crude is fractionated in one deep vacuum column designed for a sharp fractionation between vacuum gas oil, two vacuum distillates (6) and a vacuum residue, which could be also a road bitumen.

Extensive use of pinch technology minimizes heat supplied by heaters and heat removed by air and water coolers.

This process is particularly suitable for large crude capacity, i.e. above 200,000 bpsd.

It is also available for condensates and light crudes progressive distillation with a slightly adapted scheme.



Economics:

Investment (basis 230,000 bpsd including atmospheric and vacuum distillation, gas plant and rectification tower) \$750 to \$950 per bpsd (US Gulf Coast 2000).

Utility requirements, typical per bbl of crude feed:

Fuel fired, 10 ³ btu	50–65
Power, kWh	0.9–1.2
Steam 65 psig, lb	0–5
Water cooling, (15°C rise) gal	50–100
Total primary energy consumption:	
for Arabian Light or Russian Export Blend:	1.25 tons of fu
	1001

for Arabian Heavy

1.25 tons of fuel per 100 tons of Crude 1.15 tons of fuel per 100 tons of Crude

Crude distillation, continued

Installation: Technip has designed and constructed one crude unit and one condensate unit with the D2000 concept. The latest revamp project currently in operation shows an increase of capacity of the existing crude unit of 30% without heater addition.

Licensor: TOTAL and TECHNIP CONTACT

Crude distillation, atmospheric and vacuum

Application: The Shell Bulk CDU is a highly integrated concept. It separates the crude in atmospheric residue, middle distillates and a naphtha minus fraction. Compared with stand-alone units, the total integration of a crude distillation unit (CDU), hydrodesulfurization unit (HDS), high vacuum unit (HVU) and a visbreaker (VBU) results in a 50% reduction in equipment count and significantly lowered operating costs. A prominent feature embedded in this design is the Shell deepflash HVU technology. This technology can also be provided in cost-effective process designs for both feedprep and lube oil HVUs as stand-alone units. For each application, tailor-made designs can be produced.

Description: The basic concept of the bulk CDU is the separation of the naphtha minus and the long residue from the middle distillate fraction, which is routed to a bulk HDS. After desulfurization in the HDS unit, final product separation of the bulk middle distillate stream from the CDU occurs in the HDS fractionator (HDF), which consists of a main atmospheric fractionator with side strippers.

The long residue is routed hot to a feedprep HVU, which recovers the waxy distillate fraction from long residue as the feedstock for a cat-cracker or hydrocracker unit (HCU). Typical flashzone conditions are 415°C and 24 mbara. The Shell design features a deentrainment section, empty spray sections to obtain a lower flashzone pressure, and a vacuum gasoil (VGO) recovery section to recover up to 10 wt% as automotive diesel. The Shell furnace design prevents excessive cracking and enables a five-year run length between decoke.

Yields: Typical for Arabian light crude

Products		wt, %
Gas	C ₁ –C ₄	0.7
Gasoline	C ₅ –150°C	15.2



Kerosine	150°C-250°C	17.4
Gasoil (GO)	250°C-350°C	18.3
VGO	350°C-370°C	3.6
Waxy distillate (WD)	370°C-575°C	28.8
Residue	575°C+	16.0

Economics: Due to the incorporation of Shell high capacity internals and the deeply integrated designs, a CAPEX reduction in the order of 30% can be achieved. Investment costs are dependent on the required configuration and process objectives.

Installation: Over 100 Shell CDUs have been designed and operated since the early 1900s. Additionally, more than 20 Shell HVU units have been built while a similar number has been debottlenecked, including many third-party designs of feedprep and lube oil HVUs.

Licensor: Shell Global Solutions International B.V. CONTACT

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Deasphalting

Application: KBR's ROSE (Residuum Oil Supercritical Extraction) solvent deasphalting technology is used to extract maximum volumes of FCCU, or hydrocracker/hydrotreater feedstocks from atmospheric and vacuum resids, and in some special cases from whole crude oils. The extracted deasphalted oil (DAO) yields can be adjusted to optimize integration with downstream units. The ROSE DAO has "order of magnitude" lower heptane insolubles content as well as lower metals and conradson carbon than from other solvent deasphalting processes. This lower heptane insolubles content allows refiners to achieve longer run lengths in hydrotreating and hydrocracking units and reduced catalyst usage in FCC units. Moderate operating temperatures almost alleviates the need for 317SS metallurgy when processing high acid crude oils.

ROSE is also useful in production and upgrading of heavy oils. The process is also used for debottlenecking of existing vacuum distillation units and cokers.

Products: Lube blendstocks, synthetic crude, FCCU feed, hydrocracker feed, coker feed, resins and asphaltenes.

Description: Resid is charged through a mixer (M-1), where it is mixed with solvent before entering the asphaltene separator (V-1), which uses special internals to achieve maximum benefit of counter current solvent flow. The solvent extracts primarily non-asphaltenic, paraffinic deasphalted oil. The asphaltene-rich stream leaves from the bottom of the separator. The extracted oils and solvent flow overhead (V-1) through heat exchangers (E-1, E-4, E-6) so that the solvent reaches conditions where it exists as a supercritical fluid in which the oil is virtually insoluble. Recovered solvent leaves the separator top (V-3) to be cooled by heat exchange (E-4, E-1) and a cooler (E-2). The only solvent vaporized is a small amount dissolved in fractions withdrawn in the separators. This solvent is recovered in the product strippers.



Alternately an intermediate resin rich product can be produced in V2 and T2 as shown in the attached figure.

V-1, V-2 and V-3 are equipped with high-performance ROSEMAX internals. These high-efficiency, high-capacity internals offer superior product yield and quality while minimizing vessel size and capital investment. These internals can also be used to debottleneck and improve operations of existing solvent deasphalting units.

Yields: The solvent composition and operating conditions are adjusted to provide the highest product quality and yields required for downstream processing or to meet finished product specifications. Solvents range from propane through hexane and almost always are streams produced in refineries.

Deasphalting, continued

Economics:

Investment: (Basis: 30,000 bpsd, US Gulf Coast), \$1,850 per bpsd **Utilities,** typical per bbl feed:

Fuel absorbed, 103 Btu	80–110
Electricity, kWh	2.0
Steam, 150-psig, lb	12

Installations: KBR has licensed 52 units with a combined capacity of over 1 million bpd. More than 30 units are operating with several more expected to startup within the next few years.

Reference: Patel, V., R. Iqbal and O. Eng, "To vacuum or not to vacuum," *Hydrocarbon Engineering*, June 2007.

Iqbal, R., A. Khan, O. Eng and R. Floyd, "Unlocking current refinery constraints," *PTQ*, Summer 2008.

Licensor: KBR CONTACT

НОМЕ

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Deasphalting

Application: The UOP/Foster Wheeler Solvent Deasphalting (SDA) process prepares quality feed for FCC units and hydrocrackers from vacuum residue, and blending stocks for lube oil and asphalt manufacturing.

Products: Deasphalted oil (DAO) for catalytic cracking and hydrocracking feedstocks, resins for specification asphalts, and pitch for specification asphalts and residue fuels.

Description: Feed and light paraffinic solvent are mixed and then charged to the extractor (1). The DAO and pitch phases, both containing solvents, exit the extractor. The DAO and solvent mixture is separated under supercritical conditions (2). Both the pitch and DAO products are stripped of entrained solvent (3,4). A second extraction stage is utililized if resins are to be produced.

Operating conditions: Typical ranges are:

Solvent	various blends of C ₃ –C ₇ hydrocarbons
	including light naphthas
Pressure, psig	300–600
Temp., °F	120–450
Solvent to oil ratio:	4/1 to 13/1

Yields:

Feed, type	Lube oil	Cracking stock
Gravity, °API	6.6	6.5
Sulfur, wt%	4.9	3.0
CCR, wt%	20.1	21.8
Visc, SSU@210°F	7,300	8,720
Ni/V, wppm	29/100	46/125
DAO		
Yield, vol.% of feed	30	65
Gravity, °API	20.3	15.1
Sulfur, wt%	2.7	2.2



CCR, wt% Visc., SSU@210°F Ni/V, wppm	1.4 165 0.25/0.37	6.2 540 4.5/10.3
Pitch		
Softening point, R&B, °F	149	240
Penetration@77°F	12	0

Installations: Over 50 units installed; this also includes both UOP and Foster Wheeler units originally licensed separately before merging the technologies in 1996.

References: *Handbook of Petroleum Refining Processes,* Third Ed., McGraw Hill, 2003, pp. 10.37–10.61.

"When Solvent Deasphalting is the Most Appropriate Technology for Upgrading Residue," International Downstream Technology Conference, February 15–16, 2006, London.

Licensors: UOP, A Honeywell Company/Foster Wheeler USA Corp. **CONTACT**

Deep catalytic cracking (DCC)

Application: Selective conversion of gasoil and paraffinic residual feedstocks.

Products: C₂–C₅ olefins, aromatic-rich, high-octane gasoline and distillate.

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

Each operational mode utilizes unique catalyst as well as reaction conditions. Maximum propylene DCC uses both riser and bed cracking at relatively severe reactor conditions while Type II DCC uses only riser cracking like a modern fluid catalytic cracking (FCC) unit at milder conditions.

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

This technology is quite suitable for revamps as well as grassroots applications. Feed enters the unit through proprietary feed nozzles, as shown in the schematic. Integrating DCC technology into existing refineries as either a grassroots or revamp application can offer an attractive opportunity to produce large quantities of light olefins.

In a market requiring both propylene and ethylene, use of both thermal and catalytic processes is essential, due to the fundamental differences in the reaction mechanisms involved. The combination of thermal and catalytic cracking mechanisms is the only way to increase total olefins from light and heavy feedstocks while meeting the need for increased propylene to ethylene ratio. A benefit associated with DCC



rather than steam cracking for propylene production is a direct consequence of relative cost differences between DCC heavy feeds and steam cracker's light feeds. Additional capital and operating cost savings are achieved by the integration of the DCC unit and the adjacent steam cracker.

Products (wt% of fresh feed)	DCC Type I	DCC Type II	FCC
Ethylene	6.1	2.3	0.9
Propylene	20.5	14.3	6.8
Butylene	14.3	14.6	11.0
in which iC ₄ =	5.4	6.1	3.3
Amylene	—	9.8	8.5
in which iC ₅ =		6.5	4.3
		Conti	nued 🔻

Deep catalytic cracking (DCC), continued

Installation: A total of 15 DCC units have been licensed.

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

Licensor: Shaw and Research Institute of Petroleum Processing, Sinopec <u>CONTACT</u>

Deep thermal conversion

Application: The Shell Deep Thermal Conversion process closes the gap between visbreaking and coking. The process yields a maximum of distillates by applying deep thermal conversion of the vacuum residue feed and by vacuum flashing the cracked residue. High-distillate yields are obtained, while still producing a stable liquid residual product, referred to as liquid coke. The liquid coke, not suitable for blending to commercial fuel, is used for speciality products, gasification and/or combustion, e.g., to generate power and/or hydrogen.

Description: The preheated short residue is charged to the heater (1) and from there to the soaker (2), where the deep conversion takes place. The conversion is maximized by controlling the operating temperature and pressure. The soaker effluent is routed to a cyclone (3). The cyclone overheads are charged to an atmospheric fractionator (4) to produce the desired products such as gas, LPG, naphtha, kerosine and gasoil. The cyclone and fractionator bottoms are subsequently routed to a vacuum flasher (5), which recovers additional gasoil and waxy distillate. The residual liquid coke is routed for further processing depending on the outlet.

Yields: Depend on feed type and product specifications.

Feed

Type and source Viscosity, cSt @100°C	Vacuum residue, Middle East 615
Products, wt %	
Gas	3.8
Naphtha	8.2
Kerosine + Gasoil	19
(TC) Vacuum gasoil	22.8
Vacuum flashed cracked residue (liquid coke)	46.2



Economics: The typical investment for a 25,000-bpd unit will be about \$2,850 to \$3,450/bbl installed, excluding treating facilities. (Basis: Western Europe, 2009.)

Utilities, typical consumption/production for a 25,000-bpd unit, dependent on configuration and a site's marginal econmic values for steam and fuel:

Fuel as fuel oil equivalent, bpd	417
Power, MW	1.2
Net steam production (18 bar), tpd	370

Installation: To date, six Shell Deep Thermal Conversion units have been licensed. In four cases, this has involved revamping an existing Shell Soaker Visbreaker unit. Post startup services and technical services for existing units are available from Shell Global Solutions.

Reference: *Hydrocarbon Engineering,* September 2003.

Licensor: Shell Global Solutions International B.V. CONTACT

Delayed coking

Application: Upgrade residues and other heavy streams to lighter hydrocarbon fractions using the Selective Yield Delayed Coking (SYDEC) process.

Description: Charge is fed directly to the fractionator (1) where it combines with recycle and is pumped to the coker heater. The mixture is heated to coking temperature, causing partial vaporization and mild cracking. The vapor-liquid mix enters a coke drum (2 or 3) for further cracking. Drum overhead enters the fractionator (1) to be separated into gas, naphtha, and light and heavy gas oils. Gas and naphtha enter the vapor recovery unit (VRU)(4). There are at least two coking drums, one coking while the other is decoked using high-pressure water jets. The coking unit also includes a coke handling, coke cutting, water recovery and blowdown system. Vent gas from the blowdown system is recovered in the VRU.

Operating conditions: Typical ranges are:

Heater outlet temperature, °F	900–950
Coke drum pressure, psig	15–100
Recycle ratio, equiv. fresh feed	0–1.0

Increased coking temperature decreases coke production; increases liquid yield and gas oil end point. Increasing pressure and/or recycle ratio increases gas and coke make, decreases liquid yield and gas oil end point.

Yields:

Operation:			
Products, wt%	Max dist.	Anode coke	Needle coke
Gas	8.7	8.4	9.8
Naphtha	14.0	21.6	8.4
Gas oil	48.3	43.8	41.6
Coke	29.3	26.2	40.2



Economics:

Investment (basis 120,000–10,000 bpsd	d Coking and VRU)
1Q 2011 US Gulf), \$ per bpsd	5,800–12,000
Utilities, typical per bbl feed:	
Fuel, 10 ³ Btu	120
Electricity, kWh	3
Steam (exported), lb	35
Water, cooling, gal	36

Installations: Currently, 67 delayed cokers are installed worldwide with a total installed capacity over 2.5 million bpsd

Delayed coking, continued

References: *Handbook of Petroleum Refining Processes,* Third Ed., McGraw-Hill, pp. 12.33–12.89.

Elliott, J. D. and D. Wedlake, "Residue Upgrading with SYDECsM: Benefits and Economics" [Minas vs. Heavy Arabian]," presented at 1st Asia Bottom of the Barrel Technology Conference, April 2007.

Elliott, J. D., "Impact of Feed Properties and Operating Parameters on Delayed Coker Petcoke Quality,"2008 ERTC Coking and Gasification Conference, Rome, April 2008. Italy; also presented at 1st Asia Bottom of the Barrel Technology Conference, Kuala Lumpur, Malaysia, April 2007 by R. Clarke; and short presentation by J.D. Elliott, Jacobs Consulting, 2009 Petcoke Conference, San Francisco, February 2009.

Elliott, J. D., "Coker Revamps: Increase Capacity & Improve Operability," 6th International BBTC conference, Barcelona, Spain, October 2008; and also presented at the RPTC in Moscow, Russia, April 2009 by B. Robinson.

Elliott, J. D and M. McGrath, "Cost effective conversion of heavy residues," *Hydrocarbon Engineering*, March 2009.

Bernhagen, P., "Coker Heater Design: The Heart of the Coking Process,"Coking.com seminars in Galveston, Texas, March 2009; Rio de Janiero, Brazil, August 2009; and Calgary, Alberta, Canada, September 2009.

Elliott, J. D., "Managing Shot Coke: Design & Operation," ERTC Coking and Gasification Conference, Budapest, Hungary, April 2009.

Licensors: Foster Wheeler USA Corp./UOP, A Honeywell Company CONTACT

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Desulfurization

Application: GT-BTX Plu**S** accomplishes desulfurization of FCC gasoline with no octane loss and decreased hydrogen consumption by using a proprietary solvent in an extractive-distillation system. This process also recovers valuable aromatics compounds, which can be used as petro-chemical feedstock.

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 Plu**S** 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 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 benzene, toluene and xylene (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.



Process advantages:

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

• Rejects olefins from being hydrotreated in the 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) are 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 (from the ED unit) can be directed to an aromatization unit to produce additional BTX or recycled to the FCC unit to increase the light olefin production.

Economics: Feedrate 1,000 thousand tpy (22,000 bpsd); erected cost (including Fractionation and Hydrotreating) \$30 MM (ISBL, 2007 US Gulf Coast Basis).

Installation: Technology available for license.

Licensor: GTC Technology US, LLC CONTACT

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Dewaxing

Application: Bechtel's Dewaxing process is used to remove waxy components from lubrication base-oil streams to simultaneously meet desired low-temperature properties for dewaxed oils and produce slack wax as a byproduct.

Description: Waxy feedstock (raffinate, distillate or deasphalted oil) is mixed with a binary-solvent system and chilled in a very closely controlled manner in scraped-surface double-pipe exchangers (1) and refrigerated chillers (2) to form a wax/oil/solvent slurry.

The slurry is filtered through the primary filter stage (3) and dewaxed oil mixture is routed to the dewaxed oil recovery section (5) to separate solvent from oil. Prior to solvent recovery, the primary filtrate is used to cool the feed/solvent mixture (1). Wax from the primary stage is slurried with cold solvent and filtered again in the repulp filter (4) to reduce the oil content to approximately 10%.

The repulp filtrate is reused as dilution solvent in the feed chilling train. The wax mixture is routed to a solvent-recovery section (6) to remove solvent from the product streams (hard wax and soft wax). The recovered solvent is collected, dried (7) and recycled back to the chilling and filtration sections.

Economics:

Investment (Basis: 7,000-bpsd feedrate capacity, 2011 US Gulf Coast), \$/bpsd	17,500
Utilities, typical per bbl feed:	
Fuel, 10 ³ Btu (absorbed)	160
Electricity, kWh	15
Steam, lb	35
Water, cooling (25°F rise), gal	1,100



Installation: Over 100 have been licensed and built.

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT

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Dewaxing

Application: Selectively convert feedstock's waxy molecules by isomerization in the presence of ISODEWAXING Catalysts. The high-quality products can meet stringent cold flow properties and viscosity index (VI) requirements for Group II or Group III baseoils.

Description: ISODEWAXING Catalysts are very special catalysts that convert feedstocks with waxy molecules (containing long, paraffinic chains) into two or three main branch isomers that have low-pour points. The product also has low aromatics content. Typical feeds are: raffinates, slack wax, foots oil, hydrotreated VGO, hydrotreated DAO and unconverted oil from hydrocracking.

As shown in the simplified flow diagram, waxy feedstocks are mixed with recycle hydrogen and fresh makeup hydrogen, heated and charged to a reactor containing ISODEWAXING Catalyst (1). The effluent will have a much lower pour point and, depending on the operating severity, the aromatics content is reduced by 50–80% in the dewaxing reactor.

In a typical configuration, the effluent from a dewaxing reactor is cooled down and sent to a finishing reactor (2) where the remaining single ring and multiple ring aromatics are further saturated by the ISO-FINISHING Catalysts. The effluent is flashed in high-pressure and low-pressure separators (3, 4). Small amounts of light products are recovered in a fractionation system (5).

Yields: The base oil yields strongly depend on the feedstocks. For a typical low wax content feedstock, the base oil yield can be 90–95%. Higher wax feed will have a little lower base oil yield.

Economics:

Investment: This is a moderate investment process; for a typical size ISODEWAXING/ISOFINISHING Unit, the capital for ISBL is about \$9,000/bpsd.



Utilities: Typical per bbl feed:

Power, kWh	3.3
Fuel , kcal	13.4 x 10 ³
Steam, superheated, required, kg	5.3
Steam, saturated, produced, kg	2.4
Water, cooling, kg	192
Chemical-hydrogen consumption, Nm ³ /m ³ oil	30~50

Installation: More than 15 units are in operation and five units are in various stages of design or construction.

Reference: NPRA Annual Meeting, March 2005, San Francisco, Paper AM-05-39.

Licensor: Chevron Lummus Global LLC CONTACT

Dewaxing/wax deoiling

Application: Bechtel's Dewaxing/Wax Fractionation processes are used to remove waxy components from lubrication base-oil streams to simultaneously meet desired low-temperature properties for dewaxed oils and produce hard wax as a premium byproduct.

Description: Bechtel's two-stage solvent dewaxing process can be expanded to simultaneously produce hard wax by adding a third deoiling stage using the Wax Fractionation process. Waxy feedstock (raffinate, distillate or deasphalted oil) is mixed with a binary-solvent system and chilled in a very closely controlled manner in scraped-surface double-pipe exchangers (1) and refrigerated chillers (2) to form a wax/oil/solvent slurry.

The slurry is filtered through the primary filter stage (3) and dewaxed oil mixture is routed to the dewaxed oil recovery section (6) to separate solvent from oil. Prior to solvent recovery, the primary filtrate is used to cool the feed/solvent mixture (1).

Wax from the primary stage is slurried with cold solvent and filtered again in the repulp filter (4) to reduce the oil content to approximately 10%. The repulp filtrate is reused as dilution solvent in the feed chilling train. The low-oil content slack wax is warmed by mixing with warm solvent to melt the low-melting-point waxes (soft wax) and is filtered in a third stage filtration (5) to separate the hard wax from the soft wax. The hard and soft wax mixtures are each routed to solvent recovery sections (7,8) to remove solvent from the product streams (hard wax and soft wax). The recovered solvent is collected, dried (9) and recycled back to the chilling and filtration sections.

Economics:

Investment (Basis: 7,000-bpsd feedrate capacity, 2011 US Gulf Coast), \$/bpsd

20,600



Utilities, typical per bbl feed:	
Fuel, 10 ³ Btu (absorbed)	230
Electricity, kWh	25
Steam, Ib	25
Water, cooling (25°F rise), gal	1,500

Installation: Seven in service.

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT

Diesel upgrading

Application: Topsøe's Diesel Upgrading process can be applied for improvement of a variety of diesel properties, including reduction of diesel specific gravity, reduction of T90 and T95 distillation (Back-end-shift), reduction of aromatics, and improvements of cetane, cold-flow properties, (pour point, clouds point, viscosity and CFPP) and diesel color reduction (poly shift). Feeds can range from blends of straight-run and cracked gas oils up to heavy distillates, including light vacuum gasoil.

Description: Topsøe's Diesel Upgrading process is a combination of treating and upgrading. The technology combines state-of-the-art reactor internals, engineering expertise in quality design, high-activity treating catalyst and proprietary diesel upgrading catalyst. Every unit is individually designed to improve the diesel property that requires upgrading. This is done by selecting the optimum processing parameters, including unit pressure and LHSV and determining the appropriate Topsøe high-activity catalysts and plant lay-out. The process is suitable for new units or revamps of existing hydrotreating units.

In the reactor system, the treating section uses Topsøe's high-activity CoMo or NiMo catalyst, such as TK-578 BRIM or TK-607 BRIM, to remove feed impurities such as sulfur and nitrogen. These compounds limit the downstream upgrading catalyst performance, and the purified stream is treated in the downstream upgrading reactor. Reactor catalyst used in the application is dependent on the specific diesel property that requires upgrading. Reactor section is followed by separation and stripping/fractionation where final products are produced.

Like the conventional Topsøe hydrotreating process, the diesel upgrading process uses Topsøe's graded-bed loading and high-efficiency patented reactor internals to provide optimal reactor performance and catalyst utilization. Topsøe's high-efficiency internals are effective for a wide range of liquid loading. Topsøe's graded-bed technology and the



use of shape-optimized inert topping material and catalyst minimize the pressure drop build-up, thereby reducing catalyst skimming requirements and ensuring long catalyst cycle lengths.

References: Patel, R., "How are refiners meeting the ultra-low-sulfur diesel challenge?" NPRA Annual Meeting, San Antonio, March 2003.

Fuente, E., P. Christensen, and M. Johansen, "Options for meeting EU year 2005 fuels specifications," 4th ERTC, November 1999.

Installations: A total of 22 units; six in Asia-Pacific region, one in the Middle East, two in Europe and nine HDS/HDA units (see Hydrodearo-matization).

Licensor: Haldor Topsøe A/S CONTACT

НОМЕ

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Diesel—ultra-low-sulfur diesel (ULSD)

Application: Topsøe ULSD process is designed to produce ultra-lowsulfur diesel (ULSD) (< 10 wppm S) from cracked and straight-run distillates as well as renewable feeds by co-processing or standalone unit. By selecting the proper catalyst and operating conditions, the process can be designed to produce 5 wppm S diesel at low reactor pressures (<500 psig) or at higher reactor pressure when products with improved density, cetane, and polyaromatics are required.

Description: Topsøe ULSD process is a hydrotreating process that combines Topsøe's understanding of deep-desulfurization kinetics, high-activity catalyst, state-of-the-art reactor internal, and engineering expertise in the design of new and revamped ULSD units. The ULSD process can be applied over a very wide range of reactor pressures.

Our highest activity BRIM catalyst is specifically formulated with high-desulfurization activity and stability at low reactor pressure (~ 500 psig) to produce 5 wppm diesel. This catalyst is suitable for revamping existing low-pressure hydrotreaters or in new units when minimizing hydrogen consumption.

The highest activity BRIM catalyst is suitable at higher pressure when secondary objectives such as cetane improvement and density reduction are required. Topsøe offers a wide range of engineering deliverables to meet the needs of the refiners. Our offerings include process scoping study, reactor design package, process design package, or engineering design package.

Installation: Topsøe has licensed more than 70 ULSD hydrotreaters designed for less than 10 wppm sulfur in the diesel. Our reactor internals are installed in more than 80 ULSD units.

References:

Sarup, B., M. Johansen, L. Skyum and B. Cooper, "ULSD Production in Practice," 9th ERTC, Prague, November 2004.



Hoekstra, G., V. Pradhan, K. Knudsen, P. Christensen, I. Vasalos and S. Vousvoukis, "ULSD: Ensuring the unit makes on-spec. product," NPRA Annual Meeting, Salt Lake City, March 2006.

Egebjeng, R., K. Knudsen and E. Grennfelt, "Bigger is better: Industrial-scale production of renewable diesel,"NPRA Annual Meeting, San Antonio, Texas, March 2011.

Hanson, T., "Hydrotreater revamp case story: Making the most of what you have," ERTC, Instanbul, November 2010.

Licensor: Haldor Topsøe A/S CONTACT

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Dimethyl terephthalate

Application: Modifications to the traditional process for manufacturing dimethyl terephthalate (DMT) can significantly improve results including capacity increase, yield improvements, reduced energy consumption and upgrade of byproduct quality for increased commercial value.

The technology is flexible and may be implemented in increments. GTC can optimize the design or configuration to maximize use of existing equipment.

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

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



Process advantages:

- Reduction in use of raw materials (p-xylene and methanol)
- Higher specific throughput
- Lower energy consumption/ton DMT produced
- Flexible application for revamp projects

• Accumulated technical expertise available through engineering packages and follow-up services

Oxidation section

• Improved oxidation reduces side reactions and more effectively uses reaction volume, resulting in lower PX consumption.

Dimethyl terephthalate, continued

• New and more efficient scheme for the catalyst recovery in the plant helps reduce residue formation.

• Improved recovery of PX and removal of methyl benzoate: Product is upgraded to food or perfume grade.

• Carboxylic acid recovery: Recovery of formic and acetic acid as byproducts, upgrading value and reducing load in biotreatment unit.

Distillation section

• Improved distillation scheme increases purity of DMT to crystallization and reduces plant recycles.

• Improved residue treatment can increase the yields of the plant by recovering valuable materials.

Crystallization

• Typical double-crystallization scheme is simplified to increase throughputs and minimize equipment.

• New single-stage crystallization offers a low-cost alternative in revamps.

• Improved methanol recovery and handling system reduces plant losses.

• Improved isomer removal system helps reduce DMT losses.

Esterification

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

Installation: Five licensed units.

Licensor: GTC Technology US, LLC CONTACT

EB xylenes, low

Application: DX process converts ethylbenzene (EB) contained in the C₈ aromatics feedstocks to high-purity benzene plus ethane and upgrades mixed xylenes to premium grade. The feedstocks can be either pygas C₈ or reformer C₈ 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.

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

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 recycle hydrogen purity. The recycle hydrogen is then compressed, mixed with makeup hydrogen and returned to the reactor.

The liquid stream from the separator is pumped to the deheptanizer to remove light hydrocarbons. The liquid stream from the deheptanizer overhead contains benzene and toluene and is sent to distillation section to produce high-purity benzene and toluene products. The liquid stream from the deheptanizer bottoms contains mixed xylenes and a small amount of C₉⁺ aromatics. This liquid stream is sent to the PX recovery section. The mixed xylenes stream is very low in EB due to high EB conversion in the DX reactor, which debottlenecks the PX recovery unit.

Process advantages:

- Simple, low cost fixed-bed reactor design
- Flexible feedstocks and operation
- High EB conversion per pass can be nearly 100wt%
- DX products are isomerized to equilibrium composition of xylene,



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which unloads the isomerization unit

- Low ring loss at very high EB conversion
- On-specification benzene with traditional distillation
- Extremely stable catalyst

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- Low hydrogen consumption
- Moderate operating parameters
- Efficient heat integration scheme reduces energy consumption
- Turnkey package for high-purity benzene, toluene and PX production available from licensor.

Economics: Feedrate (pygas basis): 100 thousand tpy (2,200 bpsd); erected cost: \$10 MM (ISBL, 2007 US Gulf Coast Basis)

Installation: Commercialized technology available for license.

Licensor: GTC Technology US, LLC CONTACT

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Ethers

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

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

Description: A typical MTBE/ETBE unit using FCC cut is based on a single-stage scheme with a tubular (1) and an adiabatic (2) reactor. The front-end reactor uses the proprietary water cooled tubular reactor (WCTR). The WCTR is a very flexible reactor and can treat all C_4 cuts on a once-through basis. It is the optimal solution for the etherification reaction since it enables an optimal temperature profile with the best compromise between kinetic and thermodynamic.

The reactor effluent is sent to the first column (3) where the product is recovered as bottom stream while the residual C_4 are sent to the washing column (4) to separate the alcohol. The water/alcohol leaving the column is sent to alcohol-recovery column (5), to recycle both alcohol and water.

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

The industrial experience has proven that this plant with the WCTR, can be easily switched from ETBE to MTBE production, and vice versa, without stopping the plant and any reduction in feedrates. Process schemes are similar for production of heavier ethers starting from C₅ or LCN streams.



Utilities: (Referred to a feedstock at 20 wt% isobutylene concentrate—light cracked naphtha).

Steam	0.8 ÷ 0.9	t/t Ether
Water, cooling	53 ÷ 62	m³/t Ether
Power	8.4 ÷ 9.2	kWh/ t Ether

Installation: Over 25 units including MTBE, ETBE, TAME and TAEE have been licensed by Saipem.

Licensor: Saipem CONTACT

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Ethers, ETBE

Application: The CD*Etbe* catalytic distillation technology processes C₄ streams from steam cracker, refining and isobutane dehydrogenation units to produce ETBE.

Description: ETBE is formed by the catalytic etherification of isobutylene with ethanol. The patented CD*Etbe* process is based on a two-step reactor design, consisting of a fixed bed reactor followed by final conversion in a catalytic distillation column. The process utilizes an acidic ion exchange resin catalyst in both its fixed bed reactor and proprietary catalytic distillation structures.

The unique catalytic distillation column combines reaction and fractionation in a single unit operation. It allows a high conversion of isobutylene to be achieved simply and economically. By using distillation to separate the product from the reactants, the equilibrium limitation is exceeded and higher conversion of isobutylene is achieved. The ETBE produced has a very low ethanol content that does not require additional downstream processing.

Product: The produced ETBE can be blended as a high quality bio-fuel.

Process advantages:

Lummus Technology's catalytic distillation offers:

- Improved kinetics
- High conversion (beyond fixed bed-equilibrium limit)
- Low capital cost
- Low utilities
- Long catalyst life with sustained high conversion
- Reduced plot space.

Lummus Technology's boiling point reactor offers:

- Simple and effective control
- Elimination of hot spots



- Long catalyst life
- High flexibility
- Low capital cost
- Elimination of catalyst attrition
- Most effective heat removal technique
- Elimination of cooling water requirement.

Installation: Lummus Technology converted the first MTBE unit to produce ETBE in 2002 and continues to work with numerous licensors to retrofit other existing MTBE units to produce ETBE.

Licensor: Lummus Technology, a CB&I company CONTACT

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Ethers, MTBE

Application: To process C₄ streams from steam cracker, refinery and isobutane dehydrogenation units to produce methyl tertiary butyl ether (MTBE).

Description: MTBE is formed by the catalytic etherification of isobutylene with methanol. The patented CD*Mtbe* process is based on a two-step reactor design, consisting of a boiling point fixed-bed reactor followed by final conversion in a catalytic distillation column. The process uses an acidic ion-exchange resin catalyst in both its fixed-bed reactor and proprietary catalytic distillation structures.

The unique catalytic distillation column combines reaction and fractionation in a single unit operation. It allows a high conversion of isobutylene to be achieved simply and economically. By using distillation to separate the product from the reactants, the equilibrium limitation is exceeded and higher conversion of isobutylene is achieved.

Products: MTBE synthesis is a highly selective process for removal of isobutylene. It can be used for pretreatment to produce high-purity butene-1 or for recovery to make high-purity isobutylene via MTBE decomposition.

Process advantages:

Lummus Technology's catalytic distillation offers:

- Improved kinetics
- High conversion (beyond fixed bed-equilibrium limit)
- Low capital cost
- Low utilities
- Long catalyst life with sustained high conversion
- Reduced plot space

Lummus Technology's boiling point reactor offers:

- Simple and effective control
- Elimination of hot spots



- Long catalyst life
- High flexibility
- Low capital cost
- Elimination of catalyst attrition
- Most effective heat removal technique
- Elimination of cooling water requirement.

Installations: With more than 20 years of experience and a total of 117 licensed ethers units, 88 units are MTBE, with 36 still in operation.

Licensor: Lummus Technology, a CB&I company CONTACT

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Ethers—**ETBE**

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

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

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

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

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

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

ETBE is recovered as the bottoms product of the distillation unit. The ethanol-rich C_4 distillate is sent to the ethanol recovery section. Water is used to extract excess ethanol and recycle it back to process. At the top of the ethanol/water separation column, an ethanol/water azeotrope is



recycled to the reactor section. The isobutene-depleted C_4 stream may be sent to a raffinate stripper or to a molsieve-based unit to remove oxygenates such as DEE, ETBE, ethanol and tert-butanol.

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

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

Installation: The Uhde (Edeleanu) proprietary ETBE process has been successfully applied in three refineries, converting existing MTBE units. Two other MTBE plants are in the conversion stage.

Licensor: Uhde GmbH CONTACT

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Ethers—**MTBE**

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

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

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

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

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

The catalyst used in this process is a cation-exchange resin and is available from several catalyst manufacturers. Isobutene conversions of 97% are typical for FCC feedstocks. Higher conversions are attainable when processing steam-cracker C_4 cuts that contain isobutene concentrations of 25%.

MTBE is recovered as the bottoms product of the distillation unit. The methanol-rich C_4 distillate is sent to the methanol-recovery section. Water is used to extract excess methanol and recycle it back to process. The isobutene-depleted C_4 stream may be sent to a raffinate stripper or to a molsieve-based unit to remove other oxygenates such as DME, MTBE, methanol and tert-butanol.



Very high isobutene conversion, in excess of 99%, can be achieved through a debutanizer column with structured packings containing additional catalyst. This reactive distillation technique is particularly suited when the raffinate-stream from the MTBE unit will be used to produce a high-purity butene-1 product.

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

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

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

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

Licensor: Uhde GmbH CONTACT

FCC gasoline upgrading

Application: GT-BTX PluS is an extractive distillation process to convert fluid catalytic cracking (FCC) gasoline into high-value aromatics. GT-BTX PluS is especially suited for high severity or petro-FCC type operations.

Description: This process separates the aromatics plus sulfur components from cracked gasoline to permit recovery of the aromatics as petrochemical product. A mid-cut of FCC gasoline is fed to an extractive distillation operation that selectively removes the aromatics and sulfur species from the olefinic-rich gasoline. The extract is subsequently hydrodesulfurized to remove the sulfur species. The streams may be blended together as gasoline with no change in octane value from the raw cut; or the aromatics may be fed directly to the fractionation section of a paraxylene plant. The olefinic-rich non-aromatics may also be converted to aromatics via a fixed bed aromatization process.

Process advantages:

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

• Rejects olefins from being hydrotreated in the 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) are 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 (from the ED unit) can be directed to an aromatization unit to produce additional BTX or recycled to the FCC unit to increase the light olefin production.

• Effective means of benzene reduction from FCC source of gasoline without loss of octane



Economics: Feedrate—20,000 b/d 70°C–150°C range of FCC gasoline

Products—BTXA9 feed to paraxylene complex; non-aromatic raffinate for aromatization unit

Capital cost—\$30 MM USD (ISBL including extraction and HDS sections, 20/0 RSGC basis)

Installation: One licensed unit.

Licensor: GTC Technology US, LLC CONTACT

Flue gas denitrification

Application: The Topsøe SCR DeNOx process removes NO_x from flue gases through reactions with an ammonia-based reducing agent over a specially designed fixed-bed monolithic catalyst. By carefully selecting the catalyst parameters, channel size and chemical composition, the process covers a wide range of operating conditions and flue-gas dust contents and may be applied to practically all types of refinery units including furnaces, boilers, crackers and FCC units.

Products: The Topsøe SCR DeNOx converts NO_x into inert nitrogen and water vapor. The process may be designed for NO_x reductions in excess of 95% and with an ammonia leakage of just a few ppm.

Description: The reducing agent such as ammonia or urea, aqueous or pure, is injected into the flue gas stream in stoichiometric proportion to the amount of NO_x in the flue gas, controlled by measurement of flue gas flow and NO_x concentration. The injection takes place in a grid over the entire cross-section of the flue-gas duct to ensure a uniform distribution of NO_x and ammonia upstream the SCR catalyst vessel.

The process incorporates Topsøe's well-proven corrugated monolithic DNX catalyst. DNX is manufactured in small units, which may be combined into larger modules to match any requirement in terms of vessel dimensions and pressure drop, and in both horizontal and vertical vessel configurations.

The DNX catalyst is based on a fiber-reinforced ceramic carrier, which gives a unique combination of a high strength and a high microporosity. The high micro-porosity provides a superior resistance to catalyst poisons and low weight. The fibers add flexibility to the catalyst so that it can tolerate a wide range of heating and cooling rates.

Operating conditions: Typical operating conditions range from 200°C to 550°C (400°F–1,020°F), up to 3 bar (44 psia) and up to 60 g/Nm³ of dust in the flue gas.



Installation: More than 700 SCRs including more than 100 refinery units use Topsøe SCR DeNOx catalyst and technology. The refinery applications range from low-dust furnaces to high-dust FCC units and temperatures up to 500°C (930°F).

References: Damgaard, L., B. Widroth and M. Schröter: "Control refinery NO_x with SCRs," *Hydrocarbon Processing*, November 2004.

Licensor: Haldor Topsøe A/S CONTACT

Flue gas desulfurization—SNOX

Application: The SNOX process treats boiler flue gases from the combustion of high-sulfur fuels, such as heavy residual oil and petroleum coke. The SNOX process is a combination of the Topsøe WSA process and the Topsøe SCR DeNOx process. The process removes SO_2 , SO_3 and NO_x as well as dust. The sulfur is recovered in the form of concentrated commercial-grade sulfuric acid. The SNOX process is distinctly different from most other flue gas desulfurization processes in that its economy increases with increasing sulfur content in the flue gas.

Description: Dust is removed from the flue gas by means of an electrostatic precipitator or a bag filter. The flue gas is preheated in a gas/ gas heat exchanger. Thereafter, it is further heated to approximately 400°C and ammonia is added, before it enters the reactor, where two different catalysts are installed. The first catalyst makes the NO_x react with ammonia to form N₂ and water vapor, and the second catalyst makes the SO₂ react with oxygen to form SO₃. The second catalyst also removes any dust traces remaining. During the cooling in the gas/ gas heat exchanger, most of the SO₃ reacts with water vapor to form sulfuric acid vapor. The sulfuric acid vapor is condensed via further cooling in the WSA condenser, which is a heat exchanger with vertical glass tubes.

Concentrated commercial-grade sulfuric acid is collected in the bottom of the WSA condenser and is cooled and pumped to storage. Cleaned flue gas leaves the WSA condenser at 100°C and can be sent to the stack without further treatment. The WSA condenser is cooled by atmospheric air. The cooling air can be used as preheated combustion air in the boiler. This process can achieve up to 99% sulfur removal and about 96% NO_x removal.

Other features of the SNOX process are:

- No absorbent is applied
- No waste products are produced. Besides dust removed from the



flue gas, the only products are cleaned flue gas and concentrated commercial-grade sulfuric acid.

- Boilers equipped with SNOX have carbon footprints 5%–10% lower than similar boilers equipped with traditional limestone FGD.
- High degree of heat efficiency
- Modest utility consumption
- Attractive operating economy
- Simple, reliable and flexible process.

Installation: Six SNOX units have been contracted for cleaning of a total of more than five million Nm^3/h of flue gas. Additionally, 95 WSA plants have been contracted. These are similar to SNOX plants, only smaller, and some without NO_x removal, for other applications than flue gas cleaning.

Licensor: Haldor Topsøe A/S CONTACT

Fluid catalytic cracking (FCC)

Application: Selective conversion of gas oil feedstocks.

Products: High-octane gasoline, distillate and $C_3 - C_4$ olefins.

Description: Catalytic and selective cracking in a short-contact-time riser where oil feed is effectively dispersed and vaporized through a proprietary feed-injection system. Operation is carried out at a temperature consistent with targeted yields. The riser temperature profile can be optimized with the proprietary mixed temperature control (MTC) system.

Reaction products exit the riser-reactor through a high-efficiency, close-coupled, proprietary riser termination device RSS (riser separator system). Spent catalyst is pre-stripped followed by an advanced high-efficiency packed stripper prior to regeneration. The reaction product vapor may be quenched to give the lowest possible dry gas and maximum gasoline yield. Final recovery of catalyst particles occurs in cyclones before the product vapor is transferred to the fractionation section.

Catalyst regeneration is carried out in a single regenerator equipped with proprietary air and catalyst distribution systems, and may be operated for either full or partial CO combustion. Heat removal for heavier feedstocks may be accomplished by using reliable dense-phase catalyst cooler, which has been commercially proven in over 65 units. As an alternative to catalyst cooling, this unit can easily be retrofitted to a two-regenerator system (R2R) in the event that a future resid operation is desired.

The converter vessels use a cold-wall design that results in minimum capital investment and maximum mechanical reliability and safety. Reliable operation is ensured through the use of advanced fluidization technology combined with a proprietary reaction system. Unit design is tailored to the refiner's needs and can include wide turndown flexibility.

Available options include power recovery, waste-heat recovery, fluegas treatment and slurry filtration. Revamps incorporating proprietary



feed injection and riser termination devices and vapor quench result in substantial improvements in capacity, yields and feedstock flexibility within the mechanical limits of the existing unit.

Installation: Shaw and Axens have licensed 50 grassroots FCC units and performed more than 200 revamp projects.

Reference: Meyers, R., Handbook of Petroleum Refining Process, Third Ed.

Licensor: Shaw and Axens CONTACT

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Fluid catalytic cracking

Application: Conversion of gas oils and residues to light olefins, highoctane gasoline, and distillates using the compact, self supporting Orthoflow converter.

Description: Feed enters through the proprietary ATOMAX-2 feed injection system. Reaction vapors pass through a right angle turn and are quickly separated from the catalyst in a positive pressure closed-cyclone system. Closed cyclones minimize dry-gas make and increase gasoline yield. Spent catalyst flows through a stripper equipped with Dynaflux baffles to the regenerator where countercurrent flow of catalyst and air contacting is carried out.

Catalyst flow from the regenerator to the external vertical riser is controlled by riser outlet temperature, which regulates the regenerated catalyst slide valve. A plug valve located in the regenerator bottom head controls the level in the stripper by regulating the catalyst flow from the spent catalyst standpipe.

Either partial or complete CO combustion may be used in the regenerator. Flue gas flows to an external plenum and then to the flue-gas system. A Cyclofines Third Stage Separator may be used to remove particulates from the flue gas for protection of a power recovery expander and/or compliance with particulate emissions standards.

Economics: The converter is a one-piece modularized unit that combines the disengager, stripper and regenerator vessels into a single structure. This unique design minimizes the cost of construction, and also reduces the amount of field mechanical work and required plot space.

Installations: More than 150 grassroots units have been designed, resulting in a total of over 4 million bpsd fresh feed, with 12 of the latest units since 1990.



References: "Maximizing flexibility for FCC's designed to maximize propylene," 2008 NPRA Annual Meeting, March 9–11, 2008, San Diego.

"Optimize FCC Flue-Gas Emission Control—Part 2," *Hydrocarbon Processing*, Vol. 81, No. 10, October 2002, pp. 85–91.

"New developments in FCC feed injection and stripping technologies," NPRA Annual Meeting, March 2000.

Licensors: KBR and ExxonMobil CONTACT

Fluid catalytic cracking

Application: Selective and high conversion of a wide range of feedstocks into high-value products. Feedstocks include virgin or hydrotreated gasoils that may also include lube oil extract, coker gasoil and resid.

Products: High-octane gasoline, light olefins and distillate. Flexibility in unit operation allows for maximizing the most desirable product.

Description: The Lummus Technology process incorporates an advanced reaction system, high-efficiency catalyst stripper and a mechanically robust, single-stage fast fluidized bed regenerator. Oil is injected into the base of the riser via proprietary Micro-Jet feed injection nozzles (1). Catalyst and oil vapor flow upwards through a short-contact time, all-vertical riser (2) where raw oil feedstock is cracked under optimum conditions.

Reaction products exiting the riser are separated from the spent catalyst in a patented, direct-coupled cyclone system (3). Product vapors are routed directly to fractionation, thereby eliminating nonselective post-riser cracking reactions and maintaining the optimum product yield slate. Spent catalyst containing only minute quantities of hydrocarbon is discharged from the diplegs of the direct-coupled cyclones into the cyclone containment vessel (4). The catalyst flows down into the stripper containing proprietary modular grid (MG) baffles (5).

Trace hydrocarbons entrained with spent catalyst are removed in the MG stripper using stripping steam. The MG stripper efficiently removes hydrocarbons at low steam rate. The net stripper vapors are routed to the fractionator via specially designed vents in the directcoupled cyclones. Catalyst from the stripper flows down the spentcatalyst standpipe and through the slide valve (6). The spent catalyst is then transported in dilute phase to the center of the regenerator (8) through a unique square-bend-spent catalyst transfer line (7). This arrangement provides the lowest overall unit elevation. Catalyst is



regenerated by efficient contacting with air for complete combustion of coke. For resid-containing feeds, a catalyst cooler is integrated with the regenerator. The resulting flue gas exits via cyclones (9) to energy recovery/flue gas treating. The hot regenerated catalyst is withdrawn via an external withdrawal well (10). The well allows independent optimization of catalyst density in the regenerated catalyst standpipe, maximizes slide valve (11) pressure drop and ensures stable catalyst flow back to the riser feed injection zone.

The catalyst formulation can be tailored to maximize the most desired product.

Economics:

Investment (basis: 30,000 bpsd including reaction/regeneration system and product recovery. Excluding offsites, power recovery and flue gas scrubbing US Gulf Coast 2006.) \$/bpsd (typical) 2,400–3,500
Fluid catalytic cracking, continued

Utilities, typical per bbl fresh feed:	
Electricity, kWh	0.8–1.0
Steam, 600 psig (produced)	50–200
Maintenance, % of investment per year	2–3

Installation: Seventeen grassroots units licensed. Thirty-three units revamped, with five revamps in design stage.

Licensor: Lummus Technology, a CB&I company CONTACT

Fluid catalytic cracking (FCC)

Application: Selective conversion of gas oil feedstocks.

Products: High-octane gasoline, distillate and $C_3 - C_4$ olefins.

Description: Catalytic and selective cracking in a short-contact-time riser where oil feed is effectively dispersed and vaporized through a proprietary feed-injection system. Operation is carried out at a temperature consistent with targeted yields. The riser temperature profile can be optimized with the proprietary mixed temperature control (MTC) system.

Reaction products exit the riser-reactor through a high-efficiency, close-coupled, proprietary riser termination device RSS (riser separator system). Spent catalyst is pre-stripped followed by an advanced high-efficiency packed stripper prior to regeneration. The reaction product vapor may be quenched to give the lowest possible dry gas and maximum gasoline yield. Final recovery of catalyst particles occurs in cyclones before the product vapor is transferred to the fractionation section.

Catalyst regeneration is carried out in a single regenerator equipped with proprietary air and catalyst distribution systems, and may be operated for either full or partial CO combustion. Heat removal for heavier feedstocks may be accomplished by using reliable dense-phase catalyst cooler, which has been commercially proven in over 65 units. As an alternative to catalyst cooling, this unit can easily be retrofitted to a two-regenerator system (R2R) in the event that a future resid operation is desired.

The converter vessels use a cold-wall design that results in minimum capital investment and maximum mechanical reliability and safety. Reliable operation is ensured through the use of advanced fluidization technology combined with a proprietary reaction system. Unit design is tailored to the refiner's needs and can include wide turndown flexibility.

Available options include power recovery, waste-heat recovery, fluegas treatment and slurry filtration. Revamps incorporating proprietary



feed injection and riser termination devices and vapor quench result in substantial improvements in capacity, yields and feedstock flexibility within the mechanical limits of the existing unit.

Installation: Shaw and Axens have licensed 50 grassroots FCC units and performed more than 200 revamp projects.

Reference: Meyers, R., Handbook of Petroleum Refining Process, Third Ed.

Licensor: Shaw and Axens CONTACT

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Fluid catalytic cracking

Application: To convert heavy distillates and residues into high-value products, including selective propylene production when required, using the Shell fluid catalytic cracking (FCC) process.

Description: In this process, Shell's high-performance feed nozzle system feeds hydrocarbons to a short contact-time riser. This design ensures good mixing and rapid vaporization into the hot catalyst stream. Cracking selectivity is enhanced by the feed nozzles and proprietary riser-internals, which reduce catalyst back mixing while reducing overall riser pressure drop.

Riser termination design incorporates reliable close-couple cyclones that provide rapid catalyst/hydrocarbon separation. It minimizes postriser cracking and maximizes desired product yields, with no slurry clean up required. Stripping begins in the staged stripper, equipped with highcapacity baffle structure.

A single-stage partial or full-burn regenerator delivers excellent performance at low cost. Proprietary internals are used at the catalyst inlet to disperse catalyst, and the catalyst outlet to provide significant catalyst circulation enhancement. Catalyst coolers can be added for more feedstock flexibility.

Cyclone-systems in the reactor and regenerator use a proprietary design, thus providing reliability, efficiency and robustness. Flue gas cleanup can be incorporated with Shell's third-stage separator.

Shell Global Solutions FCC technologies are proven reliability champions due to simplicity of components and incorporation of Shell's extensive operating experience.



Installation: Over 30 grassroots units designed/licensed, including 7 to handle residue feeds, and over 30 units revamped.

Supplier: Shell Global Solutions International B.V. CONTACT

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Fluid catalytic cracking

Application: Selectively converts straight run and hydrotreated gasoils and residue feedstocks into higher value products using the UOP FCC process, the UOP Resid FCC (RFCC), the UOP PetroFCC process and UOP RxPro process.

Products:Light olefins (for alkylation, polymerization, etherification or petrochemicals), LPG, high-octane gasoline, distillates and fuel oils.

Description: UOP's process uses a side-by-side reactor/regenerator configuration and a patented pre-acceleration zone to condition the regenerated catalyst before feed injection. Modern Optimix feed distributors inject the feed into the riser, which terminates in a vortex separation system (VSS). A high efficiency stripper then separates the remaining hydrocarbons from the catalyst, which is then reactivated in a combustor-style regenerator. With the RxCat process technology, a portion of the catalyst that has been stripped of residual hydrocarbon can be recycled back to the riser via a standpipe and the MxR chamber.

The reactor zone features a short-contact-time riser, state-of the art riser termination device for quick separation of catalyst and vapor, with high hydrocarbon containment (VSS/VDS technology) and RxCat technology, wherein a portion of the stripped (carbonized) catalyst from the reactor is blended with the hot regenerated catalyst in a proprietary mixing chamber (MxR chamber) for delivery to the riser. Unlike other approaches for increasing the catalyst-to-oil ratio, this technology does not affect the total heat balance and, therefore, does not increase coke yield. Additionally, the recycling of cooler partially spent catalyst back to the base of the riser lowers the reactor inlet temperature which results in a reduction of undesirable thermally produced products, including dry gas. The ability to vary the carbonized/regenerated catalyst ratio provides considerable flexibility to handle changes in feedstock quality and enables a real-time switch between gasoline, olefins or distillate operating modes.



Furthermore, because the catalyst delivered to the regenerator has a higher delta coke content relative to the base, non-RxCat operation, it requires less excess oxygen at a given temperature to sustain the same kinetic combustion rate. RxCat technology is operating in six units, with another eight installations current in design and/or construction phase. The first unit to commercialize the RxCat process technology was successfully started up in 2005.

The combustor-style regenerator burns coke in a fast-fluidized environment completely to CO_2 with very low levels of CO and limited production of NO_x . The circulation of hot catalyst from the upper section to the combustor provides added control over the burn-zone temperature and kinetics. Catalyst coolers can be added to new and existing units to

Fluid catalytic cracking, continued

reduce catalyst temperature and increase unit flexibility to process feeds up to 6 wt% conradson carbon. A study of eight different combustorstyle regenerators and 15 bubbling-bed regenerators clearly showed that at the same excess oxygen level, less NO_x is emitted from the combustor-style regenerators than the other regenerator technologies.

For heavier residue feeds, the two-stage regenerator is used. In thefirst stage, the bulk of the carbon is burned from the catalyst, forming a mixture of CO and CO₂. Catalyst is transferred to the second stage, where the remaining coke is burned in complete combustion, producing low levels of carbon on regenerated catalyst. A catalyst cooler is located between the stages. This configuration maximizes oxygen use, requires only one train of cyclones and one flue gas stream, which avoids costly multiple flue gas systems and creates a hydraulically-simple system to operate. The two stage regenerator system has processed feeds up to 8.5 wt% Conradson carbon.

UOP also offers two process technologies for maximizing propylene from feedstocks traditionally processed in FCC or RFCC units. The PetroF-CC and RxPro processes are specifically designed to meet increased propylene production requirements but are flexible to also operate in maximum gasoline mode, if required. Both processes utilize commercially proven technology and mechanical features found in a conventional UOP FCC design, but are operated at process conditions that promote light olefin and/or aromatics production for petrochemical applications. The commercially-proven PetroFCC technology provides a cost-effective means for producing moderate quantities of propylene from moderate quality feedstocks. The newest entry to the enhanced propylene platform at UOP, the RxPro process, employs a multi-stage reaction system with targeted olefin recracking to achieve a highest yield of propylene (> 20 wt%FF) for a given reaction severity and feedstock quality. UOP's Advanced Fluidization (AF) spent catalyst stripper internals provide a family of options (trays, grids and packing) all with state of the art efficiency. Often the optimal selection is dependent on the unique configuration of the unit, site constructability and inspection issues. The benefits provided by the AF internals include reduced delta coke, lower regenerator temperature, higher catalyst circulation, lower dry gas make, increased conversion, and higher selectivity for desired products relative to conventional stripper designs. The AF packing option provide

Installations: All of UOP's technology and equipment are commercially proven for both process performance and mechanical reliability. UOP has been an active designer and licensor of FCC technology since the early 1940s and has licensed more than 250 FCC unit designs (including Resid FCC, MSCC, and PetroFCC process unit styles). More than 150 of these units are operating worldwide. In addition to applying our technology and skills to new units, UOP is also extensively involved in the revamping of existing units.

Licensor: UOP, A Honeywell Company CONTACT

HYDROCARBON PROCESSING®

2011 Refining Processes Handbook

Fluid catalytic cracking for maximum olefins

Application: The Indmax FCC (I-FCC) process cracks a wide range of feedstocks into light olefins. Feedstocks include virgin or hydrotreated gasoil that may include lube oil extract, coker gasoil and resid.

Products: Light olefins (principally propylene, but also ethylene and butylenes), high-octane gasoline, blending components, and distillate. Flexibility of unit operation allows for maximizing propylene, propylene plus ethylene, or propylene plus gasoline.

Catalyst: The Indmax catalyst is a unique, proprietary, multi-component, multi-functional catalyst formulation that promotes selective component cracking to provide very high conversion and yield of light olefins. It is highly metals-tolerant and produces low delta coke and dry gas – properties that are particularly important when processing residue to make light olefins.

Description: The I-FCC unit is designed for and operated at Indmax process conditions: riser reactor temperature from 560°C to 600°C, catalyst-to-oil ratio from 12 to 20, and lower hydrocarbon partial pressure compared to conventional FCC operations. The I-FCC process incorporates an advanced reaction system, high-efficiency catalyst stripper and a mechanically robust, single-stage fast fluidized bed regenerator. Oil is injected into the base of the riser via proprietary Micro-Jet feed injection nozzles (1). Catalyst and oil vapor flow upwards through a short-contact time, all-vertical riser (2) where raw oil feedstock is cracked under optimum conditions.

Reaction products exiting the riser are separated from the spent catalyst in a patented, direct-coupled cyclone system (3). Product vapors are routed directly to fractionation, thereby eliminating nonselective, post-riser cracking and maintaining the optimum product yield slate.



Spent catalyst containing only minute quantities of hydrocarbon is discharged from the diplegs of the direct-coupled cyclones into the cyclone containment vessel (4). The catalyst flows down into the stripper containing proprietary modular grid (MG) baffles (5).

Trace hydrocarbons entrained with spent catalyst are removed in the MG stripper using stripping steam. The MG stripper efficiently removes hydrocarbons at low steam rate. The net stripper vapors are routed to the fractionator via specially designed vents in the direct-coupled cyclones. Catalyst from the stripper flows down the spent-catalyst standpipe and through the slide valve (6). The spent catalyst is then transported in dilute phase to the center of the regenerator (8) through a unique square-bend-spent catalyst transfer line (7). This arrangement provides the lowest overall unit elevation. Catalyst is regenerated by efficient contacting with air for complete combustion of coke. For resid-containing feeds, the optional catalyst cooler is integrated with the

Continued ▼

Fluid catalytic cracking for maximum olefins, continued

regenerator. The resulting flue gas exits via cyclones (9) to energy recovery/flue gas treating. The hot regenerated catalyst is withdrawn via an external withdrawal well (10). The well allows independent optimization of catalyst density in the regenerated catalyst standpipe, maximizes slide valve (11) pressure drop and ensures stable catalyst flow back to the riser feed injection zone.

Economics:

Investment (basis: 30,000 bpsd including reaction/regeneration system and product recovery. Excluding offsites, power recovery and flue gas scrubbing US Gulf Coast 2006.) \$/bpsd (typical) 3,000-4,000

Installation: Two grassroots units licensed. One demonstration-scale unit is commercially operating.

Licensor: Lummus Technology, a CB&I company CONTACT

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2011 Refining Processes Handbook

Fluid catalytic cracking, high olefin

Application: MAXOFIN FCC offers refiners greater returns by maximizing propylene yields from FCC feedstocks. Over 20 wt% propylene yield can be produced from gasoils by combining the effects of enhanced ZSM-5 catalysts and proprietary hardware.

Description: This dual-riser design uses independent riser reaction conditions (cat/oil and temperatures) for heavy and light feedstocks. C_4-C_6 nonaromatic naphtha cuts can be recycled to the light hydrocarbon riser. In addition to processing light naphtha, the recycle riser can also accept coker and light-straight-run naphthas from the refinery. Both risers can operate at 100% gasoil/resid if market conditions dictate the need for petroleum products instead of petrochemicals.

The recycle riser is an external, cold wall riser similar to the primary riser. Products produced from both risers merge in the disengager vessel and travel as a common stream to the main fractionator.

Yields: The following yields were produced from a pilot plant using a hydrocracked gasoil feedstock:

Yields, wt%	Run A	Run B	Run C	Run D
Ethylene	3.2	3.9	6.4	8.2
Propylene	16.0	18.7	19.1	21.5
C ₅ + gasoline	37.9	28.8	26.2	25.0

Economics: Investment and operating costs are only slightly higher than a conventional FCC with a single riser.

Installations: All elements of MAXOFIN FCC technology have been proven. Propylene yield was dependent upon constraints in the downstream gas plant and not the converter section.



References: "KBR Catalytic Olefins Technologies Provide Refinery/Petrochemical Balance," 25th JPI Petroleum Refining Conference, Oct. 26–27, 2010, Tokyo, Japan.

"Maximizing Flexibility for FCC's Designed to Maximize Propylene," NPRA 2008 Annual Meeting, March 9–11, 2008, San Diego.

"Future refinery—FCC's role in refinery/petrochemical integration," NPRA 2001 Annual Meeting, March 2001.

Licensors: KBR and ExxonMobil CONTACT

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Fluid catalytic cracking, high severity

Application: Selective conversion of gasoil and heavy residual feedstocks.

Products: High-octane gasoline and C₃–C₄ olefins.

Description: An alliance comprising of Saudi Aramco, JX Nippon Oil & Energy Corp.(JX), King Fahad University of Petroleum and Minerals and Axens / Shaw, has developed the HS-FCC process, which is able to produce up to 25% of propylene by converting heavy hydrocarbon feedstock under severe FCC conditions, using a novel downflow reactor concept. A 3,000 bpsd HS-FCC semi-commercial plant started at the Mizushima refinery of JX group in Japan in 2011. Alongside propylene, a considerable amount of butenes, gasoline and aromatics is produced as valuable byproducts. HS-FCC product portfolio can be further increased towards propylene and aromatics by further downstream conversion of its less desired products, using proven technology approaches.

The main features of the HS-FCC process comprise a downflow reactor, high-reaction temperature, short contact time and high catalyst to oil ratio (C/O). Operating the HS-FCC process at high temperature and high C/O ratio results in two competing cracking reactions—thermal cracking and catalytic cracking. Thermal cracking contributes to dry gas production while catalytic cracking contributes to enhancing propylene yield of propylene.

A downflow reactor system has been adopted. The catalyst and the feed flow downward along with gravity to minimize back mixing in the reactor and to obtain a narrower distribution of residence time that allows maximizing intermediate products such as gasoline and light olefins. The downflow reactor allows a higher C/O ratio because the lifting of catalyst by vaporized feed is not required. The downflow reaction ensures plug flow without back mixing.



The HS-FCC process is operated under considerably higher reaction temperatures (550°C to 650°C) than conventional FCC units. Under these reaction temperatures, however, thermal cracking of hydrocarbons also takes place concurrently with catalytic cracking, resulting in increased undesirable byproducts as dry gas and coke. Short contact time (less than 0.5 sec) of feed and product hydrocarbons in the downer minimizes thermal cracking. Undesirable successive reactions such as hydrogen transfer, which consumes olefins, are suppressed.

To attain short residence time, the catalyst and products have to be separated immediately at the reactor outlet. For this purpose, a highefficiency, short-residence time product separator was developed and is

Fluid catalytic cracking, high severity, continued

capable of suppressing side reactions (oligomerization and hydrogenation of light olefins) along with coke formation.

To compensate a drop in conversion due to short contact time, the HS-FCC process is operated at high C/O ratio. Under the high C/O, there is the enhanced contribution of catalytic cracking over thermal cracking. High C/O maintains heat balance and helps minimize thermal cracking, over cracking and hydrogen transfer reactions.

Installation: One 3,000 bpsd unit in Japan.

Reference: *Oil and Gas Journal,* Sept. 26, 2005, pp. 54–59. ERTC Annual Meeting, 2010, Istanbul.

Licensor: Axens and Shaw CONTACT

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Fluid catalytic cracking, residual

Application: Conversion of low-value residual feeds and deasphalted oils from heavy crudes to high-valued light olefins, gasoline and distillates.

Description: The converter is a one-piece modularized unit that efficiently combines KBR's proven Orthoflow features with ExxonMobil's advanced reaction design features. The regenerator is a single vessel that operates in partial or complete CO combustion with a dense phase catalyst cooler depending on the coke-forming tendencies of the feedstock.

The regenerator operates with a counter current flow of air and catalyst featuring a (1) spent catalyst distributor that evenly distributes the catalyst over the regenerator bed; and a (2) proprietary baffle that limits back-mixing between the upper and lower portions of the bed, effectively achieving a staged combustion in a single regenerator. The counter-current regeneration also reduces NO_x emissions compared to other types of regenerators.

Investment: (basis 50,000 BPSD fresh feed including converter, main fractionator, vapor recovery unit, C3 splitter, and amine treating (no power recovery), battery limit, direct material and labor, 2008 Gulf Coast), \$/bbl- 4900 to 5400.

Utilities, typical per bbl fresh feed	
Electricity, kWh	0.7-1.0
Steam, 600 psig, produced, lb	40–200
Maintenance: % of plant replacement cost/y	3

Installation: Since 1990, KBR has designed more than a dozen FCC units, including those that process resid and have revamped more than 160 FCC units worldwide



Reference: "Holding the key," *Hydrocarbon Engineering*, March 2008. Niccum, P. K. et al., "Optimize FCC Flue-Gas Emission Control—Part
2," *Hydrocarbon Processing*, Vol. 81, No. 10, October 2002, pp. 85–91. "New developments in FCC feed injection and stripping technologies," 2000 NPRA Annual Meeting, March 2000.

Licensors: KBR and ExxonMobil CONTACT

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Fluid catalytic cracking—pretreatment

Application: Topsøe's FCC pretreatment technology is designed to treat a wide variety of feedstocks ranging from gasoils through heavy-vacuum gas oils and coker streams to resids. This pretreatment process can maximize FCC unit performance.

Objectives: The processing objectives range from deep desulfurization for meeting gasoline-sulfur specifications from the FCC products, to denitrogenation and metals removal, thus maximizing FCC catalyst activity. Additional objectives can include Conradson carbon reduction and saturation of polyaromatics to maximize gasoline yields.

Description: The Topsøe FCC Pretreatment technology combines understanding of kinetics, high-activity catalysts, state-of-the-art internals and engineering skills. The unit can be designed to meet specific processing objectives in a cost-effective manner by utilizing the combination of processing severity and catalyst activity.

Topsøe has experience in revamping moderate- to low-pressure units for deep desulfurization. Such efforts enable refiners to directly blend gasoline produced from the FCC and meet future low-sulfur (less than 15 ppm) gasoline specifications.

An additional option is Topsøe's Aroshift process that maximizes the conversion of polyaromatics which can be equilibrium limited at high operating temperatures. The Aroshift process increases the FCC conversion, and the yield of gasoline and C_3/C_4 olefins, while reducing the amount of light- and heavy-cycle oil. Furthermore, the quality of the FCC gasoline is improved.

Topsøe has a wide variety of catalysts for FCC pretreatment service. The catalyst types cover TK-560 BRIM and TK-562 BRIM, a CoMo catalyst with high desulfurization activity, and TK-561 BRIM, a NiMo catalyst with hydrodesulfurization and high hydrodenitrogenation activity. Topsøe offers a wide range of engineering scopes from full scoping studies, reactor design packages and process design packages to engineering design packages.



Operating conditions: Typical operating pressures range from 60 to 125 bar (900 to 1,800 psi), and temperatures from 300°C to 430°C (575°F to 800°F).

References: Andonov, G., S. Petrov, D. Stratiev and P. Zeuthen, "MCHC mode vs. HDS mode in an FCC unit in relation to Euro IV fuels specifications," 10th ERTC, Vienna, November 2005.

Patel R., H. Moore and B. Hamari, "FCC hydrotreater revamp for low-sulfur gasoline," NPRA Annual Meeting, San Antonio, March 2004.

Patel, R., P. Zeuthen and M. Schaldemose, "Advanced FCC feed pretreatment technology and catalysts improves FCC profitability," NPRA Annual Meeting, San Antonio, March 2002.

Installations: Four units in the US.

Licensor: Haldor Topsøe A/S CONTACT

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Gas treating

Application: A portfolio of gas treating technologies designed to remove sour and organic sulfur contaminants encountered in refineries, liquefied natural gas, gasification and natural gas production facilities. Suitable for natural gas, synthesis gas, liquefied hydrocarbon, e.g., LPG and the offgas from Claus plants. These process technologies enable tighter specifications to be met, increase operating capacity and reduce their energy consumption and carbon footprints.

Description: The ADIP process is ideal for the removal of hydrogen sulfide, carbon dioxide and carbonyl sulfide from hydrocarbon gas and liquid streams. It is a regenerable aqueous amine process utilizing alkanolamines such as di-isopropanolamine (DIPA) and methyl di-ethanolamine (MDEA). ADIP is also available as ADIP-X, a promoted solvent to maximize carbon dioxide and organic sulfur component removal including mercaptans. CANSOLV technology captures sulfur dioxide (SO₂) and/or carbon dioxide from combustion gases returning the sulfur dioxide into the Claus unit.

The Claus unit converts the H_2S to sulfur, combusts hydrocarbons and sour water stripper offgas, and it is designed to work in concert with Shell Claus Offgas Treating (SCOT) process. SCOT uses an amine solvent to recycle H_2S into the Claus unit after it converts the sulfur from the Claus offgas to H_2S . It is also available in a low-temperature (LT) meeting a high sulfur conversion, > 99.8% at mild steam conditions. The sulfur degassing process reduces hydrogen sulfide and hydrogen polysulfide in liquid sulfur coming from the Claus unit and the H_2S offgas can be recycled to the Claus to boost sulfur conversion.

Sulfinol and Sulfinol-X process technologies are designed to remove hydrogen sulfide, carbonyl sulfide, mercaptans and organic sulfides from sour gas using regenerable amine solvents. When used with modified dehydration molecular sieves, the integrated line-up removes all sulfur species in a single acid-gas stream. Shell Global Solution's hydrogen cyanide and carbonyl sulfide (HCN/COS) hydrolysis process catalytically neutralizes these components. The Shell-Paques process (THIOPAQ O&G) uses an aqueous soda solution containing sulfur bacteria to biologically remove H_2S from gas streams and recover H_2S as elemental sulfur.

The SulFerox process is particularly cost-effective at selectively treating gases carrying small quantities of hydrogen sulfide, while SORDECO utilizes fixed-bed absorption to improve the hydrocarbon dew point specification of natural gas.

Performance data:

• An integrated sour gas treating solution enables ultra high overall sulfur recovery efficiencies (99.9+% of the overall sulfur present in the feed gas to the processing plant) from sour gas streams, while minimizing the complexity and cost of the process line-up with low carbon footprint.

• ADIP, Sulfinol, ADIP-X and Sulfinol-X have low levels of hydrocarbon solubility, foaming, fouling, corrosion and degradation, thus facilitating efficient and stable operations in optimized Shell designed equipment, i.e. tray internals

• The Claus unit offers sulfur recovery efficiencies of up to 98%.

Note: that this depends on number of stages and H_2S content in the feed. More usual figure is 95%–96% for 2-stage Claus in refinery application (> 50% H_2S in acid gas feed).

• The SCOT process enables consistently high sulfur recovery (in excess of 99.8%), regardless of fluctuations in the Claus tail-gas composition.

• CANSOLV gas treating processes are capable of increasing Claus unit capacity by 12%

• Sulfur degassing is capable of reducing hydrogen sulfide and hydrogen polysulfide from levels of 250–300 ppmv down to less than 10 ppmv.

• THIOPAQ O&G is attractive for quantities of H_2S in the range of 0.5–150 tpd.

Gas treating, continued

Installations: Shell Group operations and more than 1,250 licensees apply the gas treating and sulfur processes that Shell Global Solutions has developed.

Licencors: Shell Global Solutions International B.V. and CANSOLV Technologies Inc. <u>CONTACT</u>

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Gas treating—H₂S removal

Application: ExxonMobil Research and Engineering Co. (EMRE) has developed and commercialized a suite of gas treating technologies and absorbents, known broadly as FLEXSORB. The FLEXSORB SE technology is designed for the selective removal of H_2S in the presence of CO₂ and utilizes proprietary severely sterically hindered amines. This allows FLEX-SORB SE solvent to achieve high H_2S cleanup selectively at low solvent circulation rates.

EMRE's FLEXSORB SE and SE PLUS solvents are used in a variety of gas treating applications including acid gas removal (AGR), acid gas enrichment (AGE) and tail gas cleanup units (TGCU). FLEXSORB technology easily fits into natural gas processing (including onshore and offshore), refining and petrochemical operations using standard gas treating equipment.

Description: The FLEXSORB technology utilizes equipment that is typical in amine-type tail gas treating units. It also incorporates features based on EMRE's extensive experience designing and operating gas treating units in all segments of the energy industry.

A simplified technology process flow diagram (PFD) is shown here. The feed gas is contacted counter-currently with lean FLEXSORB SE solution in the absorber tower (1). The rich FLEXSORB SE solution is heated in the rich/lean heat exchanger and fed to the regenerator (2). In the regeneration tower, the acid gas (H2S and CO2) is stripped from the FLEXSORB SE solution by counter-current contacting with steam generated in the reboiler. The gas exiting the stripping section of the regenerator tower is then washed in the reflux (rectifying) section, which is located at the top of the tower. The acid gas is recycled back to the front of the sulfur recovery unit. From the reboiler, the hot lean FLEXSORB SE solution is sent back through the rich/lean heat exchanger and further cooled in the lean cooler.



Economics: The FLEXSORB SE process has been shown to be the most selective and cost-effective amine solvent process. It's reliable, robust, and simple to operate. Operating experience has shown low corrosion and lower foaming than with conventional amines. Corrosion is low even at high rich loadings or high levels of heat stable salts. Conventional equipment, that is used for other amine solvents, such as counter-current towers, is used for the FLEXSORB SE process as well.

In sulfur plant tail-gas treating unit (TGTU) applications, FLEXSORB SE solvents can use about half of the circulation rate and regeneration energy typically required by MDEA-based solvents. CO₂ rejection in TGTU applications is very high, typically above 90%. FLEXSORB SE pro-

Gas treating—H₂S removal, continued

vides a reduced vapor and liquid load to the regenerator tower resulting in a smaller tower diameter compared with competing technologies.

Installations: Over 100 commercial applications have repeatedly demonstrated the advantages of FLEXSORB SE and SE PLUS over competing solvents since the first commercial unit was started up in 1983. Commercial applications include ExxonMobil affiliates as well as numerous licensee applications in locations around the world.

References: "Optimum TGT and AGE design and performance," *Hydrocarbon Processing,* Sulfur Solutions 2010.

Licensor: ExxonMobil Research and Engineering Co. CONTACT

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Gasification

Application: ExxonMobil's Reserach & Engineering's (EMRE's) continuous fluid-bed coking with integrated steam gasification technology to convert heavy hydrocarbons (vacuum residuum, extra heavy oil or bitumen) to lighter liquid products and a clean burning fuel gas, FLEXIGAS, with minimum coke production. Attractive when coking for complete resid conversion with low or no fuel oil production is preferred and when outlets for fuel coke are limited or not economic, and especially when low-cost fuel gas is needed or where natural gas cost is high.

Products: Liquid product yields are similar to delayed coking and are upgraded to transportation fuels in the refinery by hydrotreating, hydrocracking, fluid catalytic cracker (FCC), or other processes. A large quantity of clean fuel gas is produced, which can be burned in a variety of grassroots or revamp furnaces and boilers in the refinery or in nearby power plants with low SO_x and NO_x emissions.

Description: FLEXICOKING has essentially the same feed system and fluid bed reactor (1) and scrubber (2) sections as FLUID COKING, and also has the same process flexibility to directly process vacuum tower bottoms without the need for a preheat furnace. It can also handle very heavy feeds, and can adjust recycle cut point depending upon gasoil product quality requirements. A steam/air gasification fluid bed reactor (4) is added to convert coke produced in the reactor to a CO and H₂-rich fuel gas, diluted by N₂.

The heater vessel (3) serves as a fluid solids heat exchanger to provide process heat for reactions in the heater and gasifier and to initially cool and clean FLEXIGAS from the gasifier. Flexigas overhead from the heater (3) is cooled and cleaned in several steps (5) to remove fines and is then treated with FLEXSORB hindered amine to reduce H₂S to as low 10 wppm if needed. Typically 95 wt%–97 wt% of the coke generated in the reactor is gasified to produce process heat and FLEXIGAS, depending upon the amount of nickel (Ni) and vanadium (V) in the feed,



a small amount of purge or net product coke is withdrawn from the heater (3) and fines removal system (5), which can be burned in cement kilns or used for recovery of V. Partial gasification with coke withdrawal can also be used to provide additional process flexibility for increased capacity or to make fuel grade coke if attractive markets are available.

Reactor yields: Typical 1,050°F+ cut point vacuum resid (~26 wt% Conradson carbon, 4.6 wt% sulfur, 125 wppm Ni + V)

Component yield	wt%	wt%
Fuel gas (C ₂ -)	6.7	
LPG, (C ₃ /C ₄)	4.4	

Gasification, continued

Total C ₄ -		11.1
Naphtha (C ₅ -430°F)	15.3	
Distillate (430°F–650°F)	11.0	
Gas oil (650°F–975°F)	32.2	
Total C ₅ + liquids		58.6
Net product coke	1.7	
Gasified coke	28.6	
Total reactor coke		30.3
Total:	100	100

Fuel gas production: Steam and air gasification of coke produced in the reactor generates a large fuel gas stream that is rich in CO/H_2 , which can be used as fuel. Fuel gas production consistent with the above yields for a 31,000 bpd FLEXICOKING Unit is:

Flexigas production:	1,580 MBtu/hr [460 MW (th)]
Flexigas heating value:	128 Btu/SCF
H ₂ S content:	10 wppm

Competitive advantages:

• Integrated coking and gasification technology that yields the same valuable liquid products as other coking processes but produces clean fuel gas instead of high-sulfur coke.

• Fluid bed process with coke transferred pneumatically and contained within fluid solids reactors and product silos.

• Environmental advantages with lower SO_x , NO_x , and particulates emissions than conventional delayed coking processes

• Much lower investment and more reliable than delayed coking plus partial oxidation or direct gasification of solids or heavy feeds. Particularly attractive for SAGD oil sands upgrading with large fuel requirements.

Reference: Kamienski, P. W., S. Massenzio and M. de Wit, "Coking without the coke," *Hydrocarbon Engineering*, March 2008.

Chitnis, G. K. and T. L. Hilbert, "FLEXICOKING Coking and integrated steam/air gasification," International BBTC Conference, Dubronvnik, June 14, 2011.

Licensor: ExxonMobil Research and Engineering Co. CONTACT

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Gasification

Application: The Shell Gasification Process (SGP) converts heavy refinery residual liquid hydrocarbon streams with high-sulfur and metals content into a clean synthesis gas (syngas) and marketable metal oxides. Sulfur (S) is removed by normal gas treating processes and sold as elemental S.

The process converts residual streams with virtually zero value as fuelblending components into marketable, clean gas and byproducts. This gas can be used to generate power in gas turbines for making hydrogen (H₂) by the well-known shift and pressure swing adsorption (PSA) technology to produce chemicals like oxoalcohols or methane. It is one of the few environmentally acceptable solutions for residual hydrocarbon streams.

Products: Synthesis gas $(CO + H_2)$, sulfur and metal oxides.

Description: Liquid hydrocarbon feedstock (from very light such as natural gas to very heavy such as vacuum flashed cracked residue (VFCR) and ashphalt) is fed into a reactor, and gasified with pure O_2 and steam. The net reaction is exothermic and produces a gas primarily containing carbon monoxide (CO) and H_2 . Depending on the final syngas application, operating pressures, ranging from 25 bar to 65 bar, can easily be accommodated.

SGP uses refractory-lined reactors that are fitted with a gasification burner and syngas effluent cooler, designed to produce high-pressure steam—over 100 bar (about 2.5 tons per ton feedstock). Gases leaving the steam generator are at a temperature approaching the steam temperature; thus, further heat recovery occurs in an economizer.

Soot (unconverted carbon) and ash are removed from the raw gas by a two-stage waterwash. After the final scrubbing, the gas is virtually particulate-free; it is then routed to a selective-acid-gas-removal system. Net water from the scrubber section is routed to the soot ash removal unit (SARU) to filter out soot and ash from the slurry. By controlled oxidation of the filtercake, ash components are recovered as marketable oxides-principally vanadium pentoxide. The (clean) filtrate is returned to the scrubber.



Installation: Over the past 40 years, more than 150 SGP units have been installed that convert residue feedstock into synthesis gas for chemical applications. The Shell Pernis refinery near Rotterdam, The Netherlands, uses the SGP process in a close refinery integration. This highly complex refinery depends on the SGP process for its H₂ supply. ENI refinery in Sannazzaro, Italy, uses syngas for H₂ supply and power production. Similar projects have started up in Canada and China.

The Shell middle distillate synthesis plant in Bintulu, Malaysia, uses SGP to convert 100 million scfd of natural gas into synthesis gas that is used for petrochemical applications.

A related process—the Shell Coal Gasification Process (SCGP)—gasifies solids such as coal or petroleum coke. The reactor is different, but main process layout and work-up are similar. The Demkolec Power plant at Buggenum, The Netherlands, produces 250 mega watts based on the

Gasification, continued

SCGP process. In total, over 20 licenses are in different phases of project execution using SCGP, 20 SCGP gasifers are operational.

Reference: "Shell Gasification Process," Conference Defining the Future, Bahrain, June 1–2, 2004.

"Shell Gasification Process for Upgrading Gdansk Refinery," The 6th European Gasification Conference IChemE, Brighton, May 10–12, 2004.

"Overview of Shell Global Solutions Worldwide Gasification Developments," 2003 Gasification Technologies Conference, San Francisco, Oct. 12–15, 2003.

"Shell Gasification Technology—Optimal disposal solution for refineries heavy ends," ERTC Gasification Conference, Paris, 2007.

"Shell Gasification Technology: Generating Profit from the Bottom of the Barrel," NPRA, Annual Meeting, San Diego, March 9–11,2008.

"Shell Gasification Technology—Part of refinery upgrading strategies," ERTC Gasification Conference, Rome, April 21–23,2008.

Zuideveld, P. and J. Wolff, "New methods upgrade refinery residuals into lighter products," *Hydrocarbon Processing*, February 2006, pp. 73–79.

Licensor: Shell Global Solutions International B.V. CONTACT

Gasification—**PDQ**

Application: The PRENFLO (PRessurized ENtrained-FLOw) direct quench (PDQ) is an optimized design of the proven PSG gasification process for all types of solid feedstock as petcoke, solid refinery residues, coal and biomass for chemical applications (ammonia, methanol, hydrogen, synfuel.)

Description: First, the feed dust is prepared in the feed preparation unit. Approximately 80% of the dust is smaller than 0.1 mm and has a water content of approximately 1 wt%–2 wt% in the case of hard coals, and approximately 8 wt%–10 wt% for lignite.

This feed dust is gasified in the PRENFLO gasifier using oxygen and steam as the gasification agent. The gasification temperature is higher than ash-melting temperature, which allows feedstocks containing ash to be removed as slag. The cooled-type gasifier is equipped with multiple, horizontally arranged burners.

The raw gas produced, which contains mainly carbon monoxide and hydrogen, is quenched with water in a direct quench in the gasifier vessel and then cleaned in a scrubber.

Economics:

Main process data:	
Gasification pressure:	40 bar and higher
Gasification temperature:	>2,000°C
Gas temperature at outlet of	
gasifier/quench:	200°C–250°C
Carbon conversion:	>99%
Typical raw gas composition:	
$CO + H_2$	>85 vol%
CO ₂	6–8 vol%
CH ₄	<0.1 vol%



Installation: The PRENFLO PDQ process is under development for industrial-scale applications

Licensor: Uhde GmbH CONTACT

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Gasification—**PSG**

Application: The PRENFLO (PRessurized ENtrained-FLOw) process can be used to gasify all types of solid feedstocks (petcoke, solid refinery residues, coal and biomass).

Description: First, the feed dust is prepared in the feed preparation unit. Approximately 80% of the dust is smaller than 0.1 mm and has a water content of approximately 1wt%–2 wt% in the case of hard coals, and approximately 8wt%–10 wt% for lignite.

This feed dust is then gasified in the PRENFLO gasifier using oxygen and steam as gasification agents. The gasification temperature is higher than the ash-melting temperature, which allows the feedstock containing ash to be removed as slag. The cooled-type gasifier is equipped with multiple, horizontally arranged burners.

In the PRENFLO process with steam generation (PSG), the raw gas produced, which contains mainly carbon monoxide and hydrogen, is cooled in the waste-heat boiler and generates steam. The gas is dedusted in a candle filter and further treated in a scrubber unit.

Economics:

Main process data

Gasification pressure:	> 40 bar
Gasification temperature:	> 2,000°C
Gas temperature at outlet of gasifier:	1,350°C–1,600°C
Carbon conversion:	> 99%
Typical raw gas composition:	
Typical raw gas composition : $CO + H_2$	> 85 vol.%
Typical raw gas composition: CO + H ₂ CO ₂	> 85 vol.% 2–4 vol.%

Reference: PRENFLO technology has been successfully commercialized in the world's largest solid-feedstock based IGCC 300 MWe net power plant in Puertollano, Spain.



Licensor: Uhde GmbH CONTACT

Ultimate analysis	Coal	Petcoke	Mixture
C, wt%	36.3	82.2	59.2
H, wt%	2.5	3.1	2.8
N, wt%	0.8	1.9	1.4
O, wt%	6.6	_	3.3
S, wt%	0.9	5.5	3.2
Ash, wt%	41.1	0.3	20.7
Water, wt%	11.8	7.0	9.4
Total, wt%	100.0	100.0	100.0
LHV, MJ/kg	13.1	32.6	23.1

Continued ▼

Gasification—PSG, continued

Raw gas analysis	
CO ₂ , vol%	2.9
CO, vol%	59.9
H ₂ , vol%	21.7
N ₂ + Ar, vol%	14.4^{*}
CH ₄ , vol%	< 0.1
$H_2S + COS, vol\%$	1.1
Total, vol%:	100.0
LHV, dry, MJ/m ³ n	10.16

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Gasoline benzene reduction

Application: ExxonMobil's Research & Engineering (EMRE's) BenzOUT converts benzene into high-octane alkylaromatic compounds (such as isopropylbenzene) for gasoline blending by reacting a benzene-rich stream with light olefins in low-value olefin streams. The process development is based on ExxonMobil's vast experience in ethylbenzene and cumene technology widely applied in the chemical industry. This commercially demonstrated refinery process is licensed through Badger licensing LLC.

In addition to benzene reduction, the process provides several advantages that make it attractive economically.

• **Benzene reduction.** Process reduces the benzene content in the gasoline pool. High benzene conversion can be achieved.

• **Gasoline volume swell.** Upgrading of light olefins and benzene into high-octane gasoline blendstock also results in a volume swell of the gasoline products. The specific volume swell will be depend on feed composition and the level of benzene conversion.

• Octane gain. 2–5 numbers of (R+M)/2 increase is typical. The specific octane gain depends on the feed composition.

• **Reformer flexibility** for increased hydrogen production. The BenzOUT process allows refineries to feed all the C6 components (low blending octane values) to the reformer unit to achieve increased hydrogen production and significant octane gain. Benzene produced in the reformer is alkylated in the BenzOUT process

Description: BenzOUT reduces benzene by reacting a benzene-concentrate stream with a light olefin containing stream such as C_3 LPG over a proprietary catalyst. Key features of the process are:

• **Fixed-bed catalyst technology.** The process uses a simple fixedbed reactor. In revamp projects, it is possible to retrofit existing polygas tubular/chamber reactors or spare reformer reactors for this application.



• **Catalyst.** The process uses a proprietary solid-acid catalyst with long cycle lengths. In addition, the catalyst is completely regenerable exsitu thus further extending catalyst life.

• Feed requirement. The process requires conventional feed pretreatment for the olefin streams to remove potential contaminants such as sulfur and nitrogen species. Many refiners have amine, caustic treating and water washing for the olefin stream, and optimization of existing equipment is typically sufficient for achieving the process requirement. If necessary, a standard commercial pretreatment system is available for the process.

Gasoline benzene reduction, continued

Installations: Commercial demonstration and grassroots unit in construction.

Reference: El-Malki El-M. and M. Clark, "Gasoline Benzene Reduction through ExxonMobil Research and Engineering Company's Reformate Alkylation Catalytic Technology: BenzOUT," NPRA, Phoenix March 2010.

Birkhoff R. and El-M. El-Malki, "Gasoline Benzene Reduction Through Reformate Alkylation Catalytic Technology," AIChE Regional Process Technology, Galveston, Texas, October 2010.

Chitnis, G. K., El-M. El-Malki and R. Birkhoff, "Gasoline Benzene Reduction Through Reformate Alkylation Catalytic Technology," RTM Conference (India), February 2011.

Licensor: Badger Licensing LLC (ExxonMobil-Badger alliance) CONTACT

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Gasoline, high-quality

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

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

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

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

Licensor: China Petrochemical Technology Co., Ltd. CONTACT



H₂S removal

Application: ELIMINATOR technology consisting of a full line of ELIMI-NATOR products removes hydrogen sulfide (H_2S) and light mercaptans from gas streams. Suitable applications are generally sulfur loads below 200 lb/d sulfur, and/or as a standby backup unit for other sulfurremoval systems.

Description: The ELIMINATOR technology is extremely versatile, and its performance is not sensitive to operating pressure. In properly designed systems, H_2S concentrations of less than 1 ppm can easily be achieved on a continuous basis.

A number of different treatment methodologies may be used to treat sour gas streams.

• Line injection—ELIMINATOR can be sprayed directly into a gas stream with removal of the spent product in a downstream knockout pot.

• Sparge tower—Sour gas is bubbled up through a static volume of ELIMINATOR. A lead-lag vessel arrangement can be installed to allow for the removal of spent solution and the addition of fresh solution without shutting down. This arrangement also results in the optimum utilization of the solution.

• Packed tower—Sour gas is contacted with circulating solution of ELIMINATOR in a counter, packed-bed scrubber.

Products: A full line of ELIMINATOR products can treat any type of gas streams.



Economics: Operating costs are very favorable for removing less than 200 ld/d of H_2S .

Installations: Fifteen units in operation.

Licensor: Merichem Company CONTACT

H₂S removal

Application: LOCAT removes H_2S from gas streams and produces elemental sulfur. LOCAT units are in service treating refinery overhead off gas (coking, visbreaking, fluidized-bed catalytic cracking, hydrotreating, hydrofining and hydrodesulfurization), gasification syngas (coal and other organic based materials), sour-water-stripper gas, natural gas, amine acid gas (physical solvents: Rectisol, Selexol, Benfield and chemical solvents: amines: MEA, DGA, DEA, DIPA and MDEA), Claus tail gas and tank vent gas. Sulfur capacities are typically less than 25 ltpd down to several pounds per day. Key benefits of operation are high (99.9%) H_2S removal efficiency, and flexible operation, with virtually 100% turndown capability on both H_2S concentration and treated gas volumes. Sulfur is recovered as a slurry, filter cake or high-purity molten sulfur.

Description: The conventional configuration is used to process combustible gas and product gas streams. Sour gas contacts the dilute, proprietary, catalyst solution in an absorber (1), where the H_2S is absorbed and oxidized to solid sulfur. Sweet gas leaves the absorber for downstream use. The reduced catalyst solution returns to the oxidizer (2), where sparged air reoxidizes the catalyst solution. The catalyst solution is returned to the absorber. Continuous regeneration of the catalyst solution allows for very low chemical operating costs.

In the patented autocirculation configuration, the absorber (1) and oxidizer (2) are combined in one vessel, but separated internally by baffles. Sparging of the sour gas and regeneration air into the specially designed baffle system creates a series of "gas lift" pumps, eliminating the external circulation pumps. This configuration is ideally suited for treating acid gas and sour-water-stripper gas streams.

In both configurations, sulfur is concentrated in the oxidizer cone and sent to a sulfur filter, which can produce filter cake as high as 85% sulfur. If desired, the filter cake can be further washed and melted to produce pure molten sulfur. **Operating conditions:** Operating pressures range from vacuum conditions to 1,000 psi. Operating temperatures range from 40°F to 140°F. H_2S concentrations range from a few ppm to 100%. Sulfur loadings range from a few pounds per day to 25+ tpd. No restrictions on type of gas to be treated; however, some contaminants, may increase operating costs.

Installations: Presently, 204 licensed units, 82 are in operation with 12 additional units currently under construction.

Licensor: Merichem Company CONTACT



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H₂S removal

Applications: SULFUR RITE is a solid-bed scavenger for removal of H_2S from aerobic and anaerobic gas streams. Suitable applications are generally sulfur loads below 200 lb/d sulfur, and/or as a standby backup unit for other sulfur-removal systems. The spent media is nonpyrophoric.

Description: Single-bed (shown) or dual "lead-lag" configurations are possible. Sour gas is saturated prior to entering media bed. Gas enters vessel top, flows over media where H_2S is removed and reacted. Sweet gas exits the bottom of vessel. In the single-vessel configuration, when the H2S level exceeds the level allowed, the vessel must be bypassed, media removed through the lower manway, fresh media installed and vessel returned to service.

For continuous operation, a dual "lead-lag" configuration is desirable. The two vessels operate in series, with one vessel in the lead position, the other in the lag position. When the H_2S level at the outlet of the lead vessel equals the inlet H_2S level (the media is completely spent), the gas flow is changed and the vessels reverse rolls, so that the "lag" vessel becomes the "lead" vessel. The vessel with the spent media is bypassed. The media is replaced, and the vessel with fresh media is returned to service in the "lag" position.

Operating conditions: Gas streams up to 400°F can be treated. Gas streams should be at least 50% water saturated.

Installations: Sixteen units installed.

Licensor: Merichem Company CONTACT



Heavy-oil upgrading

Application: Process designed for upgrading heavy oils, including the Athabasca bitumen into an easily transportable synthetic crude oil.

Description: This process uses various proven and established refining technologies.

Bitumen with diluent is brought to the upgrader. The diluent is recovered in the diluent recovery unit (DRU) and returned to the production site. The bottom of the DRU is sent to a high deasphalted oil lift ROSE solvent deasphalting unit. The DAO is then sent to a special purpose fluid catalytic cracking unit (FCCU). The FCCU operates at low conversion, normally between 30% and 60% and uses low-cost, low-activity catalyst.

The metals in DAO are rejected with the spent catalyst. The carbon (CCR) is burnt in the regenerator to produce steam. The FCCU products can be blended into synthetic crude oil. Alternatively, the products can be hydrotreated to produce low-sulfur synthetic crude oil. Steam produced in the FCCU is used within the complex. The asphaltenes from the ROSE unit can be pelletized using KBR's AQUAFORM pelletizing technology for ease of transportation to end users. Alternatively, the asphaltenes can be gasified to produce hydrogen, steam and power for bitumen production and upgrading.

Applications: This process can be used for upgrading bitumen and other heavy and very heavy oils.

KBR has performed extensive pilot plant testing to confirm the viability of the process methodology. Below are pilot test results for KBR's ROSE portion of the scheme.

ROSE pilot results:

Feed: Athabasca Bitumen

Feed	Solvents	DAO yield, vol%	CCR in DAO, wt%
Full	nC ₄ to C ₆	70–82	7–10



ATB	C_3 to nC_5	40–87	1–9
VTB	iC ₄ to nC ₅	17–65	5–14

The synthetic crude oil of the following composition can be produced by the shown processing scheme:

C₅-350°F: 15–30 vol% Distillate: 40–65 vol% Gasoil: 20–30 vol%

Economics: KBR estimates that this process will have several percent higher rate of return on investment when compared with traditional heavy-oil upgrading technologies and methods.

Reference: "KBR KLEEN Upgrading Process," Conrad Conference, Feb. 23, 2005, Calgary, Alberta.

Licensor: KBR CONTACT

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Hydroconversion—VGO and DAO

Application: An ebullated-bed process H-Oil_{DC} is used for hydroconversion (hydrocracking and hydrotreating) of heavy vacuum gasoil and DAO having high Conradson carbon residue and metal contents and low asphaltene content. It is best suited for high severity operations and applications requiring long run lengths.

Description: The flow diagram includes integrated mid-distillate hydrotreating for an ultra-low-sulfur-diesel product. The typical battery limits scheme includes oil- and hydrogen-fired heaters, an advanced design hot high-pressure separator and ebullating pump recycle system, a recycle gas scrubber and product separation and fractionation.

Catalyst in the reactor is replaced periodically without shutdown and, for cases of feeds with low metal contents, the catalyst can be regenerated onsite to reduce catalyst consumption.

Various catalysts are available as a function of the feedstock and the required objectives. An H-Oil_{DC} unit can operate for four-year run lengths at constant catalyst activity with conversion in the 20-80% range in once-through mode and to more than 95% in recycle mode with up to 99% hydrodesulfurization.

Operating conditions:

Temperature	750-820°F/400-438°C
Hydrogen partial pressure	600–1,500 psi/40_45 bar
LHSV, hr ^{–1}	0.5–3.0
Conversion, wt%	20-80 in once-through mode

Example: VGO + DAO feed: a blend of heavy VGO and C_5 DAO containing close to 100 ppm metals is processed at 80% conversion at an overall desulfurization rate of over 96%.



2,800–4,500
60
3
0.01-0.3

Installation: The H-Oil_{DC} process has four references, three in operation, with a total cumulative capacity of 11.45 metric tpy. This technology has been commercially demonstrated based on the ebullated bed reactor making a total of 13 references for residue and VGO hydroconversion.

Licensor: Axens CONTACT

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Hydrocracking

Application: Upgrade vacuum gas oil alone or blended with various feedstocks (light-cycle oil, deasphalted oil, visbreaker or coker gasoil).

Products: Jet fuel, diesel, very-low-sulfur fuel oil, extra-quality FCC feed with limited or no FCC gasoline post-treatment or high VI lube base stocks.

Description: This process uses a refining catalyst usually followed by hydrocracking catalyst. Main features of this process are:

- High tolerance toward feedstock nitrogen
- High selectivity toward middle distillates
- High activity of the cracking catalyst, allowing for 3–4 year cycle lengths and products with low aromatics content until end of cycle.

Three different process arrangements are available: single-step/ once-through; single-step/total conversion with liquid recycle; and twostep hydrocracking. The process consists of: reaction section (1, 2), gas separator (3), stripper (4) and product fractionator (5).

Product quality: Typical for HVGO (50/50 Arabian light/heavy):

	Feed, HVGO	Jet fuel	Diesel	UCO
Sp. gr.	0.932	0.800	0.826	0.835
TBP cut point, °C	405–565	140–225	225–360	360+
Sulfur, ppm	31,700	< 10	< 10	< 20
Nitrogen, ppm	853	< 5	< 5	< 5
Metals, ppm	< 2	_	_	—
Cetane index	_	—	62	—
Flash pt., °C	_	\geq 40	125	_



Smoke pt., mm, EOR	_	26–28	_	_
Aromatics, vol%, EOR	_	< 12	< 8	_
Viscosity @ 38°C, cSt	110	_	5.3	4–5
PAH, wt%, EOR			< 2	_
Viscosity Index	_	_	_	> 125

Reference: Morel, F., J. Bonnardot and E. Benazzi, "Hydrocracking solutions squeeze more ULSD from heavy ends," November 2009.

Installation: More than 83 references, cumulative capacity exceeding 3.4 million bpsd, conversions up to 99%.

Licensor: Axens CONTACT

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Hydrocracking

Application: Convert naphthas, AGO, VGO, DAO, cracked oils from FCC units, delayed cokers and visbreakers, intermediate products from residue hydroprocessing units and synthetic gasoils and shale oil using the Chevron Lummus Global ISOCRACKING Process.

Products: Lighter, high-quality, more valuable products: LPG, gasoline, catalytic reformer feed, jet fuel, kerosene, diesel and feeds for FCC, ethylene cracker or lube oil units.

Description: A broad range of both amorphous/zeolite and zeolitic catalysts, including noble-metal zeolitic catalysts, are used to tailor the ISOCRACKING Process exactly to the refiner's objectives. In general, the process involves a staged reactor system with an initial stage of hydrotreating and partially hydrocracking the feed, and a subsequent stage continuing the conversion or product upgrade process in a more favorable environment.

Feeds can be introduced in between stages using Chevron Lummus Global (CLG) patented split-feed injection technology, or effluent flow paths can be arranged to best utilize hydrogen and minimize quench-gas requirements using proprietary SSRS (single-stage reaction sequenced) technology.

Most modern large-capacity flow schemes involving heavy sour gas oils require two reactors (1, 4) and one high-pressure separation system (2) with an optional recycle gas scrubber (5) and one recycle-gas compressor (8). The low-pressure separators (3), product stripper (6) and fractionator (7) provide the flexibility to fractionate products either in between reaction stages or at the tail-end, depending on desired product slate and selectivity requirements.



Single-stage options are used in once-through mode typically for mild hydrocracking or when a significant quantity of unconverted oil is required for FCC, lubes, or ethylene units. The single-stage recycle option is used for lower capacity units when economical. The reactors use patented internals technology called ISOMIX for near-flawless mixing and redistribution. For feeds that are high in nitrogen and other contaminants, CLG recommends the Optimized Partial Conversion (OPC) scheme that achieves gravity targets of the unconverted oil (typical FCC feed) and desired conversion at much lower capital cost and hydrogen consumption.

Hydrocracking, continued

Yields: Typical from various feeds:

Feed	VGO	VGO	VGO	VGO
Gravity, API	24.1	24.1	24.1	21.3
TBP range, °F	700–1,100	700-1,100	700-1,100	700-1,100
Nitrogen, wppm	2,500	2,500	2,500	900
Sulfur, wt %	1.9	1.9	1.9	2.5
Mode	Max. Diesel	Max. Jet	Max. Mid- Distillate	Max. Mid- Distillate + Lubes
Yields, vol %				
Naphtha	22.8	30.8	14.0	18
Jet/kerosine	_	79.7	22.0	50
Diesel	85.5	_	73.0	35
UCO	_	_	—	10
Feed	VGO	VGO	VGO	VGO
Product quality				
Kerosine smoke, mr	n	29–32	29–32	29–32
Diesel cetane numb	er 58–64		58–64	58–64
UCO BMCI				6–8
UCO Waxy V.I.				143–150
UCO Dewaxed V.I.				131–133

Economics: ISBL total installed cost of 50,000-bpsd unit at 100% conversion to middle distillates using Middle Eastern VGO feed (USGC, 2010 basis): \$342 million.

Process fuel (absorbed), MMBtu/hr	180
Electricity, MW	10
CW, gpm	2,500
Steam (export at 150 psig), M lb/hr	22

Installation: More than 100 units worldwide with over three millionbpsd total capacity.

Reference: Dahlberg, A., U. Mukherjee and C. W. Olsen, "Consider using integrated hydroprocessing methods for processing clean fuels," *Hydrocarbon Processing*, September 2007, pp. 111–120.

Mukherjee, U., J. Mayer and B. Srinivasan, "Hydroprocessing Innovation—Some Recent Applications, *Petroleum Technology Quarterly*, Summer 2004.

Bridge, A. G. and U. Mukherjee, "ISOCRACKING—Hydrocracking for Superior Fuels and Lubes Production," *Handbook of Petroleum Refining Processes,* McGraw Hill, Third Edition.

Licensor: Chevron Lummus Global LLC CONTACT

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Hydrocracking

Application: The IsoTherming process provides refiners an economical means to upgrade gasoil, heavy gasoil, coker gasoils, deasphalted oil and FCC cycle oils.

Products: Low-sulfur, low-nitrogen FCC feed, low-sulfur gasoline-kerosine type products, and low-nitrogen fuels and/or downstream feedstocks.

Description: This process uses a novel approach to introduce hydrogen in excess of reaction requirements into the liquid-full reactor. It enables much higher space velocities than conventional hydrocracking reactors. The IsoTherming process eliminates problems associated with flow maldistribution, gas-liquid mass transfer and catalyst wetting. The process eliminates the need for some high-pressure equipment in conventional hydrocracking thereby lowering cost.

Fresh feed, after heat exchange, is combined with recycle product and hydrogen in a mixer internal to the reactor. The liquid feed with soluble hydrogen is fed to IsoTherming reactor/bed one where partial desulfurization, removal of metals or mild hydrocracking occurs. The stream is resaturated with additional hydrogen in a second mixer and fed to the second IsoTherming reactor/bed where further mild hydrocracking takes place. The treated oil from the second IsoTherming bed may then be fed to additional IsoTherming beds to achieve the desired level of conversion. At this time the technology is recommended for maximum feed conversion of approximately 40%.

Treated oil from the last bed is recycled back to the inlet of bed one. This recycle stream delivers recycled hydrogen to the reactors and also acts as a heat sink; thus, a nearly isothermal reactor operation is achieved.



Economics: Revamp investment is estimated to be half that of conventional mild hydrocracking due to the primary advantages offered by Iso-Therming, which include:

• Elimination of a recycle gas compressor, high-pressure flash drum and separator, condenser and amine scrubber.

• Smaller volume(s) of catalyst required for a given feed basis.

Installation: Three units are currently in operation for mild hydrocracking of heavy oils and upgrading of light cycle oil.

Licensor: DuPont CONTACT

Hydrocracking

Application: Topsøe's hydrocracking process can be used to convert straight run vacuum gas oils and heavy cracked gasoils to high quality "sulfur-free" naphtha, kerosene, diesel, and FCC feed, meeting current and future regulatory requirements. In addition, high VI lube stocks and petrochemical feedstock can be produced to increase the refinery's profitability.

Product: By proper selection of operating conditions, process configuration, and catalysts, the Topsøe hydrocracking process can be designed for high conversion to produce high smoke point kerosine and high cetane diesel. The process can also be designed for lower conversion/upgrade mode to produce low sulfur FCC feed with the optimum hydrogen uptake or high VI (>145) lube stock. The FCC gasoline produced from a Topsøe hydrocracking unit does not require post-treatment for sulfur removal.

Description: Topsøe's hydrocracking process uses well proven cocurrent downflow fixed bed reactors with state-of-the-art reactor internals and catalysts. The process uses recycle hydrogen and can be configured in partial conversion once-through feed mode or with recycle of uncoverted oil to obtain 100% conversion to diesel and lighter products. A novel HPNA removal system can be used to eliminate unconverted oil purge. Topsøe's zeolitic and amorphous hydrocracking catalysts have been proven in several commercial hydrocrackers.

Operating conditions: Typical operating pressure and temperatures range from 55 to 170 bar (800 to 2500 psig) and 340 to 420°C (645 to 780°F).

Installations: One operating licensed hydrocracking unit. Topsøe hydrocracking catalysts have been supplied to eight hydrocrackers.

Licensor: Haldor Topsøe A/S CONTACT



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Hydrocracking

Application: To convert heavy vacuum gasoil (VGO) and other low-cost cracked and extracted feedstocks into high-value, high-quality products, such as low-sulfur diesel, jet fuel, high-octane light gasoline and reformer feed via the Shell Hydrocracking Process. Unconverted or recycle oil are prime feeds for secondary processing in fluid catalytic cracking units (FCCUs), lube base oil plants and ethylene crackers.

Description: Heavy feed hydrocarbons are preheated with reactor effluent (1). Fresh hydrogen is combined with recycle gas from the cold highpressure separator, preheated with reactor effluent, and then heated in a single-phase furnace. Reactants pass via trickle flow through multi-bed reactor(s) containing proprietary pre-treat, cracking and post-treat catalysts (2). Interbed ultra-flat quench internals and high-dispersion nozzle trays combine excellent quench, mixing and liquid flow distribution at the top of each catalyst bed, which helps maximize reactor volume utilization. After cooling by feed streams, reactor effluent enters a separator system. Hot effluent is routed to fractionation (3).

Two-stage, series flow and single-stage unit design configurations are available, capable of converting a wide range of heavy feedstocks, especially heavy coker gasoils and deasphalted oils directly into clean fuels. The catalyst systems are carefully tailored for maximum yield of the desired product slate at an optimum catalyst cycle length.

Installation: Over 30 new and revamp designs installed or under design. Revamps have been implemented in own or other licensors' designs usually to debottleneck and increase feed heaviness.

Supplier: Shell Global Solutions International B.V. CONTACT



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Hydrocracking

Application: The UOP Unicracking process converts a wide variety of feedstocks into lower-molecular-weight products.

Feed: Feedstocks include atmospheric gasoil, vacuum gasoil, FCC/RCC cycle oil, coker gasoil, deasphalted oil and naphtha for production of LPG.

Products: Processing objectives include production of gasoline, jet fuel, diesel fuel, lube stocks, ethylene-plant feedstock, high-quality FCC feedstock and LPG.

Description: Feed and hydrogen are contacted with catalysts, which induce desulfurization, denitrogenation and hydrocracking. Catalysts are based upon both amorphous and molecular-sieve containing supports. Process objectives and feedstock properties determine catalyst selection and process flow scheme for a specific unit. Product from the reactor section is condensed, separated from hydrogen-rich gas and fractionated into desired products. Unconverted oil is recycled or used as lube stock, FCC feedstock or ethylene-plant feedstock.

Yields: Example:	30,000 bpsd typical vacuum gasoil feed		
	FCC cycle	Vacuum	Fluid coker
Feed type	oil blend	gasoil	gasoil
Gravity, °API	27.8	22.3	8.4
Boiling, 10%, °F	481	690	640
End pt., °F	674	1,015	1,100
Sulfur, wt%	0.54	2.4	4.57
Nitrogen, wt%	0.024	0.15	0.269

Yields, vol% of feed with principal product of diesel

Butanes	·	 3.0
Light gasoline		6.6



Heavy naphtha	11.2
Distillate	92.3
H ₂ consump., scf/bbl	1,550

Installation: Selected for more than 200 commercial units, including several converted from competing technologies. Total capacity exceeds 4.4 million bpsd.

Licensor: UOP, A Honeywell Company CONTACT

Hydrocracking, resid

Application: Desulfurization, demetalization, CCR reduction and hydrocracking of atmospheric and vacuum resids using the LC-FINING Process.

Products: Full range of high-quality distillates. Residual products can be used as fuel oil, synthetic crude or feedstock for a resid FCC, coker, visbreaker or solvent deasphalter.

Description: Fresh hydrocarbon liquid feed is mixed with hydrogen and reacted within an expanded catalyst bed (1) maintained in turbulence by liquid upflow to achieve efficient isothermal operation. Product quality is maintained constant and at a high level by intermittent catalyst addition and withdrawal. Reactor products flow to a high-pressure separator (2), low-pressure separator (3) and product fractionator (4). Recycle hydrogen is separated (5) and purified (6).

Process features include onstream catalyst addition and withdrawal. Recovering and purifying the recycled H_2 at low pressure rather than at high pressure can reduce capital cost and allows design at lower gas rates.

Operating conditions:

Reactor temperature, °F	725–840
Reactor pressure, psig	1,400–3,500
H_2 partial pressure, psig	1,000–2,700
LSHV	0.1 to 0.6
Conversion, %	40–97+
Desulfurization, %	60–90
Demetalization, %	50–98
CCR reduction, %	35–80



Yields: For Arabian heavy/Arabian light blends:

	Atm. re	esid	Vac. re	esid
Feed				
Gravity, °API	12.40	4.73	4.73	4.73
Sulfur, wt %	3.90	4.97	4.97	4.97
Ni/V, ppmw	18/65	39/142	39/142	39/142
Conversion, vol%	45	60	75	95
(1,022°F+)				
Products, vol%				
C ₄	1.11	2.35	3.57	5.53
C ₅ –350°F	6.89	12.60	18.25	23.86
350–700°F (650°F)	(15.24)	30.62	42.65	64.81
700 (650°F)–1,022°l	F (55.27)	21.46	19.32	11.92
1,022°F+	25.33	40.00	25.00	5.0
C ₅ +, °API/wt% S	23.70/0.54	22.5/0.71	26.6/0.66	33.3/0.33

Hydrocracking, resid, continued

Economics:

Investment, estimated (US Gulf Coast, 2010)				
Size, bpsd fresh feed	92,000		49,000	
\$/bpsd typical fresh feed	5,000	7,000	8,000	9,000
Utilities, per bbl fresh feed				
Fuel fired, 10 ³ Btu	56.1	62.8	69.8	88.6
Electricity, kWh	8.4	13.9	16.5	22.9
Steam (export), lb	35.5	69.2	97.0	97.7
Water, cooling, gal.	64.2	163	164	248

Installation: Nine LC-FINING units are in operation, and one LC-FINING Units are in engineering.

Reference: Gupta, A., "Chevron Lummus Global Ebullated Bed Bottomof-theBarrel Hydroconversion (LC-FINING) Process," *Handbook of Petroleum Refining Prcesses,* McGraw Hill, Third Edition.

"LC-FINING Options for Heavy Oil Upgrading," NPRA Annual Meeting, March 9–11, 2008, San Diego, Paper AM-08-33.

Licensor: Chevron Lummus Global LLC CONTACT

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Hydrocracking, slurry-phase

Application: Eni Slurry Technology (EST) is a *breakthrough technology* for the full conversion of the bottom of the barrel to distillates. The availability at industrial level of EST enables the oil industry to solve crucial needs:

Upstream:

- Valorization of increasingly heavier oils worldwide
- More profitable marketability of the world huge reserves of extraheavy oils
 - Elimination of upstream low value petcoke production

Downstream:

- Meet the declining demand of fuel oil converting surplus of refinery residues into distillates (Zero fuel oil—zero coke refinery)
- Meet the increasing demand of cleaner distillates without increase of the CDU capacity
 - Increase the refinery flexibility to supply of heavier crudes.

Description: The fresh feed is primarily sent to the fresh feed heater and then mixed with **eni** proprietary catalyst makeup and sent to the up flow slurry bubble column reactor (1). Hot hydrogen is also sent to the slurry reactor providing the thermocatalytic hydroconversion of the fresh feed. The reactor effluent is collected in the EST hot high-pressure separator (2) where a gas-vapor stream and a VGO rich stream are separated.

The gas-vapor stream is subsequently cooled and sent to the EST cold high-pressure separator (3) to separate the gas stream, rich in hydrogen, and the hydrocarbon liquid stream. The hydrogen-rich gas stream is recycled back to the slurry reactor, together with the makeup hydrogen. The VGO-rich stream from the EST hot high-pressure separator (2) is sent to the vacuum flash column (4) in order to separate the VGO product. The bottom of the vacuum flash column (4) is mostly recycled back to the Slurry Reactor while a small amount is taken out as



purge. The VGO extracted from the vacuum flash column (4) is sent to battery limit. The liquid stream from the EST cold high-pressure separator (3) is sent to the light distillates stabilizer (5) from which light distillates could be separated and sent to battery limit.

Yields: Experimental yields from EST commercial demonstration plant are (wt% on fresh feed):

C ₁ -C ₄	6–9
Naphtha	6–20
AGO	35–55
Cat feed	12–55
Purge (Bitumen)	1–2

Hydrocracking, slurry-phase, continued

Economics: Investment (basis 23,000 bpsd capacity) \$ 8,000 per bpsd

Utility requirements, typical per bbl of fresh feed	
Fuel Fired, 10 ³ kcal	45
Power, kWh	13
Water, cooling, m ³	1.5
Steam consumption (MP), kg	35

Installations: EST industrial plant (23,000 bpsd capacity) is in progress at **eni** Sannazzaro de' Burgondi Refinery at Pavia, Italy. The Engineering Contractor is Saipem. The oil in is scheduled by first half of 2013.

EST industrial plant applies the positive results obtained from the semi-scale 1,200-bpsd commercial demonstration plant (CDP). The CDP was located inside the battery limits of **eni**'s refinery at Taranto (Italy). Since startup at the end of 2005, more than 300,000 bbl of black feed were processed successfully by the CDP unit. The commercial demonstration plant is still in operation to demonstrate useful scale information, update process schemes and optimize proper operating conditions for any new feedstock.

Licensor: Eni S.p.A. CONTACT

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Hydrocracking, slurry phase

Applications: The Veba Combi Cracker (VCC) technology is a slurry phase hydrocracking/hydrogenation process for converting petroleum residues at very high conversion rates (> 95%, 524°C+) and liquid yields (above 100 vol %) into directly marketable distillates.

The process applies the principles of the former Bergius-Pier technology for primary conversion of heavy residual oils or coal into light distillates.

Description: The slurry is mixed with hydrogen (recycle and makeup) and brought to the reactor inlet temperature conditions. The operating conditions (pressure, temperature, space velocity and additive concentration) are adjusted to accomplish a greater than 95% conversion of the residuum in a once-through mode of operation. The slurry phase reactor has no internals and is operated in an up-flow mode.

The unconverted residual oil and the additive are separated from the vaporized reaction products and the recycle gas in a hot separator. The hot-separator bottom product is fed into a vacuum flasher for additional distillate recovery. The recovered distillates are routed to a directly coupled hydrotreating stage together with the hot-separator overhead products.

The hydrotreating stage is typically a catalytic fixed-bed reactor operated under essentially the same pressure as the primary conversion stage. This second stage may be designed for either hydrotreating or hydrocracking applications.

Additional low-value refinery streams such as gasoils, deasphalted oils or FCC cycle oils may also be directly added to the second stage. Products from the second stage are cooled, and depending on the owner's needs, the recovered liquids may be stripped for synthetic crude oil production or fractionated to produce finished saleable distillate products.

The vapor stream is typically stripped of its impurities, and the resultant hydrogen-rich gas stream is recycled to the slurry reactor to maintain the desired treat rate and hydrogen partial pressure.



The unit operates essentially in a once-thru mode, and the asphaltenes conversion is typically above 90%, thus differentiating this technology from other competing processes. KBR's additive composition and structure provides for a reliable entrapment and removal of the unconverted high metals containing residual material, essentially eliminating fouling tendencies.

Economics: Since the VCC adopts a once-through slurry-phase reactor system, the unit is capable of operating at 35,000 bpsd or higher using a single-reactor-train system. When compared to ebullated-bed technologies, the diameter and weight of the reactor are substantially lower.

Based upon a comparative study on an actual refinery, KBR estimates that the net present value and the internal rate of return for the VCC process will outperform delayed cokers when benchmark crude prices exceed \$50/bbl.

Hydrocracking, slurry phase, continued

For a VCC residue upgrading refinery unit, the ISBL cost on the US Gulf Coast, Q1 2011 basis is estimated at approximately \$10,000-\$12,000/bpd capacity.

Installations: Commercial units that either licensed or practiced the VCC process are:

Location	Feed	Capacity, Metric tpy	Remarks
Leuna	Lignite, Lignite tar	600,000	Operated until 1965
Böhlen	Lignite tar pitch	250,000	
Magdeburg	Lignite tar pitch	220,000	
Scholven	Hard coal	280,000	Operated until 1964 on residue
Welheim	Tar pitch	130,000	
Gelsenberg	Hard coal	400,000	Operated until 1967 on Residue
Zeitz	Lignite tar pitch	280,000	
Lützkendorf	Tar pitch and oil	50,000	
Pölitz	Hard coal, oil	700,000	
Wesseling	Lignite	250,000	Currently operating as VGO hydrocracker
Brüx	Lignite tar pitch	600,000	
Blechhammer	Hard coal, tar	420,000	
Location	Feed	Capacity, BPD	Remarks
Bottrop	Lignite, residues, waste plastics	3,500	Operated until 2001
Scholven	Residues, bitumen	200	Currently operating as deep aromatic saturation unit
Oslo Project Canada OMW Germany China China	Canadian bitumen Refinery residues Heavy oil Refinery VR, Refinery VR+Coal	85,000 25,000 Not disclosed Not disclosed	Project cancelled after detailed engineering Project cancelled after extended basic engineering Start up 2012 Start up 2013
	Location Leuna Böhlen Magdeburg Scholven Welheim Gelsenberg Zeitz Lützkendorf Pölitz Wesseling Brüx Blechhammer Location Bottrop Scholven Oslo Project Canada OMW Germany China China	LocationFeedLeunaLignite, Lignite tarBöhlenLignite tar pitchMagdeburgLignite tar pitchScholvenHard coalWelheimTar pitchGelsenbergHard coalZeitzLignite tar pitchLützkendorfTar pitch and oilPölitzHard coal, oilWesselingLignite tar pitchBrüxLignite tar pitchBlechhammerHard coal, tarLocationFeedBottropLignite, residues, waste plasticsScholvenCanadian bitumenOslo Project CanadaCanadian bitumenOMW GermanyHeavy oilChinaHeavy oilChinaRefinery VR, Refinery VR+Coal	LocationFeedCapacity, Metric tpyLeunaLignite, Lignite tar600,000BöhlenLignite tar pitch250,000MagdeburgLignite tar pitch220,000ScholvenHard coal280,000WelheimTar pitch130,000GelsenbergHard coal400,000ZeitzLignite tar pitch280,000LützkendorfTar pitch and oil50,000PölitzHard coal, oil700,000VesselingLignite tar pitch250,000BrüxLignite tar pitch600,000BlechhammerHard coal, al700,000BottropLignite tar pitch600,000BottropLignite, residues, waste plastics Scholven3,500 200Oslo Project CanadaCanadian bitumen Refinery residues85,000 25,000OMW GermanyCanadian bitumen Refinery VR, Refinery VR+CoalNot disclosedChinaRefinery VR, Refinery VR+CoalNot disclosed

Reference: "Slurry-phase hydrocracking—possible solution to refining margins," *Hydrocarbon Processing,* February 2011, pp. 37–43.

Licensors: KBR and BP CONTACT

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Hydrocracking—residue

Application: H-Oil_{RC} is an ebullated-bed process for hydrocracking atmospheric or vacuum residue. It is the ideal solution for feedstocks having high metal, CCR and asphaltene contents. The process can have two different objectives: at high conversion, to produce stable products; or, at moderate conversion, to produce a synthetic crude oil.

Description: The flow diagram illustrates a typical H-Oil_{RC} unit that includes oil and hydrogen fired heaters, an optional inter stage separator, an internal recycle cup providing feed to the ebullating pump, high pressure separators, recycle gas scrubber and product separation and fractionation (not required for synthetic crude oil production).

Catalyst is replaced periodically in the reactor, without shutdown.

Different catalysts are available as a function of the feedstock and the required objectives. An H-Oil_{RC} unit can operate for three-year run lengths at constant catalyst activity with conversion in the 50–80% range and hydrodesulfurization as high as 85%.

Operating conditions:

Temperature	770–820°F/410–438°C
Hydrogen partial pressure	1,600–1,950 psi/110–135 bar
LHSV, hr ^{_1}	0.25–0.6
Conversion, wt%	50–80

Examples: Ural VR feed: a 540°C+ cut from Ural crude is processed at 66% conversion to obtain a stable fuel oil containing less than 1%wt sulfur, 25% diesel and 30% VGO. The diesel cut is further hydrotreated to meet ULSD specifications using an integrated Prime-D unit. **Arab Medium VR feed:** a vacuum residue from a blend 70% Arab Light-30% Arab Heavy containing 5.5wt% sulfur is processed at above 75% conversion to obtain a stable fuel oil with 2wt% sulfur.

Economics: Basis 2008 US Gulf Coast



Investment in \$ per bpsd	5,100–7,400
Utilities, per bbl of feed	
Fuel, 10 ³ Btu	70
Power, kWh	11
Catalyst makeup, lb	0.2-0.8

Installation: There are 13 H-Oil_{RC} units, six in operation and four under design/construction, with a total capacity of 19.57 metric tpy. Three additional references for H-Oil_{DC} , the ebullated bed technology for VGO and DAO, add another 11.45 metric tpy.

Reference: "Resid hydrocracker produces low-sulfur diesel from difficult feed," *Hydrocarbon Processing*, May 2006.

Licensor: Axens CONTACT

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Hydrodearomatization

Application: Topsøe's two-stage hydrodesulfurization hydrodearomatization (HDS/HDA) process is designed to produce low-aromatics distillate products. This process enables refiners to meet the new, stringent standards for environmentally friendly fuels.

Products: Ultra-low sulfur, ultra-low nitrogen, low-aromatics diesel, kerosine and solvents (ultra-low aromatics).

Description: The process consists of four sections: initial hydrotreating, intermediate stripping, final hydrotreating and product stripping. The initial hydrotreating step, or the "first stage" of the two-stage reaction process, is similar to conventional Topsøe hydrotreating, using a Topsøe high-activity base metal catalyst such as TK-607 BRIM to perform deep desulfurization and deep denitrification of the distillate feed. Liquid effluent from this first stage is sent to an intermediate stripping section, in which H₂S and ammonia are removed using steam or recycle hydrogen. Stripped distillate is sent to the final hydrotreating reactor, or the "second stage." In this reactor, distillate feed undergoes saturation of aromatics using a Topsøe noble metal catalyst, either TK-907/TK-911 or TK-915, a high-activity dearomatization catalyst. Finally, the desulfurized, dearomatized distillate product is steam stripped in the product stripping column to remove H₂S, dissolved gases and a small amount of naphtha formed.

Like the conventional Topsøe hydrotreating process, the HDS/HDA process uses Topsøe's graded bed loading and high-efficiency patented reactor internals to provide optimum reactor performance and catalyst use leading to the longest possible catalyst cycle lengths. Topsøe's high efficiency internals have a low sensitivity to unlevelness and are designed to ensure the most effective mixing of liquid and vapor streams and maximum utilization of catalyst. These internals are effective at high liquid loadings, thereby enabling high turndown ratios. Topsøe's graded-bed technology and the use of shape-optimized inert topping



and catalysts minimize the build-up of pressure drop, thereby enabling longer catalyst cycle length.

Operating conditions: Typical operating pressures range from 20 to 60 barg (300 to 900 psig), and typical operating temperatures range from 320°C to 400°C (600°F to 750°F) in the first stage reactor, and from 260°C to 330°C (500°F to 625°F) in the second stage reactor. An example of the Topsøe HDS/HDA treatment of a heavy straight-run gas oil feed is shown below:

	Feed	Product
Specific gravity	0.86	0.83
Sulfur, ppmw	3,000	1
Nitrogen, ppmw	400	< 1
Total aromatics, wt%	30	< 10
Cetane index, D-976	49	57

Hydrodearomatization, continued

References: Cooper, Hannerup and Søgaard-Andersen, "Reduction of aromatics in diesel," *Oil and Gas,* September 1994.

de la Fuente, E., P. Christensen, and M. Johansen, "Options for meeting EU year 2005 fuel specifications," 4th ERTC, Paris, November 1999.

Ghiyati, Y., "Technology options for LCO upgrading," ME-TECH, Dubai, January 2011.

Installation: A total of nine units.

Hydrofinishing

Application: Deeply saturate single- and multiple-ring aromatics in base-oil feedstocks. The product will have very low-aromatics content, very high-oxidation stability and high thermal stability.

Description: ISOFINISHING catalysts hydrogenate aromatics at relatively low reaction temperatures. They are especially effective in complete polyaromatics saturation—a reaction that is normally equilibrium limited. Typical feedstocks are the effluent from a dewaxing reactor, effluent from hydrated feeds or solvent-dewaxed feedstocks. The products are highly stabilized base-oil, technical-grade white oil or food-grade white oil.

As shown in the simplified flow diagram, feedstocks are mixed with recycle hydrogen and fresh makeup hydrogen, heated and charged to a reactor containing ISOFINISHING Catalyst (1). Effluent from the finishing reactor is flashed in high-pressure and low-pressure separators (2, 3). A very small amount of light products are recovered in a fractionation system (4).

Yields: For a typical feedstock, such as dewaxing reactor effluent, the yield can be >99%. The chemical-hydrogen consumption is usually very low, less than $\sim 10 \text{ Nm}^3/\text{m}^3$ oil.

Economics:

Investment: For a stand-alone ISOFINISHING Unit, the ISBL capital is about 3,500–5,700 \$/bpsd, depending on the pressure level and size.

Utilities: Typical per bbl feed:

Power, kW	2.6
Fuel, kcal	3.4 x 10 ³



Installation: Twenty-eight units are in various stages of operation, construction or design.

Reference: NPRA Annual Meeting, March 2004, San Antonio, Paper AM-04-68.

Licensor: Chevron Lummus Global LLC CONTACT

Hydrofinishing/hydrotreating

Application: Process to produce finished lube-base oils and special oils.

Feeds: Dewaxed solvent or hydrogen-refined lube stocks or raw vacuum distillates for lubricating oils ranging from spindle oil to machine oil and bright stock.

Products: Finished lube oils (base grades or intermediate lube oils) and special oils with specified color, thermal and oxidation stability.

Description: Feedstock is fed together with make-up and recycle hydrogen over a fixed-bed catalyst at moderate temperature and pressure. The treated oil is separated from unreacted hydrogen, which is recycled. Very high yields product are obtained.

For lube-oil hydrofinishing, the catalytic hydrogenation process is operated at medium hydrogen pressure, moderate temperature and low hydrogen consumption. The catalyst is easily regenerated with steam and air.

Operating pressures for hydrogen-finishing processes range from 25 to 80 bar. The higher-pressure range enables greater flexibility with regard to base-stock source and product qualities. Oil color and thermal stability depend on treating severity. Hydrogen consumption depends on the feed stock and desired product quality.

Utility requirements (typical, Middle East crude), units per m³ of feed:

Electricity, kWh	15
Steam, MP, kg	25
Steam, LP, kg	45
Fuel oil, kg	3
Water, cooling, m^3	10



Installation: Numerous installations using the Uhde (Edeleanu) proprietary technology are in operation worldwide. The most recent reference is a complete lube-oil production facility licensed to the state of Turkmenistan.

Licensor: Uhde GmbH CONTACT

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Hydrogen

Application: Hydrogen production with low/no export steam production from hydrocarbon feedstocks, such as natural gas, LPG, butane, naphtha, refinery offgases, etc., using the Haldor Topsøe radiant-wall Topsøe Bayonet Reformer (TBR). Plant capacities range from 5,000 Nm³/h to more than 170,000 Nm³/h hydrogen (150⁺ MMscfd H₂) and hydrogen purity of up to 99.999+%

Description: The Haldor Topsøe TBR-based hydrogen plant is developed for low export-steam hydrogen production and is tailor-made to suit the customer's needs with respect to feedstock flexibility and economics. A typical plant comprises feedstock desulfurization, pre-reforming, TBR reforming, shift reaction and pressure swing adsorption (PSA) purification to obtain product grade hydrogen. PSA offgas is used as fuel in the TBR reformer. Excess heat in the plant is efficiently used for process heating and steam generation.

A unique feature of the TBR is high thermal efficiency. Sensible heat in the process gas is recycled to the steam reforming reaction in the bayonet tube. The high thermal efficiency is utilized to design an energy efficient plant and reduce the size of the radiant-wall reformer.

Economics: TBR-based hydrogen plants provide the customer with a low investment cost and low operating expenses for hydrogen production when steam has low value. A hydrocarbon consumption of down to 3.28 Gcal/1,000 Nm³ hydrogen (348 MMBtu/scf H₂) is achieved depending on capacity and feedstock.



References: Heseler-Carstensen, J., "Additional hydrogen capacity by heat exchange reforming" NPRA, May 2010.

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Hydrogen

Application: Production of high-purity hydrogen (H_2) from hydrocarbon (HC) feedstocks, using the steam reforming process.

Feedstocks: Ranging from natural gas, LPG to naphtha as well as potential refinery offgases (ROG). Several modern hydrogen plants designed by TECHNIP have multiple feedstock flexibility.

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

Feed pre-treatment normally involves catalytic removal of sulfur, chlorine and other contaminants detrimental to downstream catalysts. The treated feed gas mixed with process steam is sent to the fired steam reformer (or adiabatic pre-reformer upstream when applied) after necessary superheating.

The net reforming reaction is strongly endothermic and the heat is supplied externally by combustion of PSA purge gas, supplemented by make-up fuel in multiple burners in a top-fired reformer. Reforming severity is optimized for each specific case mainly in terms of S/C ratio and outlet temperature. The reformer effluent is essentially an equilibrium mixture and is cooled though HP-steam generation in the PG boiler before going for shift conversion, where a major portion of carbon monoxide (CO) further converts to hydrogen.

The heat recovery fom the flugas exiting the firebox is achieved in the convection section (vertical or horizontal) and its configuration largely impacts the amount of export steam.

The process condensate resulting from heat recovery and cooling is separated and generally re-utilized in the steam system after necessary treatment. The entire steam generation is usually on natural circulation, which adds to high reliability. The cooled process gas flows to the PSA unit that provides high-purity hydrogen product (typically



< 10 ppmv total carbon oxides and in some cases < 1ppmv CO).

Typical specific energy consumptions based on feed + fuel – export steam range between 3 to 3.4 Gcal/KNm³ (320 to 360 Btu/scf) LHV, depending upon the feedstock, plant capacity and heat recovery optimization. Recent advances include high-purity export steam, gas turbine integration for steam-power synergy, environmental performance and recuperative reforming for capacity retrofit, thus lowering the hydrogen plant C-footprint.

Installation: TECHNIP, maintaining a leading market share, has designed over 260 hydrogen plants worldwide covering a wide range of capacities ranging from 12 to 530 tpd (5–220 MMscfd). Most of these installations are for refinery application with basic features for high reliability (99.5%+ excluding forced outage) as well as optimized efficiency and installed cost.

Licensor: TECHNIP CONTACT

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Hydrogen

Application: Production of hydrogen for refinery applications and petrochemical and other industrial uses.

Feed: Natural gas, refinery offgases, LPG, naphtha or mixtures thereof or any other feedstocks.

Product: High-purity hydrogen (typically >99.9%), CO, CO₂, HP steam and/or electricity may be produced as separate creditable byproduct.

Description: The plant generally comprises four process units. The feed is desulfurized, mixed with steam and converted to synthesis gas in steam reformer over a nickel containing catalyst at 20–40 bar pressure and outlet temperatures of typically 860°C–890°C for hydrogen production. The synthesis gas is further treated in the adiabatic carbon monoxide (CO) shift and the pressure swing adsorption unit to obtain high-purity hydrogen. Process options include feed evaporation, adiabatic feed prereforming and/or HT/LT shift to process, e.g., heavier feeds and/or optimize feed/fuel consumption and steam production.

Uhde's design enables maximizing process heat recovery and optimizing energy efficiency with operational safety and reliability. The Uhde's steam reformer features a well-proven top-fired design with tubes made of centrifugally cast alloy steel and a unique proprietary "cold" outlet manifold system for enhanced reliability. AA special feature further speciality is Uhde's bi-sectional steam system for the environment-friendly full recovery of process condensate and production of contaminant-free high-pressure export steam (3) with a proven process gas cooler design.

The Uhde steam reformer concept also includes a modularized shop-tested convection bank to maximize plant quality and minimize construction risks. Uhde usually offers tailor-made designs based on either their own or the customer's design standards. The hydrogen plant is often fully integrated into the refinery, particularly with respect to



steam production and use of refinery waste gases. Uhde has extensive experience and expertise in the construction of highly reliable reformers with hydrogen capacities of up to 220,000 Nm³/h (197 MMscfd). Recent developments include the reduction of CO₂-emissions while using removed CO₂ for sequestration or enhanced oil recovery (EOR).

Economics: Depending on the individual plant concept, the typical consumption figure for natural gas based plants (feed + fuel – steam) may be as low as 3.05 Gcal /1,000 Nm³ (324 MMBtu/MMscf).

Installation: Uhde is currently executing several designs for hydrogen plants. These include a 150,000 Nm³/134 MMscfd plant for Shell in Canada and a 91,000 Nm³/h/81 MMscfd plant for Bayernoil in Ger-

Hydrogen, continued

many. In addition, Uhde is building a multi-feedstock hydrogen plant for an Italian refiner and a naphtha and natural- gas fed plant for Neste Oil OYJ of Finland. Uhde has also successfully started up Europe's largest hydrogen plant for Neste Oil OYJ with a capacity of 155,000 Nm³/h (139 MMscfd). This plant features, among others, a unit to reduce CO_2 emissions.

References: Ruthardt, K. and M. Smith, "Reliability and availability," *Hydrocarbon Engineering*, February 2008.

Ruthardt, K., K. R. Radtke and J. Larsen, "Hydrogen trends," *Hydrocarbon Engineering*, November 2005, pp. 41–45.

Michel, M., "Design and Engineering Experience with Large-Scale Hydrogen Plants," *Oil Gas European Magazine,* Vol. 30 (2004) No. 2 in: Erdöl Erdgas Kohle Vol. 120 (2004) No. 6, pp. OG 85–88.

Licensor: Uhde GmbH CONTACT

НОМ

Hydrogen, recovery

Application: To recover and purify hydrogen or to reject hydrogen from refinery, petrochemical or gas processing streams using a PRISM membrane. Refinery streams include hydrotreating or hydrocracking purge, catalytic reformer offgas, fluid catalytic cracker offgas or fuel gas. Petrochemical process streams include ammonia synthesis purge, methanol synthesis purge or ethylene offgas. Synthesis gas includes those generated from steam reforming or partial oxidation.

Product: Typical hydrogen (H₂) product purity is 90%–98% and, in some cases, 99.9%. Product purity is dependent upon feed purity, available differential partial pressure and desired H₂ recovery level. Typical H₂ recovery is 80%–95% or more.

The hydrocarbon-rich nonpermeate product is returned at nearly the same pressure as the feed gas for use as fuel gas, or in the case of synthesis gas applications, as a carbon monoxide (CO) enriched feed to oxo-alcohol, organic acid, or Fisher-Tropsch synthesis.

Description: Typical PRISM membrane systems consist of a pretreatment (1) section to remove entrained liquids and preheat feed before gas enters the membrane separators (2). Various membrane separator configurations are possible to optimize purity and recovery, and operating and capital costs such as adding a second stage membrane separator (3). Pretreatment options include water scrubbing to recover ammonia from ammonia synthesis purge stream.

Membrane separators are compact bundles of hollow fibers contained in a coded pressure vessel. The pressurized feed enters the vessel and flows on the outside of the fibers (shell side). Hydrogen selectively permeates through the membrane to the inside of the hollow fibers (tube side), which is at lower pressure. PRISM membrane separators' key benefits include resistance to water exposure, particulates and low feed to nonpermeate pressure drop.



Membrane systems consist of a pre-assembled skid unit with pressure vessels, interconnecting piping, and instrumentation and are factory tested for ease of installation and commissioning.

Economics: Economic benefits are derived from high-product recoveries and purities, from high reliability and low capital cost. Additional benefits include relative ease of operation with minimal maintenance. Also, systems are expandable and adaptable to changing requirements.

Installations: Over 400 PRISM H_2 membrane systems have been commissioned or are in design. These systems include over 80 systems in refinery applications, 210 in ammonia synthesis purge and 50 in synthesis gas applications.

Licensor: Air Products and Chemicals, Inc. CONTACT

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Hydrogenation

Application: The CD*Hydro* process is used to selectively hydrogenate diolefins in the top section of a hydrocarbon distillation column. Additional applications—including mercaptan removal, hydroisomerization and hydrogenation of olefins and aromatics are also available.

Description: The patented CD*Hydro* process combines fractionation with hydrogenation. Proprietary devices containing catalyst are installed in the fractionation column's top section (1). Hydrogen is introduced beneath the catalyst zone. Fractionation carries light components into the catalyst zone where the reaction with hydrogen occurs. Fractionation also sends heavy materials to the bottom. This prevents foulants and heavy catalyst poisons in the feed from contacting the catalyst. In addition, clean hydrogenated reflux continuously washes the catalyst zone. These factors combine to give a long catalyst life. Additionally, mercaptans can react with diolefins to make heavy, thermally-stable sulfides. The sulfides are fractionated to the bottoms product. This can eliminate the need for a separate mercaptan removal step. The distillate product is ideal feedstock for alkylation or etherification processes.

The heat of reaction evaporates liquid, and the resulting vapor is condensed in the overhead condenser (2) to provide additional reflux. The natural temperature profile in the fractionation column results in a virtually isothermal catalyst bed rather than the temperature increase typical of conventional reactors.

The CD*Hydro* process can operate at much lower pressure than conventional processes. Pressures for the CD*Hydro* process are typically set by the fractionation requirements. Additionally, the elimination of a separate hydrogenation reactor and hydrogen stripper offers significant capital cost reduction relative to conventional technologies.

Feeding the CD*Hydro* process with reformate and light-straight run for benzene saturation provides the refiner with increased flexibility to produce low-benzene gasoline. Isomerization of the resulting C_5/C_6



overhead stream provides higher octane and yield due to reduced benzene and C_7^+ content compared to typical isomerization feedstocks.

Economics: Fixed-bed hydrogenation requires a distillation column followed by a fixed-bed hydrogenation unit. The CD*Hydro* process eliminates the fixed-bed unit by incorporating catalyst in the column. When a new distillation column is used, capital cost of the column is only 5% to 20% more than for a standard column depending on the CD*Hydro* application. Elimination of the fixed-bed reactor and stripper can reduce capital cost by as much as 50%.

Installation: There are 50 CD*Hydro* units are commercially licensed for C_4 , C_5 , C_6 , LCN and benzene hydrogenation applications. Twenty units have been in operation for more than five years and total commercial operating time now exceeds 100 years for CD*Hydro* technologies. Eleven units are currently in engineering/construction.

Licensor: Lummus Technology, a CB&I company CONTACT

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Hydrogenation, selective for MTBE/ETBE C₄ raffinates

Application: To achieve selective hydrogenation of butadiene to n-butenes in a catalytic distillation column.

Description: The C₄ CD*Hydro* catalytic distillation technology processes C₄ streams from refineries or steam crackers within an methyl tertiary butyl ether (MTBE)/ethyl tertiary butyl ether (ETBE) debutanizer to produce a raffinate with a high butylenes content that is essentially butadiene-free. After methanol recovery, the treated C₄ raffinate can be used for butene-1 production or alkylation feed.

Selective hydrogenation increases butenes available for alkylation or isomerization, reduces acid consumption in alkylation units, and greatly improves the quality of HF alkylate. The process uses commercially available catalyst in its proprietary catalytic distillation structures (CD*Modules*).

The C_4 stream is combined with hydrogen in the MTBE/ETBE debutanizer. Treated C_4 raffinate is taken overhead. The washing action of the reflux minimizes oligomer formation, flushing heavy compounds from the catalyst and promoting long catalyst life. Excess hydrogen and lights are vented from the overhead drum. The catalyst is sulfur tolerant. Feed sulfur compounds react with diolefins to form heavy compounds that exit in the tower bottoms with the MTBE/ETBE product. The distillate product is essentually mercaptan-sulfur free.

Process advantages include:

- Low capital cost
- Low catalyst requirements
- Low operating cost
- High product yield (low saturation to paraffins)
- No polymer recycle across catalyst
- Use of reaction heat



- Sulfur tolerant catalyst
- Essentially mercaptan-sulfur-free distillate product
- Flexible butene-1/butene-2 ratio
- Retrofit to existing C₄ columns
- All carbon steel construction.

Economics: Capital costs are considerably lower than conventional hydrotreaters since the single column design eliminates costs associated with fixed-bed systems. The C_4 CD*Hydro* process would typically be installed in a conventional or catalytic MTBE/ETBE debutanizer, either as a retrofit or in a new column.

Installation: There are 50 total commercially licensed CD*Hydro* units, 11 of which are currently in design or construction.

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Hydrogenation, selective for refinery C₅ feeds

Application: To process C_5 streams from refineries to produce a stream with high isoamylenes content that is essentially free of diolefins. The treated C_5 stream is suitable for tertiary amyl methyl ether (TAME) production or alkylation feed.

Description: The patented C_5 CD*Hydro* process achieves selective hydrogenates diolefins to amylenes in a catalytic distillation column. Selective hydrogenation is a required pretreatment step for TAME production and C_5 alkylation, improving product quality in both, and reducing acid consumption in the latter.

The process uses commercially available catalyst in proprietary catalytic distillation structures. The unique catalytic distillation column combines reaction and fractionation in a single unit operation. This constant pressure boiling system assures precise temperature control in the catalyst zone. Low reaction temperature and isothermal operation enhance selectivity and minimize yield losses to paraffins. Non-reactive 3-methyl butene-1 is isomerized to reactive 2-methyl butene-2, which increases potential TAME production. Pentene-1 is isomerized to pentene-2, which improves octane number.

Refinery C_5 streams are combined with hydrogen in the catalytic column. Treated C_5 products are taken overhead. The washing action of the reflux minimizes oligomer formation, flushing heavy compounds from the catalyst and promoting long catalyst life. The catalyst will react acidic sulfur compounds with diolefins to form heavy compounds, which exit in the tower bottoms. The distillate product is essentially mercaptan-sulfur-free.

Economics: Capital costs are considerably lower than conventional hydrotreaters since the single column design eliminates costs associated with fixed-bed systems. Additionally, the ability to remove acidic sulfur



compounds eliminates the need for sweetening. The C_5 CD*Hydro* process would typically be installed in a depentanizer, either as a retrofit or in a new column.

Process advantages include:

- Low operating pressure
- Low operating cost
- High product yield (low paraffin make)
- No polymer recycle across catalyst
- No sweetening required
- Essentially mercaptan sulfur-free distillate product
- Flexible butene-1/butene-2 ratio
- Retrofit to existing C₄ columns
- All carbon steel construction
- Isomerization option
- No hydrogen compressor.

Hydrogenation, selective for refinery C₅ feeds, continued

Installation: There are 50 total commercially licensed CD*Hydro* units, 11 of which are currently in design or construction.

Licensor: Lummus Technology, a CB&I company CONTACT

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Hydrogenation/ hydrodesulfurization

Application: The smart configuration can be applied for selective hydrogenation/hydroisomerization, aromatic saturation and hydrodesulfurization (HDS) of gasoline, kerosine and diesel/distillate desulfurization. In addition, this process can be used for the selective hydrogenation of acetylene, MAPD, $C_3/C_4/C_5/C_6/C_7$ and LCN, hydroisomerization, benzene saturation and hydrodesulfurization of gasoline, kerosine and diesel/distillate. Multiple catalyst types provide the best performance and lower cost with optimum configuration. The RHT process operates the distillation and reaction units at optimum conditions and integrates the stabilizer with the main distillation column thereby reducing CAPEX and OPEX. By taking multiple draws off from distillation column, it is possible to obtain the highest conversion, high selectivity with low operating costs. The processes apply optimum catalyst and conditions to obtain the best results. The process is optimized for energy consumption via heat integration to provide low CAPEX and OPEX.

Description:

RHT-Hydrogenation: In the RHT- Hydrogenation process (flow diagram A), the hydrocarbon feed is sent to the distillation column where the feed is treated and taken as a side draw or multiple draw offs. The feed can be treated in an optimum way for catalyst/reactor utilization. Additional liquid is needed to dilute the feed and to maintain reaction temperature. The feed is mixed with sufficient hydrogen to maintain the required for reaction before entering the reactor. The side draw is mixed with liquid from the heat sink and is heated to the reactor temperature. The reactor effluent is sent back to the distillation column to remove light ends/hydrogen at top, and the product is taken as side draw after the pasteurization section. The bottom product does not require further treatment except in the isomerization option.



The process uses metal catalyst used for hydrogenation. Most commonly used catalysts are Pt/Pd, Pd/Ag, Pd, Ni, Ni/Mo, and Co/Mo on silica or alumina base. (Catalysts such as zeolite/Pt can be used aromatic saturation). The process can be optimized for multiple or single catalyst to provide best catalyst utilization and lower cost. The multiple side draws allows heat sink and highest conversions and selectivity required

Hydrogenation/hydrodesulfurization, continued

for the process/olefins or saturation. The process uses lower pressure than conventional processes and can work in single phase or two phase reactor operation.

RHT-HDS: FCC Gasoline: The RHT- HDS process (flow diagram B) can be used for FCC gasoline. Processing scheme for straight-run naphtha, heavy gasoil and diesel is similar to conventional schemes. The FCC gasoline is mixed with hydrogen and is heated to moderate temperature. The feed is sent to the selective hydrogenation reactor to remove diolefins to prevent the formation of gums and polymers and coking on the HDS catalyst. The reactor operates in two phases or single phase down-flow reaction mode. Reactor effluent is sent to the splitter where light cut naphtha (LCN) is taken as side-draw overhead and heavy cut naphtha (HCN) is taken from the bottom and medium cut naphtha (MCN) is taken as side draw. The LCN is almost sulfur-free and contains less than 3 to 5 wppm mercaptans and other sulfur compounds. DMS is essentially eliminated or minimized.

The HCN is taken from bottom of the splitter and is mixed with hydrogen required for HDS and is heated to the desulfurization temperature in the furnace. The feed is fed to the HDS reactor in downflow mode. The HDS occurs in the catalyst zone at high temperatures to support high desulfurization rates HCN, which contains the maximum sulfur level and is the most refractory. The MCN is also mixed with hydrogen and heated to the reactor temperature and is sent the HDS reactor around the middle of reactor. The space velocity for HCN and MCN depends on the total sulfur concentration in both streams and the sulfur-containing species. Another consideration for the catalyst quantity is based on the product specifications required. The reactor effluent is sent to stabilizer, where residual sulfur is driven from the MCN and HCN product and is taken as the bottom product from stabilizer.

The catalyst used for first reactor for selective hydrogenations are Pt/Pd, Pd, Ni, Ni//W or Ni/Mo depending upon the feed and operating

conditions selected. Catalyst required for HDS include Co/ Mo, Ni/W or Ni/Mo. RHT processes do not use any internals. Additionally, if the capacity must be increased for future processes with special internals become a bottleneck and one has to install complete additional train, which is very expensive.

RHT-HDS: Gasoil/diesel: RHT has a configuration to desulfurize the crude and vacuum unit pumparound and main fractionators side draws at the location with staggered pressures so that hydrogen can be spilled into lower pressure unit, gasoil, diesel/kerosine/naphtha in that order. The flow schemes are similar to conventional processes with reactor internals designed to meet high-distribution efficiency. The catalyst is same as mentioned above earlier, e.g., Co/Mo, Ni/W, Ni/Mo. Zeolite/Pt catalyst and Ni is used for light cycle oil (LCO) aromatic saturation and ring opening.

Economics: 1Q 2006 Gulf coast Basis;

RHT-Hydrogenation:

CAPEX (ISBL facility only), \$/bbl	517
Utilities and catalyst, \$/bbl	0.25
RHT-HDS:	
Capex (ISBL facility only), \$/bbl	980
Utilities and catalyst, \$/bbl	1.26

Product properties: Hydrogenation stream meets the diolefin specification as required with high selectivity. For HDS, the product sulfur specifications are met below 10 wppm.

Installation: Technology is ready for commercialization.

Licensor: Refining Hydrocarbon Technologies LLC CONTACT

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Hydrogenation, benzene in reformate

Application: The CD*Hydro* catalytic distillation technology processes reformate streams from refineries to reduce benzene to levels required by low-benzene gasoline specifications.

Description: The patented CD*Hydro* process achieves hydrogenation of benzene to cyclohexane in a catalytic distillation column. Hydrogenation reduces benzene in the gasoline pool. The process uses commercially available catalyst in proprietary catalytic distillation structures.

Selective hydrogenation: Reformate and hydrogen are fed to the catalytic distillation column. Hydrogenation of benzene to cyclohexane can exceed 99%. Benzene conversion can easily be limited to lower levels through control of hydrogen addition. Washing action of the reflux minimizes oligomer formation, flushes heavy compounds from the catalyst and promotes long catalyst life. Treated C₆ product is taken as overhead. Excess hydrogen and lights are recycled and vented from the overhead drum. The C₇+ product is taken as bottom with essentially full recovery of heavy aromatics.

The unique catalytic distillation column combines reaction and fractionation in a single unit operation. This constant-pressure boiling system assures precise temperature control in the catalyst zone. Low reaction temperature and isothermal operation enhance safety.

Economics: Capital costs are considerably lower than conventional hydrotreaters since the single-column design eliminates costs associated with fixed-bed systems and operates at low enough pressure to avoid the need for a hydrogen compressor. The CD*Hydro* process would typically be installed in a benzene-toluene splitter, either as a retrofit or in a new column.

Advantages:

- Lower capital cost
- High conversion



- Simple operation
- Low operating pressure
- Low operating cost
- Low capital cost
- Low benzene in reformate
- All carbon steel construction
- No hydrogen compressor
- Isothermal operation
- Reduced plot area.

Installation: There are six operational units, the oldest in operation since 1995.

Licensor: Lummus Technology, a CB&I company CONTACT

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Hydrogenation, selective for refinery C₄ feeds

Application: To process C_4 streams from refineries to produce a stream with high butylenes content that is essentially butadiene-free, suitable for methyl tertiary butyl ether (MTBE) production, butene-1 production or alkylation feed.

Description: The patented C_4 CD*Hydro* process achieves selective hydrogenation of butadiene to n-butenes in a catalytic distillation column. Selective hydrogenation increases butenes available for alkylation or isomerization, reduces acid consumption in alkylation units, and greatly improves the quality of HF alkylate. The process uses commercially available catalyst in proprietary catalytic distillation structures.

The unique catalytic distillation column combines reaction and fractionation in a single unit operation. This constant pressure boiling system assures precise temperature control in the catalyst zone. Low reaction temperature and isothermal operation enhance selectivity and minimize yield losses to paraffins. Isomerization of butene-1 to butene-2 can be maximized to improve HF alkylate quality or minimized for increased butene-1 recovery.

Refinery C_4 streams are combined with hydrogen in the catalytic column. Treated C_4 products are taken overhead. The washing action of the reflux minimizes oligomer formation, flushing heavy compounds from the catalyst and promoting long catalyst life. Excess hydrogen and lights are vented from the overhead drum. The catalyst will react acidic sulfur compounds with diolefins to form heavy compounds which exit in the tower bottoms. The distillate product is essentially mercaptan-sulfur-free.

Economics: Capital costs are considerably lower than conventional hydrotreaters since the single column design eliminates costs associated with fixed-bed systems. Additionally, the ability to remove acidic sulfur compounds eliminates the need for sweetening. The C_4 CD*Hydro* process would typically be installed in a debutanizer, either as a retrofit or in a new column.



Process advantages include:

- Low operating pressure
- Low operating cost
- High product yield (low paraffin make)
- No polymer recycle across catalyst
- No sweetening required
- Essentially mercaptan sulfur-free distillate product
- Flexible butene-1/butene-2 ratio
- Retrofit to existing C₄ columns
- All carbon steel construction
- Isomerization option
- No hydrogen compressor.

Installation: There are 50 total commercially licensed CD*Hydro* units, 11 of which are in design or under construction.

Licensor: Lummus Technology, a CB&I company CONTACT

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Hydrogen—HTCR and HTCR twin plants

Application: Produce hydrogen from hydrocarbon feedstocks such as: natural gas, LPG, naphtha, refinery offgases, etc., using the Haldor Topsøe Convective Reformer (HTCR). Plant capacities range from approximately 5,000 Nm³/h to 50,000 Nm³/h (5 MM scfd to 45 MMscfd) and hydrogen purity from about 99.5–99.999+%. This is achieved without any steam export.

Description: The HTCR-based hydrogen plant can be tailor-made to suit the customer's needs with respect to feedstock flexibility. A typical plant comprises feedstock desulfurization, pre-reforming, HTCR reforming, shift reaction and pressure swing adsorption (PSA) purification to obtain product-grade hydrogen. PSA offgases are used as fuel in the HTCR. Excess heat in the plant is efficiently used for process heating and process steam generation.

A unique feature of the HTCR is the high thermal efficiency. Product gas and flue gas are cooled by providing heat to the reforming reaction to about 600°C (1,100°F). The high thermal efficiency is utilized to design energy-efficient hydrogen plants without the need for steam export. In larger plants, the reforming section consists of two HTCR reformers operating in parallel.

Economics: HTCR-based hydrogen plants provide the customer with a low-investment cost and low operating expenses for hydrogen production. The plant is supplied as a skid-mounted unit providing a short



installation time. These plants provide high operating flexibility, reliability and safety. Fully automated operation, startup and shutdown allow minimum operator attendance. A net energy efficiency of about 3.26 Gcal/1,000 Nm³ hydrogen (346 MMBtu/scf H₂) is achieved depending on size and feedstock.

Installations: Twenty-eight licensed units.

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Hydrogen—HTER

Application: Topsøe's proprietary and patented HTER-p (Haldor Topsøe Exchange Reformer) technology is a revamp option for production increase in a steam-reforming-based hydrogen plant. The technology allows hydrogen capacity increases of more than 25%. This option is especially advantageous because the significant capacity expansion is possible with minimal impact on the existing tubular reformer, which usually is the plant bottleneck.

Description: The HTER is installed in parallel with the tubular steam methane reformer (SMR) and fed independently with desulfurized feed taken upstream the reformer section. This enables individual adjustment of feedrate and steam- and process steam-to-carbon ratio to obtain the desired conversion. The hydrocarbon feed is reformed over a catalyst bed installed in the HTER. Process effluent from the SMR is transferred to the HTER and mixed internally with the product gas from the HTER catalyst. The process gas supplies the required heat for the reforming reaction in the tubes of the HTER. Thus, no additional firing is required for the reforming reactions in the HTER.

Economics: An HTER offers a compact and cost-effective hydrogen capacity expansion. The investment cost is as low as 60% of that for a new hydrogen plant. Energy consumption increases only slightly. For a 25% capacity increase, the net energy consumption is 3.13 Gcal/1,000 Nm³ H₂ (333 MM Btu/scf H₂).

References: Dybkjær, I., and S. W. Madsen, "Novel Revamp Solutions for Increased Hydrogen Demands," Eighth European Refining Technology Conference, November 17–19, 2003, London, UK



Installations: Eighteen licensed units.

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Hydrogen—steam methane reforming (SMR)

Application: Production of hydrogen from hydrocarbon feedstocks such as: natural gas, LPG, butane, naphtha, refinery offgases, etc., using the Haldor Topsøe radiant-wall Steam Methane Reformer (SMR). Plant capacities range from 5,000 Nm³/h to more than 300,000 Nm³/h hydrogen (300⁺ MMscfd H₂) and hydrogen purity of up to 99.999+%.

Description: The Haldor Topsøe SMR-based hydrogen plant is tailormade to suit the customer's needs with respect to economics, feedstock flexibility and steam export. In a typical Topsøe SMR-based hydrogen plant, a mix of hydrocarbon feedstocks or a single feedstock stream is first desulfurized. Subsequently, process steam is added, and the mixture is fed to a prereformer. Further reforming is carried out in the Haldor Topsøe radiant wall SMR. The process gas is reacted in a mediumtemperature CO shift reactor and purified by pressure swing absorption (PSA) to obtain product-grade hydrogen. PSA offgases are used as fuel in the SMR. Excess heat in the plant is efficiently used for process heating and steam generation.

The Haldor Topsøe radiant wall SMR operates at high outlet temperatures up to 950°C (1,740°F). The Topsøe reforming catalysts allow operation at low steam-to-carbon ratio. Advanced Steam Reforming uses both high outlet temperature and low steam-to-carbon ratio, which are necessary for high-energy efficiency and low hydrogen production cost. The Advanced Steam Reforming design is in operation in many industrial plants throughout the world.

Economics: The Advanced Steam Reforming conditions described can achieve a net energy efficiency as low as 2.96 Gcal/1,000 Nm³ hydrogen using natural gas feed (315 MM Btu/scf H_2).



Installations: More than 100 units.

References: Rostrup-Nielsen, J. R. and T. Rostrup-Nielsen, "Large scale hydrogen production," *CatTech*, Vol. 6, no. 4, 2002.

Dybkjær, I., and S. W. Madsen, "Advanced reforming technologies for hydrogen production," *Hydrocarbon Engineering*, December/January 1997/1998.

Gøl, J.N., and I. Dybkjær, "Options for hydrogen production," *HTI Quarterly*: Summer 1995.

Hydrogen—steam reforming

Application: Manufacture hydrogen for hydrotreating, hydrocracking or other refinery or chemical use.

Feedstock: Light saturated hydrocarbons: refinery gas or natural gas, LPG or light naphtha.

Products: Typical purity 99.99%; pressure 300 psig, with steam or CO₂ as byproducts.

Description: Hydrogen is produced by steam reforming of hydrocarbons with purification by pressure swing adsorption (PSA). Feed is heated (1) and then hydrogenated (2) over a cobalt-molybdenum catalyst bed followed by purification (3) with zinc oxide to remove sulfur. The purified feed is mixed with steam and preheated further, then reformed over nickel catalyst in the tubes of the reforming furnace (1).

Foster Wheeler's Terrace Wall reformer combines high efficiency with ease of operation and reliability. Depending on size or site requirements, Foster Wheeler can also provide a down-fired furnace. Combustion air preheat can be used to reduce fuel consumption and steam export.

Pre-reforming can be used upstream of the reformer if a mixture of naphtha and light feeds will be used, or if steam export must be minimized. The syngas from the reformer is cooled by generating steam, then reacted in the shift converter (4) where CO reacts with steam to form additional H_2 and CO_2 .

In the PSA section (5), impurities are removed by solid adsorbent, and the adsorbent beds are regenerated by depressurizing. Purge gas from the PSA section, containing CO_2 , CH_4 , CO and some H_2 , is used as fuel in the reforming furnace. Heat recovery from reformer flue gas may be via combustion air preheat or additional steam generation. Variations include a scrubbing system to recover CO_2 .



Economics:

Investment: 10–100 MMscfd, 4th Q 2010, USGC \$30–120 million **Utilities,** 50 MMscfd plant:

	Air preheat	Steam generation
Natural gas, feed + fuel, MMBtu/hr	780	885
Export steam at 600 psig/700°F, lb/hr	35,000	130,000
Boiler feedwater, lb/hr	70,000	170,000
Electricity, kW	670	170
Water, cooling, 18°F rise, gpm	350	350

Installations: Over 100 plants, ranging from less than 1 MMscfd to 95 MMscfd in a single train, with numerous multi-train installations.

Reference: *Handbook of Petroleum Refining Processes,* Third Ed., McGraw-Hill, 2003, pp 6.3–6.33.

Licensor: Foster Wheeler USA Corp CONTACT

Hydrogen (steam reforming)

Application: Hydrogen production from natural gas, refinery gas, associated gas, naphtha, LPG or any mixture of these. Appropriate purity product (up to 99.999%) can be used in refinery upgrade processes, chemical production and metallurgy (direct reduction). Possible byproducts are export steam or electricity, depending on cost and/or efficiency optimization targets.

Description: The hydrocarbon feedstock is admixed with some recycle hydrogen and preheated to 350° C- 380° C. Sulfur components are totally converted to H₂S at CoMo catalyst and then adsorbed on zinc oxide by conversion to ZnS. The desulfurized feed is mixed with process steam at an optimized steam/carbon ratio.

The desulfurized feed is mixed with process steam at an optimized steam/carbon ratio, superheated to $500^{\circ}\text{C}-650^{\circ}\text{C}$ and fed to the Lurgi Reformer. The feed/steam mixture passing the reformer tubes is converted at $800^{\circ}\text{C}-900^{\circ}\text{C}$ by presence of a nickel catalyst to a reformed gas containing H₂, CO₂, CO, CH₄ and undecomposed steam. The reformed gas is cooled to approximately 330°C in a reformed gas boiler.

The Lurgi Reformer is a top-fired reformer with a low number of burners and low heat losses, almost uniform wall temperature over the entire heated tube length and low NO_x formation by very accurate fuel and combustion air equipartition to the burners.

An adiabatic pre-reformer operating at an inlet temperature of $400^{\circ}\text{C}-500^{\circ}\text{C}$ (dependent on feedstock) may be inserted upstream of the feed superheater as a process option. Feedgas is partly converted to H₂, CO and CO₂ with high-activity catalyst; all hydrocarbons are totally converted to methane. The pre-reformer limits steam export to maximize heat recovery from the process and increases feedstock flexibility.

The CO in the reformed gas is shift-converted with an iron-chromi-



um catalyst, increasing hydrogen yield and reducing CO content to below 3 vol.%. The shift gas is cooled to 40°C and any process condensate is separated and recycled to the process. The gas is then routed to the PSA unit, where pure hydrogen is separated from the shift-gas stream. Offgas is used as fuel for steam reforming.

Recovered waste heat from the reformed and flue gases generates steam, which is used as process steam with the excess exported to battery limits.

Turndown rates of 30% or even less are achievable. The control concept allows fully automatic operation with load changes up to 3% of full capacity/minute.

Hydrogen (steam reforming), continued

Economics: Consumption figures based on light natural gas feedstock/1 millon scfd of H_2 :

Food , fuel million sefd	0.4
reeu + ruei, minion scru	0.4
Demineralized water, t	1.25
Water, cooling, m ³	3.0
Electricity, kWh	19
Export steam, t	0.7

Installations: More than 125 gas reforming plants, 33 being hydrogen plants, with single-train capacities ranging from 1 million scfd to 200 million scfd.

Licensor: Lurgi GmbH CONTACT

HYDROCARBON PROCESSING®

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Hydrogen—Steam-methane reforming (SMR)

Application: Production of hydrogen from hydrocarbon feedstocks such as natural gas, liquefied petroleum gas (LPG), refinery offgases, naphtha, etc., using the steam-methane-reforming (SMR) process.

Description: Linde has a well-proven technology for hydrogen manufacture by catalytic steam reforming of light hydrocarbons in combination with Linde's highly efficient pressure swing adsorption (PSA) process.

Product purity: Hydrogen product purities up to 99.9999 mol% are possible.

The basic process steps are hydrodesulfurization of feedstock, steam reforming, heat recovery from reformed and combustion flue gas to produce process and export steam, single-stage adiabatic high temperature CO-shift conversion (alternative shift concepts possible for plant optimization) and final hydrogen purification by PSA.

Process design and optimization for every process step and, in particular, the optimized linking of operating parameters between the two essential process steps: reforming furnace and PSA unit are based exclusively on Linde's own process and operating know-how.

Process options with pre-reforming for overall plant optimization (fuel savings over standalone primary reformer, reduced capital cost of reformer, higher primary reformer preheat temperatures, increased feedstock flexibility, lower involuntary steam production and lower overall steam/carbon ratios) are possible.

Pressure swing adsorption (PSA): The particular features of Linde's PSA technology are high product recovery rates, low operating costs and operational simplicity. Excellent availability and easy monitoring are ensured by advanced computer control. Extensive know-how and engineering expertise assisted by highly sophisticated computer programs



guarantee the design and construction of tailor-made and economical plants of the highest quality. Modular skid design of the PSA plants reduces erection time and costs at site. The fully prefabricated skids are thoroughly tested before they leave the workshop.

Reformer furnace: A compact firebox design with vertical hanging catalyst tubes arranged in multiple, parallel rows. Minimized number of forced draft top-firing burners, integrated into the firebox ceiling. Compared to other designs, the burner trimming and individual adjustment to achieve a uniform heat flow pattern throughout the reformer cross section is substantially facilitated.

Concurrent firing ensures a uniform temperature profile throughout the reformer tube length. Flame and stable combustion flow pattern is

Hydrogen—Steam-methane reforming (SMR), continued

supported by the flue-gas collecting channels arranged at ground level between the hot reformed gas headers. Thermal expansion, as well as, tube and catalyst weight are compensated by the adjustable spring hanger system arranged inside the penthouse, removing mechanical stress from the hot manifold outlet headers at ground level. The radiant reformer box is insulated with multiple layers of ceramic fiber blanket insulation, mechanically stable and resistant to thermal stress.

Convection section: Depending on the hydrogen product capacity, the convection section— a series of serial heat exchanger coils—is arranged either vertically with ID-fluegas fan and stack at reformer burner level or–specifically for the higher capacity units–horizontally at ground level for ease of access and reduced structural requirements.

Economics:

	Natural gas	LPG	Naphtha	Refinery gas
Hydrogen Product	-		-	-
Flowrate Nm ³ /h	50,000	50,000	50,000	50,000
MM SCFD	44.8	44.8	44.8	44.8
Pressure, bara	25.0	25.0	25.0	25.0
Purity, mole %	99.9	99.9	99.9	99.9
Export steam				
Flowrate, ton/hr	31	28.9	28.6	29.2
Temperature, °C	390	390	390	390
Pressure, bara	40	40	40	40
Feed and fuel consumpti	ion			
Gcal/hr	177.8	181.8	182.9	175.8
GJ/hr	744.4	761.2	765.8	736.0
Energy consumption (inc	:l. steam cre	dit)		
Gcal/1,000 Nm ³ H ₂	3.070	3.210	3.222	3.072
GJ/1,000 Nm ³ H ₂	12.853	13.440	13.490	12.862

Utilities				
Water, demin, ton/hr	55.6	57.5	60.6	53.2
Water, cooling, ton/hr	160	165	168	157
Electrical energy, kW	850	920	945	780
Design flexibility				
Export steam				
ton/1,000 Nm ³ H ₂	0.5–1.2	0.4–1.2	0.4–1.2	0.4–1.1
Fuel consumption				
GJ/1,000 Nm ³ H ₂	0.9–3.5	1.8–4.3	1.9–4.4	0.7–2.9
Investment	typical 1 dependir	to 1.2 \$mill	ion/ 1,000 N size	Jm³∕h H₂,

Installations: More than 200 new hydrogen plants have been built all over the world, for clients in the refining, chemical and fertilizer industry, with capacities ranging from below 1,000 Nm³/h to well above 100,000 Nm³/h, and for processing of all types of feedstock. Most of these plants have been built on a lump-sum turn-key basis.

Contributor: Linde AG CONTACT

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Hydroprocessing—resid

Application: The UOP Uniflex process is a high-conversion residue hydroprocessing process that maximizes the conversion of residues to transportation fuels while reducing residue byproducts around 70% compared to delayed coking. The process can increase your refinery margins \$2 to -\$4/bbl over conventional residue conversion technologies.. The normal feedstock to a Uniflex Process Unit is vacuum residue, although atmospheric residue and other streams (SDA pitch) can be processed.

Description: The feed is heated to the desired temperature by separate heating from the bulk of the recycle gas, which is heated to an elevated temperature above the desired mix temperature. Small particulate catalyst is added continuously in the feed just before the feed heater. The recycle gas is heated in its own heater then the feed plus the recycle gas are mixed in the bottom zone of the reactor. Product and catalyst leave the top of the reactor, are then immediately quenched then flow to the hot high-pressure separator (HHPS) and to further fractionation. The vapor stream from the CHPS is recycled back to the reactor after combining with make-up hydrogen. HVGO is typically recycled to almost extinction.

Experience: One unit has been in operation at the PetroCanada Montreal Refinery.

Licensor: UOP, A Honeywell Company CONTACT



Hydrotreating

Application: Hydrotreating of light and middle distillates and various gas oils, including cracked feedstocks (coker naphtha, coker LGO and HGO, visbreaker gas oil, and LCO) using the ISOTREATING Process for deep desulfurization, denitrification and aromatics saturation and to produce low-sulfur naphtha, jet fuel, ultra-low sulfur diesel (ULSD), or improved-quality FCC feed.

Description: Feedstock is mixed with hydrogen-rich treat gas, heated and reacted over high-activity hydrogenation catalyst (1). Several CoMo and NiMo catalysts are available for use in the ISOTREATING Process. One or multiple beds of catalyst(s), together with Chevron Lummus Global's advanced high-efficiency reactor internals for reactant distribution and interbed quenching, are used.

Reactor effluent is cooled and flashed (2) producing hydrogen-rich recycle gas, which, after H_2S removal by amine (3), is partially used as quench gas while the rest is combined with makeup hydrogen gas to form the required treat gas. An intermediate pressure level flash (4) can be used to recover some additional hydrogen-rich gas from the liquid effluent prior to the flashed liquids being stripped or fractionated (5) to remove light ends, H_2S and naphtha-boiling range material, and/or to fractionate the higher boiling range materials into separate products.

Operating conditions: Typical reactor operating conditions can range from 600–2,300 psig and 500–780°F, 350–2,000 psia hydrogen partial pressure, and 0.6-3 hr⁻¹ LHSV, all depending on feedstock(s) and product quality objective(s).

Yields: Depends on feedstock(s) characteristics and product requirements. Desired product recovery is maximized based on required flash point and/or specific fractionation specification. Reactor liquid product (350°F plus TBP material) is maximized through efficient hydrogenation with minimum lighter liquid product and gas production. Reactor liq-



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uid product (350°F plus) yield can vary between 98 vol% from straightrun gas oil feed to >104 vol% from predominantly cracked feedstock to produce ULSD (<10 wppm sulfur). Chemical-hydrogen consumption ranges from $450-900^+$ scf/bbl feed.

Economics: Investment will vary depending on feedstock characteristics and product requirements. For a 40,000–45,000-bpsd unit for ULSD, the ISBL investment cost (US Gulf Coast 2010) is \$3,000–\$3,500/ bspd.

Installation: Currently, there are more than 60 units operating based on ISOTREATING technology and an additional 12 units in various stages of engineering.

Licensor: Chevron Lummus Global LLC CONTACT
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Hydrotreating

Application: The IsoTherming process provides refiners an economical means to produce ultra-low-sulfur diesel (ULSD), low-sulfur and low-nitrogen feedstocks and other very low-sulfur hydrocarbon products. In addition, IsoTherming can also be used for feed upgrading in a mild-to partial-conversion hydrocracking mode in conjunction with or in lieu of conventional hydrotreating.

Products: ULSD, low-sulfur FCC feed, low-sulfur kerosine type products.

Description: This process uses a novel approach to introduce dissolved hydrogen in excess of reaction requirements into the liquid-full reactor. This approach allows operation at higher space velocities than conventional trickle-bed reactors. The IsoTherming process eliminates problems associated with flow mal-distribution, gas-liquid mass transfer and catalyst wetting. The process eliminates the need for some high pressure equipment and large hydrogen recycle compressor required in conventional hydrotreating thereby lowering cost.

The technology can be installed as a pre-treat unit ahead of an existing hydrotreater reactor or a new stand-alone process unit. Fresh feed, after heat exchange, is combined with recycled product and hydrogen in a mixer internal to the reactor. The liquid feed is saturated hydrogen and is fed to IsoTherming reactor/bed one where partial desulfurization and denitrofication occurs. The stream is resaturated with additional hydrogen in a second mixer and fed to the second IsoTherming reactor/bed where further desulfurization and denitrofication takes place.

Treated oil is recycled back to the inlet of the top bed. This recycle stream delivers recycled hydrogen to the reactors and also acts as a heat sink; thus, a nearly isothermal reactor operation is achieved.

The treated oil from the last IsoTherming reactor/bed may then be fed to additional IsoTherming reactors/beds and/or a trickle-bed hydrotreating reactor (revamp case only) acting in the polishing mode to produce an ultra-low-sulfur product.



Operating conditions: Typical diesel IsoTherming revamp conditions are:

	Diesel feed	lsoTherming pre-treat reactor	Treated product from existing conventional reactor
LCO, vol%	42		
SR, vol%	58		
Sulfur, ppm	4,300	451	7
Nitrogen, ppm	415	49	0
H_2 Consumption, scf/bbl		305	245
LHSV, Hr ^{–1} *		4	2.1
Reactor, ΔT		24	30
Reactor Pressure, psig		900	750
* Based on fresh feedrate without	ut recycle		

Continued **V**

Hydrotreating, continued

Economics: Revamp investment (basis 15,000–20,000 bpsd, 1Q2008, US Gulf Coast) \$500/bpsd diesel.

Installation: Fourteen units have been licensed globally to date. Applications of the technology include mild hyrdocracking, LSD and ULSD production, kerosine and gasoil desulfurization.

Licensor: DuPont CONTACT

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Hydrotreating

Application: Topsøe hydrotreating technology has a wide range of applications, including the purification of naphtha, distillates and residue, as well as the deep desulfurization and color improvement of diesel fuel and pretreatment of FCC and hydrocracker feedstocks.

Products: Ultra-low-sulfur diesel fuel, and clean feedstocks for FCC and hydrocracker units.

Description: Topsøe's hydrotreating process design incorporates our industrially proven high-activity TK catalysts with optimized graded-bed loading and high-performance, patented reactor internals. The combination of these features and custom design of grassroots and revamp hydrotreating units result in process solutions that meet the refiner's objectives in the most economic way.

In the Topsøe hydrotreater, feed is mixed with hydrogen, heated and partially evaporated in a feed/effluent exchanger before it enters the reactor. In the reactor, Topsøe's high-efficiency internals have a low sensitivity to unlevelness and are designed to ensure the most effective mixing of liquid and vapor streams and the maximum utilization of the catalyst volume. These internals are effective at a high range of liquid loadings, thereby enabling high turndown ratios. Topsøe's graded-bed technology and the use of shape-optimized inert topping and catalysts minimize the build-up of pressure drop, thereby enabling longer catalyst cycle length. The hydrotreating catalysts themselves are of the Topsøe TK series, and have proven their high activities and outstanding performance in numerous operating units throughout the world. The reactor effluent is cooled in the feed-effluent exchanger, and the gas and liquid are separated. The hydrogen gas is sent to an amine wash for removal of hydrogen sulfide and is then recycled to the reactor. Cold hydrogen recycle is used as guench gas between the catalyst beds, if required. The liquid product is steam stripped in a product stripper column to remove hydrogen sulfide, dissolved gases and light ends.



Operating conditions: Typical operating pressures range from 20 to 80 barg (300 to 1,200 psig), and typical operating temperatures range from 320°C to 400°C (600°F to 750°F).

References: Cooper, B. H. and K. G. Knudsen, "Production of ULSD: Catalyst, kinetics and reactor design," World Petroleum Congress, 2002.

Patel, R. and K. G. Knudsen, "How are refiners meeting the ultra-low-sulfur diesel challenge," NPRA Annual Meeting, San Antonio, March 2003.

Topsøe, H., K. Knudsen, L. Skyum and B. Cooper, "ULSD with BRIM catalyst technology," NPRA Annual Meeting, San Francisco, March 2005.

Installation: More than 60 Topsøe hydrotreating units for the various applications above are in operation or in the design phase.

Licensor: Haldor Topsøe A/S CONTACT

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Hydrotreating

Application: The CD*Hydro* and CD*HDS* processes are used to selectively desulfurize FCC gasoline with minimum octane loss.

Products: Ultra-low-sulfur FCC gasoline with maximum retention of olefins and octane.

Description: The light, mid and heavy cat naphthas (LCN, MCN, HCN) are treated separately, under optimal conditions for each. The full-range FCC gasoline sulfur reduction begins with fractionation of the light naphtha overhead in a CDHydro column. Mercaptan sulfur reacts quantitatively with excess diolefins to produce heavier sulfur compounds, and the remaining diolefins are partially saturated to olefins by reaction with hydrogen. Bottoms from the CDHydro column, containing the reacted mercaptans, are fed to the CDHDS column where the MCN and HCN are catalytically desulfurized in two separate zones. HDS conditions are optimized for each fraction to achieve the desired sulfur reduction with minimal olefin saturation. Olefins are concentrated at the bottom where the conditions result in very high levels of HDS.

No cracking reactions occur at the mild conditions, so that yield losses are easily minimized with vent-gas recovery. The three product streams are stabilized together or separately, as desired, resulting in product streams appropriate for their subsequent use. The two columns are heat integrated to minimize energy requirements. Typical reformer hydrogen is used in both columns without makeup compression. The sulfur reduction achieved will allow the blending of gasoline that meets current and future regulations.

Catalytic distillation essentially eliminates catalyst fouling because the fractionation removes heavy-coke precursors from the catalyst zone before coke can form and foul the catalyst pores. Thus, catalyst life in catalytic distillation is increased significantly beyond typical fixed-bed



life. The CD*Hydro*/CD*HDS* units can operate throughout an FCC turnaround cycle up to six years without requiring a shutdown to regenerate or to replace catalyst. Typical fixed-bed processes will require a mid FCC shutdown to regenerate/replace catalyst, requiring higher capital cost for feed, storage, pumping and additional feed capacity.

Economics: The estimated ISBL capital cost for a 50,000-bpd CD*Hydrol* CD*HDS* unit with 95% desulfurization is \$40 million (2005 US Gulf Coast).

Installation: There are 38 CD*Hydro*/CD*HDS* desulfurization units commercially licensed to treat FCC gasoline, of which 12 are currently in engineering/construction. Total licensed capacity exceeds 1.3 million bpd.

Licensor: Lummus Technology, a CB&I company CONTACT

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Hydrotreating

Application: Hydrotreating is an established refinery process for reducing sulfur, nitrogen and aromatics while enhancing cetane number, density and smoke point. This is especially critical for refiners who are looking to process heavier feedstocks, produce cleaner fuels and extend cycle length. Shell Global Solutions' hydrotreating processes are particularly effective for full range middle distillate hydrotreating (naphtha, kerosine, gasoil) and vacuum gasoil (VGO) applications. In conjunction with Criterion Catalysts & Technologies, Shell offers a portfolio of highperforming catalysts, allowing refiners to make the most of state-of-theart reactor internals.

Shell also has proven technology on distillate dewaxing application that enables refiners to increase their production of winter diesel (exhibiting excellent cold flow properties, specifically cloud point).

Description: Although capable of many configurations, this process focuses on causing oil fractions to react with hydrogen in the presence of a catalyst to produce high-value, clean products. The heart of Shell Global Solutions' hydrotreating technology is the reactor section, which features a pressurized reactor vessel utilizing proprietary catalyst and reactor internals hardware. Beginning with highly effective particulate filters installed in the reactor dome, Shell is able to mitigate pressure drop and maldistribution to the catalyst bed. These filters also optimize active catalyst volume and prevent channeling to subsequent vapor-liguid distribution trays, in turn ensuring nearly 100% catalyst wetting. To increase thermal control, Shell installs an Ultra-Flat-Quench deck at the bottom of the bed, mixing reactants with cold quench gas and redistributing them to the next bed. The compact design of these internals allows for decreased reactor height for grassroots construction or up to a 20% increase in catalytic volume for multi-bed revamps.

Naphtha hydrotreating

- Feedstocks: Straight run, visbreaker, coker
- Products: CCR/Isomerization feed quality (< 0.5 wppm sulfur, < 0.5 wppm nitrogen)

Kerosine hydrotreating

- Feedstocks: Straight run kerosine
- Products: Jet fuel quality (> 19 mm smoke point)
- Flexible designs: 1-stage or 2-stage, optimized pressure, tailored catalysts

Diesel hydrotreating

- Feedstocks: Straight run LGO, visbreaker LGO, FCC LCO, coker LGO
- Products: Euro IV/V (HDS, Cetane upgrade, cold flow improvement, density and aromatics)
- Flexible designs: 1-stage or 2-stage, optimized pressure, tailored catalysts

Bulk distillate hydrotreating

- Feedstocks: Wide boiling range straight run kerosine/LGO
- Products: Jet fuel guality, Euro IV/V
- Flexible designs: 1-stage or 2-stage, optimized pressure, tailored catalysts

Diesel hydrotreating + dewaxing

- Feedstocks: Straight run LGO, Visbreaker LGO, FCC LCO, Coker I GO
- Products: Euro IV/V Cloud point and cold flow improvement
- Flexible designs: 1-stage or 2-stage, optimized pressure, tailored catalysts, seasonal operation

VGO hydrotreating (CFHT)

- Feedstocks: Straight run VGO, coker heavy gasoil, DAO
- Products: FCCU feed (sulfur, nitrogen)
- Flexible designs: Optimized pressure, tailored catalysts

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Hydrotreating, continued

Shell's integrated stripper design, which is fully proven in commercial operations, combines hot low pressure separator (HLPS) and cold low pressure separator (CLPS), enabling improved heat integration and avoiding investment in an offgas compressor. This improved stripper design maximizes product diesel yield and is much more energy efficient over conventional trickle phase hydrodesulfurization (HDS) units and has demonstrated a reduction of up to 35% in Operational Expenditure (fuel).

Operating conditions depend on the final application. For instance, temperatures could range between 330°C and 380°C, and pressures between 50 barg and 80 barg to produce ultra-low-sulfur diesel (< 10 ppms), while for vacuum distillates temperatures range between 370°C and 420°C with pressures between 60 barg and 100 barg to produce a 450 ppmwt hydrotreated distillate as FCC feedstock.

Installation: More than 200 hydrotreater units have been designed and serviced.

Supplier: Shell Global Solutions International B.V. CONTACT

НОМ

Hydrotreating

Application: The UOP Unionfining process facilites hydrodesulfurization, hydrodenitrogenation and hydrogenation of petroleum and chemical feedstocks.

Products: Ultra-low-sulfur diesel fuel; feed for catalytic reforming, FCC pretreat; upgrading distillates (higher cetane, lower aromatics); desulfurization, denitrogenation and demetallization of vacuum and atmospheric gas oils, coker gas oils and chemical feedstocks.

Description: The UOP Maximum Quality Distillate (MQD) Unionfining process upgrades difficult, refractory, distillate-range feeds to high-quality distillate that meets stringent requirements for sulfur and aromatics content, cetane number and cold flow properties. The process is available in a single-stage configuration for most base-metal catalyst applications or a two-stage configuration to achieve the highest-quality diesel with a noble-metal catalyst.

The UOP Distillate Unionfining process improves the quality of kerosine, jet fuel and diesel fuel using state-of-the-art catalysts and carefully selected processing conditions. The product can be blended directly into fuel, and can facilitate the blending of other streams.

The UOP Vacuum Gasoil (VGO) Unionfining process is used to process straight-run VGO, heavy coker gasoil and visbreaker gasoil. The typical application of this technology is in FCC feed pre-treatment. The process provides higher yields and a better quality of FCC gasoline as well as lower yields of FCC light and heavy cycle oils.



Operating conditions: Operating conditions depend on feedstock and desired level of impurities removal. Pressures range from 500 to 2,000 psi. Temperatures and space velocities are determined by process objectives.

Installation: Several hundred units installed.

Licensor: UOP, A Honeywell Company CONTACT

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Hydrotreating

Application: The UOP RCD Unionfining process reduces the sulfur, nitrogen, Conradson carbon, asphaltene and organometallic contents of heavier residue-derived feedstocks to allow them to be used as either specification fuel oils or as feedstocks for downstream processing units such as hydrocrackers, fluidized catalytic crackers, resid catalytic crackers and cokers.

Feed: Feedstocks range from solvent-derived materials to atmospheric and vacuum residues.

Description: The process uses a fixed-bed catalytic system that operates at moderate temperatures and moderate to high hydrogen partial pressures. Typically, moderate levels of hydrogen are consumed with minimal production of light gaseous and liquid products. However, adjustments can be made to the unit's operating conditions, flowscheme configuration or catalysts to increase conversion to distillate and lighter products.

Fresh feed is combined with makeup hydrogen and recycled gas, and then heated by exchange and fired heaters before entering the unit's reactor section. Simple downflow reactors incorporating a graded bed catalyst system designed to accomplish the desired reactions while minimizing side reactions and pressure drop buildup are used. Reactor effluent flows to a series of separators to recover recycle gas and liquid products. The hydrogen-rich recycle gas is scrubbed to remove H₂S and recycled to the reactors while finished products are recovered in the fractionation section. Fractionation facilities may be designed to simply recover a full-boiling range product or to recover individual fractions of the hydrotreated product.



Installation: Twenty-eight licensed units with a combined licensed capacity of approximately one million bpsd. Commercial applications have included processing of atmospheric and vacuum residues and solvent-derived feedstocks.

Licensor: UOP, A Honeywell Company CONTACT

Hydrotreating, pyrolysis gasoline

Application: GTC Technology, in alliance with technology partners, offers an optimized technology for two-stage pyrolysis gasoline (pygas) hydrotreatment in cases where di-olefins, olefins and styrene in the raw pygas feed are saturated. The technology is simple and easy to implement into existing plant requirements. The process is applied to the C₅⁺ fraction of raw pyrolysis gasoline.

Description: The hydrotreating unit consists of three sections:

• First stage hydrotreating section saturates di-olefins to olefins

• Second stage hydrotreating section saturates olefins and desulfurizes the pygas

• Fractionation section stabilizes the hydrotreated streams and recovers the C_6-C_8 heart cut for further processing for aromatics extraction and the C_9^+ cut.

Raw pygas is first sent to the first stage hydrotreating section. The pygas feed stream along with hydrogen is preheated by the recycle liquid stream to the desired temperature and sent to the first stage hydrotreating (HDT) reactor where most diolefins in the feed are selectively saturated into 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, H₂ 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 C₅ + gasoline fraction and can be sent to the gasoline pool. To produce benzene, toluene and xylene (BTX), this C₅+



stream is sent to a fractionation section to obtain a C_6-C_8 heat cut, which will be further hydrotreated to saturate mono-olefins in the second stage hydrotreating section.

In the second stage hydrotreating section, the C_6-C_8 heart cut combined with a recycle vapor stream and makeup hydrogen is preheated in the second stage feed/effluent heat exchanger before being heated further to the desirable reaction temperature by a charge heater. The feed mixture passes through the fixed catalyst beds in the second stage HDT reactor where olefin species are saturated and sulfur species are converted to hydrogen sulfide (H₂S).

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,

Hydrotreating, pyrolysis gasoline, continued

the unreacted hydrogen and other light components are separated from the hydrotreated liquid products and recycled to the HDT reactor using a recycle gas compressor. A small vapor stream is purged as offgas to control impurities level 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, H₂ 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 C₆–C₈ cut is cooled further and sent to BL for further processing for aromatics extraction.

Process advantages:

• Flexibility in prefractionator cut point and a proprietary vaporizer allows control of polymerization potential in the hydrotreaters

• Reactor operates at high liquid content with mixed phases to minimize polymer byproduct plugging

• Optimized recycle scheme minimizes hydrocarbon vaporization and thereby extends reactor run length

• Catalyst exhibits high activity, stability, mechanical strength and poison resistance

- Aromatics saturation in second stage reactor is less than 1%
- Efficient heat integration scheme reduces energy consumption

• Turnkey package for high-purity benzene, toluene and paraxylene production available from licensor.

Economics: Feedrate 500 thousand tpy (11,000 bpsd); erected cost \$26MM (ISBL, 2007 US Gulf Coast Basis).

Installation: Commercialized technology available for license.

Licensor: GTC Technology US, LLC CONTACT

Hydrotreating—RDS/VRDS/UFR/OCR

Application: Hydrotreat atmospheric and vacuum residuum feedstocks to reduce sulfur, metals, nitrogen, carbon residue and asphaltene contents. The process converts residuum into lighter products while improving the quality of unconverted bottoms for more economic downstream use.

Products: Residuum FCC feedstock, coker feedstock, SDA feedstock or low-sulfur fuel oil. VGO product, if separated, is suitable for further upgrading by FCC units or hydrocrackers for gasoline/mid-distillate manufacture. Mid-distillate material can be directly blended into low-sulfur diesel or further hydrotreated into ultra-low-sulfur diesel (ULSD).

The process integrates well with residuum FCC units to minimize catalyst consumption, improve yields and reduce sulfur content of FCC products. RDS/VRDS also can be used to substantially improve the yields of downstream cokers and SDA units.

Description: Oil feed and hydrogen are charged to the reactors in a once-through operation. The catalyst combination can be varied significantly according to feedstock properties to meet the required product qualities. Product separation is done by the hot separator, cold separator and fractionator. Recycle hydrogen passes through an H_2S absorber.

A wide range of AR, VR and DAO feedstocks can be processed. Existing units have processed feedstocks with viscosities as high as 6,000 cSt at 100°C and feed-metals contents of 500 ppm.

Onstream Catalyst Replacement (OCR) reactor technology has been commercialized to improve catalyst utilization and increase run length with high-metals, heavy feedstocks. This technology allows spent catalyst to be removed from one or more reactors and replaced with fresh while the reactors continue to operate normally. The novel use of upflow reactors in OCR provides greatly increased tolerance of feed solids while maintaining low-pressure drop.

A related technology called UFR (upflow reactor) uses a multibed upflow reactor for minimum pressure drop in cases where onstream



catalyst replacement is not necessary. OCR and UFR are particularly well suited to revamp existing RDS/VRDS units for additional throughput or heavier feedstock.

Installation: Over 30 RDS/VRDS units are in operation. Seven units have extensive experience with VR feedstocks. Sixteen units prepare feedstock for RFCC units. Four OCR units and two UFR unit are in operation, with another nine in engineering. Total current operating capacity is about 2.2 million bpsd

References: Reynolds, "Resid Hydroprocessing with Chevron Technology," *JPI*, Tokyo, Japan, Fall 1998.

Reynolds and Brossard, "RDS/VRDS Hydrotreating Broadens Application of RFCC," *HTI Quarterly*, Winter 1995/96.

Reynolds, et al., "VRDS for conversion to middle distillate," NPRA Annual Meetng, March 1998, Paper AM-98-23.

Licensor: Chevron Lummus Global LLC CONTACT

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Hydrotreating/desulfurization

Application: The UOP SelectFining process is a gasoline desulfurization technology developed to produce ultra-low-sulfur gasoline by removing more than 99% of the sulfur present in olefinic naphtha while:

- Minimizing octane loss
- Maximizing liquid yield
- Minimizing H₂ consumption
- Eliminating recombination sulfur.

Description: The SelectFining process can hydrotreat full boiling-range (FBR) olefinic naphtha or, when used in conjunction with a naphtha splitter, any fraction of FBR naphtha.

The configuration of a single-stage SelectFining unit processing FBR olefinic naphtha (Fig. 1) is very similar to that of a conventional hydrotreater. The operating conditions of the SelectFining process are similar to those of conventional hydrotreating: it enables refiners to re-use existing idle hydroprocessing equipment.

Since FBR olefinic naphtha can contain highly reactive di-olefins (which may polymerize and foul equipment and catalyst beds), the SelectFining unit may include a separate reactor for di-olefin stabilization. Incoming naphtha is mixed with a small stream of heated hydrogen-rich recycle gas and directed to this reactor. The "stabilized" naphtha is then heated to final reaction conditions and processed in the unit's main reactor over SelectFining catalyst.

Effluent from the main reactor is washed, cooled and separated into liquid and gaseous fractions. Recovered gases are scrubbed (for H_2S removal) and recycled to the unit's reactor section, while recovered liquids are debutanized (for Rvp control) and sent to gasoline blending.

Process chemistry: While the principal reactions that occur in a hydrotreater involve conversion of sulfur and nitrogen components, conventional hydrotreaters also promote other reactions, including olefin saturation, reducing the feed's octane. UOP's S 200 SelectFining



catalyst was developed to effectively hydrotreat the olefinic naphtha while minimizing olefin saturation. It uses an amorphous alumina support (with optimized acidity) and non-noble metal promoters to achieve the optimal combination of desulfurization, olefin retention and operating stability.

In addition to processing FBR naphtha, the SelectFining technology can also be used in an integrated gasoline upgrading configuration that includes naphtha splitting, Merox extraction technology for mercaptan removal and ISAL hydroconversion technology for octane recovery.

Installation: UOP's experience in hydroprocessing and gasoline desulfurization is extensive with approximately 200 Unionfining units and more than 240 Merox units (for naphtha service) in operation. The first commercial SelectFining unit has been operating successfully since 2006.

Licensor: UOP, A Honeywell Company CONTACT

Hydrotreating, middle distillates

Application: Produce ultra-low-sulfur diesel (ULSD) and high-cetane and improved-color diesel fuel from a wide range of middle distillates feeds including large amount of cracked stock (such as LCO, light coker/vis-breaker gasoils or MHC-GO, AR/VRDS GO) using Axens' Prime-D Toolbox of proven state-of-the-art technologies (including high activity/stability HR Series catalysts and high-performances EquiFlow internals) and services.

Description: In the basic process, as shown in the diagram, feed and hydrogen are heated in the feed-reactor effluent exchanger (1) and furnace (2) and enter the reaction section (3), with possible added volume for revamp cases. The reaction effluent is cooled by the exchanger (1) and air cooler (4) and separated in the separator (5). The hydrogenrich gas phase is treated in an existing or new amine absorber for H₂S removal (6) and recycled to the reactor. The liquid phase is sent to the stripper (7) where small amounts of gas and naphtha are removed and high-quality product diesel is recovered.

Whether the need is for a new unit or for maximum reuse of existing diesel HDS units, the Prime-D Hydrotreating Toolbox meets the challenge. Process objectives ranging from low-sulfur, ultra-low-sulfur, lowaromatics, and/or high-cetane number are met with minimum cost by:

• Selection of the proper combination of catalysts from HR Series and ACT grading materials for maximized cycle length and performance. HR600 Series catalysts cover the range of the most difficult middle distillates hydrotreatment services. HR 626 CoMo exhibits high desulfurization rates at low to medium pressures; HR 648 NiMo have higher hydrogenation activities at higher pressures. HR600 Series catalysts display proven superior stability operation coupled with minimum regeneration cost.

• Use of proven, high-performance reactor internals, EquiFlow, that allow near-perfect gas and liquid distribution and outstanding radial temperature profiles (implemented in over 190 units).



• Loading catalyst in the reactor(s) with the Catapac dense loading technique for up to 20% more reactor capacity. Over 15,000 tons of catalyst have been loaded quickly, easily and safely in recent years using the Catapac technique.

• Application of Advanced Process Control for dependable operation and longer catalyst life.

• Sound engineering design based on years of R&D, process design and technical service feedback to ensure the right application of the right technology for new and revamp projects.

Whatever the diesel quality goals—ULSD, high cetane or low aromatics—Prime-D's Hydrotreating Toolbox approach will attain your goals in a cost-effective manner.

Installation: Over 200 middle distillate hydrotreaters have been licensed or revamped. They include 120 ultra-low-sulfur diesel units,

Hydrotreating, middle distillater, continued

cetane boosting units equipped with Equiflow internals and loaded with HR series catalysts.

References: "Getting Total Performance with Hydrotreating," *Petroleum Technology Quarterly,* Spring 2002.

"Premium Performance Hydrotreating with Axens HR 400 Series Hydrotreating Catalysts," NPRA Annual Meeting, March 2002, San Antonio.

"The Hydrotreating Toolbox Approach," *Hart's European Fuel News*, May 29, 2002.

"Squeezing the most from hydrotreaters," *Hydrocarbon Asia,* April/ May 2004.

"Upgrade hydrocracked resid through integrated hydrotreating," Hydrocarbon Processing, September 2008.

Licensor: Axens CONTACT

Hydrotreating—resid

Application: Upgrade and/or convert atmospheric and vacuum residues using the Hyvahl fixed-bed process.

Products: Low-sulfur fuels (0.3% to 1.0% sulfur) and RFCC feeds (removal of metals, sulfur and nitrogen, reduction of carbon residue). Thirty percent to 50% conversion of the 565°C⁺ fraction into distillates.

Description: Residue feed and hydrogen, heated in a feed/effluent exchanger and furnace, enter a reactor section—typically comprising of a guard-reactor section (PRS), main HDM and HDS reactors.

The guard reactors are onstream at the same time in series, and they protect downstream reactors by removing or converting sediment, metals and asphaltenes. For heavy feeds, they are permutable in operation (PRS technology) and allow catalyst reloading during the run. Permutation frequency is adjusted according to feed-metals content and process objectives. Regular catalyst changeout allows a high and constant protection of downstream reactors.

Following the guard reactors, the HDM section carries out the remaining demetallization and conversion functions. With most of the contaminants removed, the residue is sent to the HDS section where the sulfur level is reduced to the design specification.

The PRS technology associated with the high stability of the HDS catalytic system leads to cycle runs exceeding a year even when processing VR-type feeds to produce ultra-low-sulfur fuel oil.

Yields: Typical HDS and HDM rates are above 90%. Net production of 12% to 25% of diesel + naphtha.

Installation: In addition to three units in operation, four more were licensed in 2005/07. Total installed capacity will reach 370,000 bpsd. Two units will be operating on AR and VR feed, five on VR alone.



References: Plain, C., D. Guillaume and E. Benazzi, "Residue desulphurisation and conversion," *Petroleum Technology Quarterly,* Summer 2006.

Plain, C., D. Guillaume and E. Benazzi, "Better margins with cheaper crudes," ERTC 2005 Show Daily.

"Option for Resid Conversion," BBTC, Oct. 8–9, 2002, Istanbul.

"Maintaining on-spec products with residue hydroprocessing," 2000 NPRA Annual Meeting, March 26–28, 2000, San Antonio.

Licensor: Axens CONTACT

HYDROCARBON PROCESSING®

2011 Refining Processes Handbook

Isobutylene, from MTBE decomposition

Application: To decompose commercial-grade methyl tertiary butyl ether (MTBE) feed to high-purity isobutylene and commercial-grade methanol. Isobutylene purity of greater than 99.9% is achievable.

Description: By utilizing the CD*IB* technology, commercial MTBE feedstock is first fractionated to remove light ends and heavies. The highpurity MTBE is then fed to the decomposition reactor where MTBE is converted to isobutylene and methanol. The decomposition reaction takes place in vapor phase and is performed with high selectivity. Heat of reaction is supplied by medium-pressure steam. The methanol is extracted from the reactor effluent in a water wash. The aqueous stream is fractionated to recover the wash water and MTBE for recycle, and to produce high-quality methanol. The water-washed reactor effluent is fractionated to remove heavies (including MTBE for recycle) and light ends, leaving a high-purity (>99.9%) isobutylene product.

Economics: The CD*IB* technology can be provided in a stand-alone unit or can be coupled with a CD*Mtbe* unit to provide a very efficient integrated unit. Capital and operating costs are reduced when compared to separate units. Isobutylene product purification can be simplified by providing recycle to the MTBE unit. CD*IB* methanol recovery can be simplified by combining it with MTBE unit methanol recovery in common equipment.

Process advantages include:

- Simple and effective control
- High MTBE conversion
- High isobutylene selectivity
- High flexibility



- Low capital cost
- High purity isobutylene
- No corrosion problems
- Significant operating experience.

Installation: There are three operational units at present; two are in operation since 1987 and 1989.

Licensor: Lummus Technology, a CB&I company CONTACT

НОМ

Isobutylene, high-purity

Application: The Snamprogetti methyl tertiary butyl ether (MTBE) cracking technology allows producing high-purity isobutylene, which can be used as monomer for elastomers (polylsobutylene, butyl rubber), and/ or as intermediate for the production of chemicals (MMA, tertiary-butyl phenols, tertiary-butyl amines, etc.)

Feed: MTBE can be used as the feedstock in the plant; in case of high level of impurities, a purification section can be added before the reactor.

Description: The MTBE cracking technology is based on proprietary catalyst and reactor that carry out the reaction with excellent flexibility, mild conditions as well as without corrosion and environmental problems.

With Saipem consolidated technology, it is possible to reach the desired isobutylene purity and production with only one tubular reactor (1) filled with a proprietary catalyst characterized for the right balance between acidity and activity.

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

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



Utilities:

Steam	5	t/t isobutylene
Water, cooling	186	m³/t isobutylene
Power	17.4	kWh/t isobutylene

Installation: Four units have been licensed by Saipem.

Licensor: Saipem CONTACT

НО

Isomerization

Application: C_5/C_6 paraffin-rich hydrocarbon streams are isomerized to produce high RON and MON product suitable for addition to the gasoline pool.

Description: Several variations of the C_5/C_6 isomerization process are available. The choice can be a once-through reaction for an inexpensive-but-limited octane boost, or, for substantial octane improvement and as an alternate (in addition) to the conventional DIH recycle option, the Ipsorb Isom scheme shown to recycle the normal paraffins for their complete conversion. The Hexorb Isom configuration achieves a complete normal paraffin conversion plus substantial conversion of low (75) octane methyl pentanes gives the maximum octane results. With the most active isomerization catalyst (chlorinated alumina), particularly with the Albemarle/Axens jointly developed ATIS2L catalyst, the isomerization performance varies from 84 to 92: once-through isomerization -84, isomerization with DIH recycle-88, Ipsorb-90, Hexorb-92.

Operating conditions: The Ipsorb Isom process uses a deisopentanizer (1) to separate the isopentane from the reactor feed. A small amount of hydrogen is also added to reactor (2) feed. The isomerization reaction proceeds at moderate temperature producing an equilibrium mixture of normal and isoparaffins. The catalyst has a long service life. The reactor products are separated into isomerate product and normal paraffins in the Ipsorb molecular sieve separation section (3) which features a novel vapor phase PSA technique. This enables the product to consist entirely of branched isomers.

Installation: Sixty-five C_5/C_6 isomerization licenses have been issued over the last 20 years, with over 27 obtained in the last five years. Twenty-one units are operating including one lpsorb unit.



Reference: Axens/Albemarle, "Advanced solutions for paraffin isomerization," NPRA Annual Meeting, March 2004, San Antonio.

"Paraffins isomerization options," *Petroleum Technology Quarterly*, Q2, 2005.

Licensor: Axens CONTACT

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Isomerization

Application: Convert normal olefins to isoolefins.

Description:

C₄ olefin skeletal isomerization (ISOMPLUS)

A zeolite-based catalyst especially developed for this process provides near equilibrium conversion of normal butenes to isobutylene 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 n-butenes, such as C_4 raffinate, can be processed without steam or other diluents, nor the addition of catalyst activation agents to promote the reaction. Near-equilibrium conversion levels up to 44% of the contained n-butenes are achieved at greater than 90% selectivity to isobutylene. During the process cycle, coke gradually builds up on the catalyst, reducing the isomerization activity. At the end of the process cycle, the feed is switched to a fresh catalyst bed, and the spent catalyst bed is regenerated by oxidizing the coke with an air/nitrogen mixture. The butene isomerate is suitable for making high purity isobutylene product.

C₅ olefin skeletal isomerization (ISOMPLUS)

A zeolite-based catalyst especially developed for this process provides near-equilibrium conversion of normal pentenes to isoamylene at high selectivity and long process cycle times. Hydrocarbon feeds containing n-pentenes, such as C_5 raffinate, are processed in the skeletal isomerization reactor without steam or other diluents, nor the addition of catalyst activation agents to promote the reaction. Near-equilibrium conversion levels up to 72% of the contained normal pentenes are observed at greater than 95% selectivity to isoamylenes.

Economics: The ISOMPLUS process offers the advantages of low capital investment and operating costs coupled with a high yield of isobutylene or isoamylene. Also, the small quantity of heavy byproducts formed can



easily be blended into the gasoline pool. Capital costs (equipment, labor and detailed engineering) for three different plant sizes are:

Total installed cost:	Feedrate, Mbpd	ISBL cost, \$MM
	10	8
	15	11
	30	20

Utility consumption: per barrel of feed (assuming an electric-motordriven compressor) are:

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

Installation: Two plants are in operation. Two licensed units are in various stages of design.

Licensor: Lummus Technology, a CB&I company CONTACT

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Isomerization

Application: For more refiners, the issue of benzene in the gasoline pool is one of managing benzene production from the catalytic reformer. The two primary strategies to accomplish this goal include the minimization of benzene and benzene precursors in the catalytic reformer feed, or elimination of the benzene from the reformate after it is formed. The UOP BenSat process can be applied in either of these strategies. The process can operate in stand-along mode or in conjunction with C_5-C_6 isomerization such as the UOP Penex-Plus process configuration.

Description: The UOP BenSat process was developed as a low-cost stand-alone option to treat C_5-C_6 feedstocks that are high in benzene. Benzene is saturated to C_6 naphthenes. The catalyst used in this process is highly selective for benzene saturation to C_6 naphthenes.

Makeup hydrogen is provided in an amount slightly above the stoichiometric level required for benzene saturation. The heat of reaction associated with benzene saturation is carefully managed to control temperature rise across the reactor. Use of a relatively high space velocity in the reactor contributes to the unit's cost-effectiveness.

Feed: Typical feeds include hydrotreated light straight-run (LSR) naphtha or light reformate streams. The Ben Sat process is designed to handle 30 vol% or more benzene in the feed. Sulfur suppresses activity, as expected for any noble-metal-based catalyst. However, the suppression effect is fully reversible by subsequent processing with clean feedstocks.

Yields: For feeds with 5–10 vol% benzene, the C_5^+ volumetric product yields are 101–106% of the feed. Because of high catalyst selectivity, hydrogen consumption is minimized and is near the stoichiometric level of three moles of hydrogen per mole of benzene saturated. The BenSat process saturates benzene without an increase in Rvp.



Installation: The first BenSat unit was started in 1994. Since then 13 additional units have been commissioned either as a stand-alone unit or integrated with the Penex process in a Penex-Plus configuration. Several additional units are in design and construction.

Licensor: UOP, A Honeywell Company CONTACT

Isomerization

Application: The widely used UOP Butamer process is a high-efficiency, cost effective means of meeting the demands for the production of isobutane by isomerizing normal butane (nC_4) to isobutane (iC_4) .

Motor-fuel alkylate is one blending component that has seen a substantial increase in demand because of its paraffinic, high-octane, lowvapor pressure blending properties. Isobutane is a primary feedstock for producing motor-fuel alkylate.

Description: UOP's innovative hydrogen-once-through (HOT) Butamer process results in substantial savings in capital equipment and utility costs by eliminating the need for a product separator or recycle-gas compressor.

Typically, two reactors, in series flow, are used to achieve high onstream efficiency. The catalyst can be replaced in one reactor while operation continues in the other. The stabilizer separates the light gas from the reactor effluent.

A Butamer unit can be integrated with an alkylation unit. In this application, the Butamer unit feed is a side-cut from an isostripper column, and the stabilized isomerate is returned to the isostripper column. Unconverted n-butane is recycled to the Butamer unit, along with n-butane from the fresh feed. Virtually complete conversion of n-butane to isobutane can be achieved.

Feed: The best feeds for a Butamer unit contain the highest practical n-butane content, and only small amounts of isobutane, pentanes and heavier material. Natural gas liquids (NGL) from a UOP NGL recovery unit can be processed in a Butamer unit.

Yield: The stabilized isomerate is a near-equilibrium mixture of isobutane and n-butane with small amounts of heavier material. The lightends yield from cracking is less than 1 wt% of the butane feed.



Installation: More than 75 Butamer units have been commissioned, and additional units are in design or construction. Butamer unit feed capacities range from 800 to 35,000⁺ bpsd (74 to 3,250 tpd).

Licensor: UOP, A Honeywell Company CONTACT

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Isomerization, C₅–C₆

Application: Isomalk-2 is used to isomerize light naphtha, along with benzene reduction. It is a broad range isomerization technology developed by NPP NEFTEHIM, which has been commercially proven in all modes of recycle. This flexible process utilizes a robust platinum-based mixed metal oxide catalyst that works effectively at low temperatures, while delivering greater stability against the influence of catalyst poisons. Isomalk-2 is a competitive alternative to the three most commonly used light gasoline isomerization processes: zeolite, chlorinated alumina and sulfated oxide catalysts. Full-range octane configurations of this technology have been demonstrated in grassroots and revamp units.

Description: Isomalk-2 is a vapor-phase isomerization technology with benzene reduction. Light naphtha is hydrodesulfurized and fed to a feed vaporizer, then to the isomerization reaction section. Normal paraffins are isomerized into an equilibrium mixture of iso-paraffins to increase the octane value. Any benzene in the feed is saturated in the first of two reactors. The second reactor completes the isomerization reaction. Unlike chloride catalyst systems, Isomalk-2 does not require bone-dry feed or HC feed dryers. Process feeds include light straight run (LSR), but could also be applied to a reformate stream, and LSR/ reformate combinations.

Process advantages:

- All versions are optimized for high conversion rate while producing a close approach to thermal equilibrium
- Catalyst exhibits superior physical activity and stability
- Commercially used in all configurations of recycle
- Process capability to produce up to 93 RON with full recycle
- Regenerable catalyst with superior tolerance to process impurities and water



- No chloride addition required; no neutralization of wastes
- Operating temperature range—120°C–180°C
- Mass yield > 98%
- Up to four year cycles between regenerations
- Reduced hydrogen consumption vs. chlorided systems

Installations: Nine units in operation

Licensor: GTC Technology US, LLC CONTACT

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Isomerization

Application: The UOP Par-Isom process is an innovative application using high-performance nonchlorided-alumina catalysts for light-naphtha isomerization. The process uses PI-242 catalyst, which approaches the activity of chlorided alumina catalysts without requiring organic chloride injection. The catalyst is regenerable and is sulfur and water tolerant.

Description: The fresh C_5/C_6 feed is combined with make-up and recycle hydrogen which is directed to a heat exchanger, where the reactants are heated to reaction temperature. The heated combined feed is then sent to the reactor. Either one or two reactors can be used in series, depending on the specific application.

The reactor effluent is cooled and sent to a product separator where the recycle hydrogen is separated from the other products. Recovered recycle hydrogen is directed to the recycle compressor and back to the reaction section. Liquid product is sent to a stabilizer column where light ends and any dissolved hydrogen are removed. The stabilized isomerate product can be sent directly to gasoline blending.

Feed: Typical feed sources for the Par-Isom process include hydrotreated light straight-run naphtha, light natural gasoline or condensate and light raffinate from benzene extraction units.

Water and oxygenates at concentrations of typical hydrotreated naphtha are not detrimental, although free water in the feedstock must be avoided. Sulfur suppresses activity, as expected, for any noble-metal based catalyst. However, the suppression effect is fully reversible by subsequent processing with clean feedstocks.

Yield: Typical product C_5^+ yields are 97 wt% of the fresh feed. The product octane is 81 to 87, depending on the flow configuration and feedstock qualities.



Installation: The first commercial Par-Isom process unit was placed in operation in 1996. There are currently 13 units in operation. The first commercial application of PI-242 catalyst was in 2003. There are several units in operation with PI-242 catalyst successsfully meeting all performance expectations.

Licensor: UOP, A Honeywell Company CONTACT

Isomerization

Application: Most of the implemented legislation requires limiting benzene concentration in the gasoline pool. This has increased the demand for high-performance C_5 and C_6 naphtha isomerization technology because of its ability to reduce the benzene concentration in the gasoline pool while maintaining or increasing the pool octane. The UOP Penex process is a fixed-bed process that uses high-activity chloride-promoted catalysts to isomerize C_5/C_6 paraffins to higher octane branched components. The reaction conditions promote isomerization and minimize hydrocracking. UOP currently offers I-82 catalyst and I-84 catalyst. These catalysts represent the most active and longest life catalysts available on the market today. The catalysts differ in platinum content - selection of the most appropriate catalyst is dependent largely on the characteristics of the feed.

Description: UOP's innovative hydrogen-once-through (HOT) Penex process results in subtantial savings in capital equipment and utility costs by eliminating the need for a product separator or recycle-gas compressor. The Penex process is a fixed-bed process that uses high-activity chloride-promoted catalysts to isomerize C_5/C_6 paraffins to higher-octane-branched components. The reaction conditions promote isomerization and minimize hydrocracking.

Typically, two reactors, in series flow, are used to achieve high onstream efficiency. The catalyst can be replaced in one reactor while operation continues in the other. The stabilizer separates light gas from the reactor effluent.

Products: For typical C_5/C_6 feeds, equilibrium will limit the product to 83 to 86 RONC on a single hydrocarbon pass basis. To achieve higher octane, UOP offers several schemes in which lower octane components are separated from the reactor effluent and recycled back to the reactors. These recycle modes of operation can lead to product octane as high as 93 RONC, depending on feed quality.



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Yields:

Penex process:	Octane 86
Penex process/DIH:	Octane 90
Penex process/Molex process:	Octane 91
DIP/Penex process/DIH:	Octane 93

Feed: The Penex process can process feeds with high levels of C_6 cyclics and C_7 components. In addition, feeds with substantial levels of benzene can be processed without the need for a separate saturation section.

Installation: UOP is the leading world-wide provider of isomerization technology. More than 120 Penex units are in operation today. Capacities range from 1,000 bpsd to more than 25,000 bpsd of fresh feed capacity.

Licensor: UOP, A Honeywell Company CONTACT

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lsooctene/isooctane

Application: New processes, RHT-isooctene and RHT-isooctane, can be used to revamp existing MTBE units to isooctene/isooctane production. Feeds include C_4 iso-olefin feed from FCC, steam crackers, thermal crackers or on-purpose iso-butylene from dehydrogenation units. The processes uses a unique configuration for dimerization. A new selectivator is used, together with a dual-bed catalyst.

The configuration is capable of revamping conventional or reactive distillation MTBE units. The process provides higher conversion, better selectivity, conventional catalyst, and a new selectivator supports with longer catalyst life with a dual catalyst application.

The process is designed to apply a hydrogenation unit to convert isooctene into isooctane, if desired, by utilizing a dual-catalyst system, in the first and finishing reactors. The process operates at lower pressure and provides lower costs for the hydrogenation unit.

Description: The feed is water washed to remove any basic compounds that can poison the catalyst system. Most applications will be directed toward isooctene production. However as olefin specifications are required, the isooctene can be hydrogenated to isooctane, which is an excellent gasoline blending stock.

The RHT isooctene process has a unique configuration; it is flexible and can provide low per pass conversion through dilution, using a new selectivator. The dual catalyst system also provides multiple advantages. The isobutylene conversion is 97–99 %, with better selectivity and yield together with enhanced catalyst life. The product is over 91% C₈ olefins, and 5–9% C₁₂ olefins, with very small amount of C₁₆ olefins.

The feed after water wash, is mixed with recycle stream, which provides the dilution (also some unreacted isobutylene) and is mixed with a small amount of hydrogen. The feed is sent to the dual-bed reactor for isooctene reaction in which most of isobutylene is converted to isooctene and codimer. The residual conversion is done with single-



resin catalyst via a side reactor. The feed to the side reactor is taken as a side draw from the column and does contain unreacted isobutylene, selectivator, normal olefins and non-reactive C_4 s. The recycle stream provides the dilution, and reactor effluent is fed to the column at multiple locations. Recycling does not increase column size due to the unique configuration of the process. The isooctene is taken from the debutanizer column bottom and is sent to OSBL after cooling or as is sent to hydrogenation unit. The C_4 s are taken as overhead stream and sent to OSBL or alkylation unit. Isooctene/product, octane (R+M)/2 is expected to be about 105.

Isooctene/isooctane, continued

If isooctane is to be produced the debutanizer bottom, isooctene product is sent to hydrogenation unit. The isooctene is pumped to the required pressure (which is much lower than conventional processes), mixed with recycle stream and hydrogen and is heated to the reaction temperature before sending it the first hydrogenation reactor. This reactor uses a nickel (Ni) or palladium (Pd) catalyst.

If feed is coming directly from the isooctene unit, only a start-up heater is required. The reactor effluent is flashed, and the vent is sent to OSBL. The liquid stream is recycled to the reactor after cooling (to remove heat of reaction) and a portion is forwarded to the finishing reactor—which also applies a Ni or Pd catalyst (preferably Pd catalyst)— and residual hydrogenation to isooctane reaction occurs. The isooctane product, octane (R+M)/2 is >98.

The reaction occurs in liquid phase or two phase (preferably two phases), which results in lower pressure option. The olefins in isooctene product are hydrogenated to over 99%. The finishing reactor effluent is sent to isooctane stripper, which removes all light ends, and the product is stabilized and can be stored easily.

Economics:

	Isooctene	Isooctane ¹
CAPEX ISBL, MM USD (US Gulf Coast 1Q 06, 1,000 bpd)	8.15	5.5
Utilities basis 1,000-bpd isooctene/isooc	tane	
Power, kWh	65	105
Water, cooling, m ³ /h	154	243
Steam, HP, kg/h	3,870	4,650
Basis: FCC feed (about 15–20% isobutel	ene in C₄ mixed	stream)

¹These utilities are for isooctene/isooctane cumulative.

Installation: Technology is ready for commercial application.

Licensor: Refining Hydrocarbon Technologies LLC CONTACT

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Isooctene/isooctane, conversion of refinery MTBE units

Application: The *Dimer*₈ process uses a fixed-bed reactor followed by catalytic distillation to achieve final isobutene conversion at high dimer selectivity. The *Dimer*₈ process is the most attractive technology for converting a refinery-based methyl tertiary butyl ether (MTBE) unit to isooctene/isooctane production.

Description: The selective dimerization of isobutenes over acidic ionexchange resin produces isooctene or di-isobutylene (DIB). Oxygenates such as methanol, MTBE, water or tert-butyl-alcohol (TBA) are used as selectivators for the dimerization reaction, to prevent formation of heavier oligomers. The *Dimer*₈ process uses a fixed-bed reactor followed by catalytic distillation to achieve final isobutene conversion at high dimer selectivity.

The primary fixed-bed reactor can utilize a boiling point reactor or a water-cooled tubular reactor (WCTR) design depending on the finished product and operational requirements of the refiner. Either reactor can be used to achieve high isobutylene conversion with excellent dimer selectivity.

The unique catalytic distillation (CD) column combines reaction and distillation in a single unit operation. Continuous removal of heavier dimer product from the reaction zone enables further conversion of isobutene without loss of dimer selectivity. The use of CD eliminates the need for any downstream reaction/fractionation system to achieve such performance.

Isooctene can be used as a gasoline blendstock due to its excellent characteristics. Should olefin restrictions require a paraffinic product, the isooctene product can be saturated to isooctane in a trickle-bed hydrogenation reactor. Hydrogenation uses a base or noble metal catalyst depending on the feed contamination level.



Process advantages include:

- Easy implementation, minimum revamp changes, low capital cost, short schedule
- 90+% isobutylene conversion
- 80+% C₈ selectivity
- High flexibility
- Simple control
- High octane/low Rvp blend stock
- Low utilities.

Licensors: Jointly licensed Lummus Technology, a CB&I company, and Saipem <u>CONTACT</u>

Isooctene/isooctane

Application: The Snamprogetti dimerization/hydrogenation technology is used to produce isooctene/isooctane—high-octane compounds (rich in C_8) for gasoline blending.

Feed: C_4 streams from steam cracker, Fluid Catalytic Cracking Unit (FCC) and isobutane dehydrogenation units with isobutene contents ranging from 15 wt% to 50 wt %.

Products: Isooctene and Isooctane streams contain at least 85 wt% of C_{8} s with less than 5,000 ppm of oligomers higher than C_{12} s.

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

Oxygenates, such as methanol, Methyl Tertiary Butyl Ether (MTBE) and/or Tert-Butyl Alcohol (TBA), are used as "selectivator" to improve selectivity of the dimerization reaction while avoiding formation of heavier oligomers.

A high conversion level of isobutene (99 wt%) can be reached with a double-stage configuration where, in both stages, Water Cooled Tubular Reactors (WCTR), (1) and (2), are used for the isobutene dimerization to maintain an optimal temperature control inside the catalytic bed.

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

The isooctene product, collected as bottom of column (4), can be sent to storage or fed to the hydrogenation unit (7) to produce the saturate hydrocarbon stream—isooctane.

Due to a joint development agreement between Snamprogetti and Catalytic Distillation Technologies (CDTech) for the isobutene dimerization (*Dimer8* process) the plant configuration can be optionally modi-



fied with the introduction of a catalytic distillation (CD Column), to have an alternative scheme particularly suitable for revamping of refinery MTBE units.

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

Steam	1	t/t isooctene
Water, cooling	65	m³∕t isooctene
Power	15	kWh/t isooctene

Installation: Five industrial tests have been carried out with different feedstock, and two units have been licensed by Saipem.

Licensor: Saipem CONTACT

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Isooctene/isooctane, conversion of refinery MTBE units

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Licensors: Jointly licensed Lummus Technology, a CB&I company, and Saipem <u>CONTACT</u>

Iso-paraffins, maximizing

Application: Upgrade of fluid catalytic cracking (FCC) units for reduction of olefins, sulfur and benzene in FCC gasoline, increase of high-octane components, such as iso-paraffins, and overall gasoline yield via the maximizing iso-paraffins technology (MIP).

Products: Iso-paraffins-rich gasoline, isobutane-rich LPG and distillate

Description: FCC process produces 30%-80% of the global gasoline supply, depending on geographic location. The FCC gasoline contains a significant amount of olefins and sulfur, with a typical olefins content ranging 30%-55%.

Olefins in gasoline can lead to deposit formation and increased emissions of reactive (i.e., ozone-forming) hydrocarbons and toxic compounds. New, clean gasoline specifications require refiners to reduce the olefins in gasoline to 18 vol% and even further to 10 vol%. Conversely, olefins also are high-octane components of gasoline. The octane loss from olefins reduction must be compensated by other high-octane components, with iso-paraffins being the most desired for clean gasoline. Thus, maximizing iso-paraffins in FCC gasoline is of significant importance for meeting present high-level specifications of gasoline quality.

The MIP process scheme and operation are similar to a conventional FCC unit, but with some unique characteristics:

• A two-zone riser, with the two zones operated at different conditions, selectively promotes chemical reactions that crack heavy feedstock and convert gasoline olefins to iso-paraffins.

• Recycled catalyst or quench stream is injected into the second zone, which has larger diameter than the first zone, to lower temperature and increase reaction time.

• Optional proprietary catalysts enhance hydrogen transfer reactions while cracking heavy feeds.

The two riser zones are connected in series with a larger diameter Zone 2 on top of Zone 1, which has a smaller diameter. Zone 1 is oper-



ated at a high temperature and short residence time, while Zone 2 is operated at a low temperature and longer residence time. Such two-zone configuration provides much better control of desired reactions than a single-diameter riser that is dominantly used in conventional FCC.

In the two-zone riser of MIP technology, the primary cracking reactions are carried out in Zone 1, while the secondary reactions (hydrogen transfer, isomerization and alkylation) are favorably promoted in Zone 2 to convert the olefins to iso-paraffins and aromatics without the addition of external hydrogen. MIP has advantages over conventional FCC:

- Produces cleaner gasoline
 - o Reduces olefins by 20%-50%
 - o Reduces sulfur and benzene by 20%-40%
 - o Improved octane numbers

Iso-paraffins, maximizing, continued

- Produces higher gasoline yield
- Increases iso-butane (feedstock for alkylation) up to 40% in LPG
- Produces higher total liquid yield and less dry gas and slurry.

MIP technology can be installed in either an existing or grassroots FCC unit by modifying the unit's riser reactor section.

Products, wt% of fresh feed	FCC	MIP
Dry gas	3.8	2.9
LPG	15.4	14.6
Gasoline	44.1	49.3
Total liquid yield	82.2	85.1
Gasoline properties		
Olefins, vol%	43.1	34.1
lso-paraffins, vol%	29.5	39.6
Sulfur	Base	66% of Base
Benzene, vol%	0.437	0.307
RON	88.8	89.4
MON	79.2	80.2

Installations: A total of 17 MIP units have been installed (14 revamps of FCC and three grassroots), with capacities ranging from 0.44 to 2.8 million tpy.

Reference: Long, J. et al., "New generation of fluid catalytic cracking processes for production of clean gasoline and propylene," unpublished, *Hydrocarbon Processing,* September 2011.

Licensor: Shaw and Sinopec RIPP CONTACT

Lube extraction

Application: Bechtel's Furfural Refining process is a solvent-extraction process that uses furfural as the solvent to selectively remove undesirable components of low lubrication oil quality, which are naturally present in crude oil distillate and residual stocks. This process selectively removes aromatics and compounds containing heteroatoms (e.g., oxygen, nitrogen and sulfur). The unit produces paraffinic raffinates suitable for further processing into lube base stocks.

Products: A raffinate that may be dewaxed to produce a high-quality lube-base oil, characterized by high viscosity index, good thermal and oxidation stability, light color and excellent additive response. The byproduct extracts, being high in aromatic content, can be used, in some cases, for carbon black feedstocks, rubber extender oils and other nonlube applications where this feature is desirable.

Description: The distillate or residual feedstock and solvent are contacted in the extraction tower (1) at controlled temperatures and flowrates required for optimum countercurrent, liquid-liquid extraction of the feedstock. The extract stream, containing the bulk of the solvent, exits the bottom of the extraction tower. It is routed to a recovery section to remove solvent contained in this stream. Solvent is separated from the extract oil by multiple-effect evaporation (2) at various pressures, followed by vacuum flashing and steam stripping (3) under vacuum. The raffinate stream exits the overhead of the extraction tower and is routed to a recovery section to remove the furfural solvent contained in this stream by flashing and steam stripping (4) under vacuum.

The solvent is cooled and recycled to the extraction section. Overhead vapors from the steam strippers are condensed and combined with the solvent condensate from the recovery sections and are distilled at low pressure to remove water from the solvent. Furfural forms an azeotrope with water and requires two fractionators. One fractionator (5) separates the furfural from the azeotrope, and the second (6) separates



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water from the azeotrope. The water drains to the oily-water sewer. The solvent is cooled and recycled to the extraction section.

Economics:

Investment (Basis: 10,000-bpsd feedrate	
capacity, 2011 US Gulf Coast), \$/bpsd	6,400
Utilities, typical per bbl feed:	
Fuel, 10 ³ Btu (absorbed)	120
Electricity, kWh	2
Steam, lb	5
Water, cooling (25°F rise), gal	650

Installation: For almost 60 years, this process has been or is being used in over 100 licensed units to produce high-quality lubricating oils.

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT

Lube extraction

Application: Bechtel's MP Refining process is a solvent-extraction process that uses N-methyl-2-pyrrolidone (NMP) as the solvent to selectively remove the undesirable components of low-quality lubrication oil, which are naturally present in crude oil distillate and residual stocks. The unit produces paraffinic or naphthenic raffinates suitable for further process-ing into lube-base stocks. This process selectively removes aromatics and compounds containing heteroatoms (e.g., oxygen, nitrogen and sulfur).

Products: A raffinate that may be dewaxed to produce a high-quality lube-base oil, characterized by high viscosity index, good thermal and oxidation stability, light color and excellent additive response. The byproduct extracts, being high in aromatic content, can be used, in some cases, for carbon black feedstocks, rubber extender oils and other nonlube applications where this feature is desirable.

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Overhead vapors from the steam strippers are condensed and combined with solvent condensate from the recovery sections and are distilled at low pressure to remove water from the solvent (5). Solvent is recovered in a single tower because NMP does not form an azeotrope with water, as does furfural. The water is drained to the oily-water sewer. The solvent is cooled and recycled to the extraction section.



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Economics:

Investment (Basis: 10,000-bpsd feedrate	
capacity, 2011 US Gulf Coast), \$/bpsd	6,200
Utilities, typical per bbl feed:	
Fuel, 10 ³ Btu (absorbed)	100
Electricity, kWh	2
Steam, lb	5
Water, cooling (25°F rise), gal	600

Installation: This process is being used in 15 licensed units to produce high-quality lubricating oils. Of this number, eight are units converted from phenol or furfural, with another three units under license for conversion.

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT

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Lube hydrotreating

Application: The Bechtel Hy-Finishing process is a specialized hydrotreating technology to remove impurities and improve the quality of paraffinic and naphthenic lubricating base oils. In the normal configuration, the hydrogen finishing unit is located in the processing scheme between the solvent extraction and solvent dewaxing units for a lube plant operating on an approved lube crude. In this application, the unit operates under mild hydrotreating conditions to improve color and stability, to reduce sulfur, nitrogen, oxygen and aromatics, and to remove metals.

Another application is Hy-Starting, which is a more severe hydrotreating process (higher pressure and lower space velocity) and upgrades distillates from lower-quality crudes. This unit is usually placed before solvent extraction in the processing sequence to upgrade distillate quality and, thus, improve extraction yields at the same raffinate quality.

Description: Hydrocarbon feed is mixed with hydrogen (recycle plus makeup), preheated, and charged to a fixed-bed hydrotreating reactor (1). Reactor effluent is cooled in exchange with the mixed feed-hydrogen stream. Gas-liquid separation of the effluent occurs first in the hot separator (2) then in the cold separator (3). The hydrocarbon liquid stream from each of the two separators is sent to the product stripper (4) to remove the remaining gas and unstabilized distillate from the lube-oil product. The product is then dried in a vacuum flash (5). Gas from the cold separator is amine-scrubbed (6) to remove H2S before compression in the recycle hydrogen compressor (7).

Economics:

Investment (Basis 7,000-bpsd feedrate capacity, 2011 US Gulf Coast), \$/bpsd

7,900



Utilities, typical per bbl feed:	
Fuel, 10 ³ Btu (absorbed)	20
Electricity, kWh	5
Steam, lb	15
Water, cooling (25°F rise), gal	400

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT

Lube hydrotreating

Application: Hy-Raff is a new process to hydrotreat raffinates from an extraction unit of a solvent-based lube oil plant for upgrading standard Group I lube-base oils to produce Group II base oils. Sulfur is reduced to below 0.03 wt% and saturates are increased to greater than 90 wt%. The integration of this process into an existing base oil plant allows the operator to cost-effectively upgrade base-oil products to the new specifications rather than scrapping the existing plant and building an expensive new hydrocracker-based plant.

The product from the Hy-Raff unit is a lube-base oil of sufficient quality to meet Group II specifications. The color of the finished product is significantly improved over standard-base oils. Middle distillate byproducts are of sufficient quality for blending into diesel.

Description: Raffinate feed is mixed with hydrogen (recycle plus makeup), preheated, and charged to a fixed-bed hydrotreating reactor (1). The reactor effluent is cooled in exchange with the mixed feed-hydrogen stream. Gas-liquid separation of the effluent occurs first in the hot separator (2) then in the cold separator (3). The hydrocarbon liquid stream from each of the two separators is sent to the product stripper (4) to remove the remaining gas and unstabilized distillate from the lube-oil product, and product is dried in a vacuum flash (5). Gas from the cold separator is amine-scrubbed (6) for removal of H2S before compression in the recycle-hydrogen compressor (7).

Economics:

Investment (Basis 7,000-bpsd feedrate capacity, 2011 U.S. Gulf Coast), \$/bpsd

11,000



Utilitiies, typical per bbl feed:	
Fuel, 10 ³ Btu (absorbed)	70
Electricity, kWh	5
Steam, lb	15
Water, cooling (25°F rise), gal	200

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT

Lube oil refining, spent

Application: The Revivoil process can be used to produce high yields of premium quality lube bases from spent motor oils. Requiring neither acid nor clay treatment steps, the process can eliminate environmental and logistical problems of waste handling and disposal associated with conventional re-refining schemes.

Description: Spent oil is distilled in an atmospheric flash distillation column to remove water and gasoline and then sent to the Thermal Deasphalting (TDA) vacuum column for recovery of gas oil overhead and oil bases as side streams. The energy-efficient TDA column features excellent performance with no plugging and no moving parts. Metals and metalloids concentrate in the residue, which is sent to an optional Selectopropane unit for brightstock and asphalt recovery. This scheme is different from those for which the entire vacuum column feed goes through a deasphalting step; Revivoil's energy savings are significant, and the overall lube oil base recovery is maximized. The results are substantial improvements in selectivity, quality and yields.

The final, but very important step for base oil quality is a specific hydrofinishing process that reduces or removes remaining metals and metalloids, Conradson Carbon, organic acids, and compounds containing chlorine, sulfur and nitrogen. Color, UV and thermal stability are restored and polynuclear aromatics are reduced to values far below the latest health thresholds. Viscosity index remains equal to or better than the original feed. For metal removal (> 96%) and refining-purification duty, the multicomponent catalyst system is the industry's best.

Product quality: The oil bases are premium products; all lube oil base specifications are met by Revivoil processing from Group 1 through Group 2 of the API basestocks definitions. Besides, a diesel can be obtained, in compliance with the EURO 5 requirements (low sulfur).



Health & safety and environment: The high-pressure process is in line with future European specifications concerning carcinogenic PNA compounds in the final product at a level inferior to 5 wppm (less than 1 wt% PCA - IP346 method).

Economics: The process can be installed stepwise or entirely. A simpler scheme consists of the atmospheric flash, TDA and hydrofinishing unit and enables 70%–80% recovery of lube oil bases. The Selectopropane unit can be added at a later stage, to bring the oil recovery to the 95% level on dry basis. For two plants of equal capacity, payout times before taxes are two years in both cases.

Installation: Twelve units have been licensed using all or part of the Revivoil Technology.

Licensor: Axens and Viscolube SpA CONTACT
2011 Refining Processes Handbook

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Lube treating

Application: Process to produce lube oil raffinates with high viscosity index from vacuum distillates and deasphalted oil.

Feeds: Vacuum distillate lube cuts and deasphalted oils.

Products: Lube oil raffinates of high viscosity indices. The raffinates contain substantially all of the desirable lubricating oil components present in the feedstock. The extract contains a concentrate of aromatics that may be utilized as rubber oil or cracker feed.

Description: This liquid-liquid extraction process uses furfural or Nmethyl pyrrolidone (NMP) as the selective solvent to remove aromatics and other impurities present in the distillates and deasphalted oils. The solvents have a high solvent power for those components that are unstable to oxygen as well as for other undesirable materials including color bodies, resins, carbon-forming constituents and sulfur compounds. In the extraction tower, the feed oil is introduced below the top at a predetermined temperature. The raffinate phase leaves at the top of the tower, and the extract, which contains the bulk of the furfural, is withdrawn from the bottom. The extract phase is cooled and a so-called "pseudo raffinate" may be sent back to the extraction tower. Multistage solvent recovery systems for raffinate and extract solutions secure energy efficient operation.

Utility requirements (typical, Middle East crude), units per m³ of feed:

Electricity, kWh	10
Steam, MP, kg	10
Steam, LP, kg	35
Fuel oil, kg	20
Water, cooling, m ³	20



Installation: Numerous installations using the Uhde (Edeleanu) proprietary technology are in operation worldwide. The most recent is a complete lube-oil production facility licensed to the state of Turkmenistan.

Licensor: Uhde GmbH CONTACT

Methanol to gasoline

Application: Conversion of methanol to gasoline. In combination with syngas generation from gasification or gas reforming and conversion of syngas to methanol, the Methanol to Gasoline (MTG) process can convert coal, biomass or natural gas into conventional gasoline.

Products: Conventional regular octane gasoline and LPG. A small volume byproduct fuel gas stream is also produced.

Description: ExxonMobil's Research and Engineering's (EMRE's) MTG utilizes a two-stage catalytic conversion of methanol to hydrocarbons and water. The initial stage uses a conventional methanol to DME (dimethyl ether) conversion reactor to produce an equilibrium mixture of methanol, DME and water. The DME reactor effluent is fed to MTG reactors that complete the dehydration of the methanol and DME producing light olefins and water. The MTG catalysts promotes oligimerization of light olefins and conversion of higher olefins into branched paraffins, naphthenes and aromatics. EMRE utilizes a proprietary shape selective ZSM-5 catalyst that limits the hydrocarbon synthesis product to C_{10} hydrocarbons with a final boiling point consistent with gasoline.

The heat of reaction from the dehydration of the methanol and conversion reactions is approximately 1.7 MJ/kg. The temperature rise in the MTG reactors due to the heat of reaction is limited by a gas recycle.

The MTG reactions produce small amounts of coke, which forms on the catalyst. Coke is removed by *in-situ* regeneration, which is accommodated by using multiple MTG reactors operating in parallel.

Methanol feed is vaporized and pre-heated by heat exchange with the MTG reactor effluent. The cooled MTG reactor effluent is separated into water, raw gasoline and light gas. The raw gasoline is separated into ethylene and lower gases, C_3/C_4 , LPG and a light and heavy gasoline. The heavy gasoline is hydrotreated to reduce the concentration of durene (1,2,4,5 tetra-methyl benzene).

Operating conditions: Temperatures, °F Reactor pressures, psig

Yields:

MTG gasoline yields

Percent of feed	Percent of hydrocarbon product
1%	2%
5%	11%
38%	87%
56%	-
	Percent of feed 1% 5% 38% 56%

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Installation: The first MTG unit was built and operated by a joint venture between Mobil Corp. and the government of New Zealand. This 14,500 bpd natural gas-to-gasoline plant was started up in 1985 and operated until 1997. The first second-generation MTG unit was constructed by the Jincheng Anthracite Mining Group in Shanxi Province, China. This 2,500 bpd coal-to-gasoline unit started in June 2009.

Licensor: ExxonMobil Research and Engineering Co. CONTACT

600-800

330-400

Multipurpose gasification

Application: Production of synthesis gas, essentially H_2 and CO, from a wide range of gaseous to extra heavy liquid hydrocarbons, as well as emulsions and slurries. Recent new applications are in (chemical) waste gasification. The main advantage over comparable processes is its extreme feedstock flexibility in the quench mode. A boiler mode for highest efficiency is also available.

Description: Continuous noncatalytic partial oxidation process. The quench mode is shown above: hydrocarbon feedstock, moderator (H_2O , CO_2 or N_2) and oxidant (pure or diluted O_2 , air) are fed through a special burner into the reactor (1), a refractory-lined pressure vessel. Operating conditions are automatically controlled. Hot gas leaves the reactor at the bottom, passing the quench where water is injected to lower the temperature near the saturation temperature. Quench water washes out most particulates as unconverted carbon (soot) and ash.

Further cleaning occurs in a venturi scrubber (2) from where the gas passes to a medium-pressure steam boiler (3) for heat recovery and to the final cooler (4) before further processing. In hydrogen production, the hot, wet gas from the venturi is passed directly to a raw gas shift conversion. The soot/ash slurry from the process contains virtually all metals and ashes from the feedstock. It is withdrawn via a slurry collector (5) and processed in the metals ash recovery system (MARS) (6). There, soot/ash is filtered from the slurry and incinerated under controlled conditions, yielding a saleable metal/ash product. Filtered water is returned for quenching. Excess water is stripped and sent to conventional wastewater treatment.

Operating conditions: Actual gasification temperatures of 1,200°C to 1,500°C, pressures from atmospheric to 70 bar (or higher, if economically justified). Feedstock and oxidant preheat possible in a wide range from 100°C to 600°C, depending on type of feed. Product yields and composi-



tion vary with moderator rate and type of feed. Water quench is selected for highest feedstock flexibility. At low-salt contents, the boiler mode can recover heat as high-pressure steam, raising overall efficiency.

Economics: Characteristic consumption and production rates per ton of heavy residue feedstock: 1 to 1.1 t O_2 (100%), export 0.5 t MP steam (quench) to 2.2 t HP steam (boiler mode), 2.2 t raw syngas (dry) equiv. to 2,600 Nm³ H₂ + CO. Cold gas efficiency is 82% to 85%. In boiler mode, thermal efficiencies including HP steam generated are about 95% based on feedstock HHV. This makes the process attractive for syngas production and for an IGCC power plant. A highly integrated and efficient power complex will be in the range of \$1,200/kW total invested cost.

Continued ▼

Multipurpose gasification, continued

Installations: A large-scale industrial plant operates in Germany, demonstrating full feedstock and product flexibility by feeding to a methanol and IGCC complex. Another plant gasifies residue asphalt, producing syngas for an ammonia plant.

Reference: Liebner, W. and C. Erdmann, "MPG—Lurgi Multipurpose Gasification—Recent Applications and Experiences," World Petroleum Congress 2000, Calgary, Canada, June 2000.

Licensor: Lurgi GmbH CONTACT

NO_x reduction, low-temperature

Application: The LoTO_x low-temperature oxidation process removes NO_x from flue gases in conjunction with BELCO's EDV wet scrubbing system. Ozone is a very selective oxidizing agent; it converts relatively insoluble NO and NO₂ to higher, more soluble nitrogen oxides. These oxides are easily captured in a wet scrubber that is controlling sulfur compounds and/or particulates simultaneously.

Description: In the LoTO_x process, ozone is added to oxidize insoluble NO and NO₂ to highly oxidized, highly soluble species of NO_x that can be effectively removed by a variety of wet or semi-dry scrubbers. Ozone, a highly effective oxidizing agent, is produced onsite and on demand by passing oxygen through an ozone generator—an electric corona device with no moving parts. The rapid reaction rate of ozone with NO_x results in high selectivity for NO_x over other components within the gas stream.

Thus, the NO_x in the gas phase is converted to soluble ionic compounds in the aqueous phase; the reaction is driven to completion, thus removing NO_x with no secondary gaseous pollutants. The ozone is consumed by the process or destroyed within the system scrubber. All system components are proven, well-understood technologies with a history of safe and reliable performance.

Operating conditions: Ozone injection typically occurs in the flue-gas stream upstream of the scrubber, near atmospheric pressure and at temperatures up to roughly 150°C. For higher-temperature streams, the ozone is injected after a quench section of the scrubber, at adiabatic saturation, typically 60°C to 75°C. High-particulate saturated gas and sulfur loading (SO_x or TRS) do not cause problems.

Economics: The costs for NO_x control using this technology are especially low when used as a part of a multi-pollutant control scenario. Sulfurous and particulate-laden streams can be treated attractively as no pretreatment is required by the $LoTO_x$ system.



Installation: The technology has been developed and commercialized over several years, winning the prestigious 2001 Kirkpatrick Chemical Engineering Technology Award. At present, more than 29 units have been sold, including units on boiler, sulfuric acid plants and FCC units. Many other EDV scrubbers have been designed for future LoTO_x application. Pilot-scale demonstrations have been completed on coal- and petroleum-coke fired boilers, as well as refinery FCC units.

Reference: Confuorto, et al., "LoTO_x technology demonstration at Marathon Ashland Petroleum LLC's refinery at Texas City, Texas," NPRA Annual Meeting, March 2004, San Antonio.

Licensor: Belco Technologies Corp. CONTACT

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Olefin etherification

Application: New processing methods improve etherification of C_4-C_7 reactive olefins including light catalytic naphtha (LCN) with alcohol (e.g., methanol and ethanol). The processes, RHT-MixedEthers, RHT-MTBE, RHT-ETBE, RHT-TAME and RHT-TAEE, use unique concepts to achieve the maximum conversion without applying cumbersome catalyst in the column. The processing economics provide improvements over other available ether technologies currently available. The technology suite can be applied to ethyl tertiary butyl ether (ETBE) production in which wet ethanol can be used in place of dry ethanol. The drier can be eliminated, which is approximately half the cost for an etherification unit. The RHT ethers processes can provide the highest conversion with unique multiple equilibrium stages.

Description: The feed is water washed to remove basic compounds that are poisons for the resin catalyst of the etherification reaction. The C₄ ethers—methyl tertiary butyl ether (MTBE)/ETBE), C₅-tertiary amyl methyl ether (TAME/ tertiary amyl ethyl ether (TAEE) and C₆ /C₇ ethers are made in this process separately. The reaction is difficult; heavier ethers conversion of the reactive olefins are equilibrium conversion of about 97% for MTBE and 70% for TAME and much lower for C₆/C₇ ethers are expected.

Higher alcohols have similar effects (azeotrope hydrocarbon/alcohol relationship decreases when using methanol over ethanol). The equilibrium conversions and azeotrope effects for higher ethers are lower, as is expected. After the hydrocarbon feed is washed, it is mixed with alcohol with reactive olefin ratio control with alcohol.

The feed mixture is heated to reaction temperature (and mixed with recycle stream (for MTBE/ETBE only) and is sent to the first reactor (1), where equilibrium conversion is done in the presence of sulfonated resin catalyst, e.g. Amberlyst 15 or 35 or equivalent from other vendors.



Major vaporization is detrimental to this reaction. Vapor-phase reactive olefins are not available for reaction. Additionally at higher temperatures, there is slight thermal degradation of the catalyst occurs. The reactor effluent is sent to fractionator (debutanizer or depentanizer) to separate the ether and heavy hydrocarbons from C_4 or C_5 hydrocarbons, which are taken as overhead. Single or multiple draw offs are taken from the fractionation column. In the fractionation column, unreacted olefins (C_4 or C_5) are sent to the finishing reactor (5). This stream normally does not require alcohol, since azeotrope levels are available. But, some additional alcohol is added for the equilibrium-stage reaction. Depending on the liquid withdrawn (number of side draws), the conversion can be enhanced to a higher level than via other conventional or unconventional processes.

Olefin etherification, continued

By installing multiple reactors, it is possible to extinct the olefins within the raffinate. The cost of side draws and reactors can achieve pay-off in 6 to 18 months by the higher catalyst cost as compared to other processes. This process could provide 97–99.9% isobutene conversion in C₄ feed (depending on the configuration) and 95–98+% of isoamylenes in C₅ stream.

The ether product is taken from the bottom, cooled and sent to the storage. The raffinate is washed in extractor column (6) with and is sent to the OSBL. The water/alcohol mixture is sent to alcohol recovery column (7) where the alcohol is recovered and recycled as feed.

For ETBE and TAEE, ethanol dehydration is required for most of the processes, whereas for RHT process, wet ethanol can be used providing maximum conversions. If need be, the TBA specification can be met by optimum design with additional equipment providing high ETBE yield and conversion. Cost of ethanol dehydration is much more than the present configuration for the RHT wet-ethanol process.

The total capital cost/economics is lower with conventional catalyst usage, compared to other technologies, which use complicated structure, require installing a manway (cumbersome) and require frequently catalyst changes outs.

The RHT ether processes can provide maximum conversion as compared to other technologies with better economics. No complicated or proprietary internals for the column including single source expensive catalyst. Distillation is done at optimum conditions. Much lower steam consumption for alcohol recovery. For example, the C₅ feed case requires less alcohol with RHT configuration (azeotropic alcohol is not required) and lowers lower steam consumption.

Economics:

CAPEX ISBL, MM USD (US Gulf Coast 1Q06,	
1,000-bpd ether product)	9.1
Utilities Basis 1,000 bpd ether	
Power kWh	45.0
Water, cooling m ³ /h	250
Steam MP, Kg/h	6,000
Basis: FCC Feed (about 15–20% isobutylene in C ₄ m	ixed stream

Commercial units: Technology is ready for commercialization.

Licensor: Refining Hydrocarbon Technologies LLC CONTACT

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Olefins recovery

Application: Recover high-purity hydrogen (H_2) and C_2^+ liquid products from refinery offgases using cryogenics.

Description: Cryogenic separation of refinery offgases and purges containing 10%-80% H₂ and 15%-40% hydrocarbon liquids such as ethylene, ethane, propylene, propane and butanes. Refinery offgases are optionally compressed and then pretreated (1) to remove sulfur, carbon dioxide (CO₂), H₂O and other trace impurities. Treated feed is partially condensed in an integrated multi-passage exchanger system (2) against returning products and refrigerant.

Separated liquids are sent to a demethanizer (3) for stabilization while hydrogen is concentrated (4) to $90\%-95\%^+$ purity by further cooling. Methane, other impurities, and unrecovered products are sent to fuel or optionally split into a synthetic natural gas (SNG) product and low-Btu fuel. Refrigeration is provided by a closed-loop system (5). Mixed C₂+ liquids from the demethanizer can be further fractionated (6) into finished petrochemical feeds and products such as ethane, ethylene, propane and propylene.

Operating conditions: Feed capacities from 10 to 150+ million scfd. Feed pressures as low as 150 psig. Ethylene recoveries are greater than 95%, with higher recoveries of ethane and heavier components. Hydrogen recoveries are better than 95% recovery.

Economics: Hydrogen is economically co-produced with liquid hydrocarbon products, especially ethylene and propylene, whose high value can subsidize the capital investment. High hydrocarbon liquid products recovery is achieved without the cost for feed compression and subsequent feed expansion to fuel pressure. Power consumption is a function of hydrocarbon quantities in the feed and feed pressure. High-purity hydrogen is produced without the investment for a "back-end" PSA system. Project costs can have less than a two-year simple payback.



Installations: Five operating refinery offgas cryogenic systems processing FCC offgas, cat reformer offgas, hydrotreater purge gas, coker offgas and refinery fuel gas. Several process and refrigeration schemes used since 1987 with the most recent plant startup in 2001.

Reference: US Patents 6,266,977 and 6,560,989.

Trautmann, S. R. and R. A. Davis, "Refinery offgases—alternative sources for ethylene recovery and integration," AIChE Spring Meeting, New Orleans, March 14, 2002, Paper 102d.

Licensor: Air Products and Chemicals Inc. CONTACT

Olefins—butenes extractive distillation

Application: Separation of pure C_4 olefins from olefinic/paraffinic C_4 mixtures via extractive distillation using a selective solvent. BUTENEX is the Uhde technology to separate light olefins from various C_4 feed-stocks, which include ethylene cracker and FCC sources.

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

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

Economics:

Consumption per metric ton of FCC C₄ fraction feedstock:

Steam, t/t	0.5-0.8
Water, cooling ($\Delta T = 10^{\circ}C$), m ³ /t	15.0
Electric power, kWh/t	25.0
Product purity:	
n - Butene content	99.+ wt% min.

Solvent	content
2010 CTTC	contente

99.+ wt.– % min. 1 wt.–ppm max.



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

Licensor: Uhde GmbH CONTACT

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Olefins—dehydrogenation of light paraffins to olefins

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

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

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

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

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

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



After cooling and condensate separation, the product is subsequently compressed, light-ends are separated and the olefin product is separated from unconverted paraffins in the fractionation section.

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

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

Propane, kg/metric ton	1,200
Fuel gas, GJ/metric ton	6.4
Circul. cooling water, m ³ /metric ton	170
Electrical energy, kWh/metric ton	100

Continued **V**

Olefins—dehydrogenation of light paraffins to olefins, *continued*

Installation: Two commercial plants using the STAR process for dehydrogenation of isobutene to isobutylene have been commissioned (in the US and Argentina). A STAR process oxydehydrogenation plant for the production of 350,000 tpy propylene will go onstream in Egypt in 2009. More than 60 Uhde reformers and 25 Uhde secondary reformers have been constructed worldwide.

References: Heinritz-Adrian, M., S. Wenzel and F. Youssef, "Advanced propane dehydrogenation," *Petroleum Technology Quarterly,* Spring 2008, pp. 83–91.

Heinritz-Adrian, M., "STAR process – Advanced propane dehydrogenation for on-purpose propylene production," CMT 5th Middle East Olefins & Polyolefins Conference, Dubai, November 2007.

Wenzel, S., "STAR process—Uhde's oxydehydrogenation technology," 9th International Petrochemicals & Gas Conference and Exhibition, London, 2007.

Licensor: Uhde GmbH CONTACT

Oxygen enrichment for Claus units

Application: Overcome bottlenecks due to limited gas throughout typically for capacity increase and/or decompose detrimental hazardous materials such as ammonia

Description: As "clean fuels" regulations become effective, refiners must recover more sulfur in their Claus plants. As a byproduct of deep desulfurization, ammonia is generated and typically must be decomposed in the Claus plant. To upgrade the sulfur recovery units (SRUs) accordingly, oxygen enrichment is an effcient and low-cost option. Oxygen enrichment can increase sulfur capacity substantially and is capable of decomposing ammonia from sour-water stripper gas very efficiently.

Oxygen addition can be done in three levels, depending on the required capacity increase:

1. **Up to approximately 28% oxygen.** Oxygen is simply added to the Claus furnace air. This can raise sulfur capacity by up to 35%.

2. **Up to approximately 40% oxygen.** The burner of the Claus furnace must be replaced. Up to 60% additional sulfur capacity can be achieved by this method.

3. **Beyond 40% oxygen.** This option allows for 100% more capacity and beyond. Here major modification of Claus unit is necessary, e.g., implementing a second thermal stage.

Oxygen sources can be liquid oxygen tanks, onsite air separation units (ASUs) or pipeline supply. Oxygen consumption in Claus plants fluctuates widely in most cases; thus, tanks are the best choice due to ease of operation, flexibility and economy. For oxygen addition into the CS air duct, a number of safety rules must be observed. The oxygen metering device FLOWTRAIN contains all of the necessary safety features, including flow control, low-temperature and low-pressure alarm and switch-off, and safe standby operation. All features are connected



to the Claus plants' process control system.

An effcient mixing device ensures even oxygen distribution in the Claus air. A proprietary Claus burner was developed especially for application for air- and oxygen-enriched operations. This burner provides for a short and highly turbulent flame, which ensures good approach toward equilibrium for Claus operation and for the decomposition of ammonia.

Economics: As oxygen enrichment provides substantial additional Claus capacity, it is a low-cost alternative to building an additional Claus plant. It can save investment, manpower and maintenance. Installed cost for oxygen enrichment per level 1 is typically below \$250,000.

Oxygen enrichment for Claus units, continued

For level 2, the investment costs range from \$200,000 to \$500,000 and depend on the size of the Claus plant. Operating costs are varied and depend on the duration of oxygen usage. Typically, annual costs of oxygen enrichment are estimated as 10% to 40% of the operating cost for a Claus plant, providing the same additional sulfur capacity. Due to improved ammonia destruction maintenance work, as cleaning of heat exchanger tubes from ammonium salts and the respective corrosion become substantially less.

Installations: Over 10, plus numerous test installations to quantify the effects of capacity increase and ammonia decomposition.

Contributor: Linde AG CONTACT

Oxygen enrichment for FCC units

Application: Increase the throughput capacity by up to 50% and/or conversion in FCC units; process heavier feeds; overcome blower limitations, also temporarily.

Description: "Clean fuels" regulations are being globally implemented. Plus, the demand for transport fuels continually shifts toward more kerosine and diesel. Reasons include the regulations and the change in demand. But both contribute to the requirement of more flexibility in fluid catalytic cracking units (FCCUs). Consequently, FCCUs require more flexibility to treat a wider range of feeds, especially heavier feeds, and increasing throughput capacity. Both goals can be achieved via oxygen enrichment in the FCC regeneration.

In the FCC reactor, long-chain hydrocarbons are cleaved into shorter chains in a fluidized-bed reactor at 450°C–550°C. This reaction produces coke as a byproduct that deposits on the catalyst. To remove the coke from the catalyst, it is burned off at 650°C–750°C in the regenerator. The regenerated catalyst is returned to the reactor.

Oxygen enrichment, typically up to 27 vol% oxygen, intensifies catalyst regeneration and can substantially raise throughput capacity and/ or conversion of the FCC unit. Oxygen sources can be liquid oxygen tanks, onsite ASUs or pipeline supply. Oxygen consumption in FCC units fluctuates widely in most cases; thus, tanks are the best choice with respect to ease of operation, flexibility and economy.

For oxygen addition into the CS air duct, a number of safety rules must be observed. The oxygen metering device FLOWTRAIN contains all necessary safety features, including flow control, low-temperature and low-pressure alarm and switch-off, and safe standby operation. All of these features are connected to the FCC units' process control system. An efficient mixing device ensures even oxygen distribution in the air feed to the FCC regeneration.



Economics: Oxygen enrichment in FCC regeneration is economically favorable in many plants. For example, one refinery increased throughput by 15%. The net improvement was a 26% increase in higher-value products, such as naphtha. Likewise, lower value products increased only 5%, as fuel gas. The net profit increased substantially. Installed cost for oxygen enrichment is typically below \$250,000.

Operating costs will depend on the cost for oxygen and the duration of oxygen enrichment. Economical oxygen usage can be calculated on a case-by-case basis and should include increased yields of higher-value products and optional usage of lower-value feeds.

Installations: Currently, four units are in operation, plus test installations to quantify the effects of higher capacity and conversion levels.

Contributor: Linde AG CONTACT

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Paraxylene

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

Description: Suspension crystallization of PX in the xylene isomer mixture is used to produce PX crystals. The technology uses 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 PX content in the feed is enriched above equilibrium, such as streams originating from selective toluene conversion processes, the proprietary crystallization process technology is even more economical to produce high-purity PX product at high recoveries. The process technology takes advantage of recent advances in crystallization techniques and improvements in equipment to create this cost-effective method for paraxylene 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 PX is produced in the front section of the process at warm temperatures, taking advantage of the high concentration of PX already in the feed. At the back end of the process, high PX recovery is obtained by operating the crystallizers at colder temperatures. This scheme minimizes recycling excessive amounts of filtrate, thus reducing total energy requirements.

Process advantages:

• High PX purity and recovery

• Crystallization equipment is simple, easy to procure and operationally trouble free



• Compact design requires small plot size and lowest capital investment

• Operation is flexible to meet market requirements for PX purity

• System is easily amenable to future requirement for incremental capacity increases

• Feed concentration of PX is used efficiently through an innovative flow scheme

• Technology is flexible to process a range of feed concentrations (20–95 wt% PX) using a single or multistage system

• The aromatics complex using CrystPX technology is cost competitive with adsorption-based systems for PX recovery.

Paraxylene, continued

Economics: For 400 thousand tpy capacity from concentrated feed:

	CrystPX	Other crystallization technologies
ISBL Investment Cost	\$35 MM	\$45 MM
Paraxylene recovery	95%	95%
Electricity consumption	50 kwh/ ton PX	80 kwh/ ton PX
Operation mode	Continuous	Batch

Installation: Three commercial licenses.

Licensor: CrystPX is a proprietary process technology marketed and licensed by GTC Technology US, LLC, in alliance with Lyondell **CONTACT**

HYDROCARBON PROCESSING®

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Petroleum coke, naphtha, gasoil and gas

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

Description: Key points for the delayed coking technology include:

- Premium petroleum coke (needle coke) can be produced.
- Double-fired, multi-point steam (or water) injection, online spalling, bi-direction steam/air decoking and other techniques enable a three-year run length for the heater and 5% savings.
- The automation and safety interlock design techniques for steam stripping, water quench, coke cooling, hydraulic decoking and oil/gas preheating operations of the coke drums not only reduce work intensity and ensure safe operation, but also create conditions to reduce the drum-cycle time to 16–18 hours.
- The quench oil injection and anti-foaming agent injection with proper position and volume control prevent foaming of the coke drum and fines carry-over into the fractionator.
- During the process from steam stripping to water quench, the oil vapor and steam enter a blowdown system, which treats the vapor and steam in closed mode by stages. The blowdown system can not only recover oil and water and reduce environmental pollution, but it also can process the similar oil and wastewater of the whole refinery.
- The oil/gas preheating process of coke drum with no-coke parking valve improves the oil/gas preheating flow scheme,



reduces deformation of the coke drum during oil/gas preheating and shortens preheating time for the oil/gas.

- Equipment improvements of the coke drum include an overhead elliptical head instead of a spherical head, thus increasing the effective volume of the coke drum. The transition section between the skirt and shell connection uses a forged piece structure instead of overlay structure, thereby extending fatigue life. Alloy steel and cladding are used instead of carbon steel, thus improving corrosion resistance.
- The high-efficiency internals improve separation accuracy and enable operation flexibility; coke fine carry-over is reduced.

Petroleum coke, naphtha, gasoil and gas, continued

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

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

Licensor: China Petrochemical Technology Co., Ltd. CONTACT

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Prereforming with feed ultra purification

Application: Ultra-desulfurization and adiabatic-steam reforming of hydrocarbon feed from refinery offgas or natural gas through LPG to naphtha feeds as a prereforming step in the route to hydrogen production.

Description: Sulfur components contained in the hydrocarbon feed are converted to H_2S in the HDS vessel and then fed to two desulfurization vessels in series. Each vessel contains two catalyst types—the first for bulk sulfur removal and the second for ultrapurification down to sulfur levels of less than 1 ppb.

The two-desulfurization vessels are arranged in series in such a way that either may be located in the lead position allowing online change out of the catalysts. The novel interchanger between the two vessels allows for the lead and lag vessels to work under different optimized conditions for the duties that require two catalyst types. This arrangement may be retrofitted to existing units.

Desulfurized feed is then fed to a fixed bed of nickel-based catalyst that converts the hydrocarbon feed, in the presence of steam, to a product stream containing only methane together with H_2 , CO, CO₂ and unreacted steam which is suitable for further processing in a conventional fired reformer. The CRG prereformer enables capital cost savings in primary reforming due to reductions in the radiant box heat load. It also allows high-activity gas-reforming catalyst to be used. The ability to increase preheat temperatures and transfer radiant duty to the convection section of the primary reformer can minimize involuntary steam production.

Operating conditions: The desulfurization section typically operates between 170°C and 420°C and the CRG prereformer will operate over a wide range of temperatures from 250°C to 650°C and at pressures up to 75 bara.



Installation: CRG process technology covers over 40 years of experience with over 150 plants built and operated. Ongoing development of the catalyst has lead to almost 60 such units since 1990.

Catalyst: The CRG catalyst is manufactured under license by Johnson Matthey Catalysts.

Licensor: The process and CRG catalyst are licensed by Davy Process Technology. <u>CONTACT</u> 2011 Refining Processes Handbook

Pressure swing adsorption—rapid cycle

Applications: Proper management of hydrogen molecules within the refineries and chemical plants is becoming increasingly important due to the introduction of stringent product sulfur specifications. Hydrogen recovery/purification from fuel gas and hydrogen containing offgas streams in refining and chemical processes offers many potential benefits, including product uplift, reduced H₂ costs, avoided H₂ plant expansion and emission reductions.

Rapid-cycle pressure swing adsorption (RCPSA) technology offers a more-compact, less-expensive and more-energy-efficient solution for H_2 recovery compared to conventional PSA (cPSA) technology. This technology has been jointly developed by ExxonMobil Research and Engineering Co. (EMRE) and Xebec Adsorption Inc. The RCPSA unit for hydrogen recovery/purification is marketed as the Xebec H-6200.

Some of the potential applications of RCPSA are:

H₂ recovery/purification from:

- Fuel gas
- Recycle gas loop in hydrotreater
- Naphtha reformer hydrogen offgas
- Hydrocracker offgas and purges
- Steam cracker offgas.

Description: RCPSA technology overcomes the inherent disadvantages of cPSA, namely, slow cycle speeds, relatively large adsorbent beads and complex networks of individual switching valves. RCPSA uses two novel proprietary technologies: structured adsorbents—replacing conventional beaded cPSA adsorbents—and integrated rotary valves—replacing solenoid-actuated valves used in cPSA. Structured adsorbents provide mass transfer coefficients that are up to 100 times higher than beaded adsorbents used in cPSA; thus, significantly increasing the productivity of a unit volume of adsorbent bed. The multi-port rotary valves are used



for rapid and efficient switching of gases between adsorbent beds, effectively capturing the increased capacity of the structured adsorbent.

Multi-bed RCPSA systems can be efficiently packaged in an integrated, modular rotating bed design. The net result is that large PSA systems made up of multiple vessels of beaded adsorbent, complex process piping and multiple switching valves can be replaced with integrated modular skid-mounted Xebec H-6200 plants that are a fraction of the required footprint of a cPSA of equivalent capacity. In addition, the RCPSA's modular skid mounted design reduces installation time and cost. In the high feed pressure (p > 500 psig) applications, RCPSA can be stably operated without a tail-gas compressor resulting in further reduction of total installed cost in comparison to cPSA. Flexible product purity, enhanced recovery and better control of RCPSA can result in

Pressure swing adsorption—rapid cycle, continued

capital and operating cost savings. The modular skid mounted design of the RCPSA makes it possible for refiners to manage H_2 molecules closer to the processing units as needed, a new paradigm for distributed H_2 recovery technology for refineries and chemical plants.

Installation: The first commercial Xebec H-6200 unit was started-up at an ExxonMobil Refinery in 2008. It is installed in the diesel hydrotreater recycle loop to increase H_2 purity that results in product uplift and minimizes valuable H_2 loss from the hydrotreating unit.

Utilities: Compact RCPSA technology results in significantly less inert gas consumption in operation or in purging. Furthermore, since the switching valve function is controlled through an electric motor, instrument air is only required for the operation of each module's product control valve and automated isolation valves.

Nitrogen consumption: Estimated inert purge gas requirement: 40.4 Nm³

Typical N_2 consumption in normal start-up operation: 0.12 $\ensuremath{\text{Nm^3/h}}$ per H-6200 module

Instrument air consumption: 1.5 $\rm Nm^{3}h$ estimated for operation per H-6200 module

Power: 480–600V 3ph, 50 or 60 Hz to suit local requirements, consumption: 37 kW/module

References: "PSA technology hits the fast lane," *Chemical Processing,* August 2003.

"Recovery costs less," Hydrocarbon Engineering, November 2007.

"Rapid Cycle Pressure Swing Adsorption (RCPSA), A new, low-cost commercialized H_2 recovery process" NPRA Annual Meeting, March 9–11, 2008, San Diego.

Licensors: ExxonMobil Research and Engineering Co., and Xebec Adsorption Inc. **CONTACT**

Propylene

Application: Conversion of butene and pentene cuts into propylene.

Products: Propylene

Description: The worldwide demand for gasoline, diesel and petrochemicals is shifting toward a greater emphasis on diesel and propylene and the 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 production.

FlexEne relies on the integration of a FCC and an oligomerization unit called polynaphtha processing light FCC olefins and delivering good molecules back to the FCC. It provides the 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, thus increasing 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 and C_5 olefins. Additional diesel production may be supplied by operating the FCC unit in the maxi distillate mode.

For greater propylene production, Axens proposes to process either the polynaphtha gasoline or distillate fractions to the FCC unit where they can be easily cracked to produce propylene. Consequently, de-



pending upon market conditions, gasoline or diesel can be recycled to the FCC to produce high-value propylene from C4 and C5 olefins.

Thanks to the optimized combination of FCC and oligomerization, FlexEne delivers the largest market product flexibility when targeting production of propylene and/or gasoline and/or distillates.

Installations: Axens has licensed six grassroots FlexEne units

Reference: PTQ&A, *Petroleum Technology Quarterly*, 2Q 2011, p 16, question 2.

"The FCC Alliance celebrates its 50th license in Philippines," Axens press release March 21, 2011

Licensor: Axens CONTACT

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p-Xylene, selective toluene conversion

Application: GT-STDP process technology produces benzene and para-enriched xylenes from toluene disproportionation. The technology features a proprietary catalyst with high activity and selectivity toward paraxylene.

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

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

The liquid stream from the separator is pumped to the stripper to remove light hydrocarbons. The liquid stream from the stripper bottoms contains benzene, toluene, mixed xylenes and a small quantity of C_{9} + aromatics. This liquid stream is sent to product distillation section to obtain benzene product, toluene for recycle to the reactor, mixed xylenes to the PX recovery section and C_{9} + aromatics. The PX in the mixed xylenes stream is over 90% purity, which permits low-cost crystallization technology to be used for the PX purification.

Advantages:

- Simple, low cost fixed-bed reactor design
- Drop-in catalyst replacement for existing hydroprocessing reactors
- Paraxylene enriched to over 90% in the xylene stream



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- On-specification benzene with traditional distillation
- Physically stable catalyst
- Low hydrogen consumption

• Moderate operating parameters; catalyst can be used as replacement for traditional toluene disproportionation unit or in grassroots designs

• Efficient heat integration scheme; reduced energy consumption

• Turnkey package for high-purity benzene and paraxylene production available from licensor.

Economics: Feed rate 1,000 thousand tpy (22,000 bpsd), erected cost \$25MM (ISBL, 2008 US Gulf Coast Basis)

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

Licensor: GTC Technology US, LLC CONTACT

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Reactor internals

Application: A suite of proprietary reactor internals that offer uniform gas and liquid distribution to increase catalyst utilization and efficiently quench highly exothermic hydroprocessing catalytic reactions. The state-of-the-art reactor internals take up less space, thus enabling high reactor volume utilization while helping maximize catalyst run length. The designs are simple and robust and allow easy access to the reactor and efficient maintenance and catalyst change-out activities.

Description: Shell Global Solutions' high-dispersion (HD) trays help to optimize catalyst utilization by achieving highly uniform vapor–liquid distribution and excellent thermal distribution. Each tray nozzle is customized so that gas flow momentum is used to disperse the liquid into a mist of small droplets. This operating concept differentiates the technology from conventional downcomers or bubble caps because the nozzles fully and uniformly wet the entire catalyst surface and make efficient use of the top part of the catalyst bed.

Our reactor internals system also includes the following technology:

• Top-bed scale-catching trays to trap fouling material and prevent it from entering the catalyst beds

• Ultra-flat quench (UFQ) interbed internals for uniform process and quench mixing at the interbeds

• Catalyst support grids

• Compact bottom baskets to help maximize the catalyst volume in the bottom domes.

Performance data:

• Activity—Shell Global Solutions' reactor internals can produce 30%–50% activity gains through improved catalyst utilization and extra volume for loading catalyst.

• Efficiency—HD trays can help to utilize nearly 100% of the catalyst inventory.



• Operating window—HD trays offer high flexibility of feedrate: typically +50% to -70% for liquid as well as gas.

• Anti-fouling capacity—Shell Global Solutions' top-bed filters can efficiently remove fouling materials yet take up virtually no valuable reactor volume

• Robust design—Nuts and bolts are not used for any fixing. We offer global manufacturing options, and units are designed to withstand tilting and fouling.

Business value: The HD tray results in improved liquid and thermal distribution, ensuring maximum use of the catalyst bed. Refiners may double their cycle lengths as a result of using the new tray. These longer cycle lengths are due to the slower catalyst deactivation; the lower inlet temperatures required to produce high-specification products; and the

Reactor internals, continued

better thermal distribution that the HD trays offer. The anti-fouling trays have resulted in increases in cycle length of up to 200%.

Installation: All Shell Global Solutions' internals have been commercially proven through more than 350 hydroprocessing applications.

A South Korean refiner was experiencing hot spots in the catalyst beds of its lube-oil hydrotreater. Shell Global Solutions and its affiliate Criterion Catalysts & Technologies worked together to resolve the problem. HD trays were applied in combination with UFQ interbed internals to improve quenching and mixing between the catalyst beds. As a result, catalyst utilization improved significantly, and helped to facilitate a longer cycle and more severe operation.

Shell Global Solutions and Criterion Catalysts & Technologies tailored a system for JSC Naftan refinery when it converted a hydrotreating reactor for use as a mild hydrocracker. The system incorporated stateof-the-art internals and new-generation pre-treatment and cracking catalysts. The revamped unit was able to achieve conversion of the 370°C+ vacuum gasoil fraction at levels up to 50% higher than the design target.

Licensor: Shell Global Solutions International B.V. CONTACT

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Resid catalytic cracking

Application: Selective conversion of gasoil and heavy residual feedstocks.

Products: High-octane gasoline, distillate and C₃– C₄ olefins.

Description: For residue cracking the process is known as R2R (reactor–2 regenerators). Catalytic and selective cracking occurs in a short-contact-time riser where oil feed is effectively dispersed and vaporized through a proprietary feed-injection system. Operation is carried out at a temperature consistent with targeted yields. The riser temperature profile can be optimized with the proprietary mixed temperature control (MTC) system.

Reaction products exit the riser-reactor through a high-efficiency, close-coupled, proprietary riser termination device RSS (riser separator system). Spent catalyst is pre-stripped followed by an advanced high-efficiency packed stripper prior to regeneration. The reaction product vapor may be quenched to give the lowest dry gas and maximum gaso-line yield. Final recovery of catalyst particles occurs in cyclones before the product vapor is transferred to the fractionation section.

Catalyst regeneration is carried out in two independent stages equipped with proprietary air and catalyst distribution systems resulting in fully regenerated catalyst with minimum hydrothermal deactivation, plus superior metals tolerance relative to single-stage systems. These benefits are derived by operating the first-stage regenerator in a partial burn mode, the second-stage regenerator in a full-combustion mode and both regenerators in parallel with respect to air and flue gas flows.

The resulting system is capable of processing feeds up to about 6 wt% ConC without additional catalyst cooling means, with less air, lower catalyst deactivation and smaller regenerators than a single-stage regenerator design.

Heat removal for heavier feedstocks (above 6 CCR) may be accomplished by using a reliable dense-phase catalyst cooler, which has been commercially proven in over 65 units.



The converter vessels use a cold-wall design that results in minimum capital investment and maximum mechanical reliability and safety.

Reliable operation is ensured through the use of advanced fluidization technology combined with a proprietary reaction system. Unit design is tailored to refiner's needs and can include wide turndown flexibility.

Available options include power recovery, wasteheat recovery, fluegas treatment and slurry filtration.

Existing gasoil units can be easily retrofitted to this technology. Revamps incorporating proprietary feed injection and riser termination devices and vapor quench result in substantial improvements in capacity, yields and feedstock flexibility within the mechanical limits of the existing unit.

Installation: Shaw and Axens have licensed 50 grassroots FCC units and performed more than 200 revamp projects.

Reference: Meyers, R., Handbook of Petroleum Refining Process, Third Ed.

Licensor: Axens and Shaw CONTACT

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The resulting system is capable of processing feeds up to about 6 wt% ConC without additional catalyst cooling means, with less air, lower catalyst deactivation and smaller regenerators than a single-stage regenerator design.

Heat removal for heavier feedstocks (above 6 CCR) may be accomplished by using a reliable dense-phase catalyst cooler, which has been commercially proven in over 56 units.

The converter vessels use a cold-wall design that results in minimum



capital investment and maximum mechanical reliability and safety.

Reliable operation is ensured through the use of advanced fluidization technology combined with a proprietary reaction system. Unit design is tailored to refiner's needs and can include wide turndown flexibility.

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Reference: Meyers, R., Handbook of Petroleum Refining Process, Third Ed.

Licensor: Shaw and Axens CONTACT

Resid to propylene

Application: Selective conversion of heavy feedstocks into petrochemical products

Products: $C_3 - C_4$ olefins, in particular propylene; high-octane gasoline, aromatics

Description: Based on the R2R resid fluid catalytic cracking (RFCC) process using a riser and a double regenerator for gasoline production, this new petrochemical version is oriented toward light olefins, particularly propylene, and aromatics. The process is characterized by the utilization of two independent risers. The main riser cracks the resid feed under conditions to optimize fuels production; the second PetroRiser riser is operated to selectively crack specific recycle streams to maximize propylene production.

The RFCC applies a short contact-time riser, proprietary injection system and severe cracking conditions for bottoms conversion. The temperature and catalyst circulation rates are higher than those used for a conventional gasoline mode operation. The main riser temperature profile can be optimized with a mixed temperature control (MTC) system. Reaction products are then rapidly separated from the catalyst through a high-efficiency riser termination device (RS²).

Recycle feed is re-cracked in the PetroRiser under conditions, which are substantially more severe than in the main riser. A precise selection of recycle cuts combined with adapted commercial FCC catalysts and additives lead to high propylene yields with moderate dry-gas production.

Both the main riser and PetroRiser are equipped with a rapid separation system, and the deactivated catalysts are collected in to a single packed stripper, which enhances steam stripping efficiency of the catalyst. Catalyst regeneration is carried out in two, independent stages to minimize permanent hydrothermal activity loss. The first stage is oper-



ated in a mild partial-combustion mode that removes produced moisture and limits catalyst deactivation, while the second stage finishes the combustion at higher temperature to fully restore catalyst activity. The R2R system is able to process residue feed containing high metals and CCR using this regenerator configuration and even higher contents with the addition of a catalyst cooler.

The recycle feeds that can be used in the PetroRiser are light and medium FCC gasoline as well as olefin streams coming from a butenes oligomerization unit. This last option is of particular interesting under market conditions that favor propylene over C_4 olefins.

Resid to propylene, continued

The reaction and regeneration sections use a cold-wall design that results in minimum capital investment and maximum mechanical reliability and safety. Units are tailored to fit the market needs (feedstock and product slate) and can include a wide range of turndown flexibility. Available options include power recovery, waste-heat recovery, flue-gas treatment and slurry filtration and light olefins recovery and purification.

Installation: PetroRiser technology is available for revamp of all RFCC and FCC units. Axens and the Shaw Group have licensed more than 50 FCC units and performed more than 200 revamp projects since the alliance was created.

Reference: "Resid to propylene," ERTC Annual Meeting, 2008, Vienna.

Licensor: Axens and Shaw CONTACT

Slack wax deoiling

Application: Process to produce high-melting and low-oil containing hard wax products for a wide range of applications.

Feeds: Different types of slack waxes from lube dewaxing units, including macrocrystalline (paraffinic) and microcrystalline wax (from residual oil). Oil contents typically range from 5 wt%–25 wt%.

Products: Wax products with an oil content of less than 0.5 wt%, except for the microcrystalline paraffins, which may have a somewhat higher oil content. The deoiled wax can be processed further to produce high-quality, food-grade wax.

Description: Warm slack wax is dissolved in a mixture of solvents and cooled by heat exchange with cold main filtrate. Cold wash filtrate is added to the mixture, which is chilled to filtration temperature in scraped-type coolers. Crystallized wax is separated from the solution in a rotary drum filter (stage 1). The main filtrate is pumped to the soft-wax solvent recovery section. Oil is removed from the wax cake in the filter by thorough washing with chilled solvent.

The wax cake of the first filter stage consists mainly of hard wax and solvent but still contains some oil and soft wax. Therefore, it is blown off the filter surface and is again mixed with solvent and repulped in an agitated vessel. From there the slurry is fed to the filter stage 2 and the wax cake is washed again with oil-free solvent. The solvent containing hard wax is pumped to a solvent recovery system. The filtrate streams of filter stage 2 are returned to the process, the main filtrate as initial dilution to the crystallization section, and the wash filtrate as repulp solvent.

The solvent recovery sections serve to separate solvent from the hard wax respectively from the soft wax. These sections yield oil-free hard wax and soft wax (or foots oil).



Utility requirements (slack wax feed containing 20 wt% oil, per metric ton of feed):

Steam, LP, kg	1,500
Water, cooling, m ³	120
Electricity, kWh	250

Installation: Wax deoiling units have been added to existing solvent dewaxing units in several lube refineries. The most recent reference includes the revamp of a dewaxing unit into two-stage wax deoiling; this unit went onstream in 2005.

Licensor: Uhde GmbH CONTACT

COMPANY INDEX

SO₂ removal, regenerative

Application: Regenerative scrubbing system to recover SO_2 from flue gas containing high SO_2 levels such as gas from FCC regenerator or incinerated SRU tail gas and other high SO_2 applications. The LABSORB process is a low pressure drop system and is able to operate under varying conditions and not sensitive to variations in the upstream processes.

Products: The product from the LABSORB process is a concentrated SO_2 stream consisting of approximately 90% SO_2 and 10% moisture. This stream can be sent to the front of the SRU to be mixed with H₂S and form sulfur, or it can be concentrated for other marketable uses.

Description: Hot dirty flue gas is cooled in a flue-gas cooler or wasteheat recovery boiler prior to entering the systems. Steam produced can be used in the LABSORB plant. The gas is then quenched to adiabatic saturation (typically $50^{\circ}C-75^{\circ}C$) in a quencher/pre-scrubber; it proceeds to the absorption tower where the SO₂ is removed from the gas. The tower incorporates multiple internal and re-circulation stages to ensure sufficient absorption.

A safe, chemically stable and regenerable buffer solution is contacted with the SO₂-rich gas for absorption. The rich solution is then piped to a LABSORB buffer regeneration section where the solution is regenerated for re-use in the scrubber. Regeneration is achieved using low-pressure steam and conventional equipment such as strippers, condensers and heat exchangers.

Economics: This process is very attractive at higher SO₂ concentrations or when liquid or solid effluents are not allowed. The system's buffer loss is very low, contributing to a very low operating cost. Additionally, when utilizing LABSORB as an SRU tail-gas treater, many components normally associated with the SCOT process are not required; thus saving considerable capital.



Installation: One SRU tail-gas system and two FCCU scrubbing systems.

Reference: Confuorto, Weaver and Pedersen, "LABSORB regenerative scrubbing operating history, design and economics," Sulfur 2000, San Francisco, October 2000.

Confuorto, Eagleson and Pedersen, "LABSORB, A regenerable wet scrubbing process for controlling SO₂ emissions," Petrotech-2001, New Delhi, January 2001.

Licensor: Belco Technologies Corp. CONTACT

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Solvent deasphalting

Application: Prepare quality feeds from residues from fluid catalytic cracking (FCC), hydrocracking processes, blendstocks for lube oil and asphaltes.

Products: Deasphalted oil (DAO) for catalytic cracking and hydrocracking feedstocks, resins for specification asphalts, and pitch for specification asphalts and residue fuels.

Description: Feed and light paraffinic solvent are mixed and then charged to the extractor (1). The DAO and pitch phases, both containing solvents, exit the extractor. The DAO and solvent mixture is separated under supercritical conditions (2). Both the pitch and DAO products are stripped of entrained solvent (3,4). A second extraction stage is utililized if resins are to be produced.

Operating conditions: Typical ranges are:

Solvent	various blends of C ₃ –C ₇ hydrocarbons
	including light naphthas
Pressure, psig	300–600
Temp., °F	120–450
Solvent to oil ratio:	4/1 to 13/1

Yields:

Feed, type	Lube oil	Cracking stock
Gravity, °API	6.6	6.5
Sulfur, wt%	4.9	3.0
CCR, wt%	20.1	21.8
Visc, SSU@210°F	7,300	8,720
Ni/V, wppm	29/100	46/125
DAO		
Yield, vol.% of feed	30	65
Gravity, °API	20.3	15.1



		0.2
Visc., SSU@210°F	165	540
Ni/V, wppm	.3/.4	4.5/10.3
Pitch		
Softening point, R&B, °F	150	240
Penetration@77°F	12	0
Economics:		
Investment (basis: 40,000/2,0)00 bpsd)	
2Q 2011, US Gulf, \$/bpsd		2,000/8,000
Utilities, typical per bbl feed:		
Fuel, 10 ³ Btu (hot oil)		56–100
Electricity, kWh		1.9–2.0
Steam, 150 psig, lb		6–9
Water, cooling (25°F rise), g	al	10

Solvent deasphalting, continued

Installations: Over 50 units installed; this also includes both UOP and Foster Wheeler units originally licensed separately before merging the technologies in 1996.

References: *Handbook of Petroleum Refining Processes,* Third Ed., McGraw Hill, 2003, pp. 10.37–10.61.

"When Solvent Deasphalting is the Most Appropriate Technology for Upgrading Residue," International Downstream Technology Conference, February 15–16, 2006, London.

Licensors: Foster Wheeler USA Corp./UOP, A Honeywell Company CONTACT

Sour gas treatment

Application: The WSA process (Wet gas Sulfuric Acid) treats all types of sulfur-containing gases such as amine and Rectisol regenerator offgas, SWS gas and Claus plant tail gas in refineries, gas treatment plants, petrochemicals and coke chemicals plants. The WSA process can also be applied for SO_x removal and regeneration of spent sulfuric acid.

Sulfur, in any form, is efficiently recovered as concentrated commercial-quality sulfuric acid.

Description: Feed gas is combusted and cooled to approximately 400°C in a waste heat boiler. The gas then enters the SO₂ converter containing one or several beds of SO₂ oxidation catalyst to convert SO₂ to SO₃. The gas is cooled in a gas cooler whereby SO₃ hydrates to H₂SO₄ (gas), which is finally condensed as concentrated sulfuric acid (typically 98% w/w).

The WSA condenser is cooled by ambient air, and heated air may be used as combustion air for increased thermal efficiency. The heat released by combustion and SO_2 oxidation is recovered as steam. The process operates without removing water from the gas. Therefore, the number of equipment items is minimized, and no liquid waste is formed. Cleaned process gas leaving the WSA condenser is sent to stack without further treatment.

The WSA process is characterized by:

- Very high recovery of sulfur as commercial-grade sulfuric acid
- No generation of waste solids or wastewater
- No consumption of absorbents or auxiliary chemicals
- Efficient heat recovery ensuring economical operation
- Simple and fully automated operation adapting to variations in feed gas flow and composition.



Installation: More than 100 units worldwide.

Licensor: Haldor Topsøe A/S CONTACT

Sour-water treating

Application: Bechtel Hydrocarbon Technology Solutions, Inc. (BHTS) offers the complete suite of sulfur block technologies including sour-water treating. Typically, a sour-water stripper (SWS) is used to boil off the contaminants hydrogen sulfide (H_2S ,) ammonia (NH_3 ,) carbon dioxide (CO_2) and contaminant hydrocarbons.

Refineries have multiple water washes from a variety of units (coker, desalter units, hydrotreaters, etc.,) which must be treated before discharge or reuse. For phenol-related streams, two towers are sometimes utilized in parallel, with the stripped water being frequently reused in the refinery desalter units and similar water-washing purposes. This two-tower approach can also be used to help recover partially purified overhead gases. This is frequently done where there is a commercial value for NH_3 .

Products: Bechtel's SWS units can reduce contaminant acid gases to the typical US specification of 20 ppmw NH3 and <1 ppmw H_2S or lower if desired. These streams are environmentally friendly and suitable for discharge to the refinery waste water system.

Description: Sour-water sources frequently encountered are saturated with hydrocarbons, so a flash is utilized to make tower operation more stable. The stream is flashed from header pressure to ~5 psig (or flare header pressure) in the sour water flash drum (1). This drum serves three purposes:

• Remove entrained hydrocarbon droplets

• Allow phase separation from hydrocarbons that vaporize at the lower pressure

• Provide operational surge capacity, typically 5–10 minutes of flow. Flashed vapors can be either flared or sent to a wet gas compressor

for recovery. Recovered hydrocarbon liquids are sent to the refinery slop oil system.



The sour-water transfer pumps (2) then send the stream to the sourwater storage tank (3) for further hydrocarbon separation and removal. This final stage of separation is time consuming, so the tank is typically sized for 3–5 days of residence time. This has the added benefit of stabilizing the concentrations of contaminants in the sour water.

The stripper feed pumps (4) send the stream to a filtration system (not shown for simplicity) where particulates are removed to 10 microns or less. This helps keep the downstream equipment free of particulates, which can cause erosion, fouling and loss of performance. The sour water then flows through a feed/bottoms heat exchanger (5) for energy conservation and then to the stripper.

In the SWS (6), the contaminant gases are boiled off with heat added to the reboiler (9) in the form of refinery low-pressure (LP) steam.

Sour-water treating, continued

A generic stripper in a refinery has an overhead heat exchanger and two-phase separator for reflux. In a SWS, however, that phase change results in severe corrosion due to the H_2S , NH_3 and CO_2 in that overhead exchanger. (Amine regenerators do not have that problem because these compounds are chemically bound to the amine that is present.) The heat removal at the top of the tower is accomplished by a "pumparound loop". The pumparound pumps (7) move a liquid stream from a tray above the feed tray through the overhead air cooler (8) and back to the top tray. Pumparound flow is modulated such that the overhead gas temperature does not drop below the point where ammonium polysulfide salts deposit (usually 170°F–180°F for the gas).

From the bottom of the tower, the water flows through the feed/ bottoms exchanger to pre-heat the incoming feed. The stripped-water pumps (10) move the water through the stripped-water coolers (11), which can be a combination of air and water cooled exchangers, and out to the battery limits.

Economics:

Investment: (basis 100 gpm, 2010 US Gulf Coast)	
\$ per gpm	23,000
Utilities, typical per gal feed:	
Fuel, absorbed, 10 ³ Btu	_
Electricity, kWh	0.050
Steam, lb/gal of water	1.5
Water, cooling (25°F), gpm	7.2

Installations: This process has been used in literally thousands of units to produce low-ammonia and low-sulfur content process streams around the world.

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT
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Spent acid regeneration

Application: The WSA process (Wet gas Sulfuric Acid) treats spent sulfuric acid from alkylation as well as other types of waste sulfuric acid in the petrochemical and chemicals industry. Amine regenerator offgas and/or refinery gas may be used as auxiliary fuel. The regenerated acid will contain min. 98% H_2SO_4 and can be recycled directly to the alkylation process.

The WSA process is also applied for conversion of $\rm H_2S$ and removal of $\rm SO_x.$

Description: Spent acid is decomposed to SO_2 and water vapor in a combustor using amine regenerator offgas or refinery gas as fuel. The SO_2 containing flue gas is cooled in a waste-heat boiler and solid matter originating from the acid feed is separated in an electrostatic precipitator. By adding preheated air, the process gas temperature and oxygen content are adjusted before the catalytic converter converting SO_2 to SO_3 . The gas is cooled in the gas cooler whereby SO_3 is hydrated to H_2SO_4 (gas), which is finally condensed as 98% sulfuric acid.

The WSA condenser is cooled by ambient air. The heated air may be used as combustion air for increased thermal efficiency. The heat released by combustion and SO_2 oxidation is recovered as steam.

The process operates without removing water from the gas. Therefore, the number of equipment items is minimized and no liquid waste is formed. This is especially important in spent acid regeneration where SO_3 formed by the acid decomposition will otherwise be lost with the wastewater.

The WSA process is characterized by:

- No generation of wastewater
- No consumption of absorbents or auxiliary chemicals
- Efficient heat recovery ensuring economical operation
- Simple and fully automated operation adapting to variations in feed flow and composition.



Installation: More than 100 WSA units worldwide, including 12 for spent acid regeneration.

Licensor: Haldor Topsøe A/S CONTACT

Spent lube oil re-refining

Application: The Revivoil process can be used to produce high yields of premium quality lube bases from spent motor oils. Requiring neither acid nor clay treatment steps, the process can eliminate environmental and logistical problems of waste handling and disposal associated with conventional re-refining schemes.

Description: Spent oil is distilled in an atmospheric flash distillation column to remove water and gasoline and then sent to the Thermal Deasphalting (TDA) vacuum column for recovery of gas oil overhead and oil bases as side streams. The energy-efficient TDA column features excellent performance with no plugging and no moving parts. Metals and metalloids concentrate in the residue, which is sent to an optional Selectopropane unit for brightstock and asphalt recovery. This scheme is different from those for which the entire vacuum column feed goes through a deasphalting step; Revivoil's energy savings are significant, and the overall lube oil base recovery is maximized. The results are substantial improvements in selectivity, quality and yields.

The final, but very important step for base oil quality is a specific hydrofinishing process that reduces or removes remaining metals and metalloids, Conradson Carbon, organic acids, and compounds containing chlorine, sulfur and nitrogen. Color, UV and thermal stability are restored and polynuclear aromatics are reduced to values far below the latest health thresholds. Viscosity index remains equal to or better than the original feed. For metal removal (> 96%) and refining-purification duty, the multicomponent catalyst system is the industry's best.

Product quality: The oil bases are premium products; all lube oil base specifications are met by Revivoil processing from Group 1 through Group 2 of the API basestocks definitions. Besides, a diesel can be obtained, in compliance with the EURO 5 requirements (low sulfur).



Health & safety and environment: The high-pressure process is in line with future European specifications concerning carcinogenic PNA compounds in the final product at a level inferior to 5 wppm (less than 1 wt% PCA—IP346 method).

Economics: The process can be installed stepwise or entirely. A simpler scheme consists of the atmospheric flash, TDA and hydrofinishing unit and enables 70%-80% recovery of lube oil bases. The Selectopropane unit can be added at a later stage, to bring the oil recovery to the 95% level on dry basis. For two plants of equal capacity, payout times before taxes are two years in both cases.

Installation: Twelve units have been licensed using all or part of the Revivoil Technology.

Licensor: Axens and Viscolube SpA CONTACT

Styrene recovery

Application: GT-Styrene is an extractive distillation (ED) process that directly recovers styrene from the raw pyrolysis gasoline derived from the steam cracking of naphtha, gasoils and natural gas liquids (NGLs). The produced styrene is high purity and suitable for polymerization at a very attractive cost compared to conventional styrene production routes. If desired, the mixed xylenes can also be extracted from the pygas, upgrading their value as a chemical feedstock. The process is economically attractive for pygas feeds containing more than 15,000 tpy styrene.

Description: Raw pyrolysis gasoline is prefractionated into a heartcut C_8 stream. The resulting styrene concentrate is fed to an ED column and mixed with a selective solvent, which extracts the styrene to the tower bottoms. The rich solvent mixture is routed to a solvent recovery column SRC), which recycles the lean solvent back to the ED column and recovers the styrene overhead. A final purification step produces a 99.9% styrene product containing less than 50-ppm phenyl acetylene. The ED column overhead can be further processed to recover a high-quality mixed-xylene stream. A typical world-scale cracker can produce approximately 25,000 tpy styrene and 75,000 tpy mixed xylenes from pyrolysis gasoline.

Process advantages:

- Produces polymer-grade styrene at 99.9% purity
- Allows the recovery of isomer-quality mixed xylenes for paraxy-lene production
 - Upgrades pygas stream components to chemical value
 - Debottlenecks pygas hydrotreater and extends cycle length
 - Reduces hydrogen consumed in hydrotreating
- Optimized solvent system and design provide economical operating costs



Economics: Basis: 25,000 tpy styrene capacity

Typical USGC capital cost	\$25 million
Styrene value in pygas	\$800/ton
Styrene product sales value	\$1,400/ton
Net processing	\$160/ton
Gross margin	\$11 million/yr
Pretax ROI	44%

Installation: Four commercial licenses.

Licensor: GTC Technology US, LLC CONTACT

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Sulfur recovery

Application: Convert hydrogen sulfide (H_2S) in acid-gas streams to elemental sulfur using the modified Claus process. Applicable in natural gas plants, petroleum refineries and other processes from which H_2S is a byproduct.

Description: Acid-gas streams from an amine regenerator (A) and a sour-water stripper (B) are fed to the proprietary sulfur recovery unit (SRU) acid gas injector (1) and thermal reactor (2) where $\frac{1}{3}$ of the H₂S is converted to sulfur dioxide (SO₂). Combustion air is provided by an air blower (9). Ammonia in the sour water stripper (SWS) gas is destroyed in the thermal reactor.

Heat from the combustion is recovered in a waste-heat boiler (3). The gas stream is heated to the optium temperature in reheat exchangers (5), the H_2S and SO_2 react to form sulfur and water vapor in the three catalytic reactors (6) in series. Sulfur vapor is condensed in sulfur condensers (4 and 7) and the liquid sulfur is sent to storage thru a sulfur seals (8). Tail gas (D) from the SRU is sent to the tail gas treating unit.

Recoveries: Typical sulfur recoveries in a three catalytic bed SRU are 97%–98%.

Economics: Investment (basis 300–25 ltpd)2Q 2011 US Gulf, 10³ \$/ltpd90–400Utilities, typical per ltpd0Fuel, 10³ Btu0Electricity, KWh100Steam (exported), lb6,500Water, cooling, gal5



Installations: Over 150 units are installed worldwide with a capacity of over 15 thousand ltpd.

Reference: *Hydrocarbon Processing,* Sulfur 2011, May 2011, "Peak operating, environmental performance with sulfur recovery technology."

Licensor: Foster Wheeler USA Corp. CONTACT

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TAEE, from refinery C₅ feeds

Application: To process C_5 streams from refinery units to produce tertiary amyl ethyl ether (TAEE).

Description: TAEE is formed by the catalytic etherification of isoamylene with ethanol. The patented CD*Taee* process is based on a two-step reactor design, consisting of a boiling point fixed-bed reactor followed by final conversion in a catalytic distillation column. The process uses an acidic ion-exchange resin catalyst in both its fixed-bed reactor and proprietary catalytic distillation structures.

The unique catalytic distillation column combines reaction and fractionation in a single unit operation. It allows a high conversion of isoamylene (exceeding fixed-bed equilibrium limitations) to be achieved simply and economically. By using distillation to separate the product from the reactants, the equilibrium limitation is exceeded and higher conversion of isoamylene is achieved. Catalytic distillation also takes advantage of the improved kinetics through increased temperature without penalizing equilibrium conversion.

Lummus Technology's boiling point reactor offers:

- Simple and effective control
- Elimination of hot spots
- Long catalyst life
- High flexibility
- Low capital cost
- Elimination of catalyst attrition
- Most effective heat removal technique
- Elimination of cooling water requirement.



Installation: With 20 years of experience, Lummus Technology has 120 licensed ethers units.

Licensor: Lummus Technology, a CB&I company CONTACT

Tail gas treating

Application: Convert remaining sulfur from sulfur recovery unit (SRU) tail gas into hydrogen sulfide (H_2S ,) recover the H_2S and recycle the H_2S to the SRU.

Description: Tail gas (A) from the SRU is heated using HP steam and combined with hydrogen (H_2), then all sulfur compounds are reacted to H_2S using low-temperature catalyst. The optional waste-heat boiler (2) recovers the waste heat from the reaction stream. The reaction stream is further cooled in the quench column (3) before entering the MDEA absorber (4). The overhead gas from the absorber (C) is sent to the incinerator/stack. The rich MDEA is regenerated in the regenerator (5) and the H_2S rich overhead stream (D) is recycled to the SRU.

Recoveries: Typical stack gas emissions of sulfur dioxide (SO_2) in the incinerator stack are less than 150 ppmv. Lower emissions can be achieved using special MDEA formulations. Combining the tail-gas treating unit with the SRU can achieve overall sulfur recoveries greater than 99.98%.

Economics:

Investment (basis 300–25 ltpd)	
2Q 2011 US Gulf, 103 \$/ltpd	83–370
Utilities, typical per ltpd (SRU basis),	
based on using air cooling	
Fuel, 10 ³ Btu	3,300
Electricity, KWh	75
Steam (imported), lb	750
Water, cooling, gal	9,800
H ₂ , SCF	1,700



Installations: More than 40 units are installed worldwide at present.

Reference: *Hydrocarbon Processing,* Sulfur 2011, May 2011, "Peak operating, environmental performance with sulfur recovery technology."

Licensor: Foster Wheeler USA Corp. CONTACT

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TAME, from refinery and steamcracker C₅ feeds

Application: The CD-*Isotame* process combines skeletal isomerization and etherification steps to maximize the production of tertiary amyl methyl ether (TAME) from refinery and steam-cracker C₅ streams.

Description: TAME is formed by the catalytic etherification of reactive isoamylenes with methanol. Skeletal isomerization increases TAME production from an olefinic C_5 stream by converting normal amylenes to isoamylenes. The combination significantly reduces olefin content while also increasing octane.

This process provides the minimum capital cost at about 80% C₅ olefin reduction. The olefinic C₅ stream is fed to a selective hydrogenation step where dienes are converted to olefins. Removal of dienes reduces color and gum formation in the TAME product. In addition, unreactive 3 methyl 1-butene (3MB1) is converted to reactive isoamylene via hydroisomerization, thus increasing the TAME yield.

The primary TAME product is made in the first CD*Tame* unit where greater than 90% conversion of isoamylene is achieved. Raffinate 1 from this unit is fed to a skeletal isomerization unit (ISOMPLUS) where n-pentenes are converted to isoamylenes at high yield and selectivity. The vapor-phase reaction takes place over a robust catalyst with long cycles between regenerations.

The isomerate is then fed to a second CD*Tame* unit where additional TAME is produced at greater than 95% conversion of isoamylenes. Even higher conversion of normal pentenes to TAME can be achieved by an optional raffinate 2 recycle to the skeletal isomerization unit. A purge stream removes the saturated C₅s from the recycle stream. A common methanol recovery unit serves both CD*Tame* units.

Process advantages include:

• Selective hydrogenation of diolefins at minimum capital cost



- High conversion of isoamylenes (>95%)
- High conversion of normal pentenes (>70%)
- High selectivity of isomerization (>90%)
- Isomerization of 3MB1 to reactive isoamylene
- Improved C₅ raffinate as gasoline feedstock due to reduced, color, gum formation and olefin content
- Increased TAME production
- Increased gasoline pool octane
- Decreased gasoline pool Rvp and olefins
- Low capital and operating cost
- Superior economics and performance over C₅ alkylation
- High-quality TAME product without objectionable odor or color.

Installation: Out of the 120 licensed ethers units, approximately half of the units use the TAME technology.

Licensor: Lummus Technology, a CB&I company CONTACT

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TAME, from refinery C₅ feeds

Application: To process C_5 streams from refinery units to produce tertiary amyl methyl ether (TAME).

Description: TAME is formed by the catalytic etherification of isoamylene with methanol. The patented CD*Tame* process is based on a twostep reactor design, consisting of a boiling point fixed-bed reactor followed by final conversion in a catalytic distillation column. The process utilizes an acidic ion-exchange resin catalyst in both its fixed-bed reactor and proprietary catalytic distillation structures.

The unique catalytic distillation column combines reaction and fractionation in a single unit operation. It allows a high conversion of isoamylene (exceeding fixed-bed equilibrium limitations) to be achieved simply and economically. By using distillation also to separate the product from the reactants, the equilibrium limitation is exceeded and higher conversion of isoamylene is achieved. Catalytic distillation also takes advantage of the improved kinetics through increased temperature without penalizing equilibrium conversion. Advanced process control maximizes catalyst life and activity to provide high sustained TAME production.

Lummus Technology's ether processes offer:

- Simple and effective control
- Elimination of hot spots
- Long catalyst life
- High flexibility
- Low capital cost
- Elimination of catalyst attrition
- Most effective heat removal technique
- Elimination of cooling water requirement.



Installation: 120 licensed ethers units.

Licensor: Lummus Technology, a CB&I company CONTACT

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Treating

Application: Process to extract and convert mercaptans in hydrocarbons

Products: LPG, light naphtha

Description: Mercaptans (RSH) occur naturally in crude oils but are also generated from other sulfur compounds during crude fractionation and cracking processes. Mercaptans are undesirable in gasoline because of their obnoxious odor and their tendency to hydrolyze, forming toxic and corrosive hydrogen sulfide. The classic tests for mercaptan presence are the "doctor" test and odor threshold.

Axens' Sulfrex and sweetening processes eliminate mercaptans by extraction or by their conversion into less aggressive compounds, thus protecting downstream equipment or units such as hydrotreaters as well as meeting fuel specifications.

The extractive Sulfrex process both sweetens and reduces the total sulfur concentration. With its moderate operating conditions of pressure and ambient temperature, this continuous process is ideal for C3, C4, LPG, light gasoline and NGL feeds.

The overall reaction shown here—where R represents an aliphatic group. The process involves two steps, starting with extraction and culminating in oxidation:

Overall Sulfrex reaction

4 RSH + $O_2 \rightarrow 2$ RSSR + 2 H₂O

First step: Extraction RSH + NaOH \rightarrow NaSR + H₂O

Second step: Oxidation $4 \text{ NaSR} + 2 \text{ H}_2\text{O} + \text{O}_2 \rightarrow 4 \text{ NaOH} + 2 \text{ RSSR}$

Aqueous phase Hydrocarbon phase



In the flow diagram, the light mercaptans are extracted (extractor) by a weak caustic solution forming water and sodium mercaptide salts (NaSR). These salts are oxidized (oxidizer) by air injection in the presence of the LCPS 30 catalyst, producing an organic disulfide (RSSR) phase that separates by gravity (separator) from the aqueous solution. This phase is sent to storage or further treatment facilities. The resulting regenerated caustic solution is then returned to the extractor. The product flows through a sand filter to eliminate traces of free water and caustic.

Installations: Axens has licensed over 40 grassroots Sulfrex units.

Licensor: Axens CONTACT

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Treating—Coker LPG to low total sulfur levels

Application: AMINEX/THIOLEX and REGEN ULS treating processes are used to remove COS, H_2S and mercaptans from LPG streams with high mercaptans levels and produce treated streams with less than 5 ppm-wt of total sulfur.

Description: The removal of COS and H₂S is achieved by utilizing an AMINEX treating unit using an amine solution or with a THIOLEX treating unit using a caustic solution. When using the THIOLEX unit, mercaptan impurities are removed with a caustic solution, and the caustic is regenerated to previously unachievable purity levels in the REGEN ULS system. The combination of THIOLEX/ REGEN ULS results in minimal back extraction of disulfide oil (DSO) into the treated product. Thus, the treated product will meet specifications of less than 5 ppm-wt of total sulfur.

Installations: One licensed unit.



Treating—Condensate and crude oil sweetening

Application: MERICAT C systems remove H_2S and naphthenic acids while sweetening mercaptans to disulfide oils in condensate and crude oil streams. Treatment uses caustic, catalyst and air along with FIBER FILM Contactor technology to reduce the acidity, odor, and corrosive effects of the treated product stream.

Description: In a MERICAT C system a recycled caustic stream containing catalyst contacts an aerated hydrocarbon stream in the FIBER FILM Contactor. As the caustic and hydrocarbon phases flow down the fiber bundle, heavy mercaptans are oxidized to disulfide oils. After treatment the two phases disengage from the fibers and separate in the vessel. The treated hydrocarbon exits the top of the vessel, while the regenerated caustic solution is recycled back from the bottom of the vessel to the FIBER FILM Contactor until it is spent. Fresh caustic and catalyst are added as needed to maintain activity.

Competitive advantages:

- Ability to treat the crude oil/condensate without need for costly fractionation
- Minimal capital investment
- Minimal caustic and catalyst consumption
- Small unit design saves plant space
- Operating simplicity

The MERICAT C on-stream factor is 100%.



Installations: 15 licensed units worldwide.

Treating—Gases

Application: AMINEX and THIOLEX systems extract COS and H_2S from gases with amine or caustic solution using FIBER FILM Contactor technology.

Description: In an AMINEX system, the amine phase flows along the fibers of the FIBER FILM Contactor as it preferentially wets the fibers. The gas phase flows through the Contactor parallel to the amine-wetted fibers as the COS and H_2S is extracted into the amine. The two phases disengage in the separator vessel with the rich amine flowing to the amine regeneration unit and the treated gas flowing to its final use. Similarly, a THIOLEX system uses the same process utilizing caustic and caustic/amine solutions to preferentially wet the fibers as the COS and H_2S is extracted into the caustic phase. The rich caustic flows to sulfidic caustic storage and the treated gas flows to its final use.

Competitive advantages: FIBER FILM Contactor technology requires smaller processing vessels thus saving valuable plant space and reducing capital expenditures.

Installation: 224 licensed units worldwide in THIOLEX service.

Reference: Hydrocarbon Processing, Vol. 63, No. 4, April 1984, p. 87.



Treating—Gasoline and LPG

Application: THIOLEX/REGEN systems extract H_2S and mercaptans from gases and light liquid hydrocarbon streams, including gasolines, with caustic using FIBER FILM Contactor technology. It can also be used to hydrolyze and remove COS from LPG and propane.

Description: In a THIOLEX system, the caustic phase flows along the fibers of the FIBER FILM Contactor as it preferentially wets the fibers. Hydrocarbon flows through the caustic-wetted fibers where the H_2S and mercaptans are extracted into the caustic phase. The two phases disengage and the caustic flows to the REGEN where the caustic is regenerated using heat, air and catalyst. The disulfide oil formed in this reaction may be removed via gravity separation, FIBER FILM solvent washing or a combination of the two. The regenerated caustic flows back to the THIOLEX system for continued re-use.

COS is removed from LPG or propane by either employing AMINEX technology using an amine solution or THIOLEX technology using an MEA/caustic solution to hydrolyze the COS to H_2S and CO_2 , which are easily removed by amine or caustic.

Competitive advantages: FIBER FILM Contactor technology requires smaller processing vessels thus saving valuable plant space and reducing capital expenditures.

Installations: 382 licensed units worldwide.



References: Oil & Gas Journal, August 12, 1985, p. 78. Hydrocarbon Engineering, February 2000.

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Treating—Gasoline desulfurization, ultra deep

Application: EXOMER extracts recombinant mercaptan sulfur from selectively hydrotreated FCC gasoline streams with a proprietary treating solution. FIBER FILM Contactor technology is used for mass transfer efficiency to obtain a maximum reduction in total sulfur content. EXOMER is jointly developed with ExxonMobil Research & Engineering Co.

Description: In an EXOMER system, the lean treating solution phase flows along the fibers of the FIBER FILM Contactor along with the hydrocarbon phase, allowing the recombinant mercaptans to be extracted into the treating solution in a non-dispersive manner. The two phases disengage in the separator vessel with the treated hydrocarbon flowing to storage.

The separated rich treating solution phase is sent to the regeneration unit where sulfur-bearing components are removed. The removed sulfur is sent to another refinery unit for further processing. The regenerated lean treating solution is returned to the EXOMER extraction step for further use.

Economics: EXOMER allows refiners to meet stricter sulfur specifications while preserving octane by allowing the hydrotreater severity to be reduced. The capital expenditure for a grass roots EXOMER is 35%–50% of the cost of incremental hydrotreating capacity. Operating costs per barrel are about 60%–70% less than hydrotreating.



Installations: Three licensed units worldwide.

Reference: Hydrocarbon Processing, February 2002, p. 45.

Treating—Gasoline sweetening

Application: MERICAT systems oxidize mercaptans to disulfides by reacting mercaptans with air and caustic in the presence of catalyst using FIBER FILM Contactor technology.

Description: In a MERICAT system, the caustic phase flows along the fibers of the FIBER FILM Contactor as it preferentially wets the fibers. Prior to entering the FIBER FILM Contactor the gasoline phase mixes with air through a proprietary air sparger. The gasoline then flows through the caustic-wetted fibers in the Contactor where the mercaptans are extracted and converted to disulfides in the caustic phase. The disulfides are immediately absorbed back into the gasoline phase. The two phases disengage and the caustic is recycled back to the FIBER FILM Contactor until spent.

Competitive advantages: FIBER FILM Contactor technology uses smaller processing vessels while guaranteeing the sodium content of the product. This saves valuable plant space and reduces capital expenditure.

Installations: 133 licensed units worldwide.



Treating—Jet fuel and kerosine

Application: NAPFINING or NAPFINING HITAN / MERICAT II / AQUAFIN-ING systems eliminate H_2S , naphthenic acids and mercaptans from kerosine to meet acid number and mercaptan jet fuel specifications. Treatment uses caustic, air and catalyst along with FIBER FILM Contactor technology and an up-flow, catalyst-impregnated carbon bed.

Description: In the NAPFINING or NAPFINING HiTAN system, a recycled caustic phase flows along the fibers of the FIBER FILM Contactor as it preferentially wets the fibers. The kerosine phase simultaneously flows through the caustic-wetted fibers where naphthenic acids react with the caustic to form sodium naphthenates. The two phases disengage and the acid-free kerosine flows to the MERICAT II. NAPFINING HiTAN is an extension of the existing technology that allows for the processing of high TAN (> 0.1 mg KOH/g) feeds.

In the MERICAT II system the mercaptans react with caustic, air, and catalyst in the FIBER FILM Contactor to form disulfides. The two phases disengage again and the kerosine flows upwards through a catalyst-impregnated carbon bed where the remaining heavy mercaptans are converted to disulfides. An AQUAFINING system is then used to water wash the kerosine downstream of the MERICAT II vessel to remove caustic. Salt driers and clay filters are used downstream of the water wash to remove water, surfactants and particulates to ensure a completely clean product.

Competitive advantages: FIBER FILM Contactor technology requires smaller processing vessels thus saving valuable plant space and reducing capital expenditure. Onstream factor is 100% whereas electrostatic precipitators and down-flow fixed-bed reactors are less robust.



Installations: 214 licensed units worldwide

References: Hydrocarbon Technology International, 1993. Petroleum Technology Quarterly, Winter 1996/97.

Treating—Jet fuel and kerosine sweetening

Application: MERICAT J systems remove H_2S and some naphthenic acids while sweetening mercaptans to disulfide oils in jet fuel, kerosine, heavy naphtha, and natural gasoline streams. Treatment uses a proprietary solution (JeSOL-9), catalyst and air along with FIBER FILM Contactor technology to reduce the acidity, odor, and corrosive effects of the treated product without the need for a fixed media bed.

Description: MERICAT J is the next generation of the MERICAT process. Recycled JeSOL-9 solution containing catalyst contacts an aerated hydrocarbon stream in the FIBER FILM Contactor. As the JeSOL-9 and hydrocarbon phases flow down the fiber bundle, they contact, and heavy mercaptans are oxidized to disulfide oils. After treatment the two phases disengage from the fibers and separate in the vessel. Treated hydrocarbon exits the top of the vessel, while the regenerated JeSOL-9 solution is recycled back from the bottom of the vessel to the FIBER FILM Contactor until it is spent. Fresh JeSOL-9 solution and catalyst are added as needed to maintain activity.

Competitive advantages:

- Oxidizes heavy mercaptans without the need for a fixed media bed
- Minimal capital investment compared to units requiring fixed media beds
- No downtime, problems and maintenance costs associated with fixed media beds
- Minimal caustic and catalyst consumption
- Operating simplicity

The MERICAT J on-stream factor is 100% while competitive systems requiring periodic cleaning have less reliable on-stream factors.



Installations: Two licensed units

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Treating—Kerosine and heavy naphtha sweetening

Application: MERICAT II treating unit oxidizes mercaptan sulfur to disulfides to reduce product odor. The streams treated are jet fuel, kerosine, natural gasoline and selectively hydrotreated FCC gasolines.

Description: A MERICAT II system consists of two treaters. The FIBER FILM Contactor section removes hydrogen sulfide and naphthenic acids while converting some mercaptans to disulfides with air, oxidation catalyst and caustic solution. The partially-treated hydrocarbon exits the FI-BER FILM Contactor and passes upflow through a catalyst-impregnated carbon bed saturated with caustic to convert the remaining high-boiling mercaptans to disulfides.

Competitive advantages:

- Minimal caustic and catalyst consumption
- Operating simplicity
- Minimal capital investment
- Recausticizing of the carbon bed without interruption of treating.

The FIBER FILM section keeps organic acids from entering the carbon bed. This conserves caustic and avoids fouling of the bed with sodium naphthenate soaps. Competitive downflow reactors need more frequent carbon bed caustic washes to remove these soaps as compared to MERICAT II systems. The MERICAT II on-stream factor is 100% while competitive systems requiring periodic cleaning have unpredictable onstream factors.



Installations: 45 licensed units worldwide.

Reference: Hydrocarbon Technology International, 1993.

Treating—Phenolic caustic

Application: ECOMERICAT treating systems removes phenols from phenolic caustics by neutralization in conjunction with solvent washing using a FIBER FILM Contactor.

Description: An ECOMERICAT system contacts the spent caustic with a slipstream of sweetened gasoline containing CO_2 whereby neutralizing the spent caustic, springing the phenols and absorbing the phenols into the sweetened gasoline. This process yields neutral brine with minimal phenolic content.

Competitive advantages:

- Minimizes spent caustic disposal cost
- Reduces the phenol content of spent caustic and increases the phenol content of sweetened gasoline thus adding value
- Operates over a wide pH range
- Simple to operate
- No corrosion problems due to the buffering effect of CO₂.

Installations: Three licensed units worldwide.



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Treating—Pressure swing adsorption

Application: The UOP Polybed pressure swing adsorption (PSA) process selectively adsorbing impurities from product streams. The impurities are adsorbed in a fixed-bed adsorber at high pressure and desorbed by "swinging" the adsorber from the feed to the tail gas pressure and by using a high-purity purge. Typically, the desired component is not adsorbed and is recovered at high purity.

Description: A PSA system operates as a batch process. However, multiple adsorbers operating in a staggered sequence are used to produce constant feed, product and tail gas flows.

Step 1: Adsorption. The feed gas enters an adsorber at a high pressure, impurities are adsorbed and high-purity product is produced. Flow is normally in the upwardly direction. When an adsorber has reached its adsorption capacity, it is taken offline, and the feed automatically switched to a fresh adsorber.

Step 2: Co-current depressurization. To recover the product trapped in the adsorbent void spaces, the adsorber is co-currently (in the direction of feed flow) depressurized. The product gas withdrawn is used internally to repressurize and purge other adsorbers.

Step 3: Counter-current depressurization. At the end of the cocurrent depressurization step, the adsorbent is partially regenerated by counter-currently depressurizing the adsorber to the tail-gas pressure, and thereby rejecting the impurities.

Step 4: Purge. The adsorbent is purged with a high-purity stream (taken from another adsorber on the cocurrent depressurization step) at a constant pressure to further regenerate the bed.

Step 5: Repressurization. The repressurization gas is provided from the co-current depressurization step and a slipstream from the product.



When the adsorber has reached the adsorption pressure, the cycle has been completed. The vessel is ready for the next adsorption cycle.

The UOP Polybed PSA system offers:

- High reliability (greater than 99.8% onstream time)
- Minimal manpower requirements due to automatic operation
- Reduced equipment costs and enhanced performance based on high performance adsorbents and advanced PSA cycles
- Lower operating and equipment costs for downstream process units
- Flexibility to process more than one feedstock

Treating—Pressure swing adsorption, continued

- Modular construction for improved delivery times and low installation costs
- Minimal feed pretreatment and utility requirements
- Adsorbents last for the life of the mechanical equipment (more than 30 years).

Installation: Since commercialization in 1966, UOP has provided almost 1,000 PSA systems in more than 60 countries in the refining, petrochemical, steel and power-generation industries. The Polybed PSA System has demonstrated exceptional economic value in many applications, such as hydrogen recovery from steam methane reforming, refinery offgas, monomer recovery in polyolefin plants, hydrogen extraction from gasification syngas, helium purification for industrial gas use, adjustment of synthesis gas for ammonia production, methane purification for petrochemicals productions, and H₂/CO ratio adjustment for syngas used in oxo-alcohols production. Feed conditions typically range from 100 to 1,000 psig (7 to 70 kg/cm²g) with concentrations of the desired component typically in the range of 30 to 98+ mole%. System capacities range from less than 1 to more than 350 MMscfd (less than 1,100 to more than 390,000 Nm³/hr). UOP provides unit and complex integration development support to ensure the PSA system meets the end-user's processing objectives and worldwide service and technical support after startup.

Licensor: UOP, A Honeywell Company CONTACT

Treating—**Propane**

Application: AMINEX treating system extracts H₂S and COS from propane with an amine solution using FIBER FILM Contactor technology.

Description: In an AMINEX system, the amine phase flows along the fibers of the FIBER FILM Contactor as it preferentially wets the fibers. The propane phase flows through the amine-wetted fibers as the H_2S and COS are extracted into the amine phase. The two phases disengage in the separator vessel with the rich amine flowing to the amine regeneration unit and the treated propane flowing to storage.

Competitive advantages: FIBER FILM Contactor technology requires smaller processing vessels thus saving valuable plant space and reducing capital expenditure.

Installations: 29 licensed units worldwide.

Reference: Hydrocarbon Processing, Vol. 63, No. 4, April 1984, p. 87.

Licensor: Merichem Company CONTACT



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Treating—**Reformer products**

Application: CHLOREX treating system removes inorganic chloride compounds from liquid and gas reformer products using a FIBER FILM Contactor and an alkaline water treating solution.

Description: The CHLOREX system uses an alkaline water solution to extract chloride impurities contained in the reformate stabilizer feed or the stabilizer overhead product. CHLOREX can also be used to remove chlorides from reformer offgas. Fresh caustic and fresh process water are added to the system to maintain the proper pH of the recycle solution.

Competitive advantages: CHLOREX produces an easily handled waste when compared to disposal of sacrificial solid bed absorbents.

Installations: Four licensed units worldwide.



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Treating—Spent caustic deep neutralization

Application: MERICON systems neutralize spent caustics containing sulfides, mercaptans, naphthenic acids, and phenols.

Description: A MERICON system neutralizes spent caustic with acid to a low pH. The resulting acid gases and acid oils are separated from the acidic brine. The acid gases (H_2S and mercaptans) flow to a sulfur plant. The sprung acid oils are returned to the refinery for processing. The acidic brine is further stripped with fuel gas to remove traces of H_2S and mercaptans. Finally, the acidic brine is mixed with caustic to return it to a neutral pH for final disposal.

Competitive advantages:

- Minimal operator attention and 100% onstream factor between turnarounds
- Minimal capital investment
- Maximum COD reduction
- Non-odorous neutralized brine product
- Recovery of valuable hydrocarbons.

Installations: 30 licensed units worldwide.

Reference: Petroleum Technology Quarterly, Spring 2001, p. 55.



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Vacuum distillation

Application: Process to produce vacuum distillates that are suitable for lubricating oil production by downstream units, and as feedstocks to FCC and hydrocracker units.

Feed: Atmospheric bottoms from crude oils (atmospheric residue) or hydrocracker bottoms.

Product: Vacuum distillates of precisely defined viscosities and flash points (for lube production) and low metals content (for FCC and hydrocracker units) as well as vacuum residue with specified softening point, penetration and flash point.

Description: Feed is preheated in a heat-exchanger train and fed to the fired heater. The heater outlet temperature is controlled to produce the required quality of vacuum distillates and residue. Structured packings are typically used as tower internals to achieve low flashzone pressure and, hence, to maximize distillate yields. Circulating reflux streams enable maximum heat recovery and reduced column diameter.

A wash section immediately above the flash zone ensures that the metals content in the lowest side draw is minimized. Heavy distillate from the wash trays is recycled to the heater inlet or withdrawn as metals cut.

When processing naphthenic residues, a neutralization section may be added to the fractionator.

Utility requirements (typical, North Sea Crude), units per m³ of feed:

Electricity, kWh	5
Steam, MP, kg	15
Steam production, LP, kg	60
Fuel oil, kg	7
Water, cooling, m ³	3



Installation: Numerous installations using the Uhde (Edeleanu) proprietary technology are in operation worldwide. The most recent reference is a 86,000-bpd unit for a German refinery, which was commissioned in 2004; the unit produces vacuum distillates as feedstock for FCC and hydrocracker units.

Licensor: Uhde GmbH CONTACT

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Visbreaking

Application: Manufacture incremental gas and distillate products and simultaneously reduce fuel oil viscosity and pour point. Also, reduce the amount of cutter stock required to dilute the resid to meet the fuel oil specifications. Foster Wheeler/UOP offer both "coil" and "soaker" type visbreaking processes. The following information pertains to the "coil" process.

Products: Gas, naphtha, gas oil, visbroken resid (tar).

Description: In a "coil" type operation, charge is fed to the visbreaker heater (1) where it is heated to a high temperature, causing partial vaporization and mild cracking. The heater outlet stream is quenched with gas oil or fractionator bottoms to stop the cracking reaction. The vapor-liquid mixture enters the fractionator (2) to be separated into gas, naphtha, gas oil and visbroken resid (tar). The tar may also be vacuum flashed for recovery of visbroken vacuum gas oil.

Operating conditions: Typical ranges are:

Heater outlet temperature, °F	850-910
Quenched temperature, °F	710-800

An increase in heater outlet temperature will result in an increase in overall severity, further viscosity reduction and an increase in conversion.

Feed, source	Light Arabian	Light Arabian
Туре	Atm. Resid	Vac. Resid
Gravity, °API	15.9	7.1
Sulfur, wt%	3.0	4.0
Concarbon, wt%	8.5	20.3
Viscosity, CKS @130°F	150	30,000
CKS @ 210°F	25	900
Products, wt%		
Gas	3.1	2.4



Naphtha (C ₅ –330 °F)	7.9	6.0
Gasoil	14.5	15.5
Visbroken resid	74.5 (600°F+)	76.1 (662°F+)

Economics:

Investment (basis: 40,000-10,000 bpsd, 4th	Q 2010, US Gulf),
\$ per bpsd	1,800-3,500
Utilities, typical per bbl feed:	
Fuel, MMBtu	0.1195
Power, kW/bpsd	0.0358
Steam, MP, Ib	6.4
Water, cooling, gal	71.0

Installation: Over 50 units worldwide.

Reference: Handbook of Petroleum Refining Processes, Third Ed., McGraw-Hill, 2003, pp. 12.91–12.105.

Licensors: Foster Wheeler USA Corp./UOP, A Honeywell Company CONTACT

Visbreaking

Application: The Shell Soaker Visbreaking process is most suitable to reduce the viscosity of vacuum (and atmospheric) residues in (semi) complex refineries. The products are primarily distillates and stable fuel oil. The total fuel oil production is reduced by decreasing the quantity of cutter stock required. Optionally, a Shell vacuum flasher may be installed to recover additional gasoil and vacuum gasoil as cat cracker or hydrocracker feed from the cracked residue. The Shell Soaker Visbreaking technology has also proven to be a very cost-effective revamp option for existing units.

Description: The preheated vacuum residue is charged to the visbreaker heater (1) and from there to the soaker (2). The conversion takes place in both the heater and the soaker. The operating temperature and pressure are controlled such as to reach the desired conversion level and/ or unit capacity. The cracked feed is then charged to an atmospheric fractionator (3) to produce the desired products like gas, LPG, naphtha, kerosine, gasoils and cracked residue. If a vacuum flasher is installed, additional gasoil and vacuum gasoil are recovered from the cracked residue.

Yields: Depend on feed type and product specifications.

Type and source Viscosity, cSt @100°C	Vacuum residue, Middle East 615
Products, wt %	
Gas	2.28
Naphtha	4.8
Kerosine + gasoil	13.6
(TC) Vacuum gasoil	23.4
Vacuum flashed cracked residue	56



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Economics: The typical investment for a 25,000-bpd unit will be about \$1,800 to \$2,250/bbl installed, excluding treating facilities. (Basis: Western Europe, 2009.)

Utilities, typical consumption consumption/production for a 25,000-bpd unit, dependent on configuration and a site's marginal economic values for steam and fuel:

Fuel as fuel oil equivalent, bpd	400
Power, MW	1.2
Net steam production (18 bar), tpd	370

Installation: More than 70 Shell Soaker Visbreakers have been built. Post startup services and technical services for existing units are available from Shell Global Solutions.

Licensor: Shell Global Solutions International B.V. and CB&I Lummus B.V. CONTACT

HOM

Visbreaking

Application: The FWUSA/UOP Visbreaking process is a non-catalytic thermal process that converts atmospheric or vacuum residues via thermal cracking to gas, naphtha, distillates, and visbroken residue. Atmospheric and vacuum residues are typically charged to a visbreaker to reduce fuel oil viscosity and increase distillate yield in the refinery. The process will typically achieve a conversion to gas, gasoline, and distillates of 10% to 50%, depending on the severity and feedstock characteristics. Visbreaking reduces the quantity of cutter stock required to meet fuel oil specifications and, depending upon sulfur specs, can decrease fuel oil production by 20%.

Products: Gas, naphtha, gas oil, visbroken resid (tar).

Description: The thermal conversion of the residue chargestock is accomplished by heating at high temperatures in a specially designed furnace. The residence time, temperature, and pressure of the furnace's soaking zone is controlled to optimize the thermal free radical cracking to produce the desired products. The heater effluent is quenched to stop the reaction and the quenched products flow to the fractionator for separation of the visbroken naphtha, distillate, and residue. After steam stripping, the distillate is recombined with the visbroken residue for heavy fuel oil production.

Operating conditions: Typical ranges are:

Heater outlet temperature, °F	850-910
Quenched temperature, °F	710-800

An increase in heater outlet temperature will result in an increase in overall severity, further viscosity reduction and an increase in conversion.



Installation: Over 50 units worldwide.

Licensors: UOP, A Honeywell Company/Foster Wheeler USA Corp. **CONTACT**

Wax hydrotreating

Application: Hydrogen finishing technology has largely replaced clay treatment of low-oil-content waxes to produce food- and medicinal-grade product specifications (color, UV absorbency and sulfur) in new units. Advantages include lower operating costs, elimination of environmental concerns regarding clay disposal and regeneration, and higher net wax product yields.

Description: Hard-wax feed is mixed with hydrogen (recycle plus makeup), preheated, and charged to a fixed-bed hydrotreating reactor (1). The reactor effluent is cooled in exchange with the mixed feed-hydrogen stream. Gas-liquid separation of the effluent occurs first in the hot separator (2) then in the cold separator (3). The hydrocarbon liquid stream from each of the two separators is sent to the product stripper (4) to remove the remaining gas and unstabilized distillate from the wax product, and the product is dried in a vacuum flash (5). Gas from the cold separator is either compressed and recycled to the reactor or purged from the unit if the design is for once-through hydrogen.

Economics:

Investment (Basis 2,000-bpsd feedrate capacity, 2011 US Gulf Coast), \$/bpsd	11,300
Utilitiies, typical per bbl feed: Fuel, 10 ³ Btu (absorbed)	30
Steam, Ib	25
Water, cooling (25°F rise), gal	300

Licensor: Bechtel Hydrocarbon Technology Solutions, Inc. CONTACT



Wet scrubbing system, EDV

Application: EDV Technology is a low pressure drop scrubbing system, to scrub particulate matter (including PM2.5), SO_2 and SO_3 from flue gases. It is especially well suited where the application requires high reliability, flexibility and the ability to operate for 4–7 years continuously without maintenance shutdowns. The EDV technology is highly suited for FCCU regenerator flue-gas applications.

Products: The effluents from the process will vary based on the reagent selected for use with the scrubber. In the case where a sodium-based reagent is used, the product will be a solution of sodium salts. Similarly, a magnesium-based reagent will result in magnesium salts. A lime/ limestone-based system will produce a gypsum waste. The EDV technology can also be designed for use with the LABSORB buffer thus making the system regenerative. The product, in that case, would be a usable condensed SO₂ stream.

Description: The flue gas enters the spray tower through the quench section where it is immediately quenched to saturation temperature. It proceeds to the absorber section for particulate and SO₂ reduction. The spray tower is an open tower with multiple levels of BELCO-G-Nozzles. These nonplugging and abrasion-resistant nozzles remove particulates by impacting on the water/reagent curtains. At the same time, these curtains also reduce SO₂ and SO₃ emissions. The BELCO-G-Nozzles are designed not to produce mist; thus a conventional mist eliminator is not required.

Upon leaving the absorber section, the saturated gases are directed to the EDV filtering modules to remove the fine particulates and additional SO_3 . The filtering module is designed to cause condensation of the saturated gas onto the fine particles and onto the acid mist, thus allowing it to be collected by the BELCO-F-Nozzle located at the top.

To ensure droplet-free stack, the flue gas enters a droplet separator. This is an open design that contains fixed-spin vanes that induce a cyclonic flow of the gas. As the gases spiral down the droplet separa-



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tor, the centrifugal forces drive any free droplets to the wall, separating them from the gas stream.

Economics: The EDV wet scrubbing system has been extremely successful in the incineration and refining industries due to the very high scrubbing capabilities, very reliable operation and reasonable price.

Installation: More than 200 applications worldwide on various processes including more than 80 applications on FCCU, heater, SRU tailgas unit, fluidized coker and coal-fired boilers.

Reference: Confuorto and Weaver, "Flue gas scrubbing of FCCU regenerator flue gas—performance, reliability, and flexibility—a case history," *Hydrocarbon Engineering*, 1999.

Eagleson and Dharia, "Controlling FCCU emissions," 11th Refining Technology Meeting, HPCL, Hyderabad, 2000.

Licensor: Belco Technologies Corp. CONTACT

White oil and wax hydrotreating

Application: Process to produce white oils and waxes.

Feeds: Nonrefined as well as solvent- or hydrogen-refined naphthenic or paraffinic vacuum distillates or deoiled waxes.

Products: Technical- and medical-grade white oils and waxes for plasticizer, textile, cosmetic, pharmaceutical and food industries. Products are in accordance with the US Food and Drug Administration (FDA) regulations and the German Pharmacopoeia (DAB 8 and DAB 9) specifications.

Description: This catalytic hydrotreating process uses two reactors. Hydrogen and feed are heated upstream of the first reaction zone (containing a special presulfided NiMo/alumina catalyst) and are separated downstream of the reactors into the main product and byproducts (hydrogen sulfide and light hydrocarbons). A stripping column permits adjusting product specifications for technical-grade white oil or feed to the second hydrogenation stage.

When hydrotreating waxes, however, medical quality is obtained in the one-stage process. In the second reactor, the feed is passed over a highly active hydrogenation catalyst to achieve a very low level of aromatics, especially of polynuclear compounds. This scheme permits each stage to operate independently and to produce technical- or medical-grade white oils separately. Yields after the first stage range from 85% to 99% depending on feedstock. Yields from the second hydrogenation step are nearly 100%. When treating waxes, the yield is approximately 98%.

Utility requirements (typical, Middle East Crude), units per m³ of feed:

	1st stage for	2nd stage for	Food-grade
	techn. white oil	med. white oil	wax
Electricity, kWh	197	130	70
Steam, LP, kg	665	495	140
Water, cooling, m	³ 48	20	7
Hydrogen, kg	10.0	2.6	1.6



Installation: Four installations use the Uhde (Edeleanu) proprietary technology, one of which has the largest capacity worldwide.

Licensor: Uhde GmbH CONTACT

ΛE

Xylene isomerization

Application: GT-IsomPX is GTC's xylene isomerization technology. It is available in two versions: EB isomerization type and EB dealkylation type. Both versions gain high ethylbenzene (EB) conversion rates while producing equilibrium mixed xylenes. Catalysts that exhibit superior physical activity and stability are the key to this technology. 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: reactor section and product distillation section. In this process, paraxylene (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 isomerization reaction unit, where m-xylene,o-xylene and PX are isomerized to equilibrium and EB is de-alkylated to benzene.

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

• With the EB-dealkylation catalyst, the byproduct benzene is produced at high purity by simple distillation.



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- Low H₂/HC ratio, high WHSV and low xylenes loss
- Long cycle length
- Efficient heat integration scheme reduces energy consumption

• Turnkey package for high-purity benzene, toluene and PX production available from licensor.

Economics: Feedrate: 4,000 thousand tpy (88,000 bpsd); erected cost: \$29 MM (ISBL, 2007 US Gulf Coast Basis).

Installation: Technology available for license.

Licensor: GTC Technology US, LLC CONTACT

HOME

Xylenes and benzene

Application: The S-TDT process can produce mixed xylenes and benzene in an aromatics complex through disproportionation of toluene and transalkylation of toluene and C_9^+ aromatics (C_9^+ A) using toluene and C_9^+ A as feedstocks.

Description: The commercially proven HAT series catalysts are the core of the S-TDT process. The catalyst provides high activity, high selectivity, good operation stability and feedstock flexibility. The excellent performance of HAT series catalysts provides technological supports for some aromatics complexes to expand their capacities without a reactor revamp, increase in catalyst inventory and hydrogen compressor replacement.

Commercial examples: The capacities for two plants were 398,000 metric tpy and 1.007 million metric tpy, respectively. After using the HAT catalysts and operation conditions of the S-TDT process, outputs for both benzene and mixed xylenes increased by 40% without any changes to the reactor, compressor and catalyst inventory for both facilities.

Either pure toluene or high content of $C_9^+ A$ (70 wt%) can be used as feedstocks for the process. In particular, C_{10} aromatics ($C_{10}A$) in the feedstock can be as much as 10 wt%. $C_{10}A$ can also be converted into lower carbon aromatics, so that more benzene and mixed-xylenes can be produced and plant profitability is increased.

The purity of the benzene product from the benzene and toluene (BT) fractionation section is such that no further extraction is needed. The mixed-xylenes product containing only 1%–4% ethylbenzene is a good feedstock for paraxylene (PX) production.

To reduce operating costs and save energy, the plant's waste heat is utilized as much as possible with heat integration technology and highefficiency heat exchangers.



Commercial plants: The S-TDT process has been licensed to six plants, among which three were commissioned in China and the Middle East, and the other three are under design.

The HAT series catalysts not only have exhibited excellent performance in the S-TDT process units, but also have been successfully used as a drop-in catalyst in many other company-licensed process units in China.

Licensor: China Petrochemical Technology Co., Ltd. CONTACT