

Hydrocarbon Processing's Refining Processes Handbooks

reflect the dynamic advancements now available in licensed process technologies, catalysts and equipment. The global 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. Hence, global 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, coking, (crude) distillation, catalytic cracking (fluid and resid), hydrocracking, hydrotreating, hydrogen, isomerization, desulfurization, lube treating, visbreaking, etc.

To maintain as complete listing as possible, the **Refining Processes 2004** handbook is available on CD-Rom only. Additional copies may be ordered from our website.

- **Refining Processes Index**
- **Company Index**
- **Refining Articles**
- **Equipment and Services Providers**

Refining Processes Index - 1

[Alkylation](#)[Alkylation, catalytic](#)[Alkylation, sulfuric acid](#)[Alkylation—feed preparation](#)[Alkylation—HF](#)[Aromatics](#)[Aromatics extractive distillation](#)[Aromatics recovery](#)[Asphalt—oxidation](#)[Benzene reduction](#)[Catalytic cracking \(MSCC\)](#)[Catalytic dewaxing](#)[Catalytic reforming](#)[Coking](#)[Coking, flexi](#)[Coking, fluid](#)[Crude distillation](#)[Crude topping units](#)[Deasphalting](#)[Deep catalytic cracking](#)[Deep thermal conversion](#)[Desulfurization](#)[Dewaxing](#)[Dewaxing/wax deoiling](#)[Diesel upgrading](#)[Diesel—ultra-low-sulfur diesel \(ULSD\)](#)[Electrical desalting](#)[Ethers](#)[Ethers—ETBE](#)[Ethers—MTBE](#)[Fluid catalytic cracking](#)[Fluid catalytic cracking—pretreatment](#)[Gas treating—H₂S removal](#)[Gasification](#)[Gasoline desulfurization](#)[Gasoline desulfurization, ultra-deep](#)[H₂S and SWS gas conversion](#)[H₂S removal](#)[H₂S removal, Thiopaq](#)[Hydrocracking](#)[Hydrocracking, resid](#)[Hydrocracking/hydrotreating—VGO/DAO](#)[Hydrodearomatization](#)[Hydrodesulfurization](#)[Hydrodesulfurization—UDHDS](#)[Hydrofinishing](#)[Hydrofinishing/hydrotreating](#)[Hydrogen](#)[Hydrogenation](#)[Hydrogen—HTCR-based](#)[Hydrogen—HTER-p based](#)[Hydrogen—Methanol-to-Shift](#)[Hydrogen—recovery](#)[Hydrogen—steam methane reforming \(SMR\)](#)[Hydroprocessing, residue](#)[Hydroprocessing, ULSD](#)[Hydrotreating](#)

Refining Processes Index - 2

[Hydrotreating—aromatic saturation](#)[Hydrotreating—catalytic dewaxing](#)[Hydrotreating, diesel](#)[Hydrotreating—lube and wax](#)[Hydrotreating—RDS/VRDS/UFR/OCR](#)[Hydrotreating—resid](#)[Isomerization](#)[Isooctane](#)[Isooctane/isooctene](#)[Isooctene/Isooctane/ETBE](#)[LPG recovery](#)[Lube and wax processing](#)[Lube extraction](#)[Lube hydrotreating](#)[Lube oil refining, spent](#)[Lube treating](#)[Mercaptan removal](#)[NOx abatement](#)[NOx reduction, low-temperature](#)[Olefins recovery](#)[Olefins-butenes extractive distillation](#)[Olefins-dehydrogenation](#)[Oligomerization of C₃C₄ cuts](#)[Oligomerization—polynaphtha](#)[Oxygen enrichment for Claus units](#)[Oxygen enrichment for FCC units](#)[Paraxylene](#)[Prereforming with feed ultra purification](#)[Resid catalytic cracking](#)[SBS SO₃ removal process](#)[SO₂ removal, regenerative](#)[Sour gas treatment](#)[Spent acid regeneration](#)[Spent oil lube re-refining](#)[Sulfur degassing](#)[Sulfur recovery](#)[Thermal gasoil process](#)[Treating—gases](#)[Treating—gasoline](#)[Treating—gasoline and light hydrocarbon liquids](#)[Treating—gasoline desulfurization, ultra deep](#)[Treating—jet fuel/kerosine](#)[Treating—light liquids](#)[Treating—Phenolic caustic](#)[Treating—reformer products](#)[Treating—spent caustic deep neutralization](#)[Treating—sweetening](#)[Vacuum distillation](#)[Visbreaking](#)[Wax hydrotreating](#)[Wet gas scrubbing \(WGS\)](#)[Wet scrubbing system, EDV](#)[White oil and wax hydrotreating](#)

Company Index

[ABB Lummus Global, Inc.](#)[Air Products and Chemicals Inc.](#)[Aker Kvaerner](#)[Akzo Nobel Catalysts](#)[Akzo Nobel Catalysts bv](#)[Axens](#)[BARCO](#)[Bechtel Corp.](#)[Belco Technologies Corp.](#)[Black & Veatch Pritchard, Inc.](#)[BOC Group, Inc.](#)[CB&I Howe-Baker Process and
Technologies](#)[CDTECH](#)[Chevron Lummus Global LLC](#)[ChevronTexaco Corp.](#)[Codan Development LLC](#)[ConocoPhillips, Technology Solutions
Division](#)[Costain Oil, Gas & Process Ltd.](#)[Criterion Catalyst Co., LP](#)[Davy Process Technology Ltd.](#)[ExxonMobil Research and
Engineering Co.](#)[Fina Research S.A.](#)[Fortum Oil and Gas](#)[Foster Wheeler](#)[Future Energy GmbH](#)[Gas Technology Products LLC](#)[GE Energy](#)[Goar, Allison & Associates, Inc.](#)[GTC Technology Inc.](#)[Haldor Topsøe A/S](#)[Hydrocarbon Technologies, Inc.](#)[IFP Group Technologies](#)[Kellogg Brown & Root, Inc.](#)[Linde AG, Gas Division](#)[Linde BOC Process Plants LLC](#)[Lyondell Chemical Co.](#)[Merichem Chemicals & Refinery
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[Burckhardt Compression AG](#)

[DMC Clad Metal Div., Dynamic Materials Corp.](#)

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[Fischer Valve Div., Emerson Process Management](#)

[Gas Technology Products LLC](#)

[KBC Advanced Technologies](#)

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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 isobutene-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.

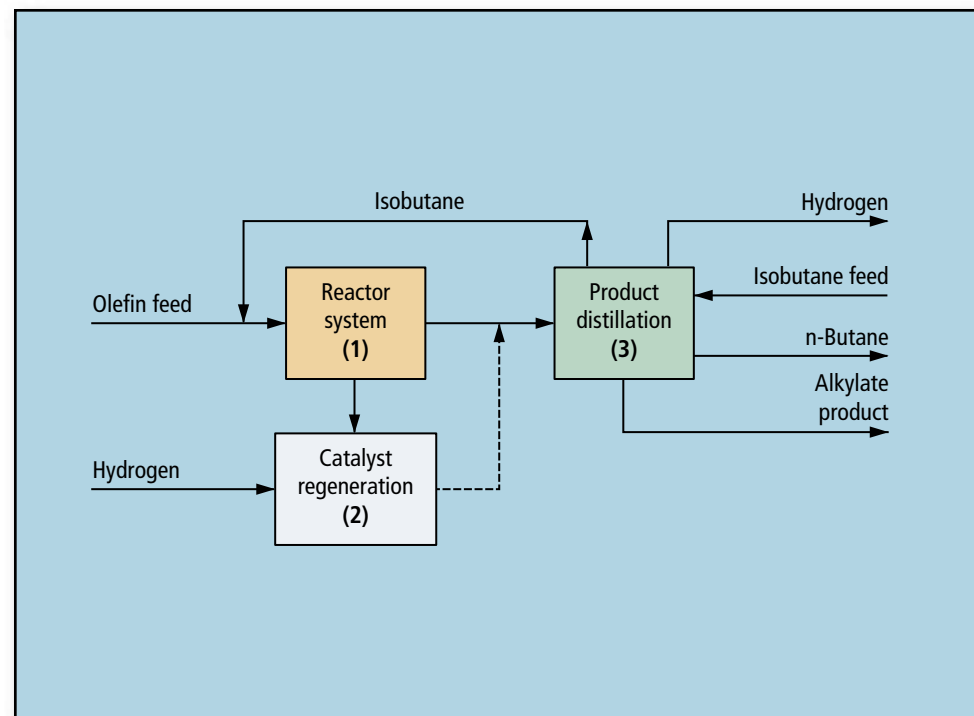
Description: The light olefin feed is combined with the isobutene make-up and recycle and sent to the alkylation reactors which convert the olefins into alkylate using a solid acid catalyst (1). The AlkyClean process uses a true solid acid catalyst to produce alkylate, eliminating the safety and environmental hazards associated with liquid acid technologies. Simultaneously, reactors are undergoing a mild liquid-phase regeneration using isobutene 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 propane, n-butane and alkylate, while also recycling isobutene 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 C₅⁺ alkylate has a RON of 93–98 depending on processing conditions and feed composition.

Economics:

Investment (basis 10,000-bpsd unit) \$/bpsd	3,100
Operating cost , \$/gal	0.47

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



Reference: "The Process: A new solid acid catalyst gasoline alkylation technology," NPRA 2002 Annual Meeting, March 17–19, 2002.

Licensors: ABB Lummus Global, Akzo Nobel Catalysts and Fortum Oil and Gas.

Alkylation

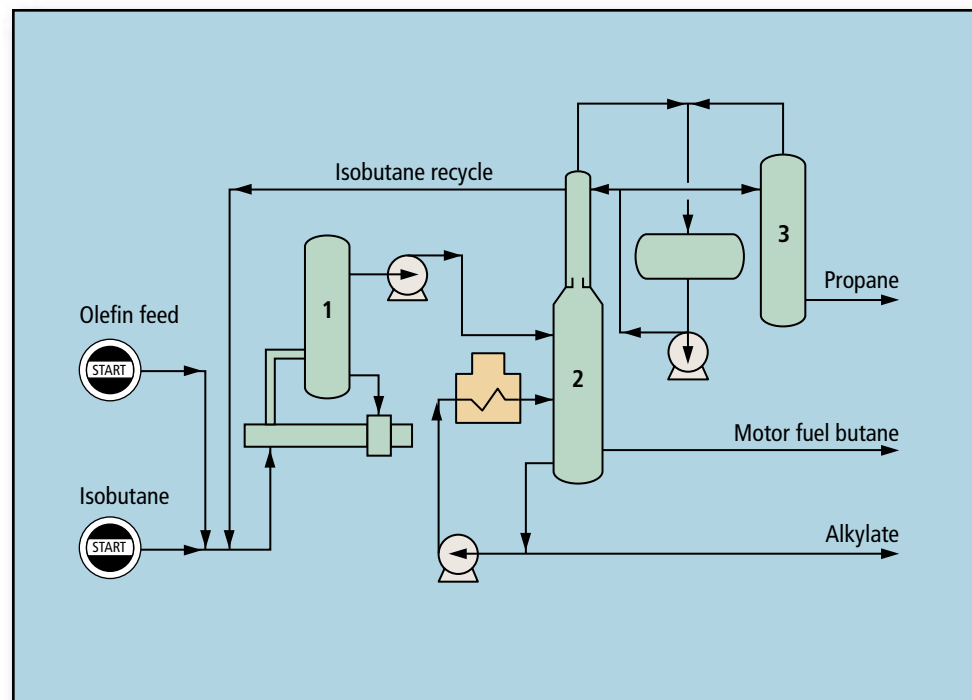
Application: Convert propylene, amylenes, butylenes and isobutane to the highest quality motor fuel using ReVAP (**Re**duce **V**olatility **A**lkylation **P**rocess) alkylation.

Products: An ultra-low-sulfur, high-octane and low-Rvp blending stock for motor and aviation fuels.

Description: Dry liquid feed containing olefins and isobutane is charged to a combined reactor-settler (1). The reactor uses the principle of differential gravity head to effect catalyst circulation through a cooler prior to contacting highly dispersed hydrocarbon in the reactor pipe. The hydrocarbon phase that is produced in the settler is fed to the main fractionator (2), which separates LPG-quality propane, isobutane recycle, n-butane and alkylate products. A small amount of dissolved catalyst is removed from the propane product by a small stripper tower (3). Major process features are:

- Gravity catalyst circulation (no catalyst circulation pumps required)
- Low catalyst consumption
- Low operating cost
- Superior alkylate qualities from propylene, isobutylene and amylenes feedstocks
- Onsite catalyst regeneration
- Environmentally responsible (very low emissions/waste)
- Between 60% and 90% reduction in airborne catalyst release over traditional catalysts
- Can be installed in all licensors' HF alkylation units.

With the proposed reduction of MTBE in gasoline, ReVAP offers significant advantages over sending the isobutylene to a sulfuric-acid-alkylation unit or a dimerization plant. ReVAP alkylation produces higher octane, lower Rvp and endpoint product than a sulfuric-acid-alkylation unit and nearly twice as many octane barrels as can be produced from a dimerization unit.



Yields:

Composition (lv%)	Feed type	
	Butylene	Propylene-butylene mix
Propylene	0.8	24.6
Propane	1.5	12.5
Butylene	47.0	30.3
i-Butane	33.8	21.8
n-Butane	14.7	9.5
i-Pentane	2.2	1.3
Alkylate product		
Gravity, API	70.1	71.1
Rvp, psi	6-7	6-7
ASTM 10%, °F	185	170
ASTM 90%, °F	236	253
RONC	96.0	93.5

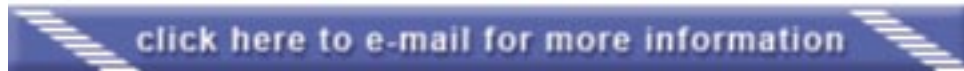
Alkylation, *continued*

Per bbl olefin converted

i-Butane consumed, bbl	1.139	1.175
Alkylate produced, bbl	1.780	1.755

Installation: 140 worldwide licenses.

Licensors: Technology Solutions Division of ConocoPhillips.



Alkylation

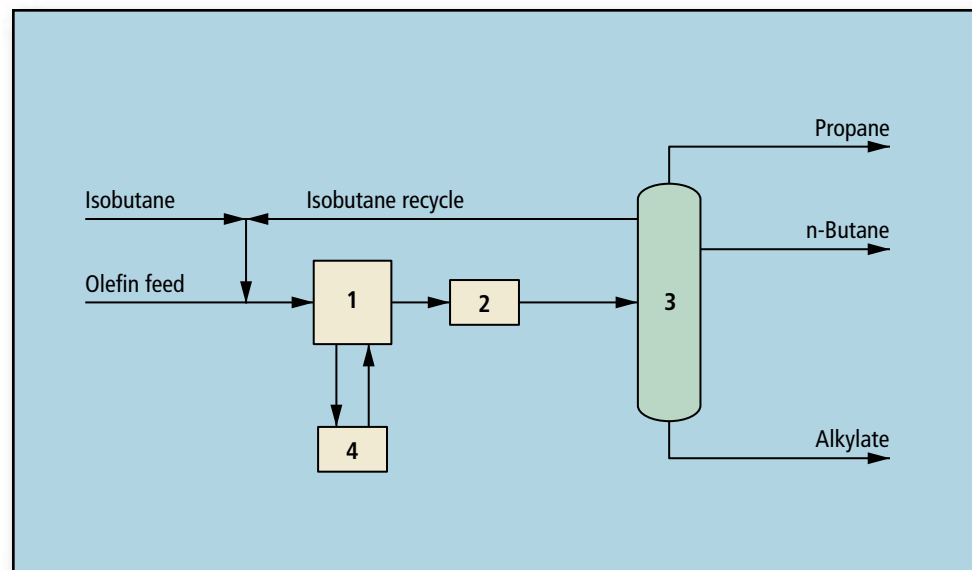
Application: The Topsøe fixed-bed alkylation (FBA) technology applies a unique fixed-bed reactor system with a liquid superacid catalyst absorbed on a solid support. FBA converts isobutane with propylene, butylene and amylene to produce branched chain hydrocarbons. As an alternative, FBA can conveniently be used to alkylate isopentane as a means of disposing isopentane for Rvp control purpose.

Products: A high-octane, low-Rvp and ultra-low-sulfur blending stock for motor and aviation gasoline.

Description: The FBA process combines the benefits of a liquid catalyst with the advantages of a fixed-bed reactor system. Olefin and isobutane feedstocks are mixed with a recycle stream of isobutane and charged to the reactor section (1). The olefins are fully converted over a supported liquid-phase catalyst confined within a mobile, well-defined catalyst zone. The simple fixed-bed reactor system allows easy monitoring and maintenance of the catalyst zone with no handling of solids.

Traces of dissolved acid in the net reactor effluent are removed quantitatively in a compact and simple-to-operate effluent treatment unit (2). In the fractionation section (3), the acid-free net reactor effluent is split into propane, isobutane, n-butane and alkylate. The unique reactor concept allows an easy and selective withdrawal of small amounts of passivated acid. The acid catalyst is fully recovered in a compact catalyst activity maintenance unit (4). The integrated, inexpensive and onsite-maintenance of catalyst activity is a distinct feature of the FBA process. Other significant characteristics of FBA include:

- High flexibility (feedstock, operation temperature)
- Low operating costs
- Low catalyst consumption.



Process performance:

Alkylate product	MTBE raffinate	Olefin feed type FCC C ₄ cut	C ₃ -C ₅ cut
RON (C ₅ +)	98	95	93
MON (C ₅ +)	95	92	91

Economics: (Basis: MTBE raffinate, inclusive feed pretreatment and on-site catalyst activity maintenance)

Investment (basis: 6,000 bpsd unit), \$ per bpsd	5,600
Utilities , typical per bbl alkylate:	
Electricity, kWh	10
Steam, MP (150 psig), lb	60
Steam, LP (50 psig), lb	200
Water, cooling (20°F rise), gal10 ³	2.2

Licensors: Haldor Topsøe A/S.

Alkylation

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

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

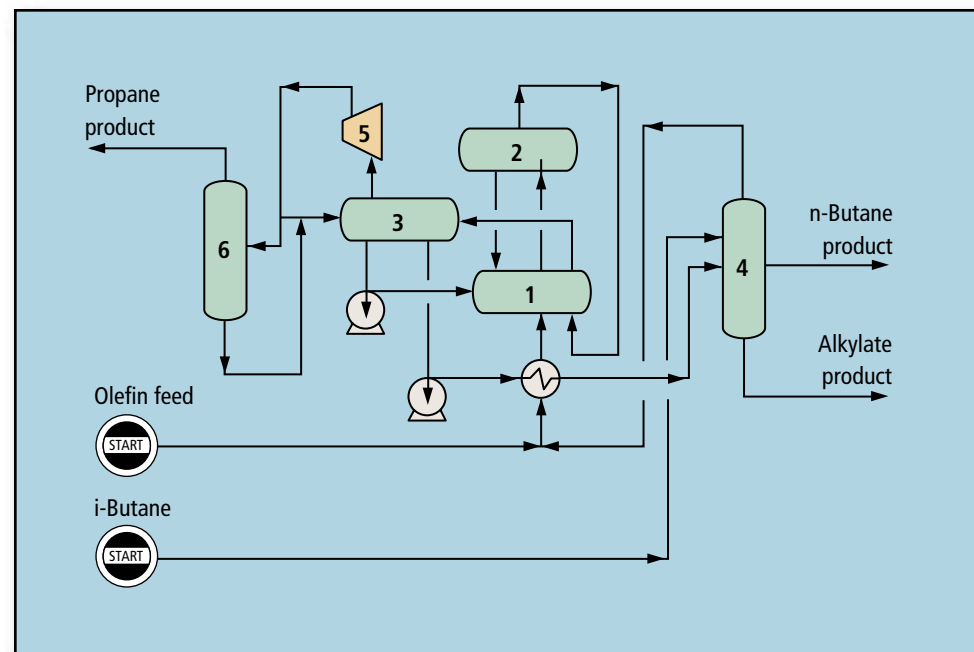
Description: Plants are designed to process a mixture of propylene, butylenes and amylene. Olefins and isobutane-rich streams along with a recycle stream of H_2SO_4 are charged to the STRATCO Contactor reactor (1). The liquid contents of the Contactor reactor are circulated at high velocities and an 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 amylene in most cases.

Economics (basis: butylene feed):

Investment (basis: 10,000-bpsd unit), \$ per bpsd 3,500



Utilities, typical per bbl alkylate:

Electricity, kWh	13.5
Steam, 150 psig, lb	180
Water, cooling (20°F rise), 10 ³ gal	1.85
Acid, lb	15
Caustic, lb	0.1

Installation: Nearly 600,000 bpsd installed capacity.

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

Licensors: STRATCO, DuPont.

Alkylation

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

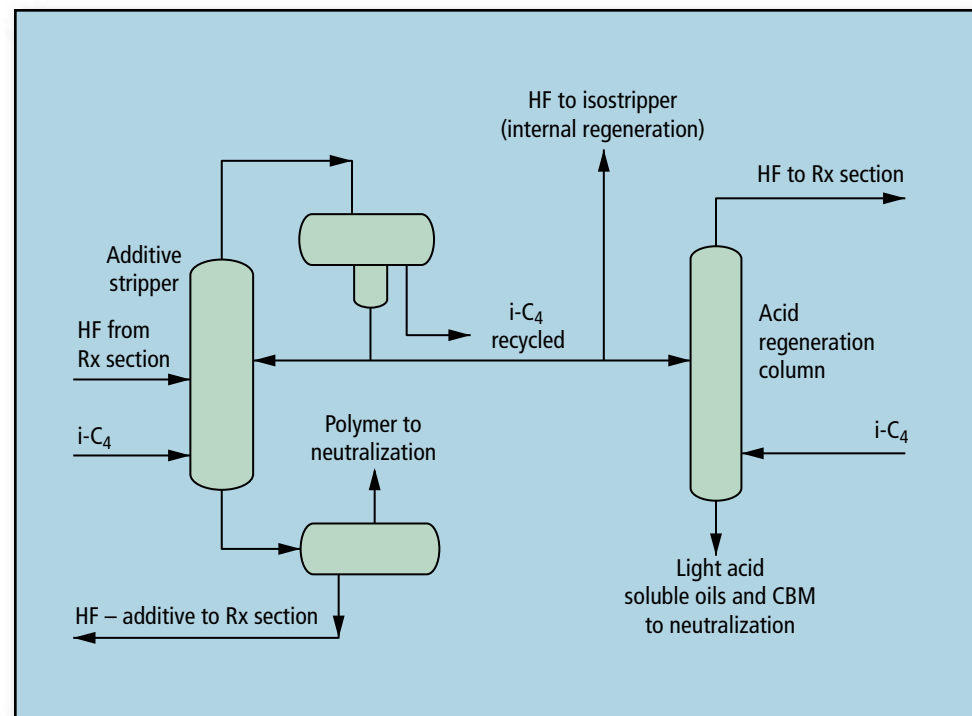
Description: The additive stripper sends acid, water and light-acid soluble oils overhead and on to the acid regenerator. Heavy acid soluble oils and the concentrated HF-additive complex are sent to the additive stripper bottoms separator. From this separator the polymer is sent to neutralization, and 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.

Experience: ChevronTexaco, the co-developer of the Alkad process, installed facilities to use this technology in the HF Alkylation unit at their former El Dorado, Kansas, refinery. This unit began initial operations in 1994.

Installation: One unit is under construction.

Licensors: UOP LLC and ChevronTexaco Corp.



Alkylation

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

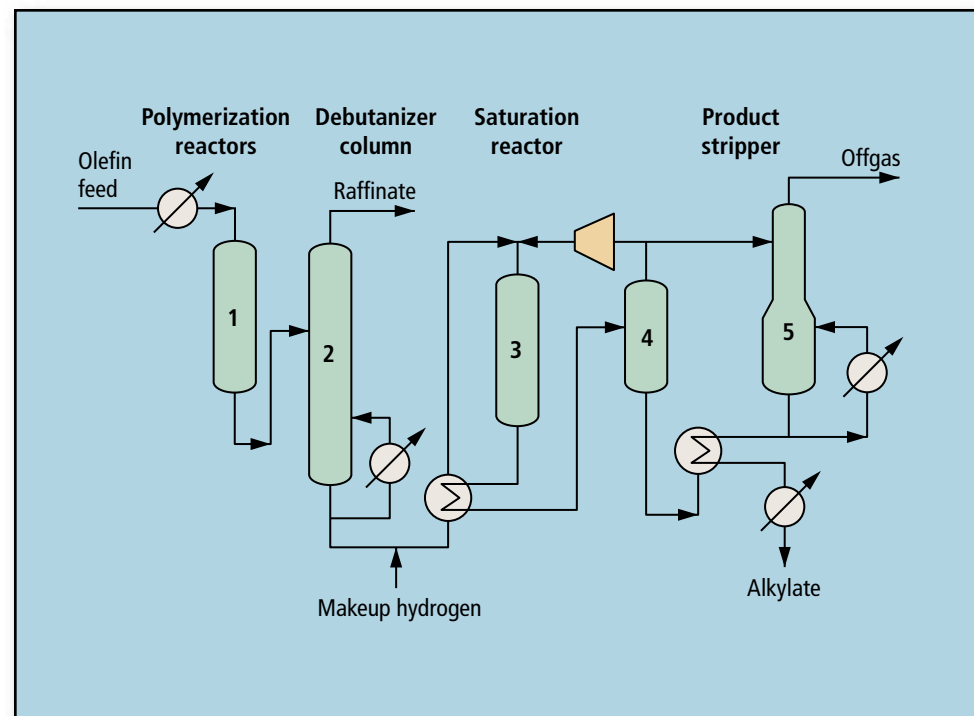
Description: The InAlk process makes premium alkylate using a combination of commercially proven technologies. Iso-butene reacts with itself or with other C_3 – C_5 olefins via polymerization. The resulting mixture of higher molecular weight iso-olefins may then be hydrogenated to form a high-octane 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. Currently five InAlk units are in operation.

Licensors: UOP LLC.



Alkylation, catalytic

Application: CDAlky process is an advanced sulfuric acid-catalyzed alkylation process that reacts light olefin streams from refinery sources, such as fluid catalytic cracking (FCC) units or from steam-cracking units, with iso-paraffins to produce motor fuel alkylate.

Description: The patented CDAlky process is an advanced sulfuric acid-catalyzed alkylation process for the production of motor fuel alkylate. The process flow diagram shows the basic configuration to process a mixed C₄-olefin feed and produce a bright, clear, high-quality motor fuel alkylate, without the need for water/caustic washes or bauxite treatment.

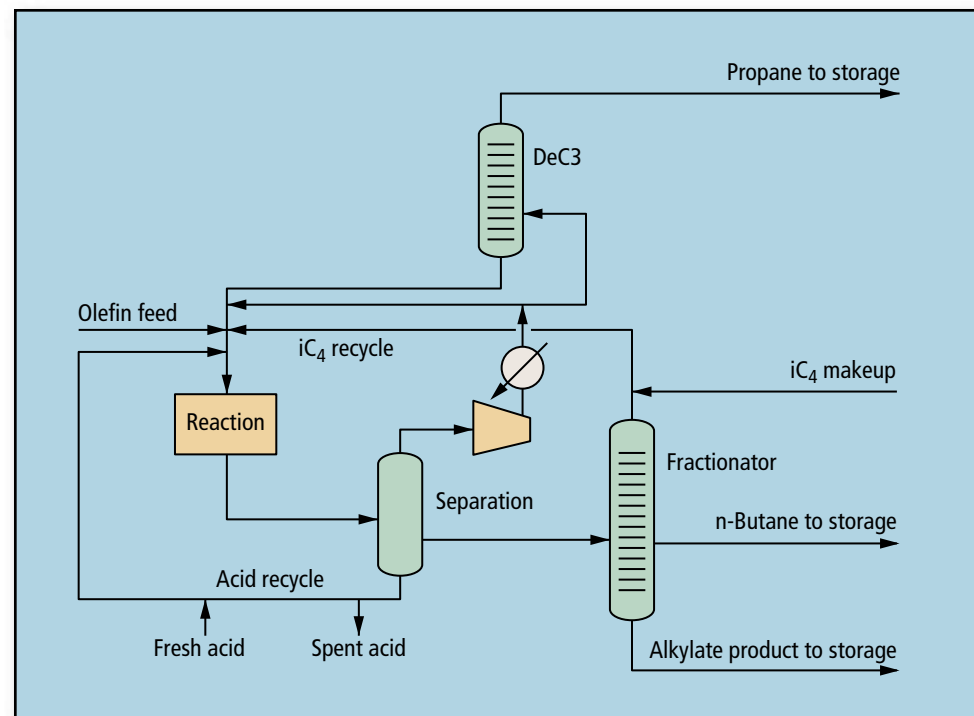
This process yields a higher-quality product while consuming significantly less acid than conventional technologies. The flow scheme is also less complex than conventional designs, which reduces capital and operating costs.

Conventional sulfuric-acid alkylation units use mechanical mixing in their contactors to achieve the required contact between acid and hydrocarbon phases, and are characterized by high acid consumption. In addition, conventional technologies are unable to take the full benefit of operating at lower temperature, which substantially improves alkylate quality and lowers acid consumption.

CDTECH has developed a novel contactor that operates at lower temperatures and substantially reduced acid consumption—50%+. The CDAlky process uses conventional product fractionation, which can consist of a single column or two columns. This process has been designed to make it possible to reuse equipment from idled facilities.

The benefits of the CDAlky process include:

- 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

Installation: Consistent with time-tested methodology for developing new processes, CDTECH has been operating a 2-bpd pilot plant in this novel mode of operation for an extended time period without the penalties associated with conventional technologies.

Licensors: CDTECH.

Alkylation, sulfuric acid

Application: Auto-refrigerated sulfuric-acid catalyzed process that combines butylene (and propylene or pentylene if desired) with isobutane to produce high-octane gasoline components that are particularly attractive in locations that are MON limited. Technology can be installed grassroots or retrofit into existing alkylation facilities.

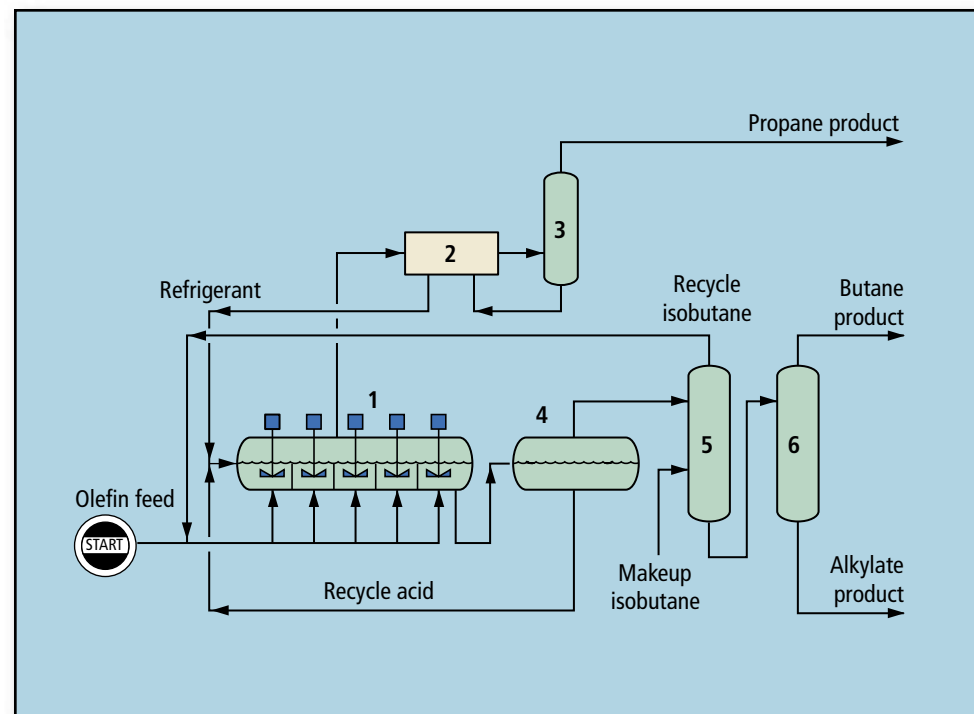
Products: A low-sulfur, low-Rvp, highly isoparaaffinic, high-octane (especially MON) gasoline blendstock is produced from this alkylation process.

Description: Olefin feed and recycled isobutane are introduced into the stirred, autorefrigerated reactor (1). Mixers provide intimate contact between the reactants and the acid catalyst. Highly efficient autorefrigeration removes heat of reaction heat from the reactor. Hydrocarbons vaporized from the reactor to provide cooling are compressed (2) and returned to the reactor. A depropanizer (3), which is fed by a slipstream from the refrigeration section, is designed to remove any propane introduced to the plant with the feeds.

Hydrocarbon products are separated from the acid in the settler containing proprietary internals (4). In the deisobutanizer (5) isobutane is recovered and recycled along with makeup isobutane to the reactor. Butane is removed from alkylate in the debutanizer (6) to produce a low Rvp, high-octane alkylate product. A small acid stream containing acid-soluble oil byproducts is removed from the unit and is either regenerated on site or sent to an off-site sulfuric acid regeneration facility to recover acid strength.

Yields:

Alkylate yield	1.8 bbl C ₅ +/bbl butylene feed
Isobutane required	1.2 bbl/bbl butylene feed
Alkylate quality	97 RON / 94 MON
Rvp, psi	3



Utilities: Typical per barrel of alkylate produced:

Water, cooling, Mgal	2
Power, kWh	9
Steam, lb	200
H ₂ SO ₄ , lb	19
NaOH, 100%, lb	0.1

Operating experience: Extensive commercial experience in both Exxon-Mobil and licensee refineries, and a total operating capacity of 119,000-bpsd at 11 locations worldwide. Unit capacities range from 2,000 to 30,000 bpd, and single reactor/settler trains with capacities up to 9,500 bpsd. Recent commercial applications include a revamp at ExxonMobil's Altona, Australia, refinery and a new unit at TNK-BP's Ryazan, Russia refinery, which is currently under construction. Continued ▼

Alkylation, sulfuric acid, *continued*

Technical advantages:

- **Autorefrigeration** is thermodynamically more efficient, allows lower reactor temperatures that favor better product quality, and lowers energy usage.
- **Staged reactor** results in a high average isobutane concentration, which favors high product quality.
- **Low space velocity** results in high product quality and reduced ester formation eliminating corrosion problems in fractionation equipment.
- **Low reactor operating pressure** translates into high reliability for the mechanical seals for the mixers, which operate in the vapor phase.

Economic advantages:

- **Lower capital investment**—Simple reactor/settler configuration, less compression requirements translate into a significant investment savings compared to indirect refrigeration systems
- **Lower operating costs**—Autorefrigeration, lower mixing and compression power requirements translate into lower operating costs
- **Better economy of scale**—Reactor system is simple and easily expandable, with 9,500 bpsd single train capacities easily achievable.

Reference: Lerner, H., "Exxon sulfuric acid alkylation technology," *Handbook of Petroleum Refining Processes*, 2nd edition, R. A. Meyers, Ed., pp. 1.3–1.14.

Licensors: ExxonMobil Research and Engineering Co.

[click here to e-mail for more information](#)

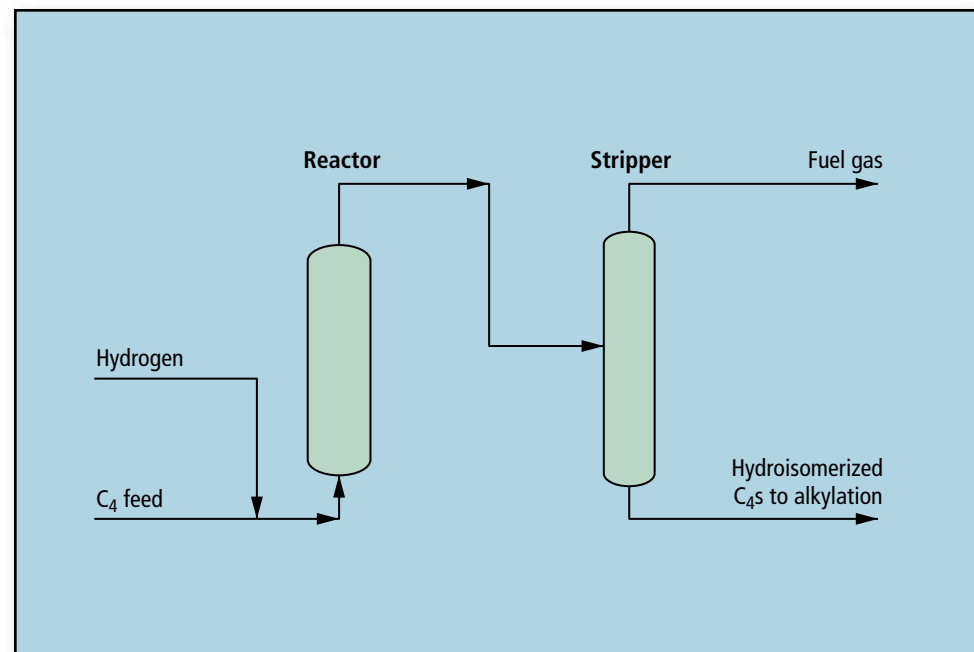
Alkylation—feed preparation

Application: Upgrades alkylation plant feeds with Alkyfining process.

Description: Diolefins and acetylenes in the C_4 (or C_3-C_4) feed react selectively with hydrogen in the liquid-phase, fixed-bed reactor under mild temperature and pressure conditions. Butadiene and, if C_3 s are present, methylacetylene and propadiene are converted to olefins.

The high isomerization activity of the catalyst transforms 1-butene into cis- and trans-2-butenes, which affords higher octane-barrel production.

Good hydrogen distribution and reactor design eliminate channeling while enabling high turndown ratios. Butene yields are maximized, hydrogen is completely consumed and, essentially, no gaseous byproducts or heavier compounds are formed. Additional savings are possible when pure hydrogen is available, eliminating the need for a stabilizer. The process integrates easily with the C_3/C_4 splitter.



Alkyfining performance and impact on HF alkylation product:

The results of an Alkyfining unit treating an FCC C_4 HF alkylation unit feed containing 0.8% 1,3-butadiene are:

Butadiene in alkylate, ppm	< 10
1-butene isomerization, %	70
Butenes yield, %	100.5
RON increase in alkylate	2
MON increase in alkylate	1
Alkylate end point reduction, °C	–20

The increases in MON, RON and butenes yield are reflected in a substantial octane-barrel increase while the lower alkylate end point reduces ASO production and HF consumption.

Economics:

Investment:

Grassroots ISBL cost:	
For an HF unit, \$/bpsd	430
For an H_2SO_4 unit, \$/bpsd	210

Annual savings for a 10,000-bpsd alkylation unit:

HF unit, US\$	4.1 million
H_2SO_4 unit, US\$	5.5 million

Installation: Over 80 units are operating with a total installed capacity of 700,000 bpsd.

Licensors: Axens.

Alkylation—HF

Application: HF Alkylation 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 HF catalyst under conditions selected to maximize alkylate yield and quality.

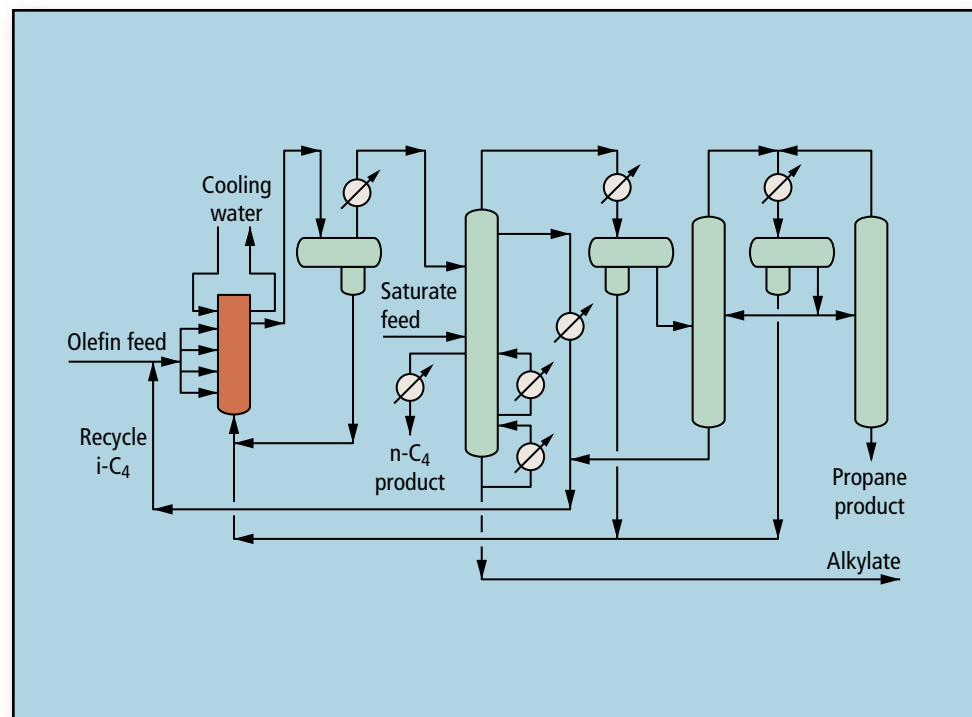
The reactor system is carefully designed to ensure efficient contacting and mixing of hydrocarbon feed with the acid catalyst. Efficient heat transfer conserves cooling water supply. Acid inventory in the reactor system is minimized by combining high heat-transfer rates and lower total acid circulation.

Acid regeneration occurs in the acid regenerator or via a patented internal-acid-regeneration method. Internal regeneration allows the refiner to shutdown the acid regenerator, thereby realizing a utility savings as well as reducing acid consumption and eliminating polymer 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 is recommended to reduce acid regeneration requirements, catalyst (acid) consumption and 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. And unlike sulfuric alkylation units, HF Alkylation does not require refrigeration equipment to maintain a low reactor temperature.



Installations: Over 20 UOP licensed HF alkylation units are in operation.

Licensors: UOP LLC.

Aromatics

Application: The technology 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.

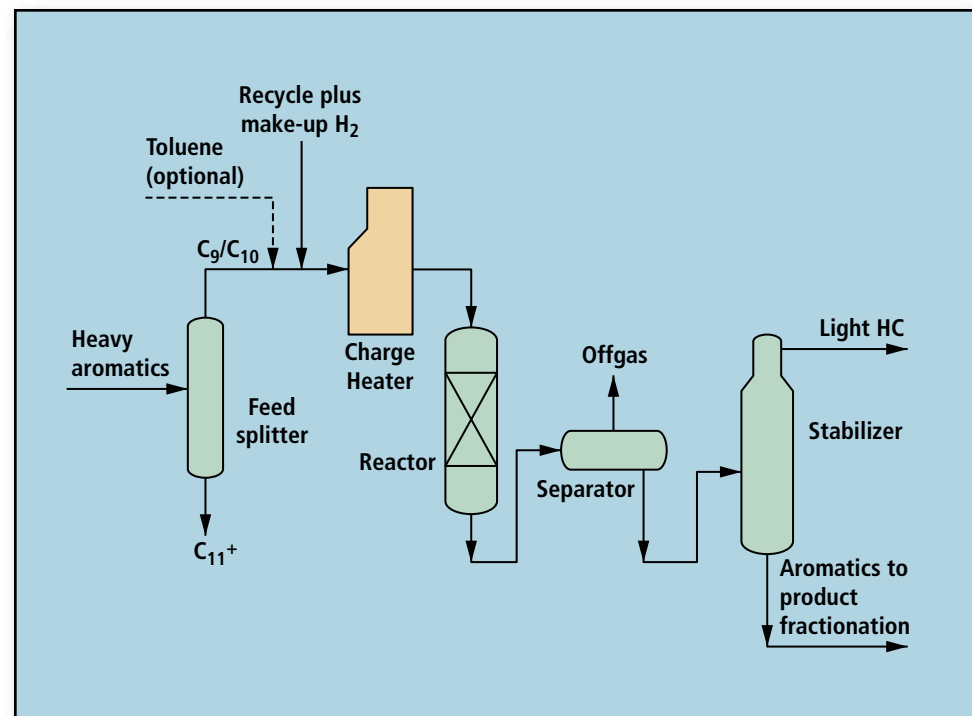
Description: The technology encompasses three main processing areas: feed preparation, reactor and product stabilization sections. The heavy aromatics stream (usually derived from catalytic reformat) is fed to a C_{10}/C_{11} splitter. The overhead portion, along with any toluene that may be available, is the feed to the transalkylation reactor section. The combined feed is mixed with hydrogen, vaporized, and fed to the reactor. The un-reacted hydrogen is recycled for re-use. The product stream is stabilized to remove fuel gas and other light components.

The process reactor is charged with a proprietary catalyst, which exhibits good flexibility to feed stream variations, including 100% C_9+ aromatics. Depending on the feed composition, the xylene yield can vary from 27 to 35% and C_9 conversion from 53 to 67%.

Process advantages include:

- Simple, low cost fixed-bed reactor design
- Selective toward xylene production, with high toluene/ C_9 conversion rates
- Physically stable catalyst
- Flexible to handle up to 100% C_9+ components in feed
- Flexible to handle benzene recycle to increase xylene yields
- Moderate operating parameters; catalyst can be used as replacement to other transalkylation units, or in grassroots designs
- Decreased hydrogen consumption due to low cracking rates
- Efficient heat integration scheme, reduces energy consumption.

Licensors: GTC Technology Inc., using catalyst supplied by Süd-Chemie Inc.



Aromatics extractive distillation

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

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

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

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

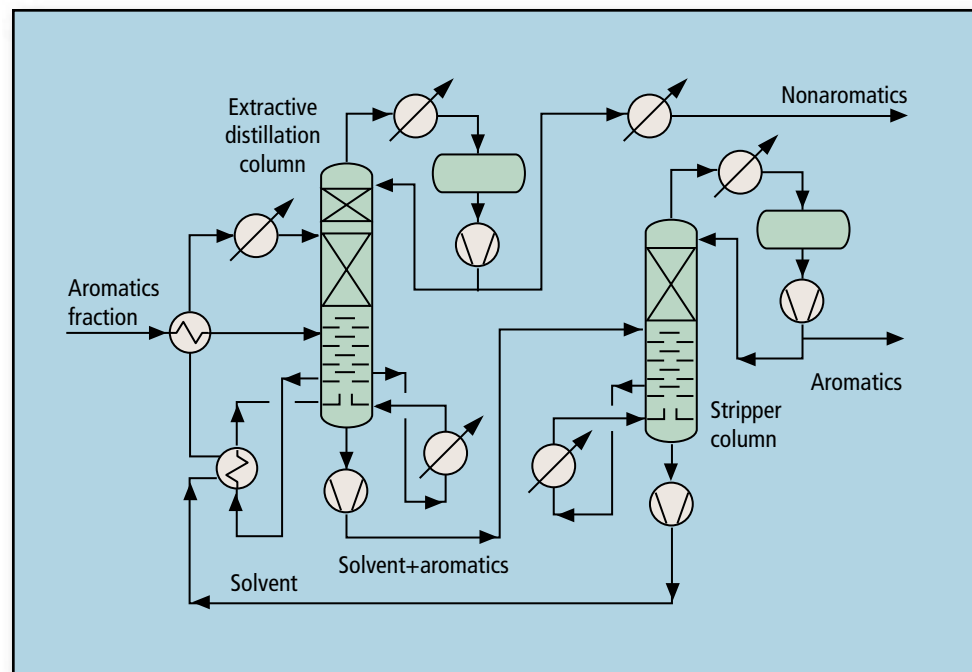
Economics:

Pygas feedstock:

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

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

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



*Maximum content of nonaromatics

**Including benzene/toluene splitter

Installation: Fifty Morphylane plants (total capacity of more than 6 MMtpy).

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

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

Licensors: Uhde GmbH.

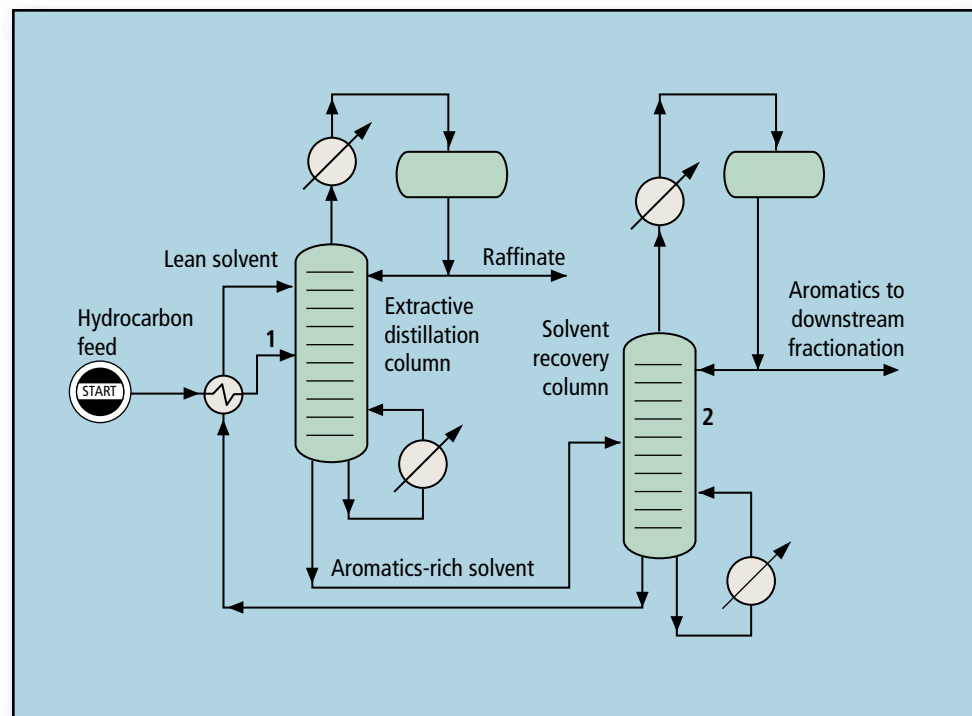
Aromatics recovery

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

Description: The technology has several advantages:

- Less equipment required, thus, significantly lower capital cost compared to conventional liquid-liquid extraction systems
- Energy integration reduces operating costs
- Higher product purity and aromatic recovery
- Recovers aromatics from full-range BTX feedstock without pre-fractionation
- Distillation-based operation provides better control and simplified operation
- Proprietary formulation of commercially available solvents 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
- Flexibility of design options for grassroots plants or expansion of existing liquid-liquid extraction units.

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 the raffinate product, requiring no further treatment.

Rich solvent from the bottom of the EDC is routed to the solvent-recovery column (SRC), where the aromatics are stripped overhead. Stripping steam from a closed-loop water circuit facilitates hydrocarbon removal. 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.

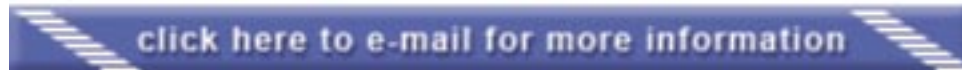
The SRC overhead mixed aromatics product is routed to the purification section, where it is fractionated to produce chemical-grade benzene, toluene and xylenes.

Aromatics recovery, *continued*

Economics: Estimated installed cost for a 15,000-bpd GT-BTX extraction unit processing BT-reformate feedstock is \$12 million (US Gulf Coast 2004 basis).

Installations: Three grassroots applications with other cases in design and construction.

Licensors: GTC Technology Inc.



Asphalt—oxidation

Application: Biturox, a continuous oxidation process, converts suitable feedstock blends at elevated pressure and temperature by a specially designed reactor into road paving and industrial asphalt (bitumen) with optimized properties (e.g. PEN Index).

Feed: Long and short residues from crudes with densities below 36°API, and refinery side streams such as VGO, deasphalting pitch, solvent refining extracts, visbreaker bottoms, etc., as composed blend.

Description: The different feed components (A,B,C) are blended within the unit and pumped via a feed/product heat-exchanger (1) to the reactor vessel (2). The reactor is a vertical carbon-steel cylinder, equipped with a multi-stage stirrer (3) and a baffle system (4), that control the recirculation of the liquid and air dispersion within the reactor.

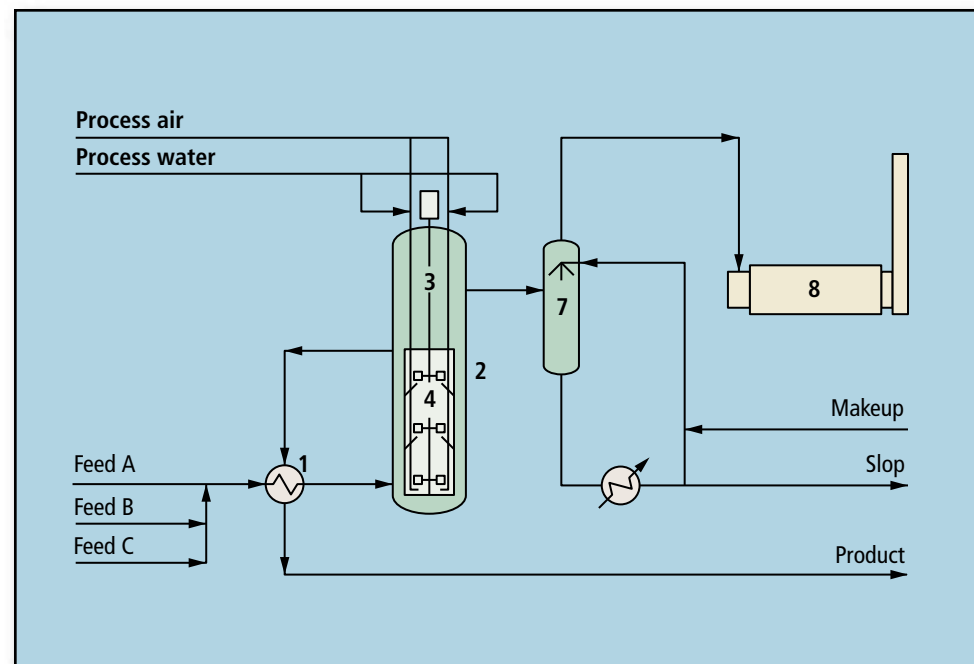
The oxidation processes operate on flow-controlled compressed air (5), which is injected together with a small amount of water (6). The internal cooling via water avoids local over-heating and prevents coke formation and deposits within the reactor. A stable, homogenous process temperature is crucial for the production of high-quality asphalt. The finished product is pumped via the feed/product heat-exchanger (1) to storage.

Offgas from the reaction (oxygen content approx. 2%) is scrubbed (7) and is thermally treated in an incinerator (8) or sent to another refinery offgas treating system.

For specific conditions related to feed and/or finished products peculiarities, a two-stage Biturox-process is recommended.

Operating conditions:

Pressure, psig	29	
Temperature, °F	520	
Oxygen utilization, %	90	
Residence time	paving grades	approx. 2 hrs
	industrial grades	approx. 5 hrs



Yields: The Biturox process enables the user—starting from a great variety of (inexpensive) feedstock components—to manufacture stable and homogenous bitumen of improved PEN Indices, exceeding the standards and requirements of chemical and construction industries.

Economics:

Investment, US\$/bpsd: approx. 850
(basis 6000 bpsd, incl. standard offgas treatment)

Utilities for reactor section (per reactor cuft)

Air, cf/h	30
Water, gal/h	0.15
Electricity, kW	0.06
Steam (50 psig), lb/h:	0.12

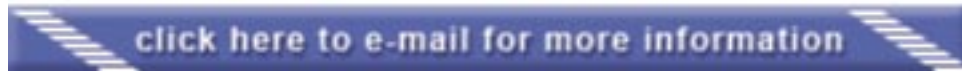
Maintenance minimum
Turnaround interval, yr 2

Asphalt—oxidation, *continued*

Installation: Poerner has licensed over 25 Biturox Oxidation Units world-wide with a total capacity of 28.9 million bbl/y and performed over 200 pilot tests on all important bitumen crude bases and blends.

Reference: Poerner, A., "How to use less expensive crudes for making quality bitumen," The Singapore Asphalt Conference 1996.

Licensors: Poerner Ingenieurgesellschaft GmbH.



Benzene reduction

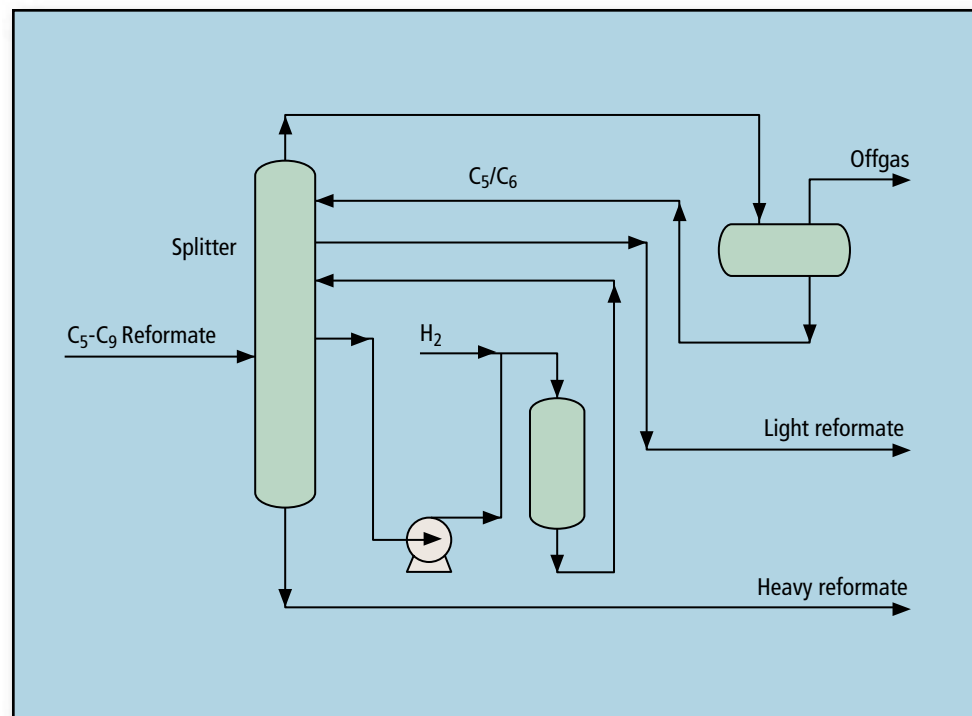
Application: Benzene reduction from reformat, with the Benfree process, using integrated reactive distillation.

Description: Full-range reformat from either a semiregenerative or CCR reformer is fed to the reformat splitter column, shown above. The splitter operates as a dehexanizer lifting C_6 and lower-boiling components to the overhead section of the column. Benzene is lifted with the light ends, but toluene is not. Since benzene forms azeotropic mixtures with some C_7 paraffin isomers, these fractions are also entrained with the light fraction.

Above the feed injection tray, a benzene-rich light fraction is withdrawn and pumped to the hydrogenation reactor outside the column. A pump enables the reactor to operate at higher pressure than the column, thus ensuring increased solubility of hydrogen in the feed.

A slightly higher-than-chemical stoichiometric ratio of hydrogen to benzene is added to the feed to ensure that the benzene content of the resulting gasoline pool is below mandated levels, i.e., below 1.0 vol% for many major markets. The low hydrogen flow minimizes losses of gasoline product in the offgas of the column. Benzene conversion to cyclohexane can easily be increased if even lower benzene content is desired. The reactor effluent, essentially benzene-free, is returned to the column.

The absence of benzene disrupts the benzene-iso- C_7 azeotropes, thereby ensuring that the latter components leave with the bottoms fraction of the column. This is particularly advantageous when the light reformat is destined to be isomerized, because iso- C_7 paraffins tend to be cracked to C_3 and C_4 components, thus leading to a loss of gasoline production.



Economics:

Investment, Grassroots ISBL cost, \$/bpsd:	300
Combined utilities, \$/bbl	0.17
Hydrogen	Stoichiometric to benzene
Catalyst, \$/bbl	0.01

Installation: Twenty-six benzene reduction units have been licensed.

Licensors: Axens.

Catalytic cracking (MSCC)

Application: To selectively convert gas oils and residual feedstocks to higher-value cracked products such as light olefins, gasoline and distillates.

Description: The MSCC process uses a fluid catalyst and a novel contacting arrangement to crack heavier materials into a highly selective yield of light olefins, gasoline and distillates. A distinguishing feature of the process is that the initial contact of oil and catalyst occurs without a riser in a very short residence time followed by a rapid separation of initial reaction products. Because there is no riser and the catalyst is downflowing, startup and operability are outstanding.

The configuration of an MSCC unit has the regenerator (1) at a higher elevation than the reactor (2). Regenerated catalyst falls down a standpipe (3), through a shaped opening (4) that creates a falling curtain of catalyst, and across a well-distributed feed stream. The products from this initial reaction are quickly separated from the catalyst. The catalyst then passes into a second reaction zone (5), where further reaction and stripping occurs. This second zone can be operated at a higher temperature, which is achieved through contact with regenerated catalyst.

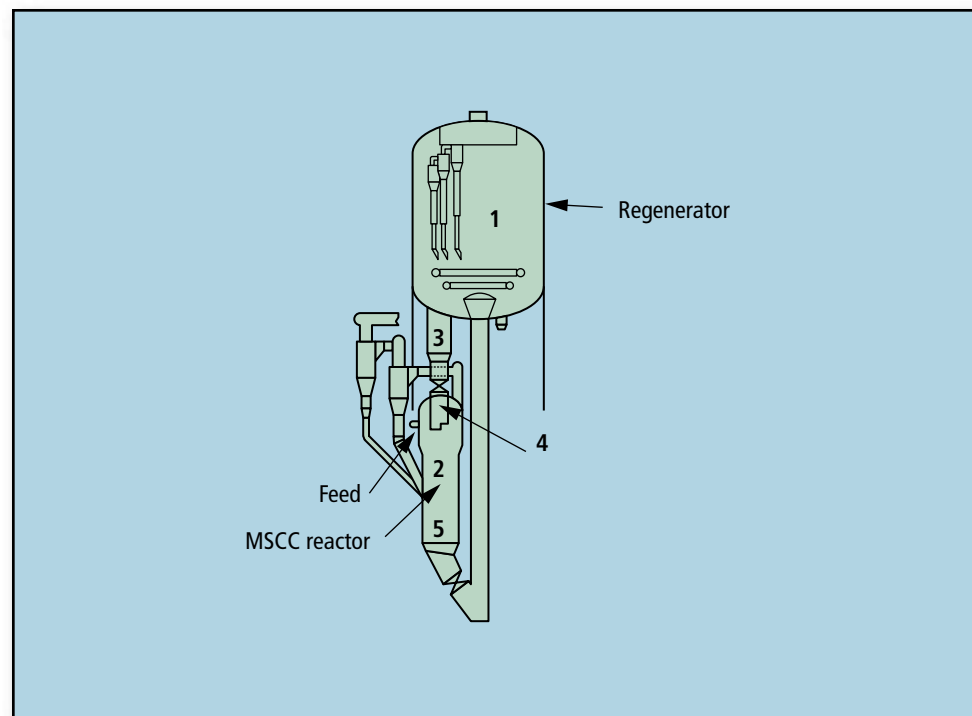
Since a large portion of the reaction product is produced under very short time conditions, the reaction mixture maintains good product olefinicity and retains hydrogen content in the heavier liquid products. Additional reaction time is available for the more-difficult-to-crack species in the second reaction zone/stripper.

Stripped catalyst is airlifted back to the regenerator where coke deposits are burned, creating clean, hot catalyst to begin the sequence again.

Installations: Four MSCC units are currently in operation with another in design/construction.

Reference: "Short-Contact-Time FCC," AIChE 1998 Spring Meeting, New Orleans.

Licensors: UOP LLC (in cooperation with BARCO).



Catalytic dewaxing

Application: Use the ExxonMobil 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: 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.

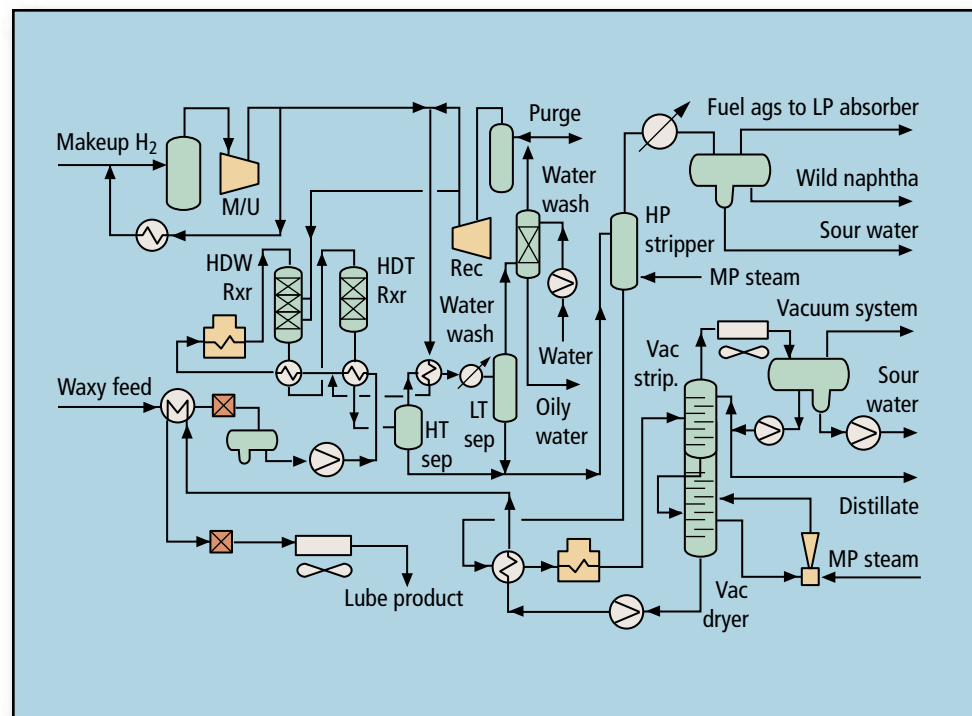
Operating conditions:

Temperatures, °F	550 to 800
Hydrogen partial pressures, psig	500 to 2,500
LHSV	0.4 to 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

Economics: \$3,000–5,500 per bpsd installed cost (US Gulf Coast).



Installation: Eight units are operating and four are in design.

Licensors: ExxonMobil Research and Engineering Co.

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 its higher selectivity, trimetallic catalysts RG582 and RG682 make an excellent catalyst replacement for semi-regenerative reformers.

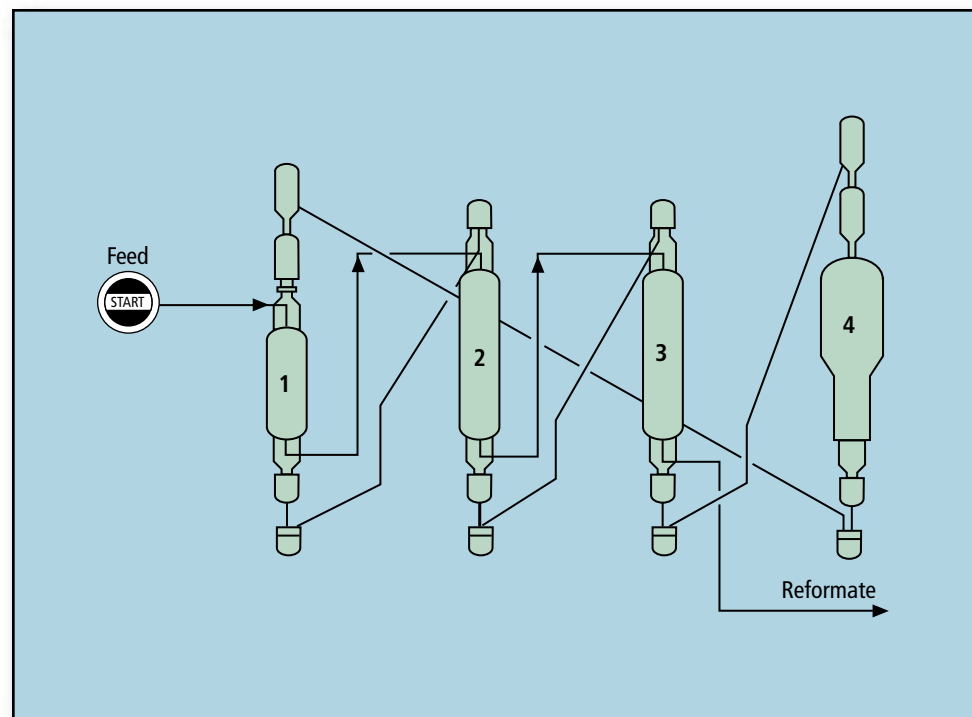
The second, the advanced Octanizing process, uses continuous catalyst regeneration allowing operating pressures as low as 3.5 kg/cm² (50 psig). This is made possible by smooth-flowing moving bed reactors (1–3) which use a highly stable and selective catalyst suitable for continuous regeneration (4). 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 Regen C₂ 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 CR401 (gasoline mode) and AR501 (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, C₅+ 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
Oper. press., kg/cm ²	10–15	<5
Yield, wt% of feed:		
Hydrogen	2.8	3.8
C ₅ +	83	88
RONC	100	102
MONC	89	90.5



Economics:

Investment: Basis 25,000 bpsd continuous octanizing unit, battery limits, erected cost, US\$ per bpsd 1,800

Utilities: typical per bbl feed:

Fuel, 10 ³ kcal	65
Electricity, kWh	0.96
Steam, net, HP, kg	12.5
Water, boiler feed, m ³	0.03

Installation: Of 111 units licensed, 64 units are designed with continuous regeneration technology capability.

Reference: "Continuing Innovation In Cat Reforming," NPRA Annual Meeting, March 15–17, 1998, San Antonio. Continued ▼

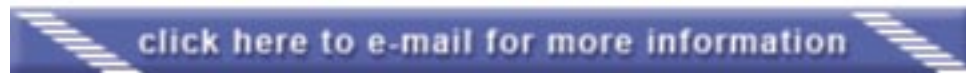
Catalytic reforming, *continued*

"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.

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

Licensors: Axens.



Catalytic reforming

Application: Increase the octane of straight-run or cracked naphthas for gasoline production.

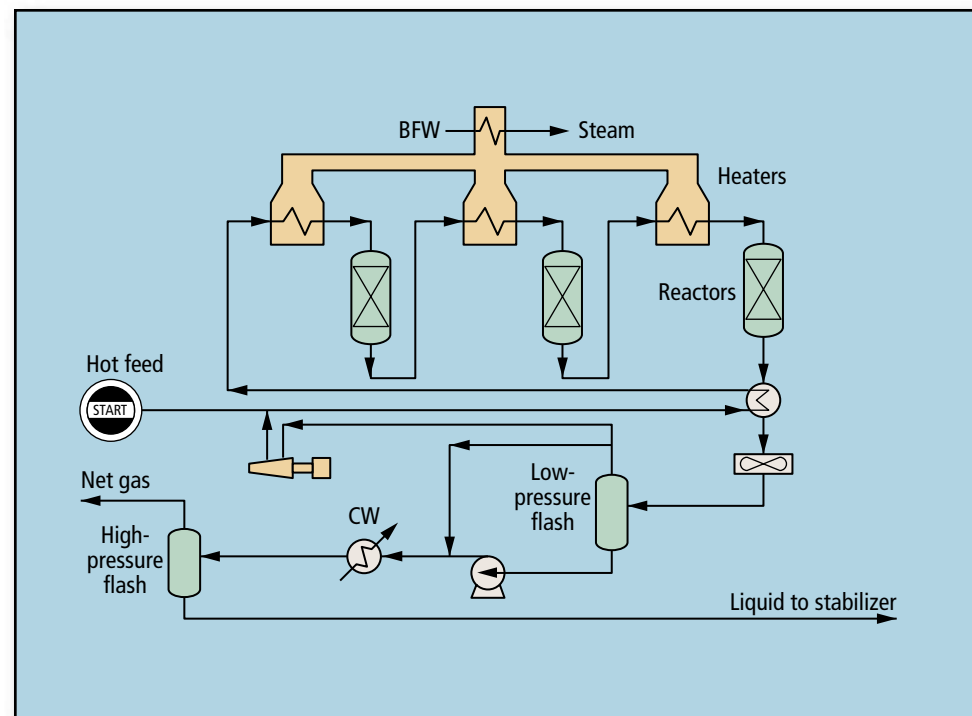
Products: High-octane gasoline and hydrogen-rich gas. Byproducts may be LPG, fuel gas and steam.

Description: Semi-regenerative multibed reforming over platinum or bi-metallic catalysts. Hydrogen recycled to reactors at the rate of 3 mols/mol to 7 mols/mol of feed. Straight-run and/or cracked feeds are typically hydrotreated, but low-sulfur feeds (<10 ppm) may be reformed without hydrotreatment.

Operating conditions: 875°F to 1,000°F and 150 psig to 400 psig reactor conditions.

Yields: Depend on feed characteristics, product octane and reactor pressure. The following yields are one example. The feed contains 51.4% paraffins, 41.5% naphthenes and 7.1% aromatics, and boils from 208°F to 375°F (ASTM D86). Product octane is 99.7 RONC and average reactor pressure is 200 psig.

Component	wt%	vol%
H ₂	2.3	1,150 scf/bbl
C ₁	1.1	—
C ₂	1.8	—
C ₃	3.2	—
iC ₄	1.6	—
nC ₄	2.3	—
C ₅ +	87.1	—
LPG	—	3.7
Reformate	—	83.2



Economics:

Utilities, (per bbl feed)	
Fuel, 10 ³ Btu release	275
Electricity, kWh	7.2
Water, cooling (20°F rise), gal	216
Steam produced (175 psig sat), lb	100

Licensors: CB&I Howe-Baker Process and Technology.

Catalytic reforming

Application: The 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.

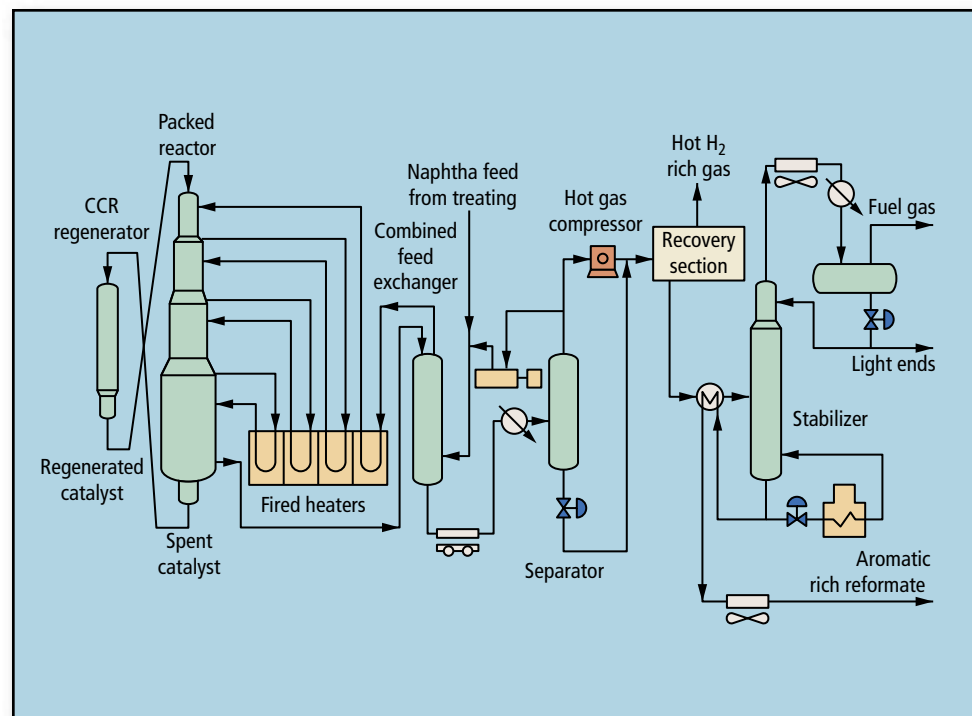
Radial-flow reactors are arranged in a vertical stack. The predominant reactions are endothermic; so an interheater is used between each reactor to reheat the charge to reaction temperature. The effluent from the last reactor is heat exchanged against combined feed, cooled and split into vapor and liquid 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 commissioned more than 180 units (more than 3.9 million bpd of capacity) with another 30 in various stages of design, construction and commissioning.

Efficiency/product quality: Commercial onstream efficiencies of more than 95% are routinely achieved in CCR Platforming units.

Licensors: UOP LLC.



Coking

Application: Conversion of vacuum residues (virgin and hydrotreated), various petroleum tars and coal tar pitch through delayed coking.

Products: Fuel gas, LPG, naphtha, gas oils and fuel, anode or needle grade coke (depending on feedstock and operating conditions).

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 through the coker heater (2) where the desired coking temperature is achieved, to one of two coke drums (3). 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; two gas oil sidestreams; and the recycle that rejoins the feed.

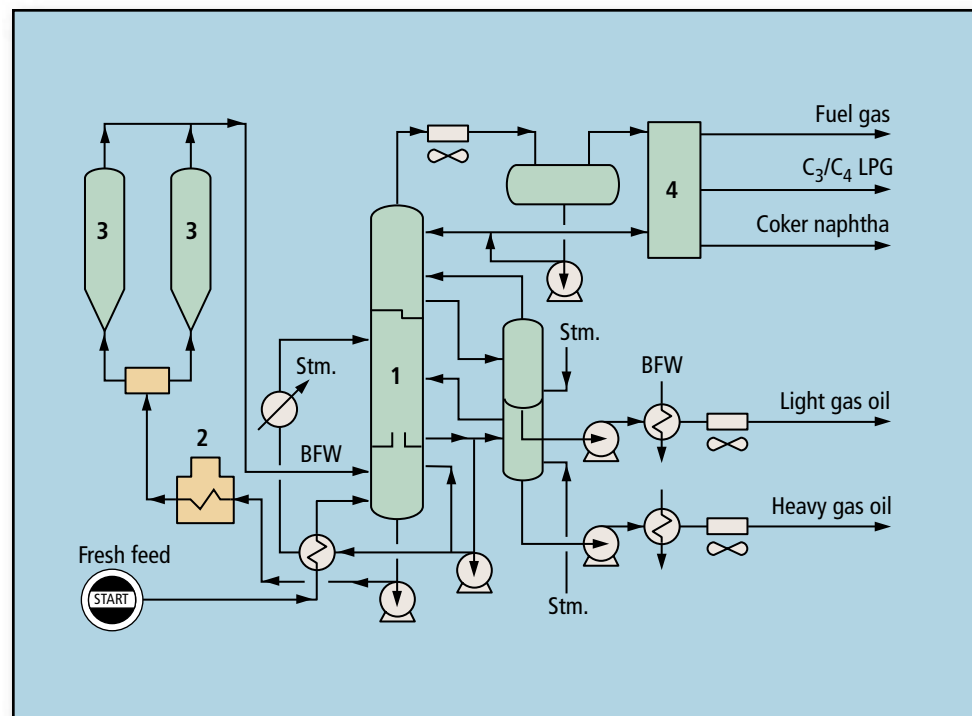
The overhead stream is sent to a vapor recovery unit (4) where the individual product streams are separated. The coke that forms in one of at least two (parallel connected) drums is then removed using high-pressure water. The plant also includes a blow-down system, coke handling and a water recovery 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	Coal tar pitch
Gravity, °API	7.4	1.3	211.0
Sulfur, wt%	4.2	2.3	0.5



Conradson carbon, wt%	20.0	27.6	—
Products, wt%			
Gas + LPG	7.9	9.0	3.9
Naphtha	12.6	11.1	—
Gas oils	50.8	44.0	31.0
Coke	28.7	35.9	65.1

Economics:

Investment (basis: 20,000 bpsd straight-run vacuum residue feed, US Gulf Coast 2002, fuel-grade coke, includes vapor recovery), US\$ per bpsd (typical) 4,000

Coking, *continued*

Economics (continued):

Utilities, typical/bbl of feed:

Fuel, 10^3 Btu	145
Electricity, kWh	3.9
Steam (exported), lb	20
Water, cooling, gal	180

Installation: More than 55 units.

Reference: Mallik, Ram, Gary and Hamilton, "Delayed coker design considerations and project execution," NPRA 2002 Annual Meeting, March 17–19, 2002.

Licensors: ABB Lummus Global.

[click here to e-mail for more information](#)

Coking

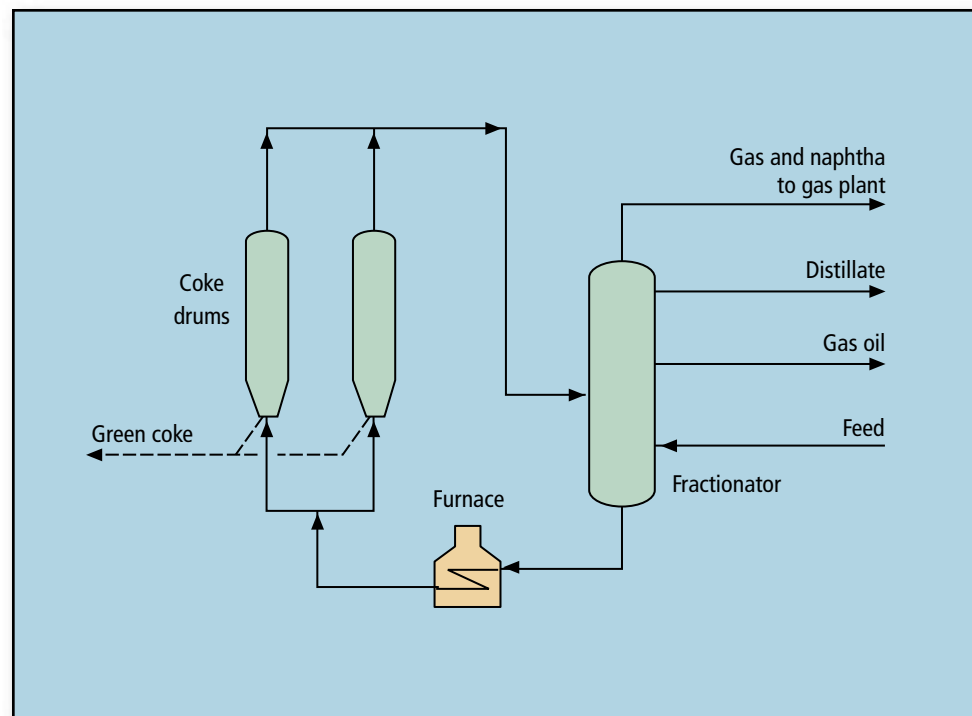
Application: Upgrading of petroleum residues (vacuum residue, bitumen, solvent-deasphalter pitch and fuel oil) to more valuable liquid products (LPG, naphtha, distillate and gas oil). Fuel gas and petroleum coke are also produced.

Description: The delayed coking process is a thermal process and consists of fired heater(s), coke drums and main fractionator. The cracking and coking reactions are initiated in the fired heater under controlled time-temperature-pressure conditions. The reactions continue as the process stream moves to the coke drums. Being highly endothermic, the coking-reaction rate drops dramatically as coke-drum temperature decreases. Coke is deposited in the coke drums. The vapor is routed to the fractionator, where it is condensed and fractionated into product streams—typically fuel gas, LPG, naphtha, distillate and gas oil.

When one of the pair of coke drums is full of coke, the heater outlet stream is directed to the other coke drum. The full drum is taken offline, cooled with steam and water and opened. The coke is removed by hydraulic cutting. The empty drum is then closed, warmed-up and made ready to receive feed while the other drum becomes full.

Benefits of ConocoPhillips' delayed coking technology are:

- Maximum liquid-product yields and minimum coke yield through low-pressure operation, patented distillate recycle technology and zero (patented) or minimum natural recycle operation
- Maximum flexibility; distillate recycle operation can be used to adjust the liquid-product slate or can be withdrawn to maximize unit capacity
- Extended furnace runlengths between decokings
- Ultra-low-cycle-time operation maximizes capacity and asset utilization
- Higher reliability and maintainability enables higher onstream time and lowers maintenance costs
- Lower investment cost.



Economics: For a delayed coker processing 35,000 bpsd of heavy, high-sulfur vacuum residue, the U.S. Gulf Coast investment cost is approximately U.S.\$145–160 million.

Installation: Low investment cost and attractive yield structure has made delayed coking the technology of choice for bottom-of-the-barrel upgrading. Numerous delayed coking units are operating in petroleum refineries worldwide.

Licensors: Technology Solutions Division of ConocoPhillips.

Coking

Application: Manufacture petroleum coke and upgrade residues to lighter hydrocarbon fractions using the Selective Yield Delayed Coking (SYDEC) process.

Products: Coke, gas, LPG, naphtha and gas oils.

Description: Charge is fed directly to the fractionator (1) where it combines with recycle and is pumped to the coker heater where it 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. There are at least two coking drums, one coking while the other is decoked using high-pressure water jets.

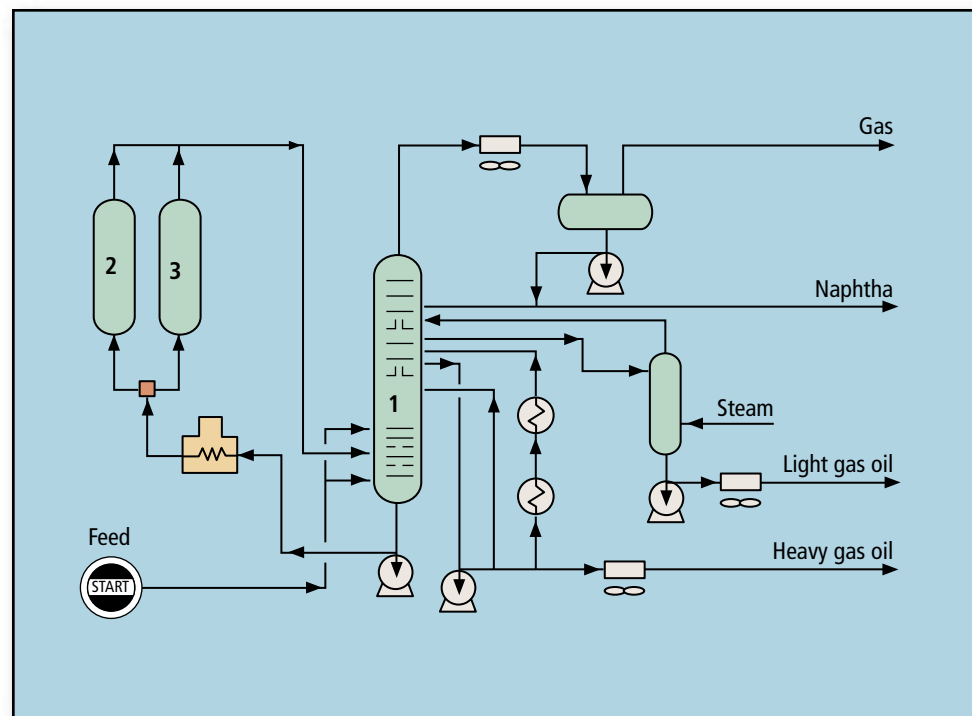
Operating conditions: Typical ranges are:

Heater outlet temperature, °F	900–950
Coke drum pressure, psig	15–100
Recycle ratio, equiv. fresh feed	0.05–1.0

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: 65,000–10,000 bpsd,
2Q 2004, US Gulf), \$ per bpsd 2,750–5,000

Utilities, typical per bbl feed:

Fuel, 10 ³ Btu	120
Electricity, kWh	3
Steam (exported), lb	35
Water, cooling, gal	36

Installation: More than 65,000 tpd of fuel, anode and needle coke.

References: *Handbook of Petroleum Refining Processes*, 3rd Ed., pp. 12.33–12.89.

Continued ▼

Coking, *continued*

"Optimize coker operations," *Hydrocarbon Processing*, September 2003.

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

"Drivers for additional delayed coking capacity in the refining industry," *Petroleum Economist*, September 2003.

Licensors: Foster Wheeler/UOP LLC.



Coking, flexi

Application: Continuous fluid bed technology to convert heavy hydrocarbons (vacuum residuum, extra heavy oil or bitumen) to full-range lighter liquid products and low-Btu fuel gas. Applicable for resid conversion in refineries with limited outlets for coke, for heavy feed conversion at the resource location and for producing a fuel substitute where natural gas has high value.

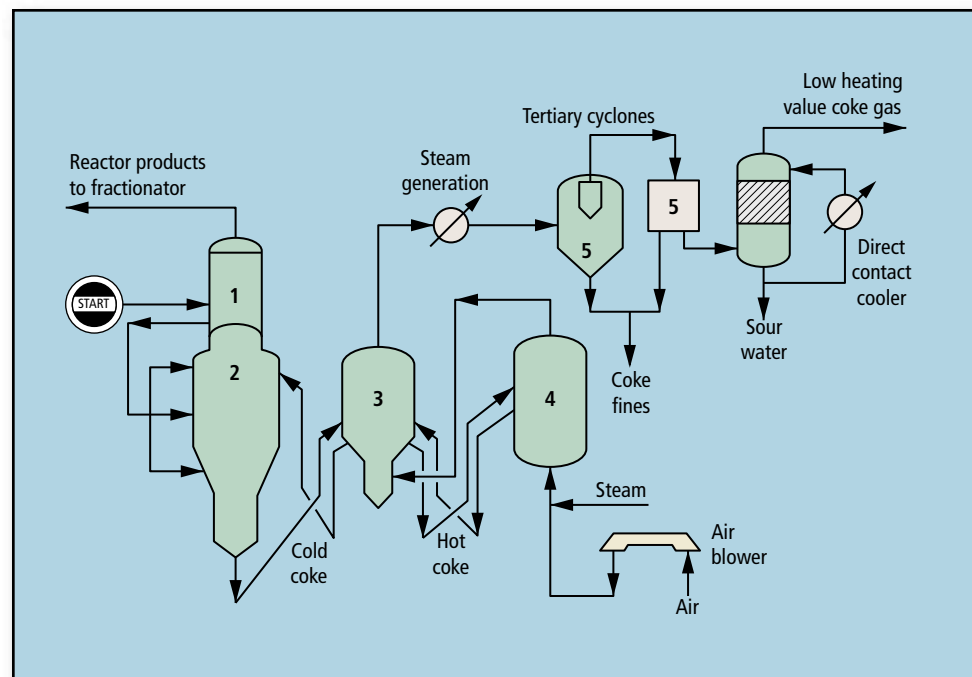
Products: Liquid and gas products can be upgraded through conventional treating. Low-Btu gas created from gasification of coke can be burned in furnaces or boilers, replacing other fuels at refineries or upstream production facilities.

Description: FLEXICOKING has essentially the same reactor (1)/scrubber (2) sections as FLUID COKING, and also has the same process flexibility options: recycle, once-through and VPS integrated.

Process heat is supplied by circulating hot coke between the heater (3) and reactor. Coke reacts with air and steam in the gasifier (4) to produce heat and low-Btu gas that can be used as fuel in furnaces and boilers, backing out fuel gas. About 97% of the coke generated is consumed in the process; a small amount of coke is withdrawn from the heater (3) and fines system (5), which can be disposed in cement kilns or used in metals recovery. Partial gasification and oxygen-enrichment can be used to provide additional process flexibility. A dual-gasification option can produce a hydrogen-rich stream.

Yields: Example, typical Middle East vacuum resid (~ 25 wt% Concarbon, ~5 wt% sulfur):

	Recycle	Once-through
Light ends, wt%	11.8	10.4
Naphtha (C ₅ , 350°F), wt%	11.5	9.5
Distillate (350–650°F), wt%	14.5	13.1
Heavy gas oil (650°F+), wt%	32.1	39.7
Low-Btu gas, MBtu/bbl	1.2	1.1
C ₅ + Liquids, wt%	58.1	62.3



Investment: TPC, US Gulf Coast, 2Q 2003 estimate with all environmental controls included (range dependent on unit capacity)

Capital investment, \$/bpsd 3,000–4,700

Competitive advantages:

- Fully continuous, commercially proven fluid-bed coking and fluid bed gasification process that is internally fueled and heat integrated with no purchase of fuel gas.
- Low-value coke is converted to fuel gas for use onsite or sale.
- Processes wide range of feeds, especially high metals, sulfur, CCR and single-train capacities >100 Kbpsd
- Continued technology developments providing enhancements for yields, capacity, reliability and run length
- More cost effective than delayed coking-partial oxidation or direct gasification of heavy feeds.

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Coking, flexi, *continued*

Licensors: ExxonMobil Research and Engineering Co.



Coking, fluid

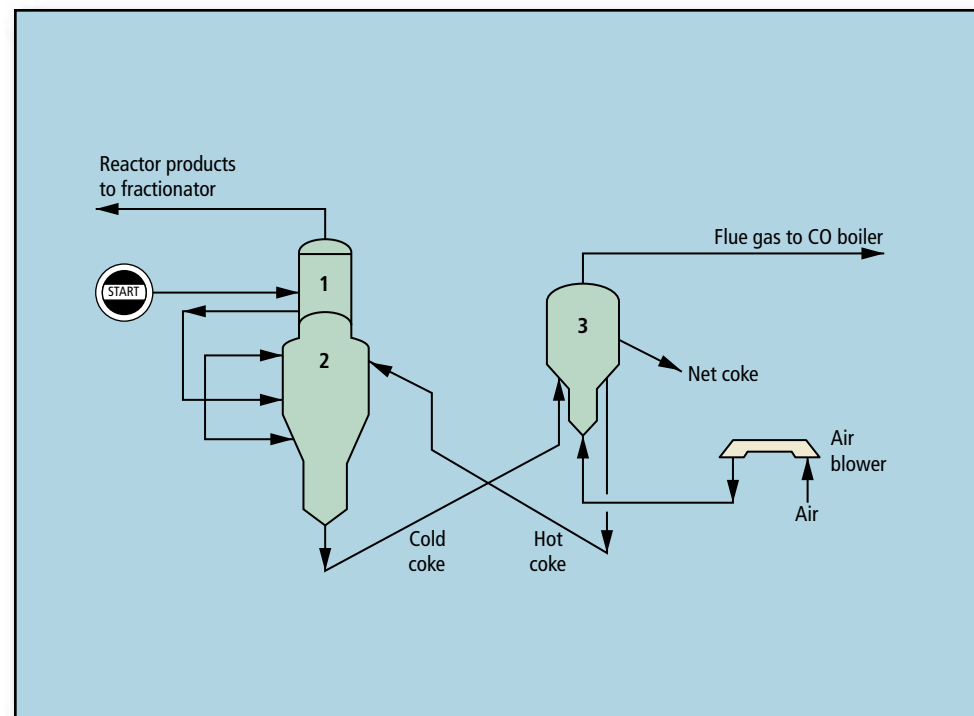
Application: Continuous fluid bed technology to convert heavy hydrocarbons (vacuum residuum, extra heavy oil or bitumen) to full-range lighter liquid products and coke. Coke can be sold as fuel or burned in an integrated fluid bed boiler to produce power and steam.

Products: Liquid and gas products can be upgraded through conventional treating. Fluid coke is widely used as a solid fuel, with particular advantages in cement kilns and in fluid bed boilers.

Description: Feed (typically 1,050°F+ vacuum resid) enters the scrubber (1) for heat exchange with reactor overhead effluent vapors. The scrubber typically cuts 975°F+ higher boiling reactor effluent hydrocarbons for recycle back to the reactor with fresh feed. Alternative scrubber configurations provide process flexibility by integrating the recycle stream with the VPS or by operating once-through, which produces higher liquid yields. Lighter overhead vapors from the scrubber are sent to conventional fractionation and light ends recovery. In the reactor (2), feed is thermally cracked to a full-range of lighter products and coke.

The heat for the thermal cracking reactions is supplied by circulating coke between the burner (3) and reactor. About 20% of the coke is burned with air to supply process heat requirements, eliminating the need for an external fuel supply. The rest of the coke is withdrawn and either sold as a product or burned in a fluid bed boiler. Properties of the fluid coke enable ease of transport and direct use in fuel applications, including stand-alone or integrated cogeneration facilities.

Yields: Example, typical Middle East vacuum resid (~25 wt% Concarbon, ~5 wt% sulfur):



Net product coke, wt%	25.7	23.9
Coke consumed for heat, wt%	4.4	3.4
C ₅ + liquids, wt%	58.1	62.3

Investment: TPC, U.S. Gulf Coast, 2Q03 estimate with all environmental controls included (range dependent on unit capacity)

Capital investment, \$/bp/sd 2,200–3,600

Competitive advantages:

- Fully continuous commercially proven fluid-bed coking process
- Single-train capacities >100 KB/SD; greater than other processes
- Process wide range of feeds, especially high metals, sulfur, CCR
- Internally heat integrated, minimal purchase of fuel gas; lower coke production than delayed coking

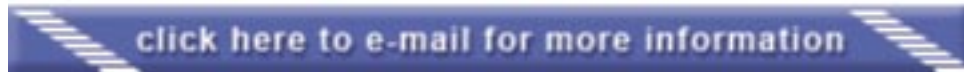
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	Recycle	Once-through
Light ends, wt%	11.8	10.4
Naphtha (C ₅ , 350°F), wt%	11.5	9.5
Distillate (350–650°F), wt%	14.5	13.1
Heavy Gas Oil (650°F+), wt%	32.1	39.7

Coking, fluid, *continued*

- Continued technology developments (yields, run length, reliability)
- Lower investment and better economy of scale than delayed coking
- Efficient integration with fluid bed boilers for COGEN.

Licensors: ExxonMobil Research and Engineering Co.



Crude distillation

Application: Separates and recovers the relatively lighter fractions from a fresh crude oil charge (e.g., naphtha, kerosine, diesel and cracking stock). 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 750°F to 775°F.

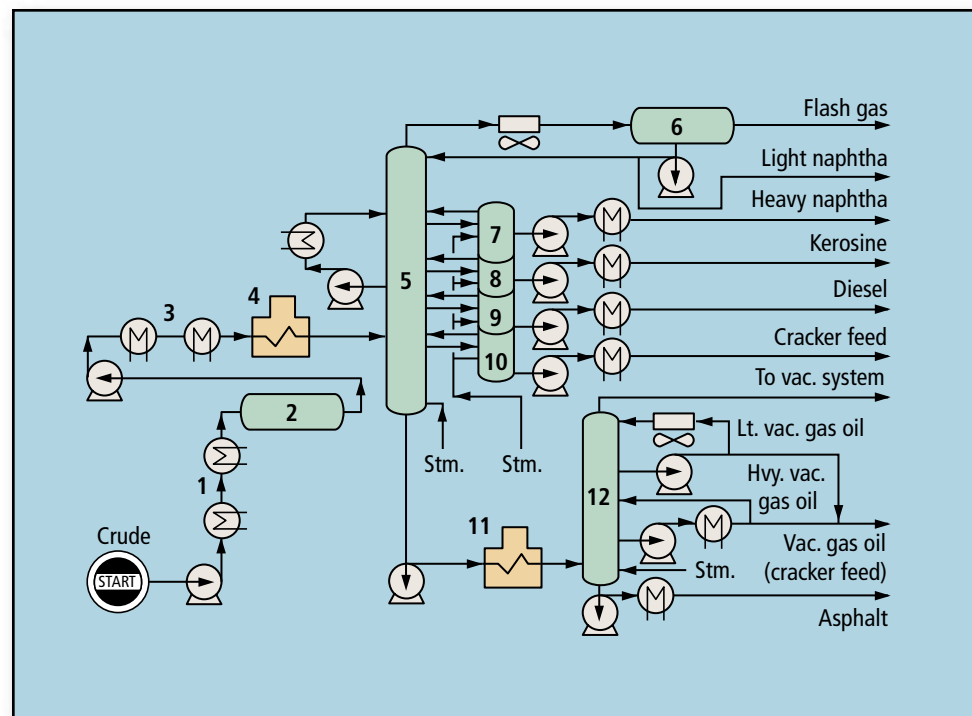
From the heater outlet, the stream is fed into a vacuum tower (12), where the distillate is condensed in two sections and withdrawn as two sidestreams. The two sidestreams are combined to form cracking feed-stock. An asphalt base stock is pumped from the bottom of the tower. Two circulating reflux streams 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. gas oil	2.6	23.4	35
Hvy. vac. gas oil	10.9	19.5	85
Vac. bottoms	<u>53.9</u>	<u>5.8</u>	<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, 2nd Q, 2004, US Gulf), \$ per bpsd 800–1,180

Utility requirements, typical per bbl fresh feed

Steam, lb	24
Fuel (liberated), 10 ³ Btu	(80–120)
Power, kWh	0.6
Water, cooling, gal	300–400

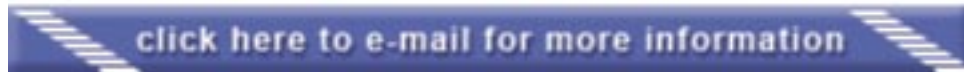
Installation: Foster Wheeler has designed and constructed crude units having a total crude capacity in excess of 15 MMbpsd.

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Crude distillation, *continued*

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

Licensors: Foster Wheeler.



Crude distillation

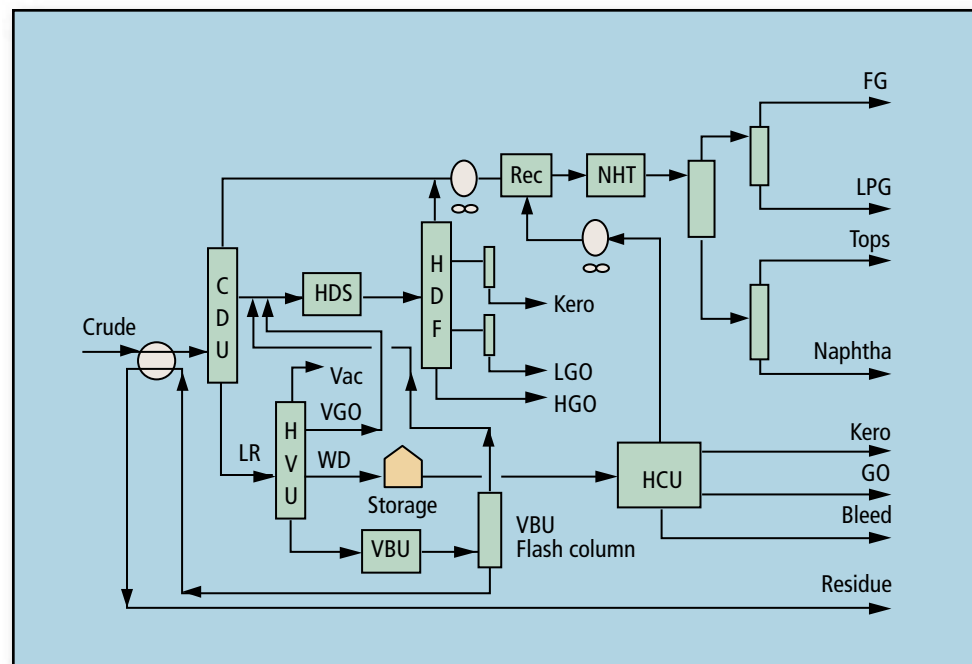
Application: The Shell Bulk CDU is a highly integrated concept. It separates the crude in long residue, waxy distillate, middle distillates and a naphtha minus fraction. Compared with stand-alone units, the overall integration of a crude distillation unit (CDU), hydrosulfurization unit (HDS), high vacuum unit (HVU) and a visbreaker (VBU) results in a 50% reduction in equipment count and significantly reduced 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 the HDS. After desulfurization in the HDS unit, final product separation of the bulk middle distillate stream from the CDU takes place 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, spray sections to obtain a lower flashzone pressure, and a VGO recovery section to recover up to 10 wt% as automotive diesel. The Shell furnace design prevents excessive cracking and enables a 5-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	150–250°C	17.4
Gasoil (GO)	250–350°C	18.3
VGO	350–370°C	3.6



Waxy distillate (WD)	370–575°C	28.8
Residue	575°C+	16.0

Economics: Due to the incorporation of Shell high capacity internals and the deeply integrated designs, an attractive CAPEX reduction 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, a total of some 50 HVU units have been built while a similar number has been debottlenecked, including many third-party designs of feedprep and lube oil HVUs.

Licensors: Shell Global Solutions International B.V.

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 $\frac{2}{3}$ 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.

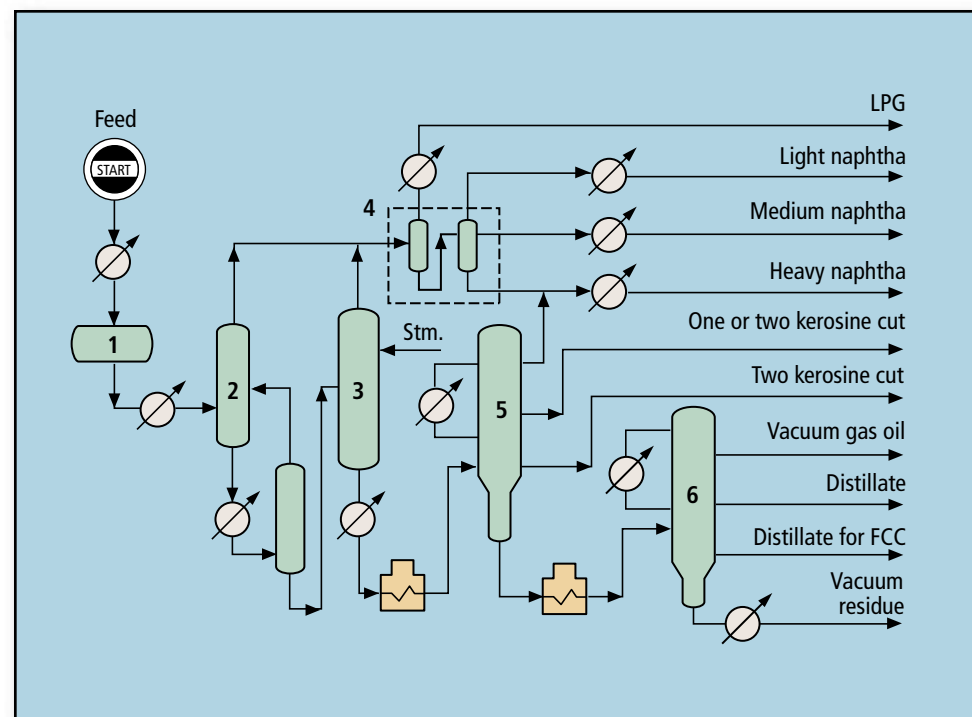
Extensive use of pinch technology minimizes heat supplied by heaters and heat removed by air and water coolers.

This process is particularly suitable for large crude capacity from 150,000 to 250,000 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:

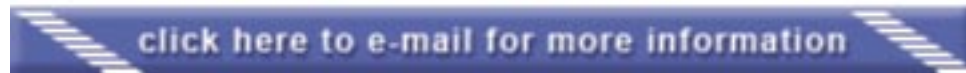
for Arabian Light or Russian Export Blend:	1.25 tons of fuel
	per 100 tons of Crude
for Arabian Heavy	1.15 tons of fuel
	per 100 tons of Crude

Continued ▼

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.

Licensors: TOTALFINAELF and Technip.



Crude topping units

Application: Crude topping units are typically installed in remote areas to provide fuel for local consumption, often for use at pipeline pumping stations and at production facilities.

Products: Diesel is typically the desired product, but kerosine, turbine fuel and naphtha are also produced.

Description: Crude topping units comprise of four main sections: pre-heat/heat recovery section, fired heater, crude fractionation (distillation), and product cooling and accumulation. The fired heater provides heat for the plant. Fuel for the heater can be residual products, offgas, natural gas, distillate product, or combinations of these fuels, depending on the installation. Heat integration reduces emissions and minimizes process-energy requirements. Depending on the individual site, an electrostatic desalter may or may not be required to prevent fouling and plugging, and control corrosion in the fractionation section.

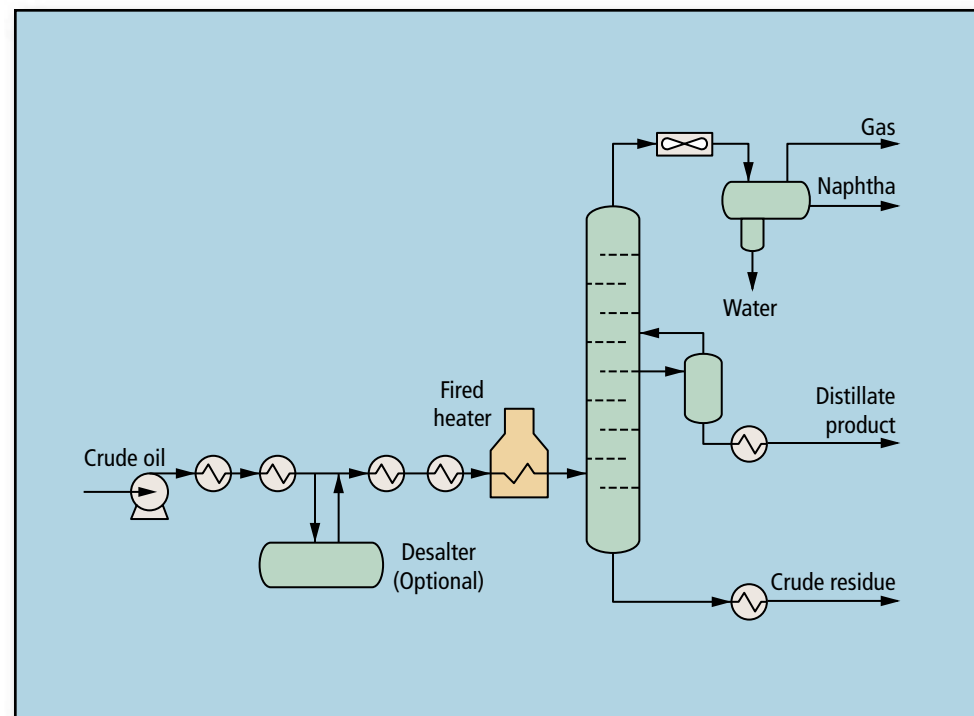
Crude topping units are modularized, which reduces construction cost and complexity. Modular units also allow installation in remote areas with minimal mobilization. These units are typically custom designed to meet individual customer requirements.

Crude topping units are self-contained, requiring few utilities for operation. Utility packages, wastewater treatment facilities and other associated offsites are often supplied, depending on the individual site requirements.

Operating conditions:

Column pressure, psig	0–20
Temperature, °F	550–650

Licensors: CB&I Howe-Baker Process and Technology.



Deasphalting

Application: Prepare 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 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 utilized if resins are to be produced.

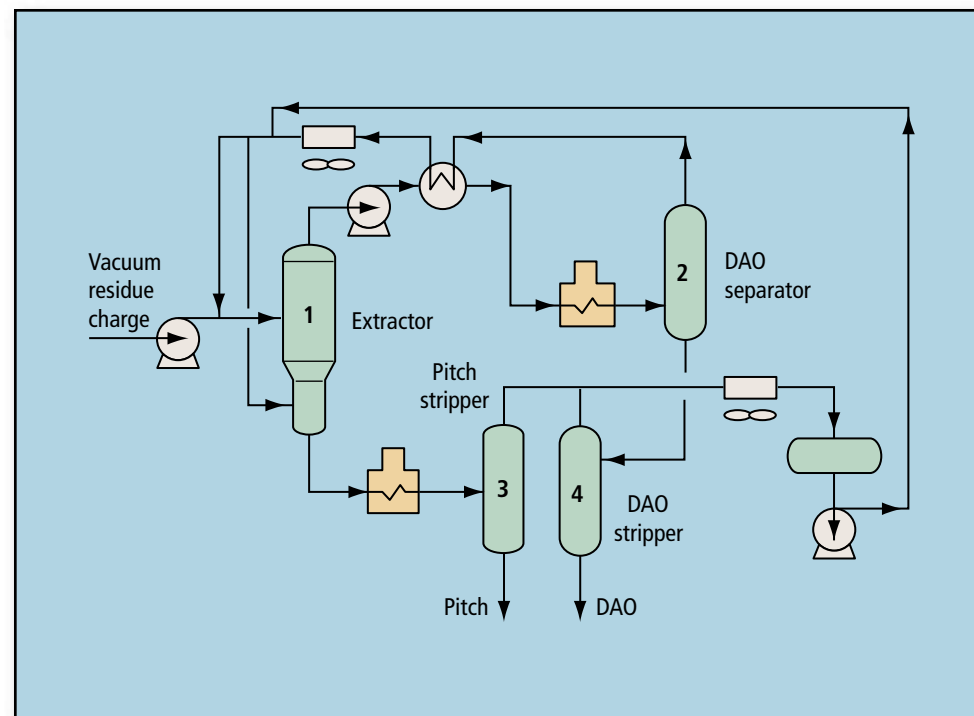
Operating conditions: Typical ranges are: solvent, various blends of C₃–C₇ hydrocarbons including light naphthas. Pressure: 300 to 600 psig. Temp.: 120°F to 450°F. Solvent-to-oil ratio: 4/1 to 13/1.

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	53	65
Gravity, °API	20.3	17.6	15.1
Sulfur, wt%	2.7	1.9	2.2
CCR, wt%	1.4	3.5	6.2
Visc., SSU@ 210°F	165	307	540
Ni/V, wppm	0.25/0.37	1.8/3.4	4.5/10.3



Pitch

Softening point, R&B, °F	149	226	240
Penetration@77°F	12	0	0

Economics:

Investment (basis: 2,000–40,000 bpsd
2Q 2004, US Gulf), \$/bpsd

Utilities, typical per bbl feed:	Lube oil	Cracking stock
Fuel, 10 ³ Btu	81	56
Electricity, kWh	1.5	1.8
Steam, 150-psig, lb	116	11
Water, cooling (25°F rise), gal	15	nil

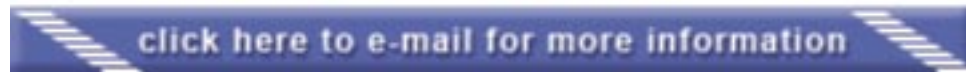
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Deasphalting, *continued*

Installations: 50+. This also includes both UOP and Foster Wheeler units originally licensed separately before merging the technologies in 1996.

Reference: *Handbook of Petroleum Refining Processes*, 2nd Ed., McGraw Hill, 1997, pp.10.15–10.60.

Licensors: UOP LLC/Foster Wheeler.



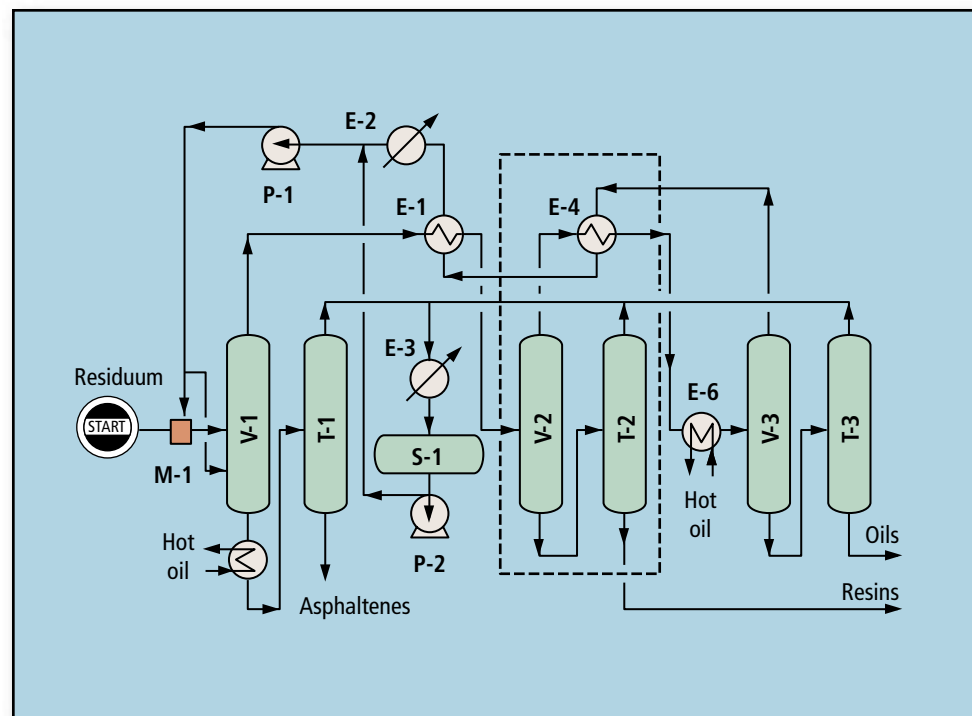
Deasphalting

Application: Extract lubricating oil blend stocks and FCCU or hydrocracker feedstocks with low metal and Conradson carbon contents from atmospheric and vacuum resid using ROSE Supercritical Fluid Technology. Can be used to upgrade existing solvent deasphalters. ROSE may also be used to economically upgrade heavy crude oil.

Products: Lube blend stocks, FCCU feed, hydrocracker 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). Counter-current solvent flow extracts lighter components from the resid while rejecting asphaltenes with a small amount of solvent. Asphaltenes are then heated and stripped of solvent (T-1). Remaining solvent solution goes overhead (V-1) through heat exchange (E-1) and a second separation (V-2), yielding an intermediate product (resins) that is stripped of solvent (T-2). The overhead is heated (E-4, E-6) so the solvent 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). Deasphalted oil from the oil separator (V-3) is stripped (T-3) of dissolved solvent. The only solvent vaporized is a small amount dissolved in fractions withdrawn in the separators. This solvent is recovered in the product strippers. 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. They can also debottleneck and improve operations of existing solvent deasphalting units.

The system can be simplified by removing equipment in the outlined box to make two products. The intermediate fraction can be shifted into the final oil fraction by adjusting operating conditions. Only one exchanger (E-6) provides heat to warm the resid charge and the small amount of extraction solvent recovered in the product strippers.



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

Economics:

Investment: (Basis: 30,000 bpsd, US Gulf Coast),
\$ per bpsd 1,250

Utilities, typical per bbl feed:

Fuel absorbed, 10 ³ Btu	80–110
Electricity, kWh	2.0
Steam, 150-psig, lb	12

Deasphalting, *continued*

Installation: Thirty-six licensed units with a combined capacity of over 600,000 bpd.

Reference: Northup, A. H., and H. D. Sloan, "Advances in solvent deasphalting technology," 1996 NPRA Annual Meeting, San Antonio.

Licensors: Kellogg Brown & Root, Inc.



Deep catalytic cracking

Application: Selective conversion of gasoil and paraffinic residual feedstocks.

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

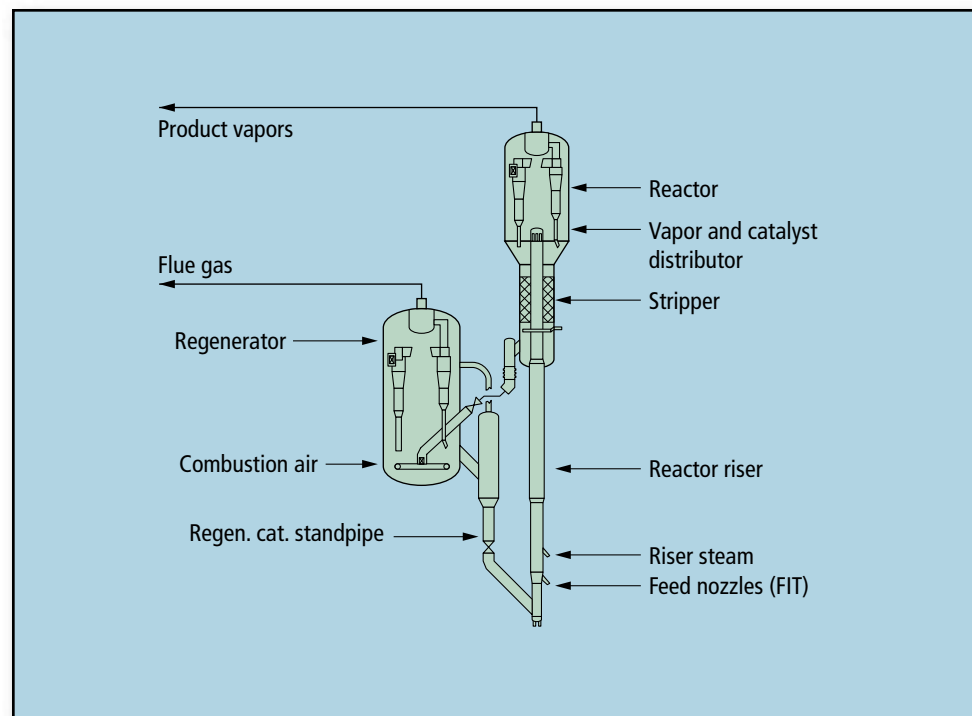
Description: DCC is a fluidized process for selectively cracking a wide variety of feedstocks to light olefins. Propylene yields over 24 wt% are achievable with paraffinic feeds. A traditional reactor/regenerator unit design uses a catalyst with physical properties similar to traditional FCC catalyst.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

Each operational mode utilizes unique catalyst as well as reaction conditions. Maximum propylene DCC uses both riser and bed cracking at severe reactor conditions while Type II DCC uses only riser cracking like a modern 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 heavier feeds while meeting the need for an increased propylene to ethylene ratio. The integrated DCC/steam cracking complex offers significant capital savings over a conventional stand-alone



refinery for propylene production.

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

Installation: Six units are currently operating in China and one in Thailand. Several more units are under design in China.

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

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Deep catalytic cracking, *continued*

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



Deep thermal conversion

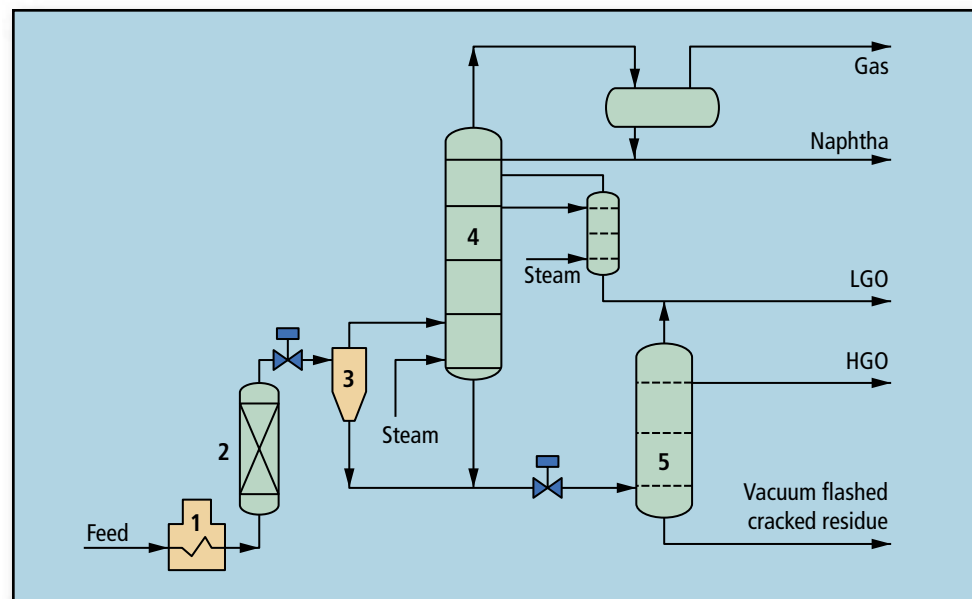
Application: The Shell Deep Thermal Conversion process closes the gap between visbreaking and coking. The process yields a maximum of distillates by applying deep thermal conversion of the vacuum residue feed and by vacuum flashing the cracked residue. High-distillate yields are obtained, while still 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 like gas, LPG, naphtha, kero 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, vacuum residue	Middle East
Viscosity, cSt @100°C	770
Products in % wt. on feed	
Gas	4.0
Gasoline ECP 165°C	8.0
Gas oil ECP 350°C	18.1
Waxy distillate ECP 520°C	22.5
Residue ECP 520°C+	47.4

Economics: The investment ranges from 1,300 to 1,600 US\$/bbl installed excl. treating facilities and depending on the capacity and configuration (basis: 1998).



Utilities, typical per bbl @180°C

Fuel, Mcal	26
Electricity, kWh	0.5
Steam, net production, kg	20
Water, cooling, m ³	0.15

Installation: Presently, four Deep Thermal Conversion units have been licensed. In two cases, this involved a revamp of an existing Shell Soaker Visbreaker unit. In addition, two units are planned for revamp, while one grassroots unit is currently under construction. Post startup services and technical services on existing units are available from Shell.

Reference: Visbreaking Technology, Erdöl and Kohle, January 1986.

Licensors: Shell Global Solutions International B.V. and ABB Lummus Global B.V.

Desulfurization

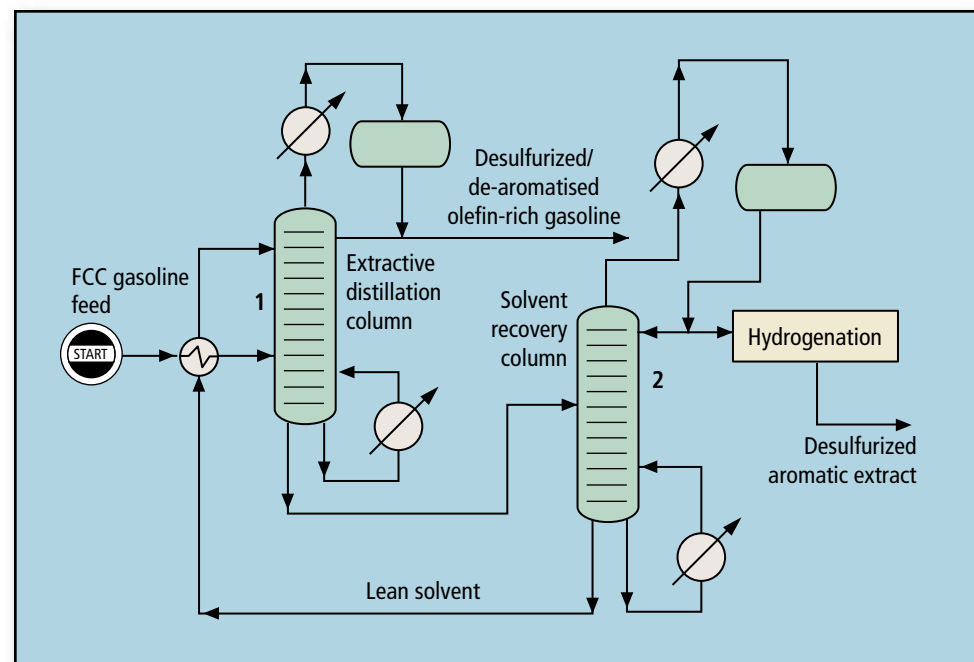
Application: GT-DeSulf addresses overall plant profitability by desulfurizing the FCC stream with no octane loss and decreased hydrogen consumption by using a proprietary solvent in an extractive distillation system. This process also recovers valuable aromatics compounds.

Description: FCC gasoline, with endpoint up to 210°C, is fed to the GT-DeSulf unit, which extracts sulfur and aromatics from the hydrocarbon stream. The sulfur and aromatic components are processed in a conventional hydrotreater to convert the sulfur into H₂S. 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 process the majority of the gasoline through hydrotreating and caustic-washing units to eliminate the sulfur. That method inevitably results in olefin saturation, octane downgrade and yield loss.

GT-DeSulf has these advantages:

- Segregates and eliminates FCC-gasoline sulfur species to meet a pool gasoline target of 20 ppm
- Preserves more than 90% of the olefins from being hydrotreated in the HDS unit; and thus, prevents significant octane loss and reduces hydrogen consumption
- Fewer components are sent to the HDS unit; consequently, a smaller HDS unit is needed and there is less yield loss
- High-purity BTX products can be produced from the aromatic-rich extract stream after hydrotreating
- Olefin-rich raffinate stream (from the ED unit) can be recycled to the FCC unit to increase the light olefin production.

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 nonaromatics into the overhead as raffinate. Nearly all of the nonaromatics, including olefins, are effectively sepa-



rated into the raffinate stream. The raffinate stream can be optionally caustic washed before routing to the gasoline pool, or to a C₃= producing unit.

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 used as desulfurized gasoline, or directed to an aromatics production plant. Lean solvent from the SRC bottoms are treated and recycled back to the EDC.

Economics: Estimated installed cost of \$1,000/bpd of feed and production cost of \$0.50/bbl of feed for desulfurization and dearomatization.

Licensors: GTC Technology Inc.

Desulfurization

Application: The S-Brane process selectively separates sulfur from gasoline streams by using a membrane technology. This method can be used to meet clean-gasoline requirements with minimal octane loss. S-Brane also substantially reduces the refiners' need to hydrotreat naphtha.

Products: A low-sulfur stream (typically 80% of the feed) that can be directly blended into a gasoline pool and a small stream with concentrated sulfur that requires further processing.

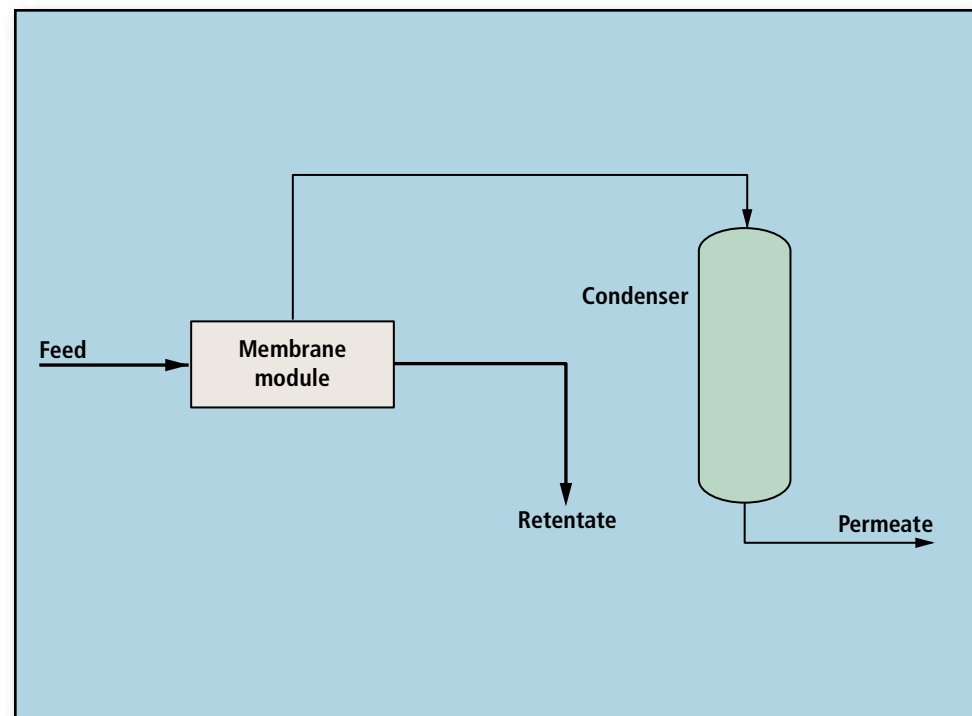
Description: S-Brane is a simple physical separation process that separates a feed gasoline stream into two product streams. The feed stream (ideally a C₅-350°F FCC gasoline stream) is passed over a membrane that is selective for sulfur-containing hydrocarbon molecules. As the gasoline passes over the membrane, sulfur-containing molecules and some hydrocarbon molecules dissolve into the membrane and, subsequently, diffuse through it. A low-sulfur stream (retentate), about 75–80% of the inlet gasoline volume, can be directly blended into the gasoline pool.

A smaller stream (permeate) contains the majority of the sulfur and must be processed further before being blended into the gasoline pool.

S-Brane operates as a pervaporation-mode-membrane process. The driving force that moves molecules through the membrane is a vacuum on the backside (permeate side) of the membrane that causes a vapor pressure gradient for each molecule type.

The shell side of the assembly is operated under vacuum conditions (about 0.75–1.5 psia). Once through the membrane, permeate molecules are condensed and passed along for further processing to treat the now concentrated sulfur species. In the S-Brane process, the feed and retentate are at about 230°F and 100 psig while the permeate is first a vapor and then condensed into liquid form.

The process provides an effective way to reduce refiners' hydrotreating requirements and substantially avoid octane loss associated with hydrotreating-based technologies.



Economics: The capital cost of S-Brane is about 30% of a corresponding size hydrotreating unit. The exact number is dependent on both the processing capacity and also the sulfur levels of both the feed and the desired product.

Membrane service-life:	3 years
Catalyst:	None
Hydrogen requirement:	None
Utilities (per bbl feed)	
Electricity	0.91 kW
Water, cooling (20°F rise)	128 gal
Steam, 50 lb	9.3 lbs
Steam, 300 lb	5.1 lbs

Desulfurization, *continued*

Installation: A 300-bpd demonstration plant has been in operation since June 2003.

Reference: "S-BraneTechnology Brings Flexibility To Refiners' Clean Fuels Solutions," 2004 NPRA Annual Meeting, San Antonio, March 22–23, 2004.

Licensors: W. R. Grace & Co.



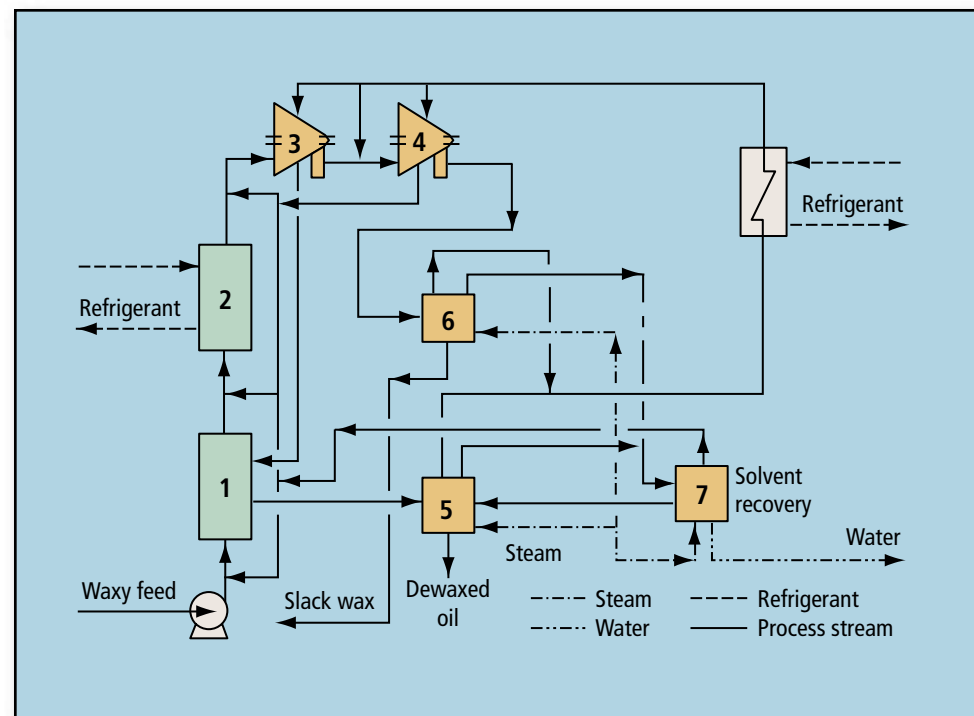
Dewaxing

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, 2004 US Gulf Coast), \$/bpsd 9,300

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 Corp.

Dewaxing

Application: Selectively convert feedstock's waxy molecules by isomerization in the presence of ISODEWAXING Catalysts. The products are high-quality base oils that can meet stringent cold flow properties.

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.

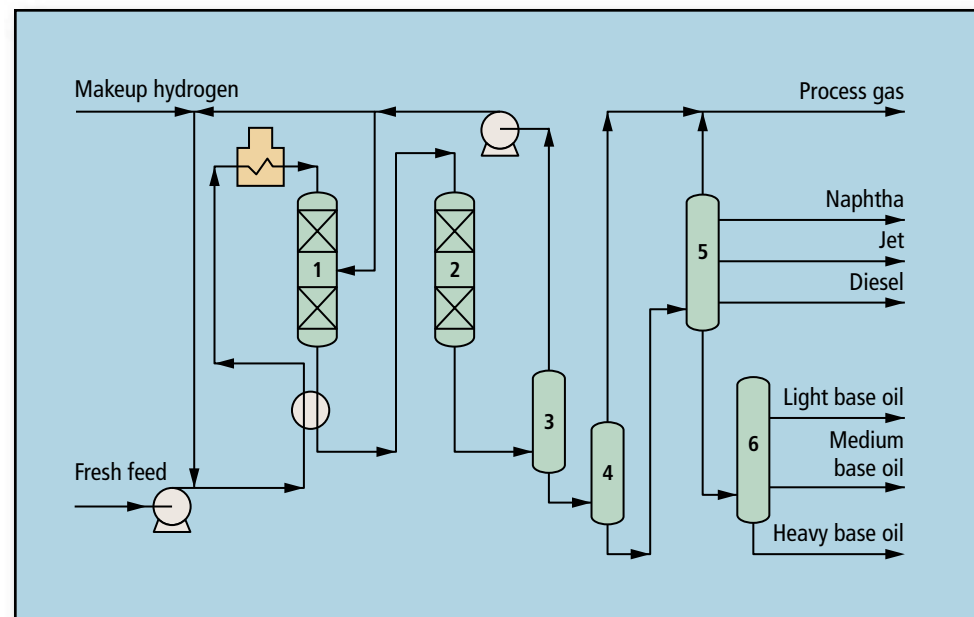
As shown in the simplified flow diagram, waxy feedstocks are mixed with recycle hydrogen and fresh makeup hydrogen, heated and charged to a reactor containing ISODEWAXING Catalyst (1). The effluent will have a much lower pour point and, depending on the operating severity, the aromatics content is reduced 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 6,000 \$/bpsd.



Utilities:

Typical per bbl feed:	
Power, kW	3.3
Fuel, kcal	13.4×10^3
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: Ten units are in operation and eight units are in various stages of design or construction.

Reference: NPRA Annual Meeting, March 2004, San Antonio, Paper AM-04-68.

Licensors: Chevron Lummus Global LLC.

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.

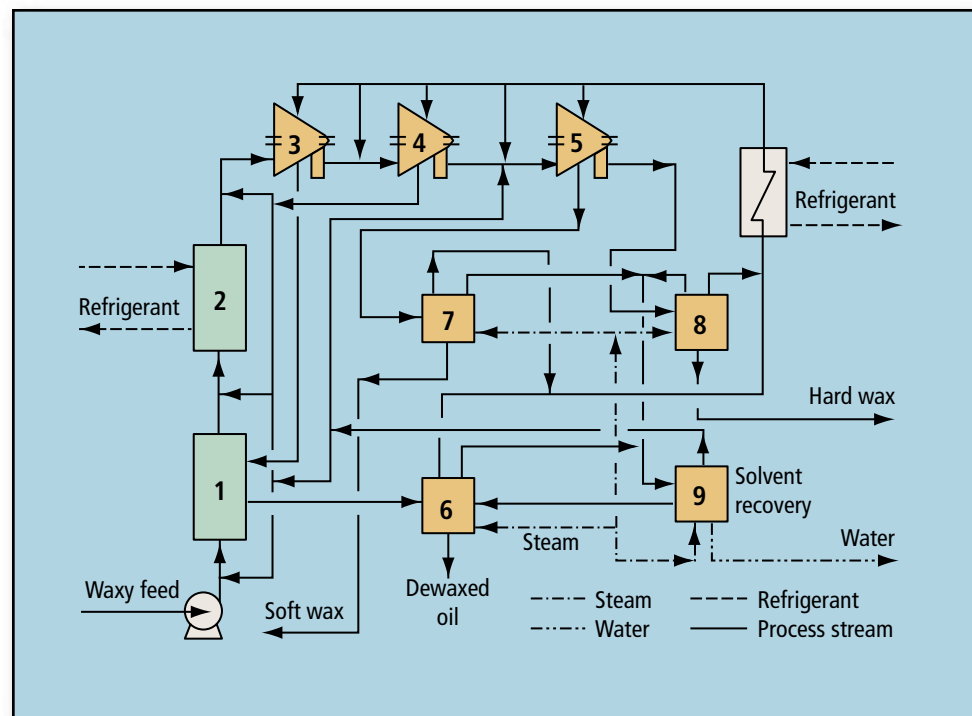
Description: Bechtel's two-stage solvent dewaxing process can be expanded to simultaneously produce hard wax by adding a third deoiling stage using the Wax Fractionation process. Waxy feedstock (raffinate, distillate or deasphalted oil) is mixed with a binary-solvent system and chilled in a very closely 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, 2004 US Gulf Coast), \$/bpsd 10,900



Utilities, typical per bbl feed:

Fuel, 10 ³ Btu (absorbed)	230
Electricity, kWh	25
Steam, lb	25
Water, cooling (25°F rise), gal	1,500

Installation: Seven in service.

Licensors: Bechtel Corp.

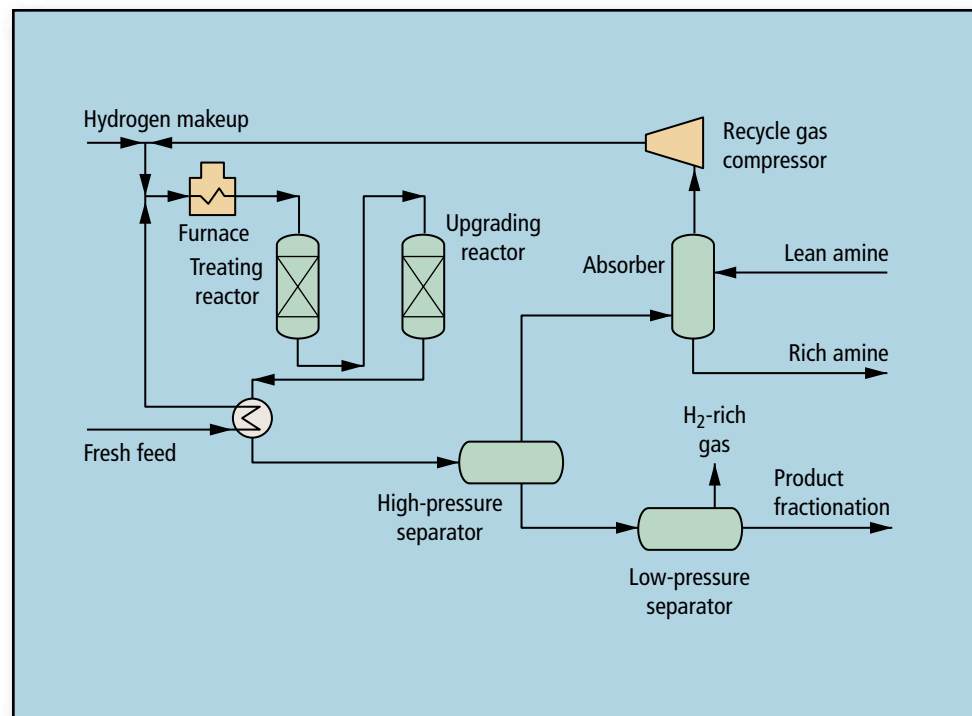
Diesel upgrading

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 gas oil.

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. 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-573 or TK-574, 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 2003 Annual Meeting, San Antonio, March 2003.

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

Installations: A total of 13 units are in operation; five in Asia-Pacific region, one in the Middle East, two in Europe and five HDS/HDA units (see Hydrodearomatization).

Licensors: Haldor Topsøe A/S.

Diesel—ultra-low-sulfur diesel (ULSD)

Application: Topsøe ULSD process is designed to produce ultra-low-sulfur diesel (ULSD)—5–50 wppm S—from cracked and straight-run distillates. 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.

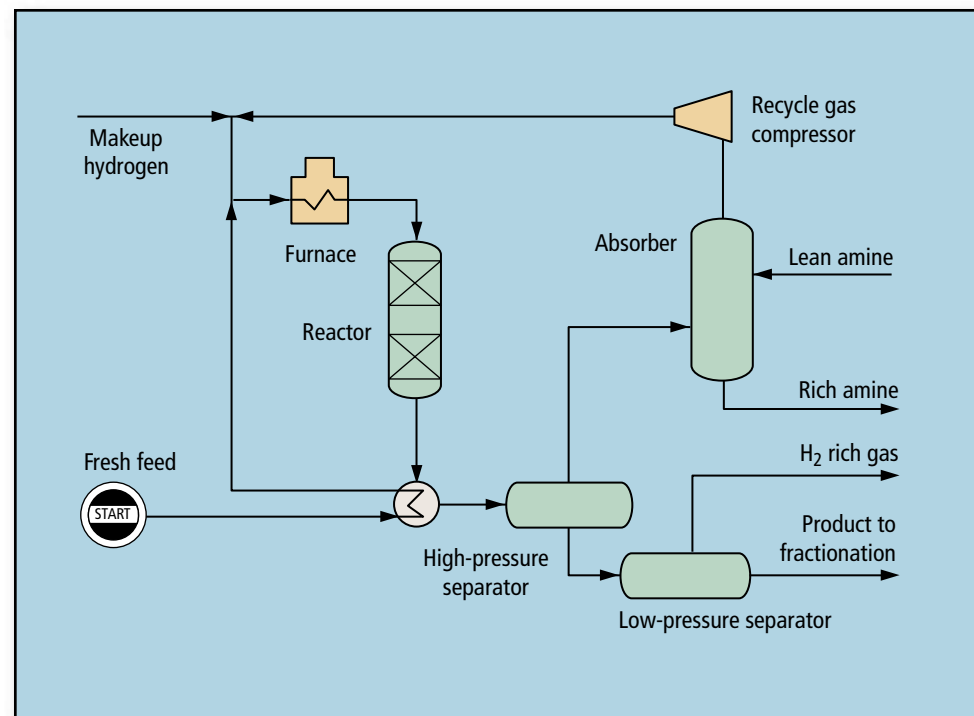
Our highest activity CoMo catalyst is specifically formulated with high-desulfurization activity and stability at low reactor pressure (~ 500 psig) to produce 5 wppm diesel. This catalyst is suitable for revamping existing low-pressure hydrotreaters or in new units when minimizing hydrogen consumption.

The highest activity NiMo 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 34 ULSD hydrotreaters of which 26 units are designed for less than 10 wppm sulfur in the diesel. Our reactor internals are installed in more than 60 units.

References: "Cost-Effectively Improve Hydrotreater Designs," *Hydrocarbon Processing*, November 2001 pp. 43–46.

"The importance of good liquid distribution and proper selection of catalyst for ultra deep diesel HDS," JPI Petroleum Refining Conference, October 2000, Tokyo.



Low, G., J. Townsend, and T. Shooter, "Systematic approach for the revamp of a low-pressure hydrotreater to produce 10-ppm, sulfur-free diesel at BP Conynton Refinery," 7th ERTC, November 2002, Paris.

Licensors: Haldor Topsøe A/S.

Electrical desalting

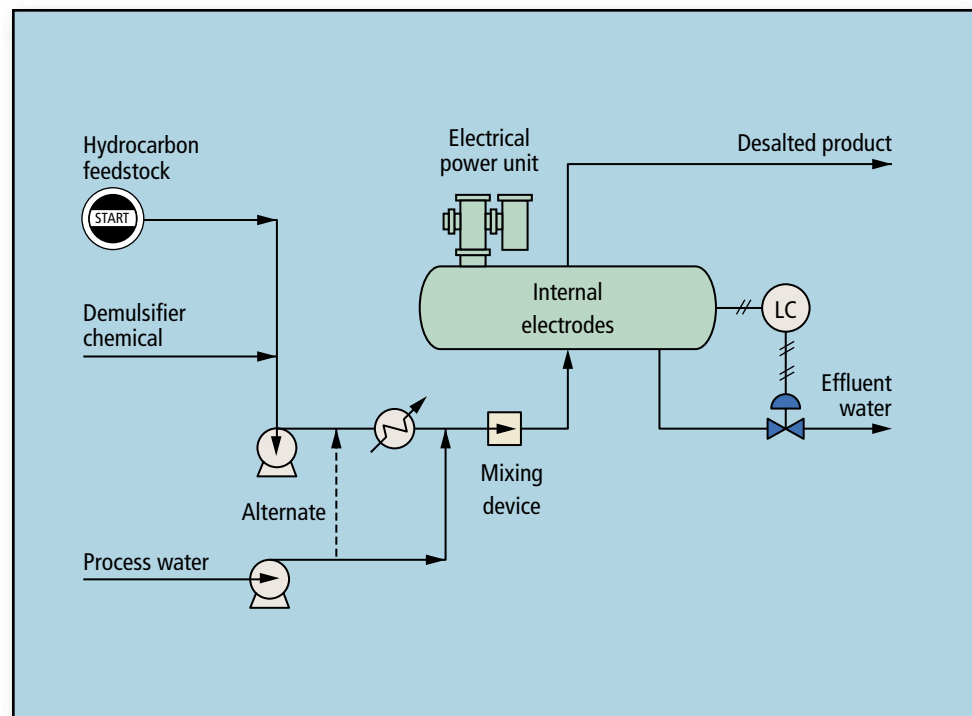
Application: For removal of undesirable impurities such as salt, water, suspended solids and metallic contaminants from unrefined crude oil, residuums and FCC feedstocks.

Description: Salts such as sodium, calcium and magnesium chlorides are generally contained in the residual water suspended in the oil phase of hydrocarbon feedstocks. All feedstocks also contain, as mechanical suspensions, such impurities as silt, iron oxides, sand and crystalline salt. These undesirable components can be removed from hydrocarbon feedstocks by dissolving them in washwater or causing them to be water-wetted. Emulsion formation is the best way to produce highly intimate contact between the oil and washwater phases.

The electrical desalting process consists of adding process (wash) water to the feedstock, generating an emulsion to assure maximum contact and then utilizing a highly efficient AC electrical field to resolve the emulsion. The impurity-laden water phase can then be easily withdrawn as underflow.

Depending on the characteristics of the hydrocarbon feedstock being processed, optimum desalting temperatures will be in the range of 150°F to 300°F. For unrefined crude feedstocks, the desalter is located in the crude unit preheat train such that the desired temperature is achieved by heat exchange with the crude unit products or pumparound reflux. Washwater, usually 3–6 vol%, is added upstream and/or downstream of the heat exchanger(s). The combined streams pass through a mixing device thereby creating a stable water-in-oil emulsion. Properties of the emulsion are controlled by adjusting the pressure drop across the mixing device.

The emulsion enters the desalter vessel where it is subjected to a high-voltage electrostatic field. The electrostatic field causes the dispersed water droplets to coalesce, agglomerate and settle to the lower portion of the vessel. The water phase, containing the various impurities removed from the hydrocarbon feedstock, is continuously discharged to



the effluent system. A portion of the water stream may be recycled back to the desalter to assist in water conservation efforts. Clean, desalted hydrocarbon product flows from the top of the desalter vessel to subsequent processing facilities.

Desalting and dehydration efficiency of the oil phase is enhanced by using EDGE (Enhanced Deep-Grid Electrode) technology which creates both high- and low-intensity AC electrical fields inside the vessel. Demulsifying chemicals may be used in small quantities to assist in oil/water separation and to assure low oil contents in the effluent water.

Licensors: CB&I Howe-Baker Process and Technology.

Ethers

Application: Production of high-octane reformulated gasoline components (MTBE, ETBE, TAME and/or higher molecular-weight ethers) from C_1 to C_2 alcohols and reactive hydrocarbons in C_4 to C_6 cuts.

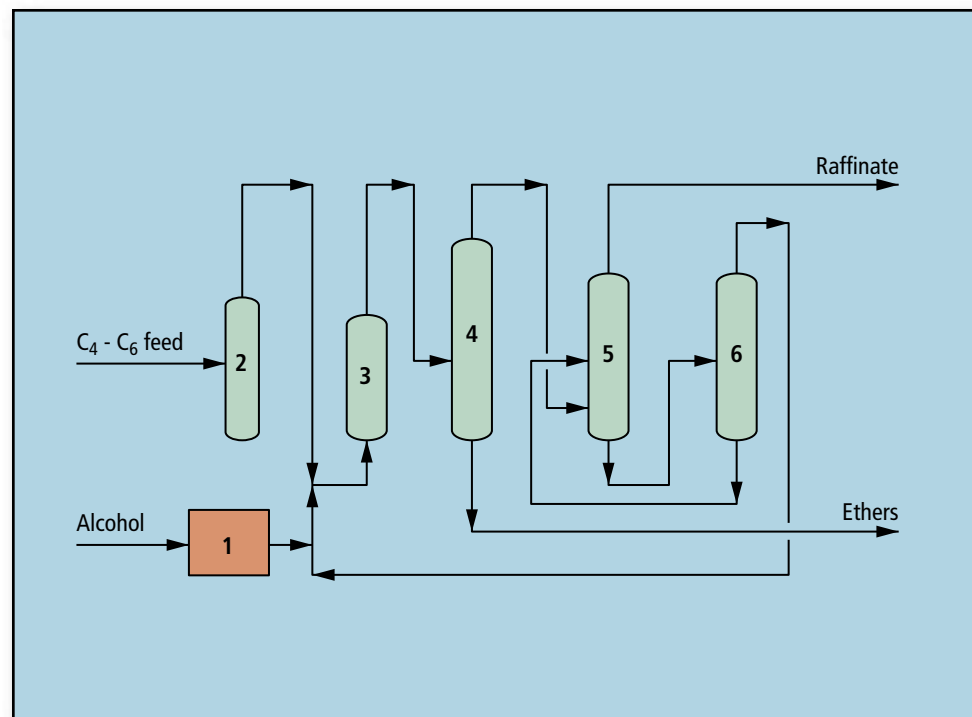
Description: Different arrangements have been demonstrated depending on the nature of the feeds. All use acid resins in the reaction section. The process includes alcohol purification (1), hydrocarbon purification (2), followed by the main reaction section. This main reactor (3) operates under adiabatic upflow conditions using an expanded-bed technology and cooled recycle. Reactants are converted at moderate well-controlled temperatures and moderate pressures, maximizing yield and catalyst life. The main effluents are purified for further applications or recycle.

More than 90% of the total per pass conversion occurs in the expanded-bed reactor. The effluent then flows to a reactive distillation system (4), Catacol. This system, operated like a conventional distillation column, combines catalysis and distillation. The catalytic zones of the Catacol use fixed-bed arrangements of an inexpensive acidic resin catalyst that is available in bulk quantities and easy to load and unload.

The last part of the unit removes alcohol from the crude raffinate using a conventional waterwash system (5) and a standard distillation column (6).

Yields: Ether yields are not only highly dependent on the reactive olefins' content and the alcohol's chemical structure, but also on operating goals: maximum ether production and/or high final raffinate purity (for instance, for downstream 1-butene extraction) are achieved.

Economics: Plants and their operations are simple. The same inexpensive (purchased in bulk quantities) and long-lived, non-sophisticated catalysts are used in the main reactor section catalytic region of the Catacol column, if any.



Installation: Over 25 units, including ETBE and TAME, have been licensed. Twenty-four units, including four Catacol units, are in operation.

Licensors: Axens.

Ethers

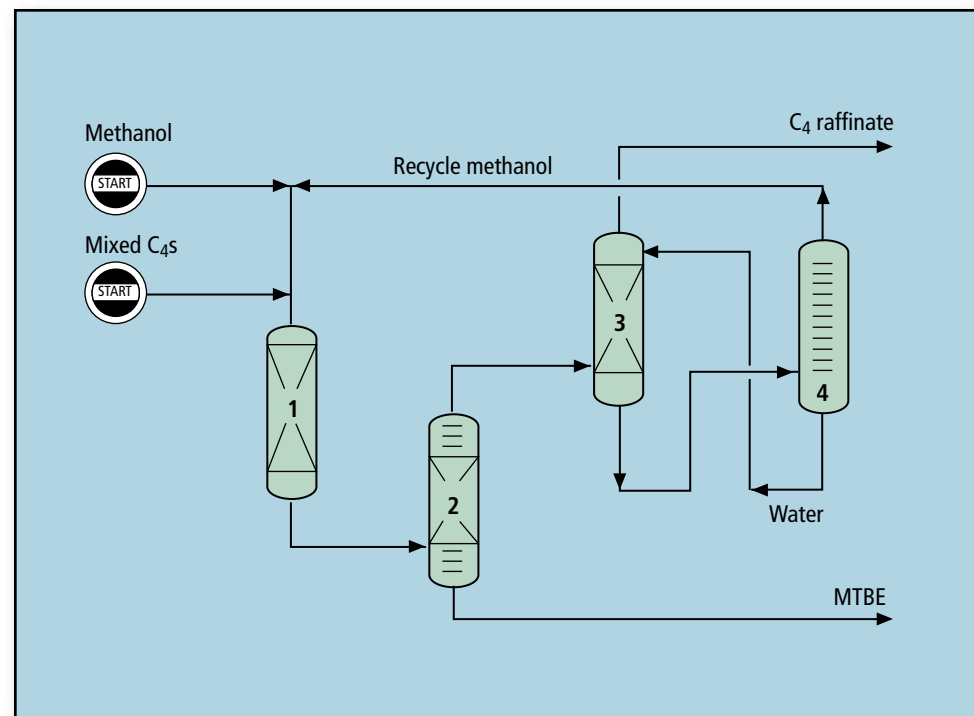
Application: To produce high-octane, low-vapor-pressure oxygenates such as methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME) or heavier tertiary ethers for gasoline blending to reduce olefin content and/or meet oxygen/octane/vapor pressure specifications. The processes use boiling-point/tubular reactor and catalytic distillation (CD) technologies to react methanol (MeOH) or ethanol with tertiary isoolefins to produce respective ethers.

Description: For an MTBE unit, the process can be described as follows. Process description is similar for production of heavier ethers. The C₄s and methanol are fed to the boiling-point reactor (1)—a fixed-bed, downflow adiabatic reactor. In the reactor, the liquid is heated to its boiling point by the heat of reaction, and limited vaporization occurs. System pressure is controlled to set the boiling point of the reactor contents and hence, the maximum temperatures. An isothermal tubular reactor is used, when optimum, to allow maximum temperature control. The equilibrium-converted reactor effluent flows to the CD column (2) where the reaction continues. Concurrently, MTBE is separated from unreacted C₄s as the bottom product.

This scheme can provide overall isobutylene conversions up to 99.99%. Heat input to the column is reduced due to the heat produced in the boiling-point reactor and reaction zone. Over time, the boiling-point reactor catalyst loses activity. As the boiling-point reactor conversion decreases, the CD reaction column recovers lost conversion, so that high overall conversion is sustained. CD column overhead is washed in an extraction column (3) with a countercurrent water stream to extract methanol. The water extract stream is sent to a methanol recovery column (4) to recycle both methanol and water.

C₄s ex-FCCU require a well-designed feed waterwash to remove catalyst poisons for economic catalyst life and MTBE production.

Conversion: The information below is for 98% isobutylene conversion, typical for refinery feedstocks. Conversion is slightly less for ETBE than for



MTBE. For TAME and TAE, isoamylene conversions of 95%+ are achievable. For heavier ethers, conversion to equilibrium limits are achieved.

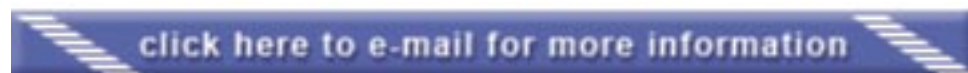
Economics: Based on a 1,500-bpsd MTBE unit (6,460-bpsd C₄s ex-FCCU, 19% vol. isobutylene, 520-bpsd MeOH feeds) located on the US Gulf Coast, the inside battery limits investment is:

Investment, \$ per bpsd of MTBE product	3,500
Typical utility requirements, per bbl of product	
Electricity, kWh	0.5
Steam, 150-psig, lb	210
Steam, 50-psig, lb	35
Water, cooling (30°F rise), gal	1,050

Ethers, *continued*

Installation: Over 60 units are in operation using catalytic distillation to produce MTBE, TAME and ETBE. More than 100 ether projects have been awarded to CDTECH since the first unit came onstream in 1981. Snamprogetti has over 20 operating ether units using tubular reactors.

Licensors: Snamprogetti S.p.A.



Ethers—ETBE

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

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

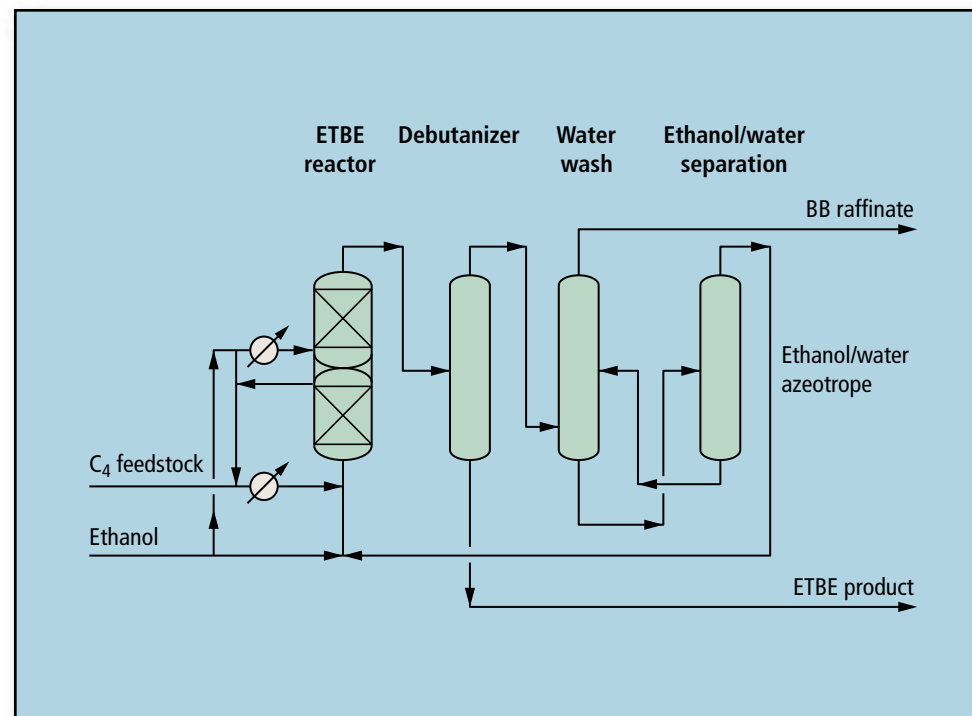
Products: ETBE and other tertiary alkyl ethers are primarily used in gasoline blending as an octane enhancer to improve hydrocarbon combustion efficiency. Moreover, blending of ETBE to the gasoline pool will lower vapor pressure (Rvp).

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

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

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

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



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

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

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

Licensors: Uhde GmbH.

Ethers—MTBE

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

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

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

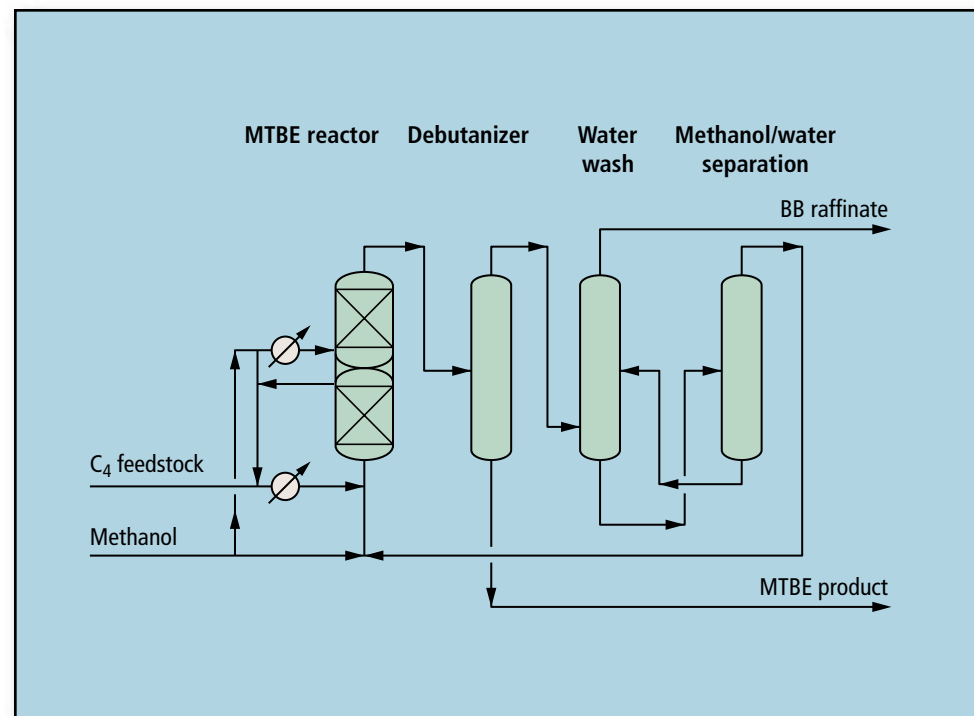
Description: The technology features a two-stage reactor system of which the first reactor is operated in the recycle mode. With this method, a slight expansion of the catalyst bed is achieved which ensures very uniform concentration profiles within the reactor and, most important, avoids hot spot formation.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

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

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

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

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



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

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

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

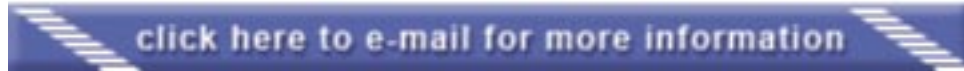
Steam, MP, kg	100
Electricity, kWh	35
Water, cooling, m ³	15
Steam, LP, kg	900

Continued ▼

Ethers—MTBE, *continued*

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

Licensors: Uhde GmbH.



Fluid catalytic cracking

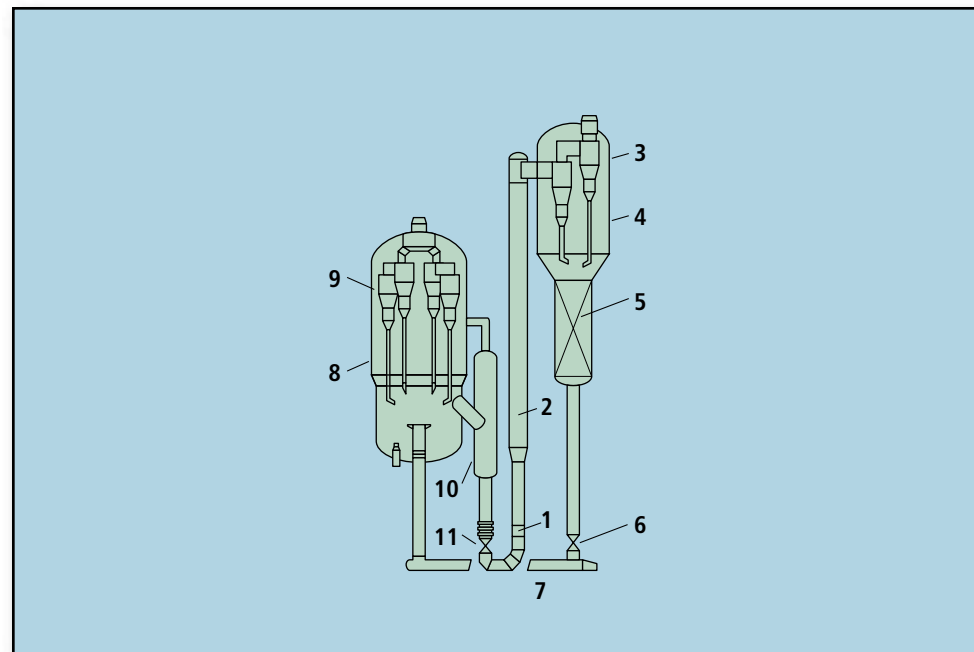
Application: Selective conversion of a wide range of gas oils into high-value products. Typical feedstocks are virgin or hydrotreated gas oils but may also include lube oil extract, coker gas oil and resid.

Products: High-octane gasoline, light olefins and distillate. Flexibility of mode of operation allows for maximizing the most desirable product. The new Selective Component Cracking (SCC) technology maximizes propylene production.

Description: The Lummus 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 (5).

Trace hydrocarbons entrained with spent catalyst are removed in the stripper using stripping steam. 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 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 2001.)

\$/bpsd (typical)	2,200–3,000
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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

Continued ▼

Fluid catalytic cracking, *continued*

Installation: Fourteen grassroots units in operation and one in design stage. Fifteen units revamped and two in design stage.

Licensors: ABB Lummus Global.



Fluid catalytic cracking

Application: To convert heavy distillates and residues into high-value products, including selective propylene production when required, using the Shell 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 back mixing at lower pressure drop.

Riser termination design incorporates reliable close-couple cyclones that provide rapid catalyst/hydrocarbon separation. It maximizes desired product yields, with no slurry clean up required. Stripping begins inside the first cyclone, followed by a high-capacity baffle structure.

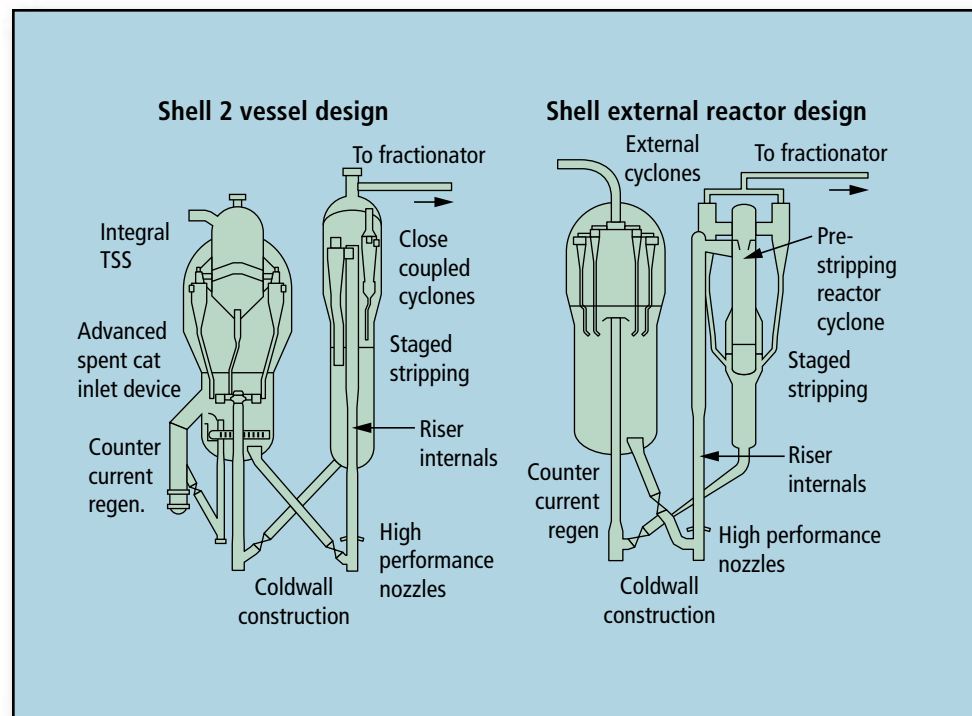
A single-stage partial or full-burn regenerator delivers excellent performance at low cost. Proprietary internals are used at the catalyst inlet to disperse catalyst, and the catalyst outlet to provide significant catalyst circulation enhancement. Catalyst coolers can be added for more feed-stock flexibility.

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.

Two FCC design options are available. The Shell 2 Vessel design is recommended to handle less heavy feeds with mild coking tendencies; the Shell External Reactor is preferred for heavy feeds with high coking tendencies. These designs are proven reliability champions due to simplicity of components and incorporation of Shell's extensive operating experience.

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

Supplier: Shell Global Solutions International B.V.



Fluid catalytic cracking

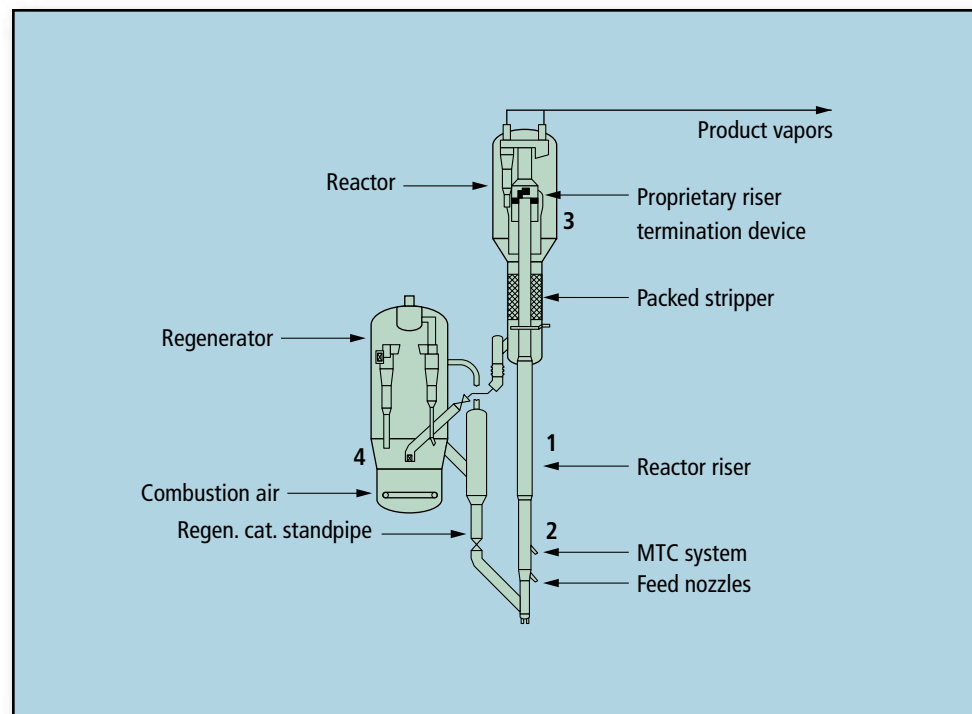
Application: Selective conversion of gas oil feedstocks.

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

Description: Catalytic and selective cracking in a short-contact-time riser (1) 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 (2). Reaction products exit the riser-reactor through a high-efficiency, close-coupled, proprietary riser termination device RS² (Riser Separator Stripper) (3). Spent catalyst is pre-stripped followed by an advanced high-efficiency packed stripper prior to regeneration. The reaction product vapor may be quenched using BP's proprietary technology 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 (4) 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 24 units and is licensed exclusively by Stone & Webster/Axens. As an alternative to catalyst cooling, this unit can easily be retrofitted to a two-regenerator system 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, wasteheat recovery, flue gas treatment and slurry filtration. Revamps incorporating proprietary feed injection and riser termination devices and vapor quench result in sub-



stantial improvements in capacity, yields and feedstock flexibility within the mechanical limits of the existing unit.

Installation: Stone & Webster and Axens have licensed 27 full-technology units and performed more than 150 revamp projects.

Reference: Letzsch, W. S., "1999 FCC Technology Advances," 1999 Stone & Webster Eleventh Annual Refining Seminar at NPRA Q&A, Dallas, Oct. 5, 1999.

Licensors: Stone & Webster Inc., a Shaw Group Co./Axens, IFP Group Technologies.

Fluid catalytic cracking

Application: Selectively convert gas oils and resid feedstocks into higher-value products using the FCC/RFCC/PETROFCC process.

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

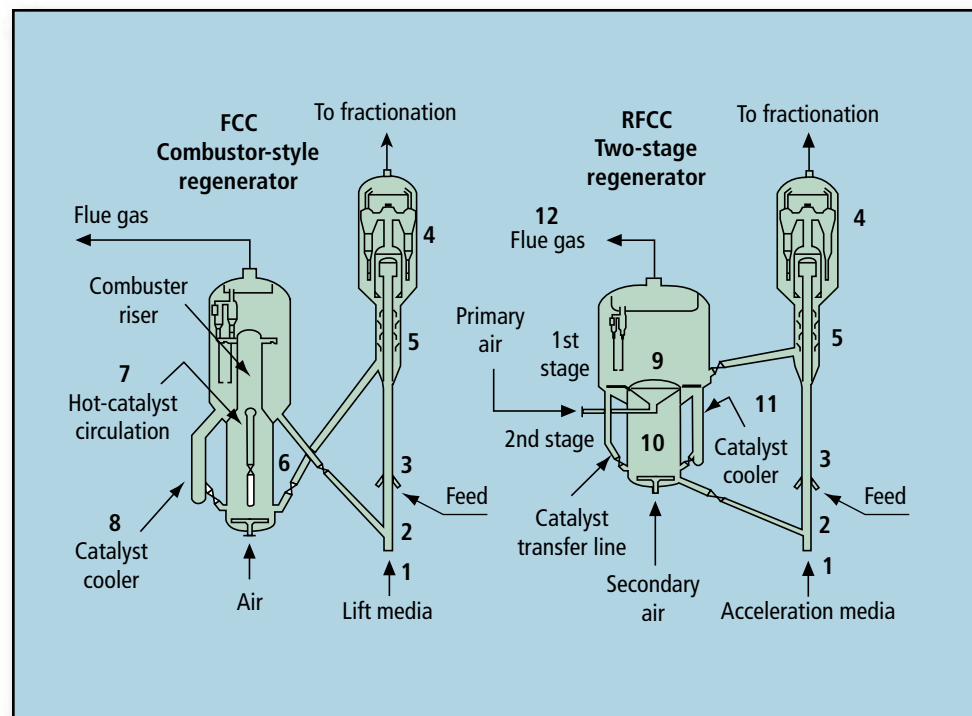
Description: The combustor-style unit is used to process gas oils and moderately contaminated resids, while the two-stage unit is used for more contaminated resids.

In either unit style, the reactor section is similar. An acceleration media of light hydrocarbons, steam or a mixture of both contacts regenerated catalyst at the base of the riser (1). This patented acceleration zone (2), with elevated Optimix feed distributors (3), enhances the yield structure by effectively contacting catalyst with finely atomized oil droplets.

The reactor zone features a short-contact-time riser and a state-of-the-art riser termination device (4) for quick separation of catalyst and vapor, with high hydrocarbon containment (VSS/VDS technology). This design offers high light olefin and gasoline yields and selectivity with low dry gas yields. Steam is used in an annular stripper (5) to displace and remove entrained hydrocarbons (AF stripper technology) from the catalyst. Existing units can be revamped to include these features (1–5).

The combustor-style regenerator (6) burns coke in a fast-fluidized environment completely to CO_2 with very low levels of CO. The circulation of hot catalyst (7) from the upper section to the combustor provides added control over the burn-zone temperature and kinetics and enhances radial mixing. Catalyst coolers (8) can be added to new and existing units to reduce catalyst temperature and increase unit flexibility for commercial operations of feeds up to 6 wt% Conradson carbon.

For heavier resid feeds, the two-stage regenerator is used. In the first stage, upper zone (9), the bulk of the carbon is burned from the catalyst, forming a mixture of CO and CO_2 . Catalyst is transferred to the second stage, lower zone (10), where the remaining coke is burned in complete combustion, producing low levels of carbon on regener-



ated catalyst. A catalyst cooler (11) is located between the stages. This configuration maximizes oxygen use, requires only one train of cyclones and one flue gas stream (12), avoids costly multiple flue gas systems and creates a hydraulically-simple and well-circulating layout. The two-stage regenerator system has processed feeds up to 10 wt% Conradson carbon.

PETROFCC is a customized application using mechanical features such as RxCAT technology for recontacting carbonized catalyst, high-severity processing conditions and selected catalyst and additives to produce high yields of propylene, light olefins and aromatics for petrochemical applications.

Installations: All of UOP's technology and equipment are commercially proven for both process performance and mechanical reliability. UOP

Fluid catalytic cracking, *continued*

has been an active designer and licensor of FCC technology since the early 1940s and has licensed more than 215 FCC, Resid FCC, and MSCC process units. Today, more than 150 of these units are operating world-wide. In addition to applying our technology and skills to new units, UOP is also extensively involved in the revamping of existing units. During the past 15 years, UOP's FCC Engineering department has undertaken 40 to 60 revamp projects or studies per year.

Licensor: UOP LLC.



Fluid catalytic cracking

Application: Conversion of gas oils and residues to high-value products using the efficient and flexible Orthoflow catalytic cracking process.

Products: Light olefins, high-octane gasoline, and distillate.

Description: The converter is a one-piece modularized unit that efficiently combines KBR's proven Orthoflow features with ExxonMobil's advanced design features. Regenerated catalyst flows through a wye (1) to the base of the external vertical riser (2). Feed enters through the proprietary ATOMAX-2 feed injection system. Reaction vapors pass through a patented right-angle turn (3) and are quickly separated from the catalyst in a patented closed-cyclone system (4). Spent catalyst flows through a two-stage stripper equipped with DynaFlux baffles (5) to the regenerator (6) where advanced catalyst distribution and air distribution are used. Either partial or complete CO combustion may be used in the regenerator, depending on the coke-forming tendency of the feedstock. The system uses a patented external flue gas plenum (7) to improve mechanical reliability. Catalyst flow is controlled by one slide valve (8) and one plug valve (9). An advanced dense-phase catalyst cooler (10) is used to optimize profitability when heavier feeds are processed.

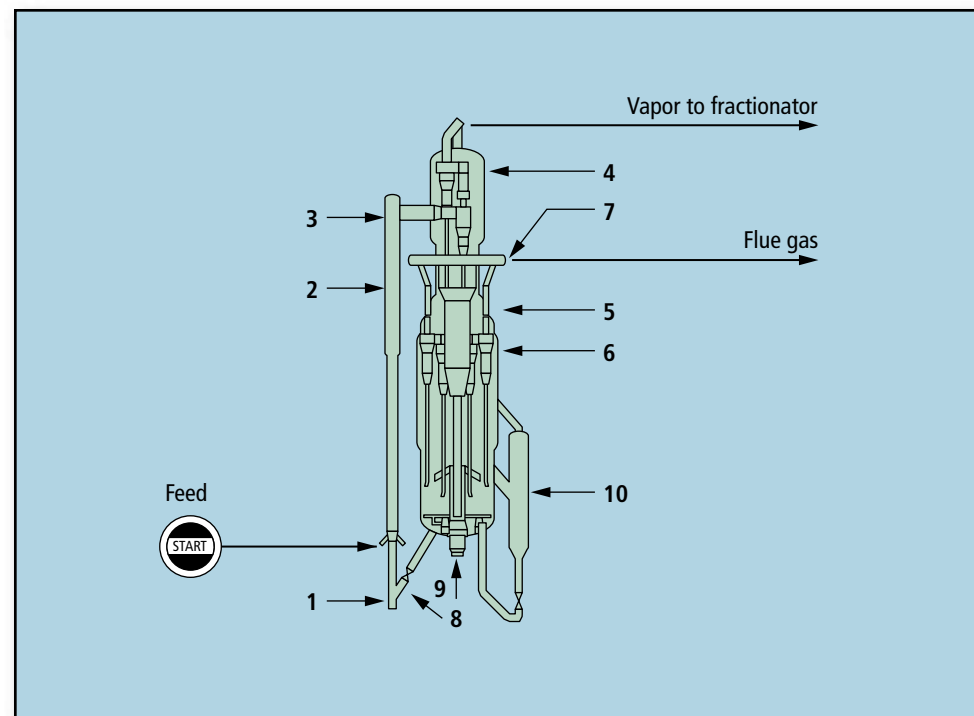
Economics:

Investment (basis: 50,000-bpsd fresh feed including converter, fractionator, vapor recovery and amine treating, but not power recovery; battery limit, direct material and labor, 2002 Gulf Coast)
\$ per bpsd 1,950–2,150

Utilities, typical per bbl fresh feed
Electricity, kWh 0.7–1.0
Steam, 600 psig (produced) lb 40–200

Catalyst, makeup, lb/bbl 0.10–0.15

Maintenance, % of plant replacement cost/yr 3



Installation: More than 150, resulting in a total of over 4 million bpd fresh feed, with 20 designed in the past 12 years.

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

"RegenMax technology: staged combustion in a single regenerator," NPRA 1999 Annual Meeting, March 1999.

Licensors: Kellogg Brown & Root, Inc.

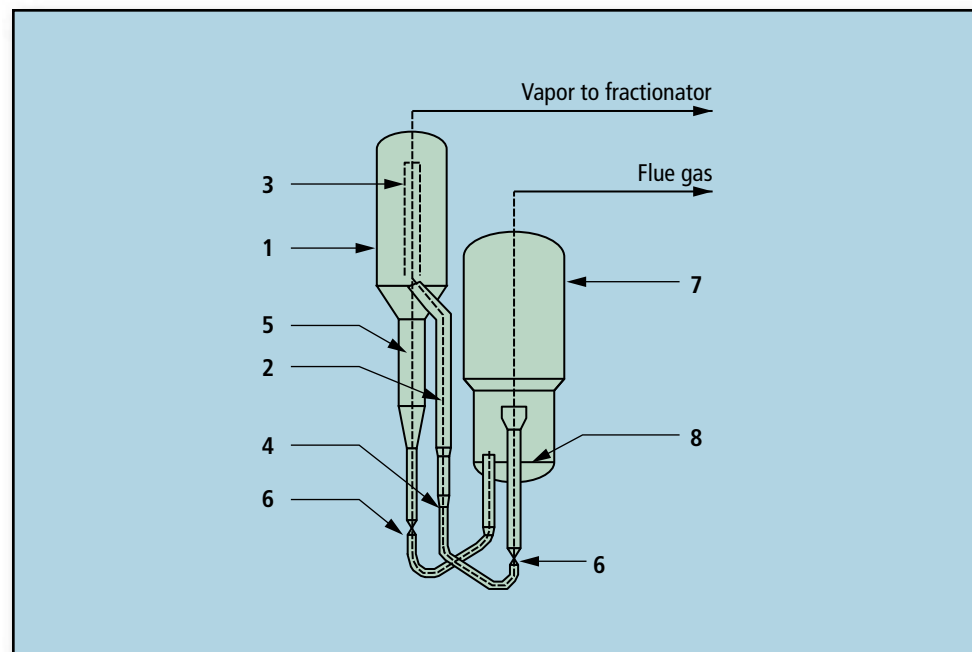
Fluid catalytic cracking

Application: FLEXICRACKING IIIR converts high-boiling hydrocarbons including residues, gas oils, lube extracts and/or deasphalted oils to higher value products.

Products: Light olefins for gasoline processes and petrochemicals, LPG, blend stocks for high-octane gasoline, distillates and fuel oils.

Description: The FLEXICRACKING IIIR technology includes process design, hardware details, special mechanical and safety features, control systems, flue gas processing options and a full range of technical services and support. The reactor (1) incorporates many features to enhance performance, reliability and flexibility, including a riser (2) with patented high-efficiency close-coupled riser termination (3), enhanced feed injection system (4) and efficient stripper design (5). The reactor design and operation maximizes the selectivity of desired products, such as naphtha and propylene.

The technology uses an improved catalyst circulation system with advanced control features, including cold-walled slide valves (6). The single vessel regenerator (7) has proprietary process and mechanical features for maximum reliability and efficient air/catalyst distribution and contacting (8). Either full or partial combustion is used. With increasing residue processing and the need for additional heat balance control, partial burn operation with outboard CO combustion is possible, or KBR dense phase catalyst cooler technology may be applied. The ExxonMobil wet gas scrubbing or the ExxonMobil-KBR Cyclofinex TSS technologies can meet flue gas emission requirements.



Yields: Typical examples:

	Resid feed mogas operation	VGO + lube extracts distillate operation	VGO feed mogas operation
Feed			
Gravity, °API	22.9	22.2	25.4
Con carbon, wt%	3.9	0.7	0.4
Quality	80% Atm. Resid (Hydrotreated)	20% Lube Extracts	50% TBP-794°F
Product yields			
Naphtha, lv% ff (C ₄ /FBP)	78.2 (C ₄ /430°F)	40.6 (C ₄ /260°F)	77.6 (C ₄ /430°F)
Mid Dist., lv% ff (IBP/FBP)	13.7 (430/645°F)	49.5 (260/745°F)	19.2 (430/629°F)

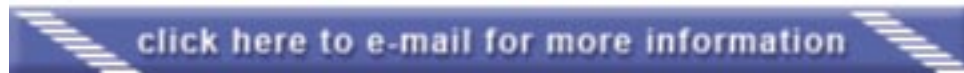
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Fluid catalytic cracking, *continued*

Installation: More than 70 units with a design capacity of over 2.5-million bpd fresh feed.

References: Ladwig, P. K., "Exxon FLEXICRACKING IIIR fluid catalytic cracking technology," *Handbook of Petroleum Refining Processes*, Second Ed., R. A. Meyers, Ed., pp. 3.3–3.28.

Licensors: ExxonMobil Research and Engineering Co. and Kellogg Brown & Root, Inc. (KBR).



Fluid catalytic cracking—pretreatment

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

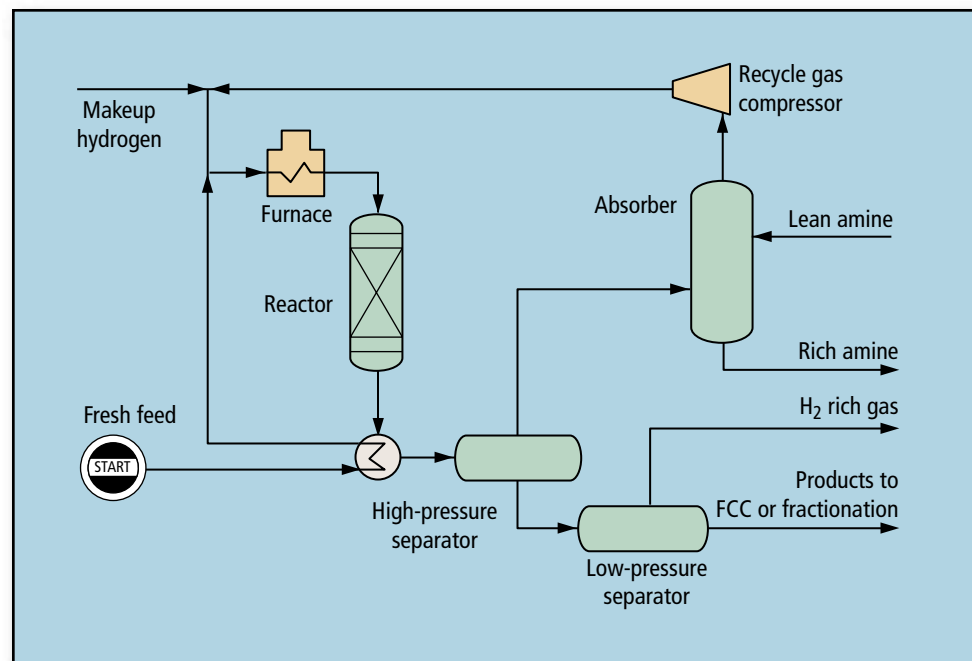
Objectives: The processing objectives range from deep desulfurization for meeting gasoline-sulfur specifications from the FCC products, to denitrogenation and metals removal, thus maximizing FCC catalyst activity. Additional objectives can include Conradson carbon reduction and saturation of polyaromatics 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 enabled refiners to directly blend gasoline produced from the FCC and meet future low-sulfur (less than 30 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-558, a CoMo catalyst with high desulfurization activity, and TK-559, a NiMo catalyst with hydrodesulfurization and hydrodenitrogenation activity. Topsøe offers a wide range of engineering scopes from scoping studies, reactor design packages and process design packages to engineering design packages.



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

References: Patel R., H. Moore and B. Hamari, "FCC hydrotreater re-vamp for low-sulfur gasoline," NPRA Annual Meeting, San Antonio, March 21–23, 2004.

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

Installations: Four units are operating in the US.

Licensor: Haldor Topsøe A/S.

Gas treating—H₂S removal

Application: Remove H₂S selectively, or remove a group of acidic impurities (H₂S, CO₂, COS, CS₂ and mercaptans) from a variety of streams, depending on the solvent used. FLEXSORB SE technology has been used in refineries, natural gas production facilities and petrochemical operations.

FLEXSORB SE or SE Plus solvent is used on: hydrogenated Claus plant tail gas to give H₂S, ranging down to H₂S <10 ppmv; pipeline natural gas to give H₂S <0.25 gr/100 scf; or Flexicoking low-Btu fuel gas. The resulting acid gas byproduct stream is rich in H₂S.

Hybrid FLEXSORB SE solvent is used to selectively remove H₂S, as well as organic sulfur impurities commonly found in natural gas.

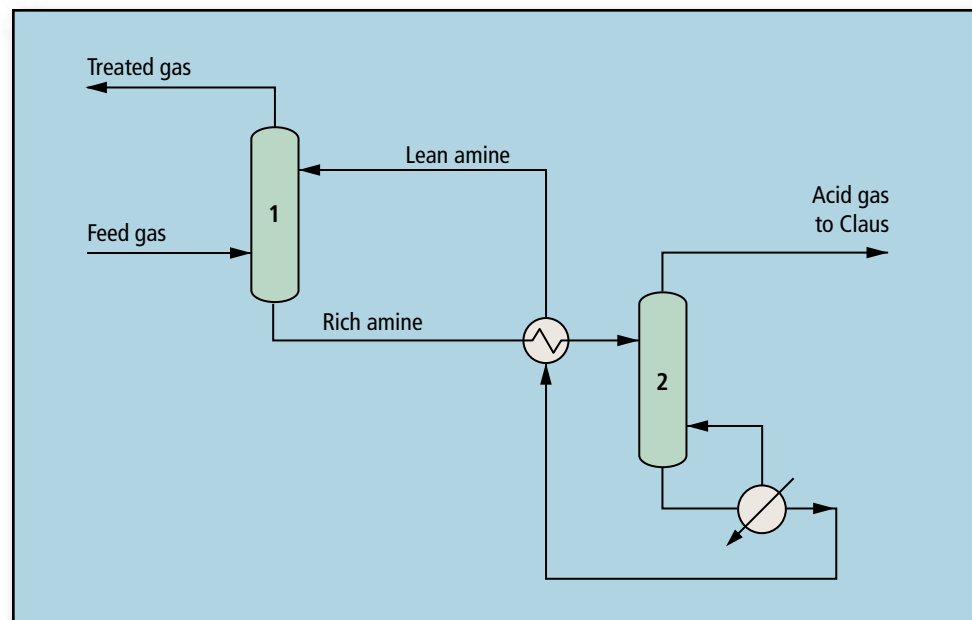
FLEXSORB PS solvent yields a treated gas with: H₂S <0.25 gr/100 scf, CO₂ <50 ppmv, COS and CS₂ <1 ppmv, mercaptans removal >95%. This solvent is primarily aimed at natural gas or syngas cleanup. The byproduct stream is concentrated acid gases.

Description: A typical amine system flow scheme is used. The feed gas contacts the treating solvent in the absorber (1). The resulting rich solvent bottom stream is heated and sent to the regenerator (2). Regenerator heat is supplied by any suitable heat source. Lean solvent from the regenerator is sent through rich/lean solvent exchangers and coolers before returning to the absorber.

FLEXSORB SE solvent is an aqueous solution of a hindered amine. FLEXSORB SE Plus solvent is an enhanced aqueous solution, which has improved H₂S regenerability yielding <10 vppm H₂S in the treated gas. Hybrid FLEXSORB SE solvent is a hybrid solution containing FLEXSORB SE amine, a physical solvent and water. FLEXSORB PS solvent is a hybrid consisting of a different hindered amine, a physical solvent and water.

Economics: Lower investment and energy requirements based primarily on requiring 30% to 50% lower solution circulation rates.

Installations: Total gases treated by FLEXSORB solvents are about 2 billion scfd and the total sulfur recovery is about 900 long tpd.



FLEXSORB SE—31 plants operating, two in design

FLEXSORB SE Plus—16 plants operating, two startups in 2004, six in design

Hybrid FLEXSORB SE—two plants operating, two in design

FLEXSORB PS—four plants operating.

Reference: Garrison, J., et al., "Keyspan Energy Canada Rimbey acid gas enrichment with FLEXSORB SE Plus technology," 2002 Laurance Reid Gas Conditioning Conference, Norman, Oklahoma.

Adams-Smith, J., et al., Chevron USA Production Company, "Carter Creek Gas Plant FLEXSORB tail gas treating unit," 2002 GPA Annual Meeting, Dallas.

Fedich, R., et al., "Selective H₂S Removal," *Hydrocarbon Engineering*, May 2004.

Licensors: ExxonMobil Research and Engineering Co.

[click here to e-mail for more information](#)

Gasification

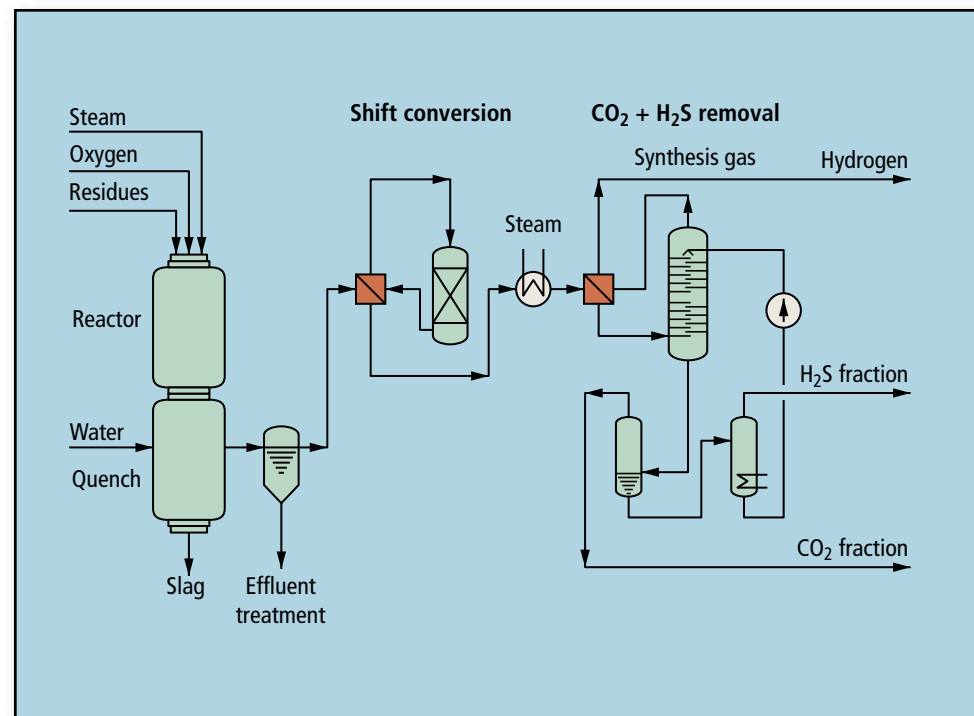
Application: The FUTURE ENERGY (FE) Gasification process (formerly known as the "GSP" process or "NOELL" process and now owned by FE) processes liquid, solid or gaseous waste materials from the refinery (petcoke, heavy residues), chemical industry and coals (hard coal, lignite) into a clean, tar-free synthesis gas, which can be further converted into value materials such as methanol, hydrogen, fertilizers or energy. Byproducts are a vitrified granulated slag, elemental sulfur and soluble heavy metal sulfides recovered in the wastewater treatment.

Due to the reducing atmosphere prevailing in all process stages, gasification, in contrast to incineration, allows treatment of waste materials and residues meeting high environmental standards and to utilize the product syngas for chemical production or power generation. Toxic components are decomposed, and there will not be a de-novo synthesis.

Description: The basic version of FE's entrained-flow gasifier was developed for the gasification of pulverized brown coal. Later, this gasifier technology was shaped up for the universal use of ash-containing fuels. The reactants are fed to the gasifier via special-design burners on top of the reaction chamber and are converted in a flame reaction.

The oxygen-to-fuel ratio is trimmed to keep the gasification temperature at a level at which the inorganic matter melts and flows vertically downward in parallel with the gasification gas and leaves the gasifier through a special discharge unit. Carbon conversion rates of more than 99% are achieved. Dependent on the further use of the gas produced, a direct-contact water-spray-quench system or an indirect-cooling heat recovery steam generator system can be installed downstream of the gasifier.

The gasification chamber is enclosed by a cooling screen which consists of gas-tight welded cooling tubes. These are studded and refractory-lined with a thin layer of a special SiC ramming mass. Liquid slag on this cooling screen cools down and solidifies and forms a compact slag layer that performs similar to a refractory lining. The solidified slag layer grows in thickness until the ash-fusion temperatures are exceeded.



Slag then hitting the wall remains in liquid condition, flows downward the wall and discharges at the bottom together with the gasification gas. The reactor design with cooling screen described requires gasification feeds with ash contents of more than 1 wt% allowing the solidified slag layer to constantly regenerate. This is not given if the ash content is lower. In this case, a cooling wall reactor design is used, where a refractory lining replaces the missing slag layer. A water jacket is substituted for the tube screen.

Economics: Unit costs are very much dependent on the value/tipping fee of the feed material and the total plant design, as well as the final product/single processing steps desired.

Gasification, *continued*

Installations: The FE gasifier has been operating successfully at SVZ Schwarze Pumpe, Spreeetal/Spreewitz, Germany, since 1984, first on brown coal and then on sludges, ash-containing oils and slurries. The cooling screen design ensures long gasifier availability periods before requiring repair or relining. Over eight years, it has been proven on an industrial scale. Compared with a conventional refractory lining, the cooling screen is insensitive to high ash content or fluctuating ash composition. The gasifier can be started up or shut down within a few minutes.

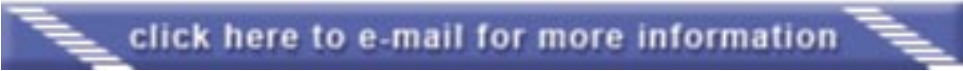
A further example is the Seal Sands gasification facility, Middlesbrough, UK, of BASF plc., which was constructed to process 110,000 tpy of liquid waste (mixtures of nitriles and amines, as well as cyanide and ammonia compounds). A 140 MWth Autothermal Oil Conversion Plant for Sokolovská uhelná, a.s., Vresová, Czech Republic, is under construction.

References: "Gasification—An opportunity to design environmentally compatible processes in the chemical and pulp & paper industry," *Chem. Eng. Technology*, Vol. 26 (2003), Wiley-VCH, Verlag, Weinheim.

"Experience during erection and commissioning of the gasification plant Seal Sands, UK," 2001 Gasification Technologies Conference, San Francisco, Oct. 7–10, 2001.

"Gasification of solids bearing tars in the entrained flow gasifiers of FUTURE ENERGY," 6th European Gasification Conference, Brighton, May 10–12, 2004.

Licensors: FUTURE ENERGY GmbH.



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Gasification

Application: The GE Gasification Process (formerly known as the Texaco Gasification Process) converts residual liquid refinery bottoms streams containing high sulfur and metals to hydrogen, fuel gas, chemical synthesis gas ($\text{CO} + \text{H}_2$) and high-pressure steam. Refinery liquid-waste streams may be used as supplemental feed. A coke water slurry may also be used as an alternate feed.

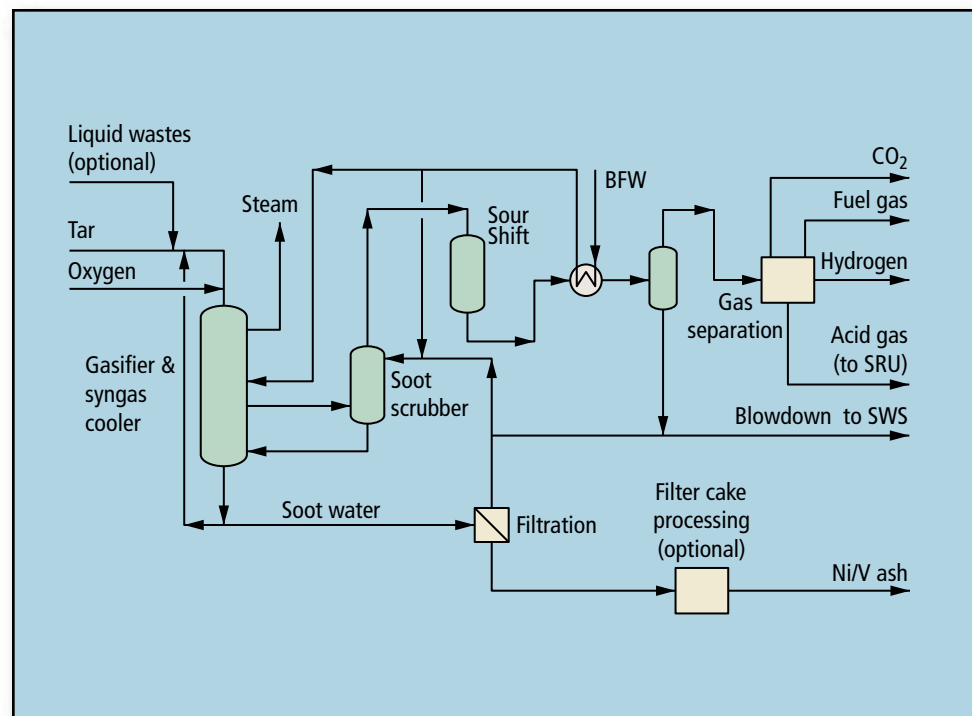
The sulfur is removed as H_2S compatible with standard refinery sulfur recovery units (SRUs) or acid-gas reinjection. Metals are removed in a filter cake, which may be optionally processed (offsite or onsite) for nickel (Ni) and vanadium (V) recovery. If desired up to 95% of the carbon in the feed can be recovered as a byproduct purified- CO_2 stream compatible with enhanced oil or gas recovery.

The process converts the lowest value residual streams—visbreaker tar, deasphalter tar or coke—into high-value products. Typically 80–90% of the energy in the tar is recovered in product and HP-export steam streams. Fuel gas produced in gasification is well suited for combustion turbines. It has a higher mass flow than natural gas and typically generates 10–20% more power than natural gas in a combustion turbine. The gasification process is an environmentally acceptable and energy efficient solution for residual refinery bottoms streams.

Products: Hydrogen, synthesis gas ($\text{CO} + \text{H}_2$), fuel gas, sulfur (as acid gas) and filter cake (for metals recovery).

Process: Liquid-bottoms tar stream is mixed with hot soot water and fed with oxygen to the pressurized refractory-lined gasifier. The gasifier operates at high pressure (400–800 psig) and temperatures (2,300–2,700°F), which breaks down all hydrocarbons into CO and H_2 with a small amount of soot (unconverted carbon) and ash. Gasifier pressures up to 1,250 psig are possible in an alternate water-quench design.

A syngas cooler chills the gasifier outlet gas and produces high-pressure steam (up to 2,000 psig). The cooled gas is scrubbed with water



to remove the soot and ash. All or a portion of the moisturized gas is reacted in a fixed-bed catalytic shift reactor; CO reacts with steam to produce additional hydrogen and CO_2 . This allows the adjustment of the H_2/CO ratio in the syngas to any value greater than 1. More heat is recovered from the exothermic-shift reaction by superheating steam and economizing boiler feedwater. Excess condensate is blown down to an offsite sour-water stripper (SWS).

The dry gas is then separated into its various components using conventional amine, physical solvent or cryogenic gas separations. A conventional PSA unit is used for final hydrogen purification.

A portion of the byproduct soot water is recycled to the gasifier; the remainder is filtered to remove the soot and ash. The filter cake can be

Gasification, *continued*

optionally processed using commercial metals reclaiming processes to recover the Ni and V.

Yields:

Feed, source	Maya Crude	Oil Sands
Type	SDA Tar	Visbr Tar
API	-4.4	0
Sulfur, wt%	7	7
Ni + V, ppm	1,200	600
Products		
Hydrogen, Mscf/bbl	14	14
CO ₂ , tons/bbl	0.5	0.5
Fuel gas, 10 ⁶ Btu/bbl	0.8	0.8

Economics:

Investment , \$ per bpsd	16,000	14,000
(basis 10,000 bpsd, on plot facilities only, exclude contingency, owner's cost, sales tax 1st Q, 2004, US Gulf)		

Utilities , typical per bbl feed		
Steam SH HP, export, lb	500	600
Steam Sat'd LP, cons, lb	0	100
Power (excl CO ₂ compression), kWh	12	12
Oxygen, tons	0.2	0.2
Water, cooling, gal	1,800	1,400

Installation: More than 50 resid-bottoms units utilizing the GE Gasification Process are in commercial operation worldwide in various applications including hydrogen production, combustion turbine fuel gas production and syngas for chemical synthesis.

Licensors: GE Energy.

[click here to e-mail for more information](#)

Gasification

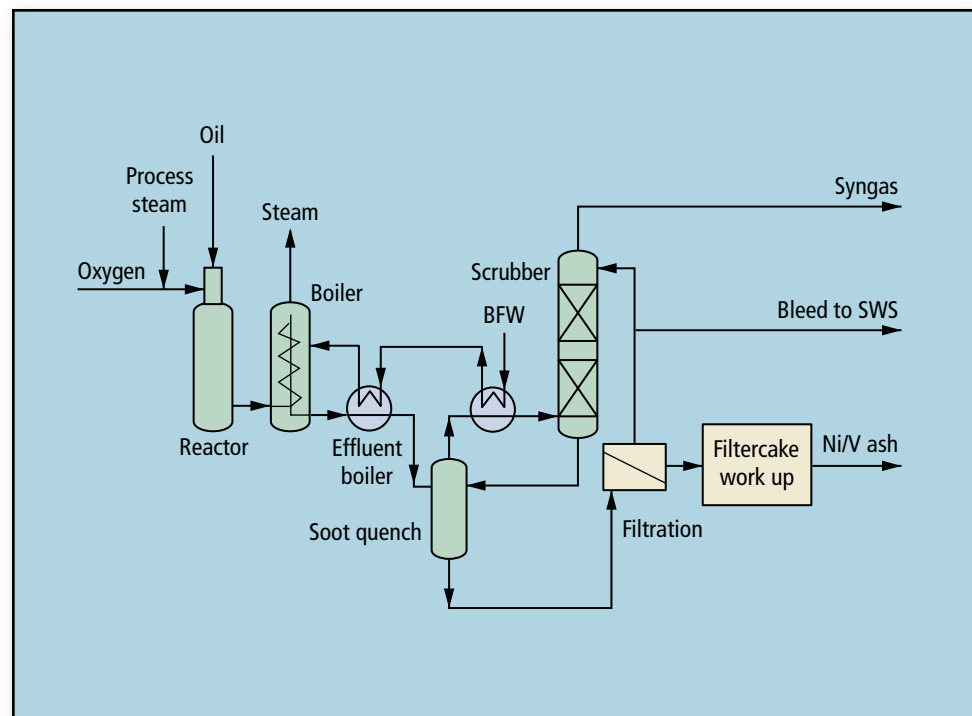
Application: The Shell Gasification Process (SGP) converts the heaviest residual liquid hydrocarbon streams with high-sulfur and metals content into a clean synthesis gas and valuable metal oxides. Sulfur (S) is removed by normal gas treating processes and sold as elemental S.

The process converts residual streams with virtually zero value as fuel-blending components into valuable, clean gas and byproducts. This gas can be used to generate power in gas turbines and for making H₂ by the well-known shift and PSA technology. It is one of the few ultimate, environmentally acceptable solutions for residual hydrocarbon streams.

Products: Synthesis gas (CO+H₂), sulfur and metal oxides.

Process description: Liquid hydrocarbon feedstock (from very light such as natural gas to very heavy such as vacuum flashed cracked residue, VFCR and asphalt) is fed into a reactor, and gasified with pure O₂ and steam. The net reaction is exothermic and produces a gas primarily containing CO and H₂. Depending on the final syngas application, operating pressures, ranging from atmospheric up to 65 bar, can easily be accommodated. SGP uses refractory-lined reactors that are fitted with both burners and a heat-recovery-steam generator, 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, the ash components are recovered as valuable oxides—principally vanadium pentoxide. The (clean) filtrate is returned to the scrubber.



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.

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 latest, flagship installation is in the Shell Pernis refinery near Rotterdam, The Netherlands. This highly complex refinery depends on the SGP process for its H₂ supply. Similar projects are underway in Canada and Italy.

The Demkolec Power plant at Buggenum, The Netherlands produces 250 Mwe based on the SCGP process. The Shell middle distillate

Gasification, *continued*

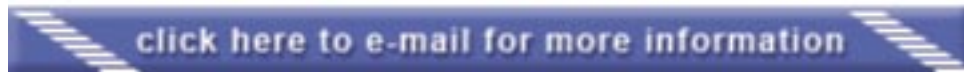
synthesis plant in Bintulu, Malaysia, uses SGP to convert 100 million scfd of natural gas into synthesis gas that is used for petrochemical applications.

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.

Licensors: Shell Global Solutions International B.V.



Gasoline desulfurization

Application: Convert high-sulfur gasoline streams into a low-sulfur gasoline blendstock while minimizing octane loss, yield loss and operating cost using S Zorb sulfur removal technology.

Products: A zero sulfur blending stock for gasoline motor fuels.

Description: Gasoline from the fluid catalytic cracker unit is combined with a small hydrogen stream and heated. Vaporized gasoline is injected into the fluid-bed reactor (1), where the proprietary sorbent removes sulfur from the feed. A disengaging zone in the reactor removes suspended sorbent from the vapor, which exits the reactor to be cooled.

Regeneration: The sorbent (catalyst) is continuously withdrawn from the reactor and transferred to the regenerator section (2), where the sulfur is removed as SO_2 and sent to a sulfur-recovery unit. The cleansed sorbent is reconditioned and returned to the reactor. The rate of sorbent circulation is controlled to help maintain the desired sulfur concentration in the product.

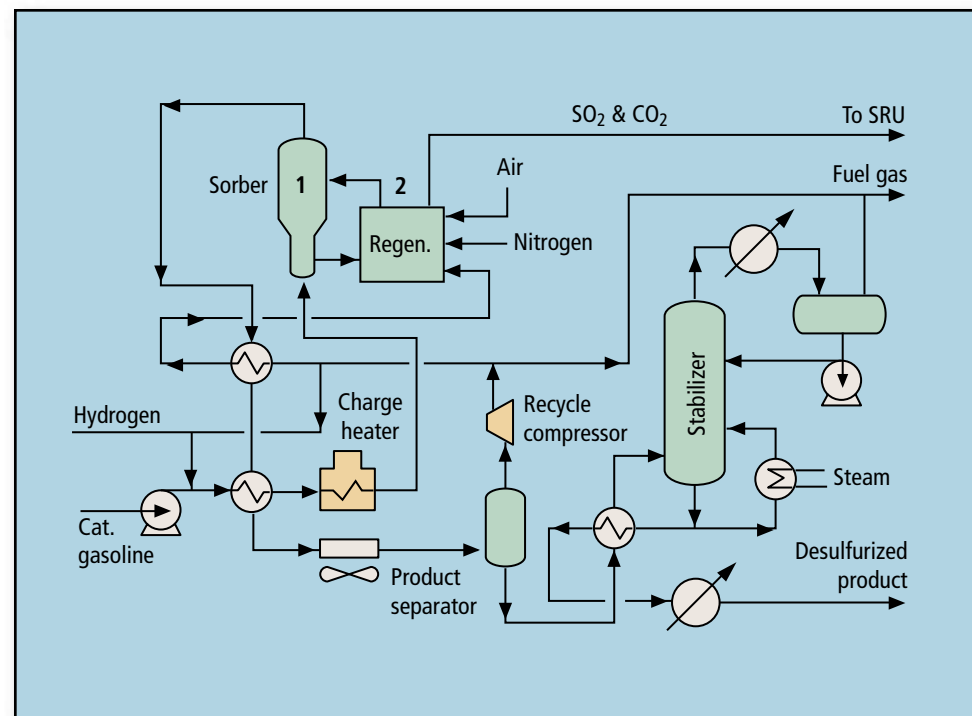
Economics:

Typical operating conditions:

Temperature, °F	750–825
Pressure, psig	100–500
Space velocity, whsv	4–8
Hydrogen purity, %	70–99
Total H_2 usage, scf/bbl	40–60

Case study premises:

25,000-bpd feed
775-ppm feed sulfur
25-ppm product sulfur (97% removal)
No cat gasoline splitter



Results:

C_5+ yield, vol% of feed	>100%
Lights yield, wt% of feed	< 0.1
<u>(R+M) loss</u>	
2	<0.3
Operating cost, ¢/gal*	0.9

* Includes utilities, 4% per year maintenance and sorbent costs.

Installation: Forty-three sites licensed as of 1Q 2004.

Licensors: Technology Solutions Division of ConocoPhillips.

Gasoline desulfurization, ultra-deep

Application: Ultra-deep desulfurization of FCC gasoline with minimal octane penalty using Prime-G+ process.

Description: FCC debutanizer bottoms are fed directly to a first reactor wherein, under mild conditions, diolefins are selectively hydrogenated and mercaptans are converted to heavier sulfur species. The selective hydrogenation reactor effluent is then usually split to produce an LCN (light cat naphtha) cut and an HCN (heavy cat naphtha).

The LCN stream is mercaptans-free with a low-sulfur and diolefin concentration, enabling further processing in an etherification or alkylation unit. The HCN then enters the main Prime-G+ section where it undergoes in a dual catalyst reactor system; a deep HDS with very limited olefins saturation and no aromatics losses produces an ultra-low-sulfur gasoline.

The process provides flexibility to advantageously co-process other sulfur-containing naphthas such as light coker naphtha, steam cracker naphtha or light straight-run naphtha.

Industrial results:

Full-range FCC Gasoline, 40°C–220°C

	Feed	Prime-G+ Product
Sulfur, ppm	2,100	50*
(RON + MON)/2	87.5	86.5
Δ (RON + MON)/2		1.0
% HDS		97.6

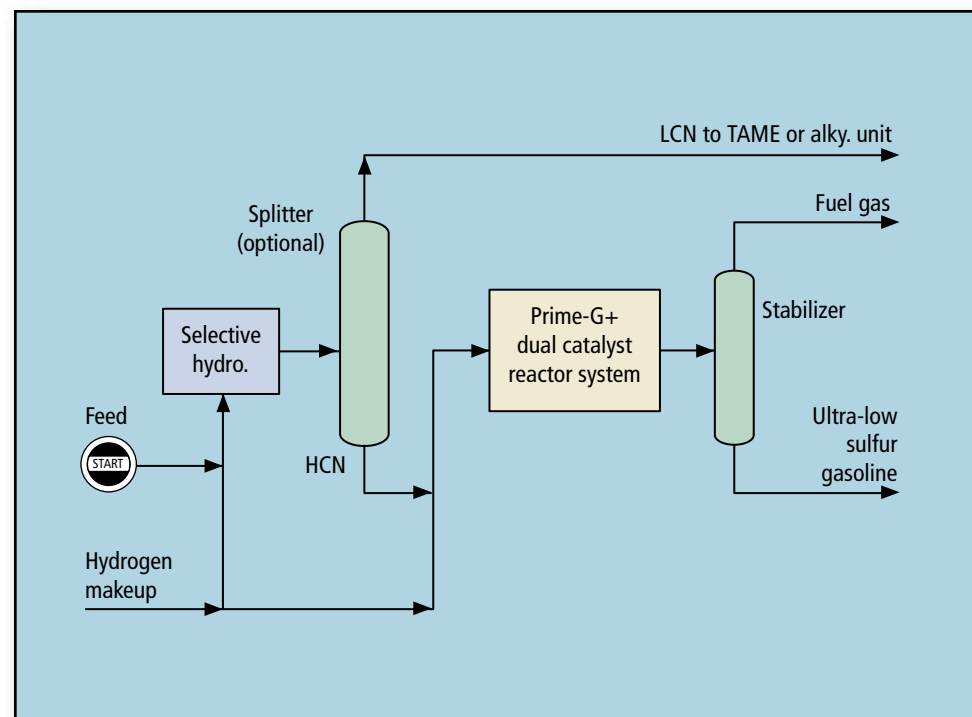
≤ 30 ppm pool sulfur after blending

Pool sulfur specifications as low as less than 10 ppm are attained with the Prime-G+ process in two units in Germany.

Economics:

Investment: Grassroots ISBL cost, \$/bpsd 600–800

Installation: Ninety-two units have been licensed for a total capacity of 2.4 million bpsd. Thirty-two Prime-G+ units are already in operation, pro-



ducing ultra-low-sulfur gasoline. Twenty other units will come onstream at the end of 2004.

OATS process: In addition to the Prime-G+ technology, the OATS (olefins alkylation of thiophenic sulfur), initially developed by BP, is also exclusively offered for license by Axens for ultra-low-sulfur gasoline production.

Reference: "Prime-G+: From pilot to start-up of world's first commercial 10 ppm FCC gasoline desulfurization process," NPRA Annual Meeting, March 17–19, 2002, San Antonio.

Licensors: Axens.

Gasoline desulfurization, ultra-deep

Application: Reduce sulfur in gasoline to less than 10 ppm by hydrodesulfurization followed by cracking and isomerization to recover octane with the OCTGAIN process.

Description: The basic flow scheme of the OCTGAIN process is similar to that of a conventional naphtha hydrotreater. Feed and recycle hydrogen mix is preheated in feed/effluent exchangers and a fired heater then introduced into a fixed-bed reactor. Over the first catalyst bed, the sulfur in the feed is converted to hydrogen sulfide (H_2S) with near complete olefin saturation. In the second bed, over a different catalyst, octane is recovered by cracking and isomerization reactions. The reactor effluent is cooled and the liquid product separated from the recycle gas using high- and low-temperature separators.

The vapor from the separators is combined with makeup gas, compressed and recycled. The liquid from the separators is sent to the product stripper where the light ends are recovered overhead and desulfurized naphtha from the bottoms. The product sulfur level can be as low as 5 ppm. The OCTGAIN process can be retrofitted into existing refinery hydrotreating units. The design and operation permit the desired level of octane recovery and yields.

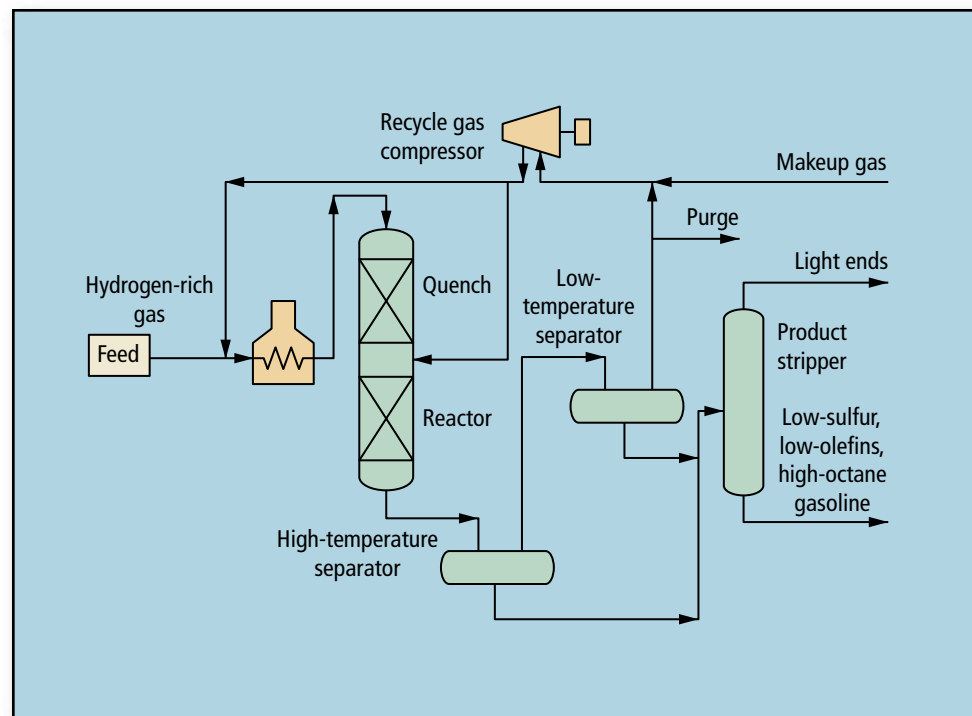
EMRE has an alliance with Kellogg Brown & Root (KBR) to provide this technology to refiners.

Yields: Yield depends on feed olefins and desired product octane.

Installations: Commercial experience with two operating units.

Reference: Halbert, T., et al., "Technology Options For Meeting Low-Sulfur Mogas Targets," NPRA Annual Meeting, March 2000.

Licensors: ExxonMobil Research and Engineering (EMRE) Co.



Gasoline desulfurization, ultra-deep

Application: Reduce sulfur in FCC gasoline to levels as low as <10 wppm by selective hydrotreating to maximize octane retention with the SCANfining technology.

Description: The feed is mixed with hydrogen, heated with reactor effluent exchange and passed through a pretreat reactor for diolefin saturation. After further heat exchange with reactor effluent and preheat using a utility, the hydrocarbon/hydrogen mixture enters the main reaction section which features ExxonMobil Research and Engineering Co. (EMRE) proprietary selective catalyst systems. In this section of the plant, sulfur is removed in the form of H_2S under tailored process conditions, which strongly favor hydrodesulfurization while minimizing olefin saturation.

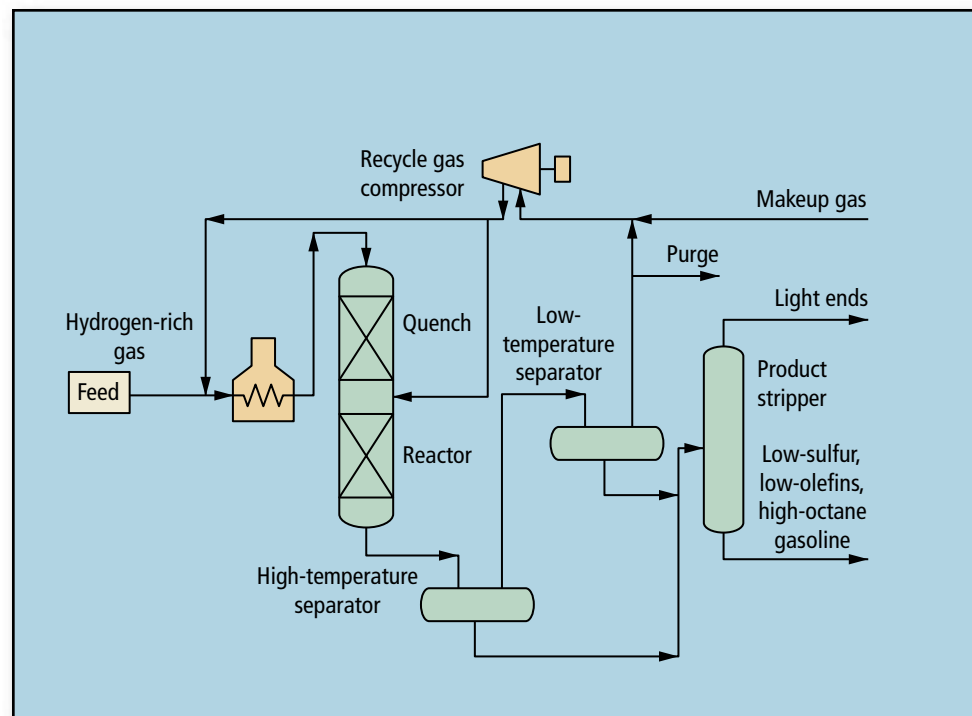
The feed may be full-range, intermediate or heavy FCC-naphtha fraction. Other sulfur-containing streams such as light-coker naphtha, steam cracker or light straight-run naphthas can also be processed with FCC naphthas. SCANfining technology can be retrofitted to existing units such as naphtha or diesel hydrotreaters and reformers. SCANfining technology also features ExxonMobil's proprietary reactor internals such as Automatic Bed Bypass Technology for onstream mitigation of reactor plugging/pressure drop buildup.

For high-sulfur feeds and/or very low-sulfur product, with low levels of product mercaptans variations in the plant design from SCANfining I Process to the SCANfining II Process for greater HDS selectivity, or addition of a ZEROMER process step for mercaptan conversion, or addition of an EXOMER process unit for mercaptan extraction.

EMRE has an alliance with Kellogg Brown & Root (KBR) to provide SCANfining technology to refiners and an alliance with Merichem Chemicals & Refinery Services LLC to provide EXOMER technology to refiners.

Yields: Yield of C_5+ liquid product is typically over 100 LV%.

Installation: Thirty-one units under design, construction or operation



having combined capacity of over 900,000 bpsd.

References: Sapre, A.V., et al., "Case History: Desulfurization of FCC naphtha," *Hydrocarbon Processing*, February 2004.

Ellis, E. S., et al., "Meeting the Low Sulfur Mogas Challenge," World Refining Association Third European Fuels Conference, March 2002.

Licensors: ExxonMobil Research and Engineering Co.

H₂S and SWS gas conversion

Application: The ATS process recovers H₂S and NH₃ in amine regenerator offgas and sour water stripper gas (SWS gas) as a 60% aqueous solution of ATS—ammonium thiosulfate (NH₄)₂S₂O₃, which is the standard commercial specification. The ATS process can be combined with a Claus unit; thus increasing processing capacity while obtaining a total sulfur recovery of >99.95%. The ATS process can also handle SWS gas alone without ammonia import while the S/N balance is adjusted by exchanging H₂S surplus and deficit with a Claus unit.

ATS is increasingly used as a fertilizer (12-0-0-26S) for direct application and as a component in liquid fertilizer formulations.

Description: Amine regenerator off gas is combusted in a burner/waste heat boiler. The resulting SO₂ is absorbed with ammonia in a two-stage absorber to form ammonium hydrogen sulfite (AHS). NH₃ and H₂S contained in the SWS gas plus imported ammonia (if required) is reacted with the AHS solution in the ATS reactor. The ATS product is withdrawn as a 60% aqueous solution that meets all commercial specifications for usage as a fertilizer. Unreacted H₂S is returned to the H₂S burner.

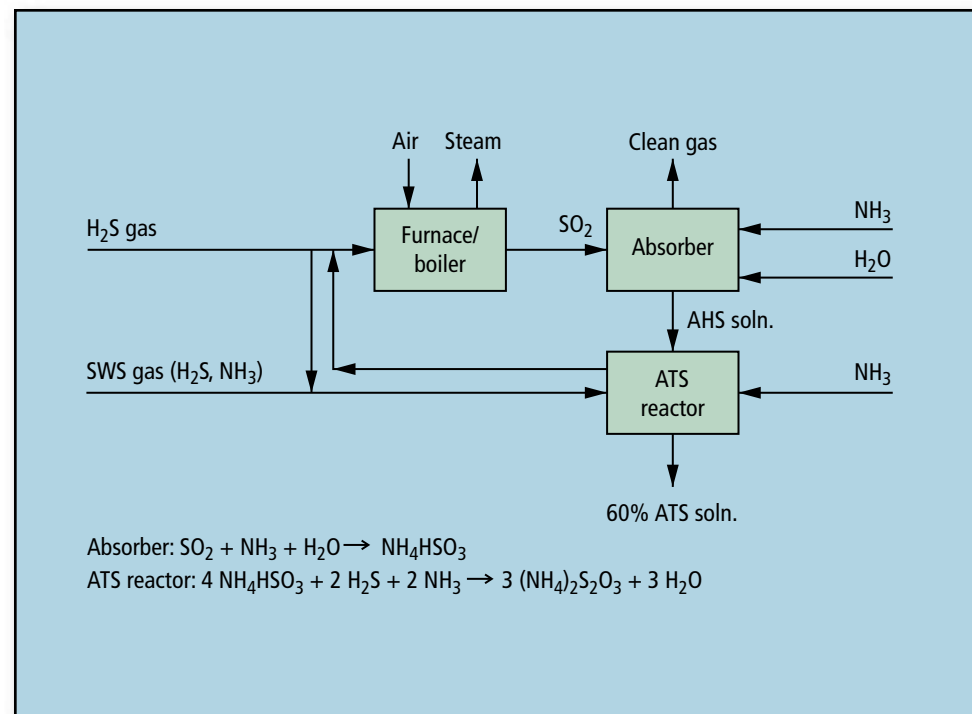
Except for the H₂S burner/waste heat boiler, all process steps occur in the liquid phase at moderate temperatures and neutral pressure. The AHS absorber and ATS reactor systems are chilled with cooling water.

More than 99.95% of the sulfur and practically 100% of the ammonia contained in the feed gas streams are recovered. Typical emission values are:

SO _x	<100 ppmv
NO _x	<50 ppmv
H ₂ S	<1 ppmv
NH ₃	<20 ppmv

Installation: One Topsøe 30,000 mtpy ATS plant is operating in Northern Europe.

Licensors: Haldor Topsøe A/S.



H₂S removal

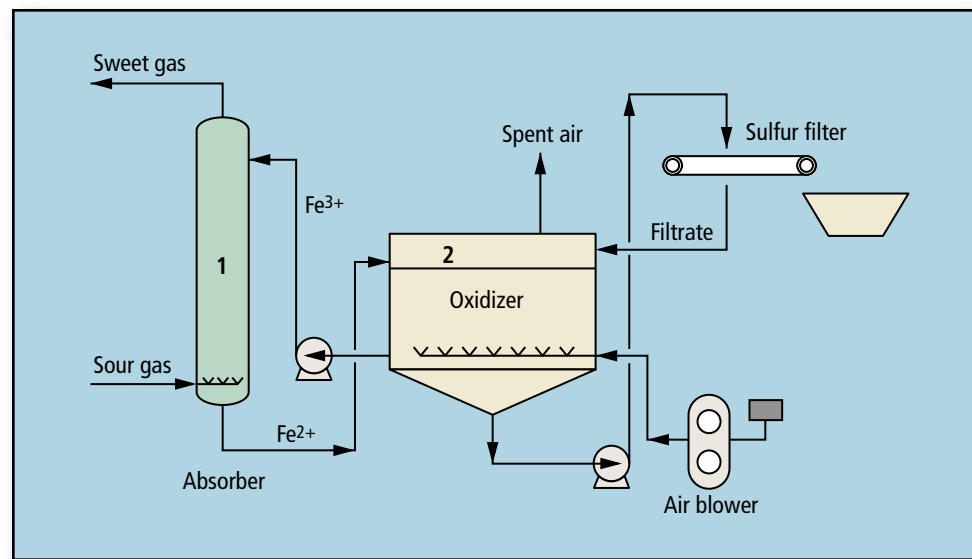
Application: LO-CAT removes H₂S from gas streams and produces elemental sulfur. LO-CAT units are in service treating refinery fuel gas, hydrodesulfurization offgas, sour-water-stripper gas, amine acid gas, claus tail gas and sulfur tank vent gas. Sulfur capacities are typically less than 25 ltpd down to several pounds per day. Key benefits of operation are high (99.9%) H₂S removal efficiency, and flexible operation, with virtually 100% turndown capability of H₂S composition and total gas flow. Sulfur is recovered as a slurry, filter cake or high-purity molten sulfur. The sulfur cake is increasingly being used in agriculture, but can also be deposited in a nonhazardous landfill.

Description: The conventional configuration is used to process combustible gas and product gas streams. Sour gas contacts the dilute, proprietary, iron chelate catalyst solution in an absorber (1), where the H₂S is absorbed and oxidized to solid sulfur. Sweet gas leaves the absorber for use by the refinery. 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 amine 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. Hydrogen sulfide concentrations range from a few ppm to 100%. Sul-



fur loadings range from a few pounds per day to 25+ tons per day. No restrictions on type of gas to be treated; however, some contaminants, such as SO₂, may increase operating costs.

Installations: Presently, 160 licensed units are in operation with four units under construction.

Reference: Heguy, D. L. and G. L. Nagl, "Consider optimized Iron-Redox processes to remove sulfur," *Hydrocarbon Processing*, January 2003, pp. 53–57.

Licensors: Gas Technology Products LLC, a Merichem Co.

H₂S removal

Applications: Sulfur-Rite is a solid-bed scavenger for removal of H₂S from aerobic and anaerobic gas streams. Suitable applications are generally sulfur loads below 200 lb/d sulfur, and/or remote refinery locations. Sulfur vents, loading and unloading facilities, or backup insurance for other refinery sulfur-removal systems are examples.

The spent media is nonpyrophoric, and is suitable for disposition in nonhazardous landfills.

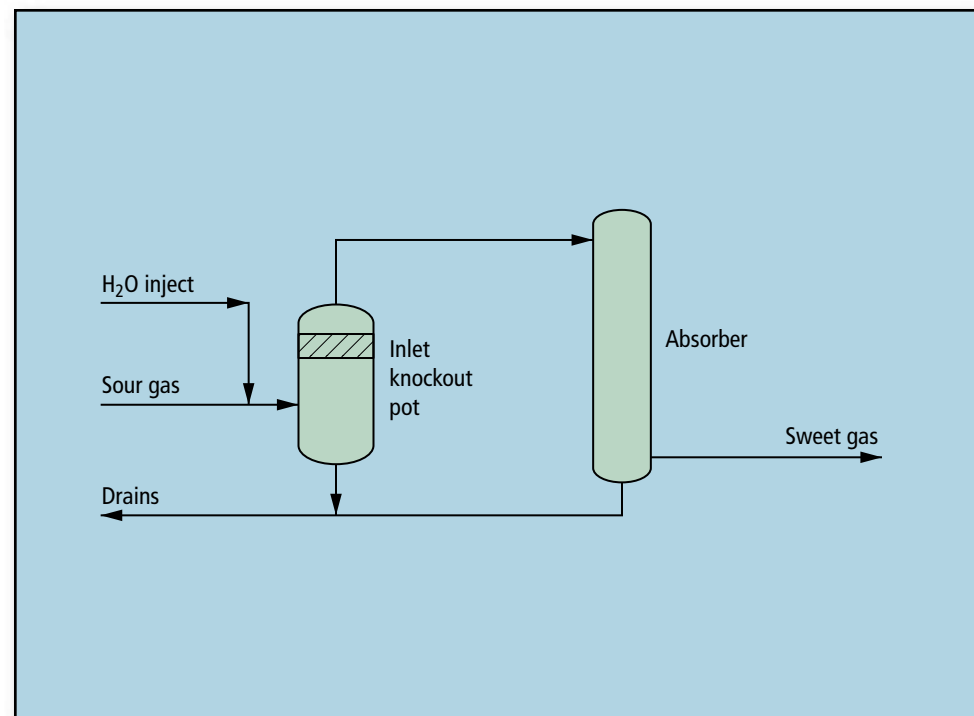
Description: Single-bed (shown) or dual “lead-lag” configurations are possible. Sour gas is saturated prior to entering media bed. Gas enters vessel top, flows over media where H₂S is removed and reacted. Sweet gas exits the bottom of vessel. In the single-vessel configuration, when the H₂S level exceeds 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 H₂S level at the outlet of the lead vessel equals the inlet H₂S 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: Five units installed.

Licensors: Gas Technology Products LLC, a Merichem Co.



H₂S removal, Thiopaq

Application: The biological Thiopaq process selectively removes and converts H₂S and light mercaptans from gas streams, aqueous streams and/or light hydrocarbons to elemental sulfur or sulfate.

Product: The sulfur produced is hydrophilic; thus, it prevents equipment from fouling and blocking. Moreover, this characteristic makes the product suitable for agricultural use as fertilizer or as an insecticide. Alternatively, the sulfur can be molten to a high-purity product meeting international Claus sulfur specifications.

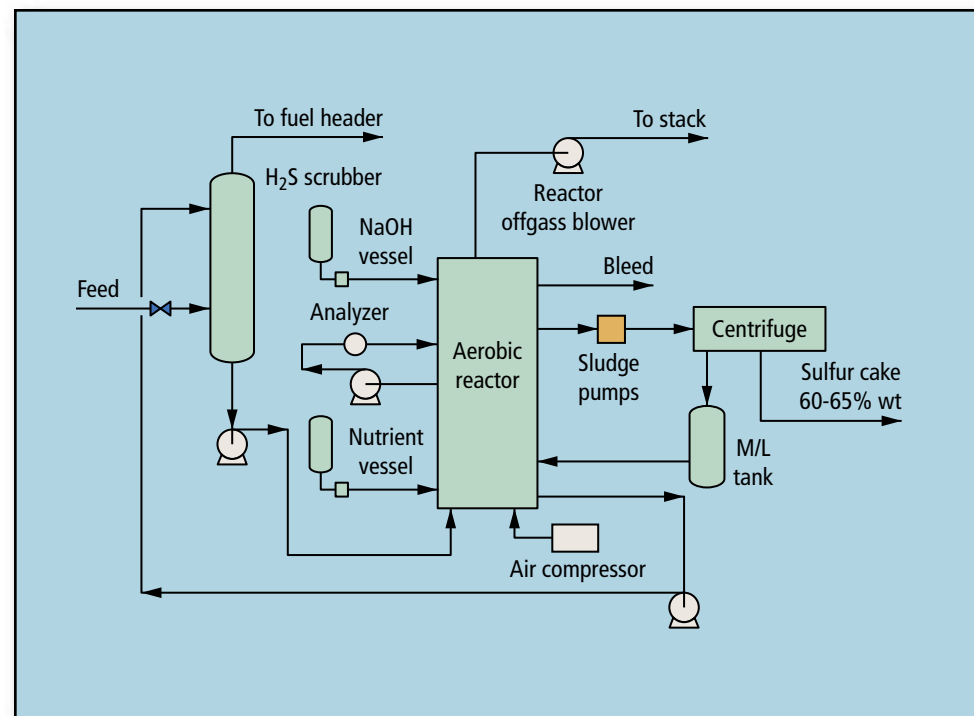
Description: The Thiopaq process consists of three integrated process sections: an absorption section to remove the H₂S from the gas stream, bioreactor(s) and a sulfur-separation section.

The heart of this process is the proprietary bioreactor. In this air-lift-loop reactor, sulfide (HS⁻) is oxidized under controlled conditions to elemental sulfur in the presence of microorganisms. These aerobic (oxygen consuming) organisms use the released energy from the sulfide oxidation for metabolic processes. The elemental sulfur produced has a hydrophilic nature and is separated from the aqueous effluent in a proprietary three-phase separator.

The scrubbing step to remove H₂S from the gas streams is integrated into the Thiopaq process and regenerates the scrubbing solution, rather than its disposal. Regeneration is possible because the alkalinity consumption due to the absorption of H₂S is compensated by the oxidation of H₂S to elemental sulfur.

Operating conditions: The absorber operates at the pressure of feed and at bioreactor temperature. The bioreactor operates at atmospheric pressure and 30–35°C. If the feed is available at a higher temperature, then it requires cooling before entering the absorber.

Economics: The costs associated with using Thiopaq to treat typical refinery spent caustic of a flowrate of 9,510 gpd containing 2,970 lbs/day of sulfide:



Capital cost, budget	\$1,500,000
Annual operating cost	\$158,000

The cost of an LPG flow of 1,500 BSD and recovery of 1,500 lbs/d of sulfur and achieving < 5ppm H₂S in the treated LPG:

Capital cost, budget	\$1,330,600
Annual operating cost	\$180,000

The costs for an offgas flowrate of 24,200 lbs/hr and recovery of 7.8 tpd of sulfur:

Capital cost, budget	\$2,600,000
Annual operating cost	\$300,000

H₂S removal, Thiopaq, *continued*

Installations: Thirty-two units are operating worldwide to remove sulfur from gas and liquid streams in a variety of industries. This includes a 13-mtpd unit in a refinery service in Egypt.

Licensors: UOP LLC, Shell International Oil Products B.V., and Paques Bio System B.V.



Hydrocracking

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

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

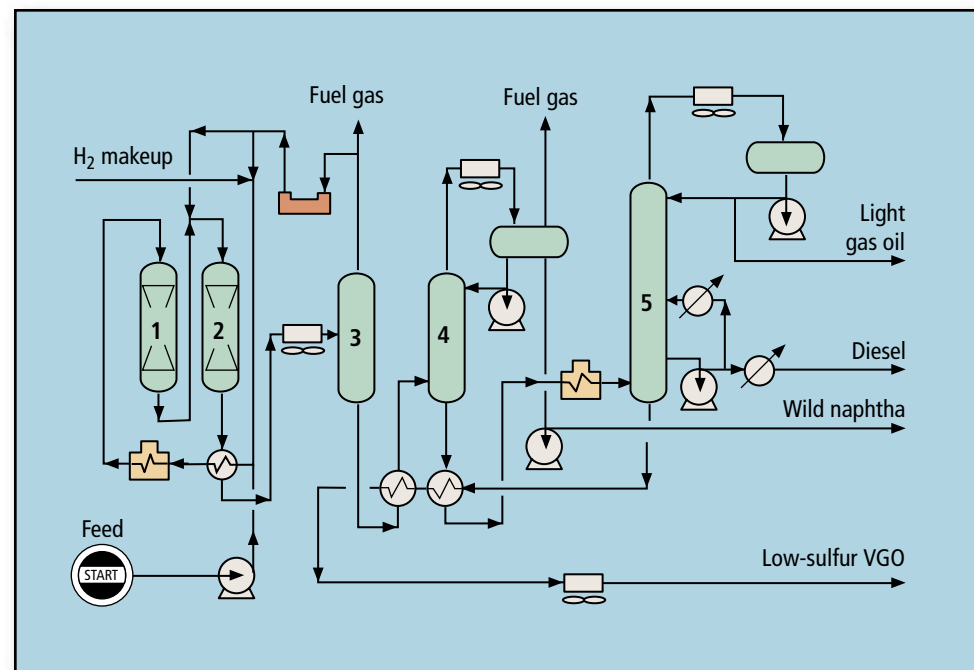
Description: This process uses a refining catalyst usually followed by a zeolite-type hydrocracking catalyst. Main features of this process are:

- High tolerance toward feedstock nitrogen
- High selectivity toward middle distillates
- High activity of the zeolite, 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 two-step 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
Sp. gr.	0.932	0.800	0.826
TBP cut point, °C	405–565	140–225	225–360
Sulfur, ppm	31,700	<10	<10
Nitrogen, ppm	853	<5	<5
Metals, ppm	<2	–	–
Cetane index	–	–	62
Flash pt., °C	–	≥ 40	125
Smoke pt., mm, EOR	–	26–28	–
Aromatics, vol%, EOR	–	< 12	< 8
Viscosity @ 38°C, cSt	110	–	5.3
PAH, wt%, EOR	–	–	<2



Economics:

Investment: (Basis: 40,000-bpsd unit, once-through, 90% conversion, battery limits, erected, engineering fees included, 2000 Gulf Coast), \$ per bpsd 2,000–2,500

Utilities, typical per bbl feed:

Fuel oil, kg	5.3
Electricity, kWh	6.9
Water, cooling, m ³	0.64
Steam, MP	balance

Installation: More than 50 references, cumulative capacity exceeding 1 million bpsd, conversion ranging from 50% to 99%.

Licensors: Axens.

Hydrocracking

Application: Convert naphthas, AGO, VGO, DAO, cracked oils from FCC units, delayed cokers and visbreakers, and intermediate products from residue hydroprocessing units using the Chevron Lummus Global ISO-CRACKING Process.

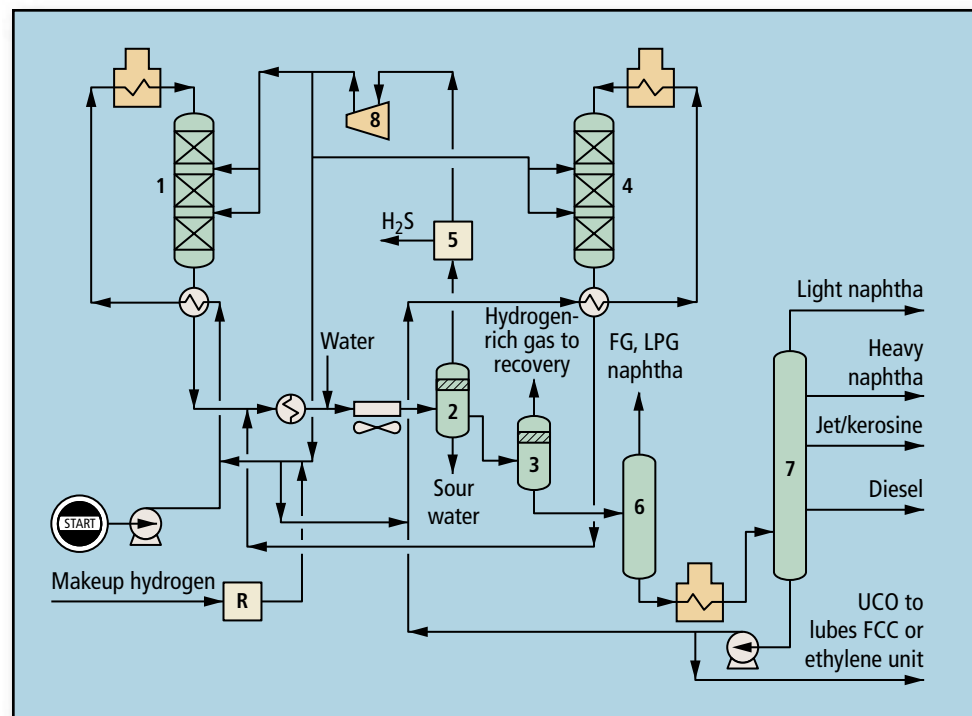
Products: Lighter, high-quality, more valuable products: LPG, gasoline, catalytic reformer feed, jet fuel, kerosene, diesel and feeds for FCC, ethylene cracker or lube oil units.

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 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.



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

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Hydrocracking, continued

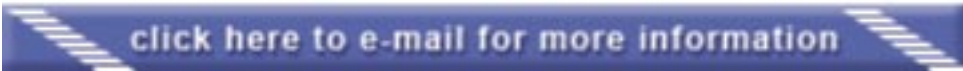
Feed	VGO	VGO	VGO	VGO
Product quality				
Kerosine smoke, mm		29–32	29–32	29–32
Diesel cetane number	58–64		58–64	58–64
UCO BMCI				6–8
UCO Waxy V.I.				143–145
UCO Dewaxed V.I.				131–133

Economics: ISBL total installed cost of 35,000-BPSD unit at 100% conversion to middle distillates using Middle Eastern VGO feed (USGC, mid-2004 basis): \$110 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 50 units worldwide with over 800,000-bpsd total capacity.

Licensors: Chevron Lummus Global LLC.



Hydrocracking

Application: Desulfurization, demetalization, CCR reduction and hydrocracking of atmospheric and vacuum resid 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.

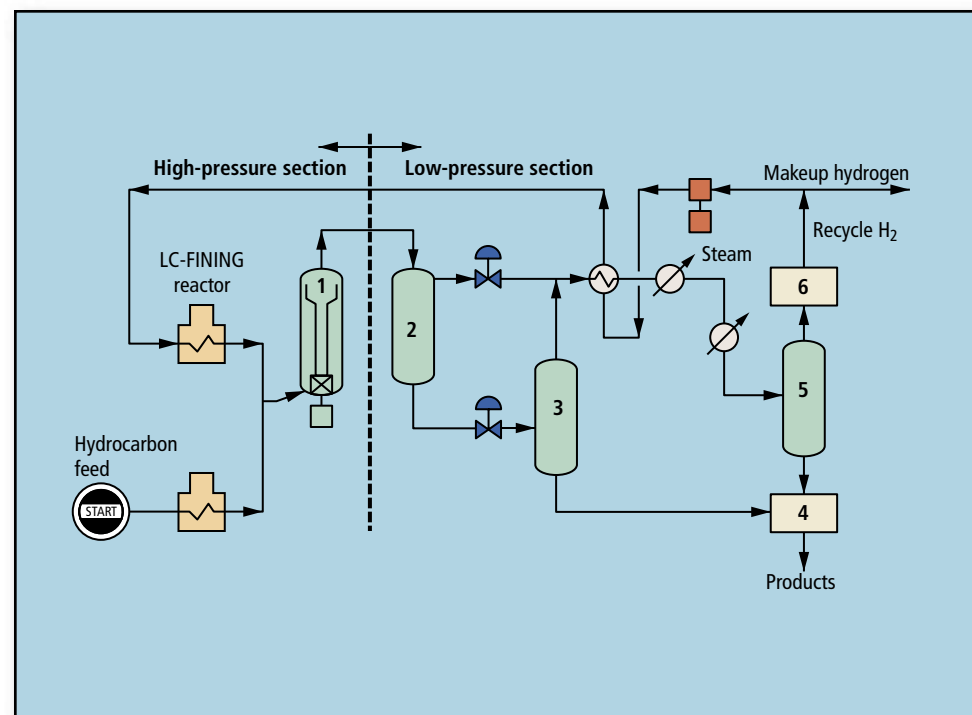
Description: Fresh hydrocarbon liquid feed is mixed with hydrogen and reacted within an expanded catalyst bed (1) maintained in turbulence by liquid upflow to achieve efficient isothermal operation. Product quality is maintained constant and at a high level by intermittent catalyst addition and withdrawal. 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. resid		Vac. resid	
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% (1,022°F+)	45	60	75	95
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°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

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Hydrocracking, *continued*

Economics:

Investment, estimated (US Gulf Coast, 2000)

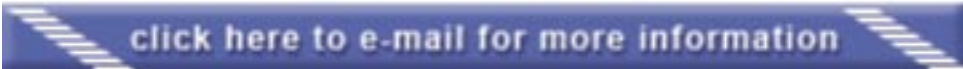
Size, bpsd fresh feed	92,000		49,000	
\$/bpsd typical fresh feed	2,200	3,500	4,200	5,200

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: Five LC-FINING units are in operation, one LC-FINING Unit is in construction and two LC-FINING Units are in engineering.

Licensors: Chevron Lummus Global LLC.



Hydrocracking

Application: Convert a wide variety of feedstocks including vacuum deep-cut gas oil, coker gas oils, de-asphalted oil (DAO), and FCC cycle oils into high-quality, low-sulfur fuels using ExxonMobil Research and Engineering Company's (EMRE) moderate pressure hydrocracking (MPHC) process.

Products: Products include a wide range of high-quality, low-sulfur distillates and blending stocks including LPG, high-octane gasoline, high-quality reformer naphtha. Unconverted bottoms product from the MPHC unit is very low in sulfur and is an excellent feedstock for fluid catalytic cracking (FCC), lube-oil basestock production, steam cracking and low-sulfur fuel oil.

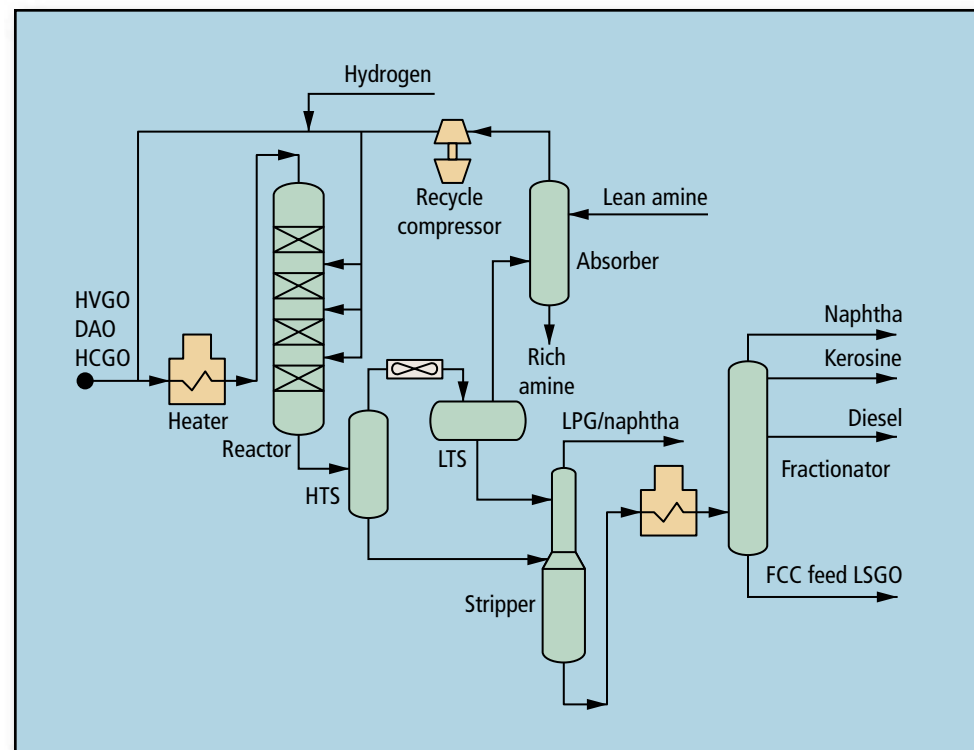
Description: The process uses a multiple catalyst system in multi-bed reactor(s) that incorporates proprietary advanced quench and redistribution internals (Spider Vortex). Heavy hydrocarbons and recycle gas are preheated and contact the catalyst in the trickle-phase fixed-bed reactor(s). Reactor effluent is flashed in high- and low-temperature separators. An amine scrubber removes H₂S from the recycle gas before it gets compressed and re-circulated back to the unit. An optimized, low cost stripper/fractionator arrangement is used for product recovery.

When higher-quality distillates are required, the addition of a low-cost, highly integrated distillate post-treating unit (PTU) can be incorporated in the design to meet or exceed high-pressure hydrocracking product quality at lower capital cost and hydrogen consumption

Operating conditions and yields: Typical operating conditions on a Middle East VGO for a once-through MPHC operation are shown:

Operation conditions:

Configuration	MPHC	MPHC	MPHC
Nominal conversion, %	35	50	50
H ₂ pressure, psig	800	800	1,250



Yields:

Naphtha, wt%	4	10	10
Kero/jet, wt%	6	10	10
Diesel, wt%	22	26	27
LSGO (FCC feed), wt%	65	50	50
H ₂ consumption, wt%	1.0–1.5	1.3–1.8	1.5–2.0

Product quality:

Kero sulfur, wppm	20–200	20–200	20–200
Kero smoke Pt, mm	13–18	15–20	17–22
Diesel sulfur, wppm	30–500	30–300	30–200
Diesel cetane no.	45–50	47–52	50–55

Continued ▼

Hydrocracking, *continued*

Utilities, per bbl of feed:

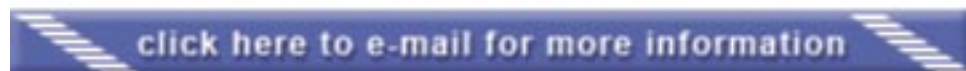
Electric power, kW	4.1	7.2
Fuel (absorbed), Btu	67,100	69,600
Steam, MP (export), lb	(15.9)	(21.1)
Water, cooling, gal	101	178
Wash water, gal	1.5	2.2
Lean amine, gal	36.1	36.1

EMRE's MPHC process is equally amenable to revamp or grassroots applications. EMRE has an alliance with Kellogg Brown & Root (KBR) to provide MPHC technology to refiners.

Economics: Investment \$/bpsd 2,000–3,000

Installation: Four operating units; two in construction.

Licensors: ExxonMobil Research and Engineering Co.



Hydrocracking

Application: Topsøe's hydrocracking process (ULTRACRACKING) can be used to convert straight run vacuum gas oils and heavy cracked gas oils 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.

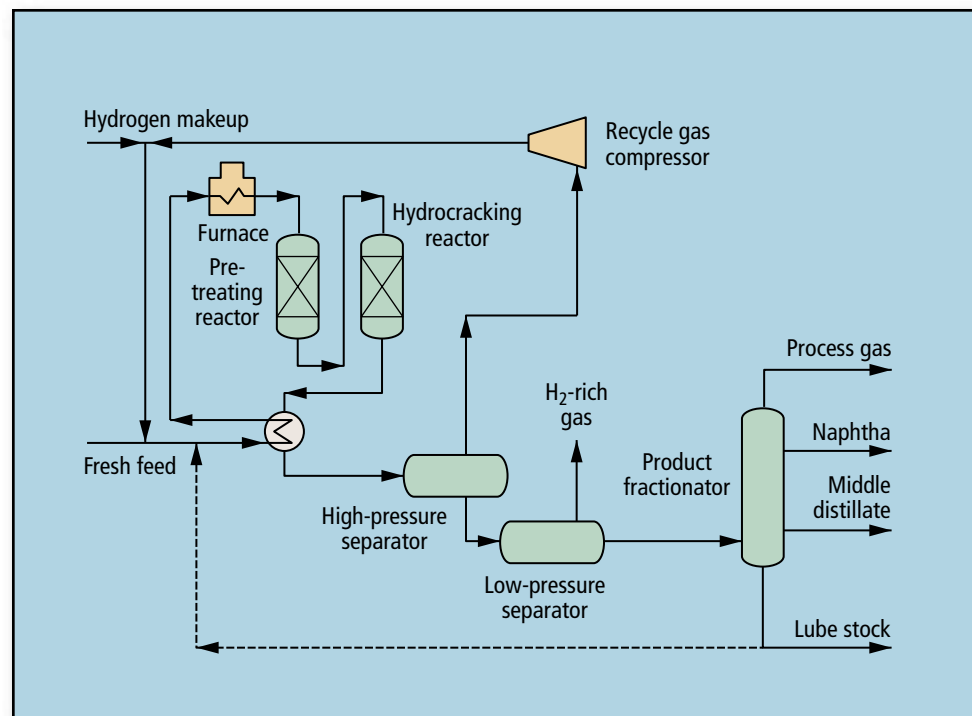
Product: By proper selection of operating conditions, process configuration, and catalysts, the Topsøe ULTRACRACKING process can be designed for high conversion to produce high smoke point kerosene and high cetane diesel. The process can also be designed for lower conversion/upgrade mode to produce low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

Description: The ULTRACRACKING process uses well proven co-current 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 partially converted oil to obtain 100% conversion to diesel and lighter products. 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 hydrocracker. Topsøe hydrocracking catalysts are in use in five hydrocrackers.

Licensors: Haldor Topsøe A/S.



Hydrocracking

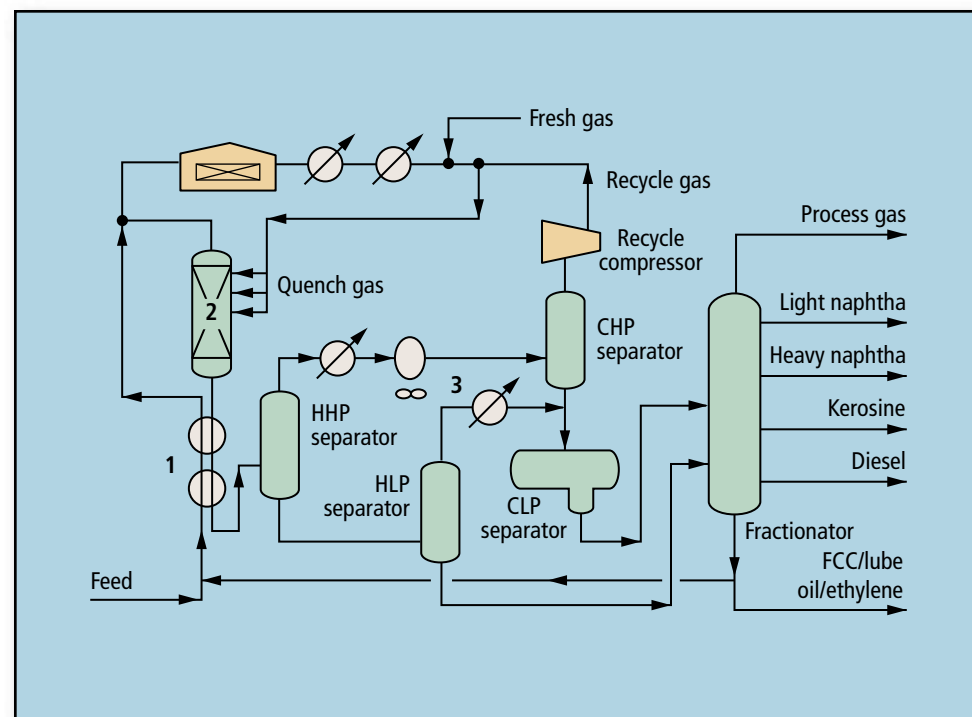
Application: To convert heavy VGO and other low-cost cracked and extracted feedstocks into high-value, high-quality products, such as low-sulfur diesel, jet fuel, high-octane light gasoline and reformer feed via the Shell Hydrocracking Process. Unconverted or recycle oil are prime feeds for secondary processing in 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 high-pressure 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 while maximizing 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 including a single-reactor, stacked-bed design suitable for capacities up to 10,000 tpd in partial or full-conversion modes. The catalyst systems are carefully tailored for the desired product slate and catalyst cycle length.

Installations: 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.



Hydrocracking

Application: Convert a wide variety of feedstocks into lower-molecular-weight products using the Unicracking and HyCycle Unicracking process.

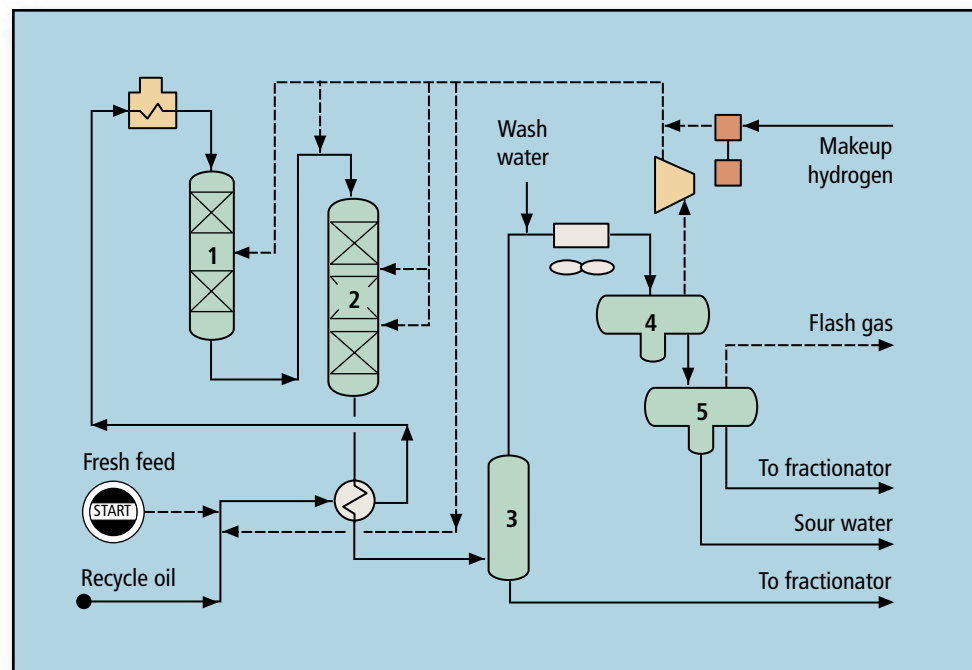
Feed: Feedstocks include atmospheric gas oil, vacuum gas oil, FCC/RCC cycle oil, coker gas oil, deasphalted oil and naphtha for production of LPG.

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 determine catalyst selection 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:

Feed type	FCC cycle oil blend	Vacuum gas oil	Fluid coker gas oil	
Gravity, °API	27.8	22.7	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	0.08	0.269	
Principal products	Gasoline	Jet	Diesel	FCC feed
Yields, vol% of feed				
Butanes	16.0	6.3	3.8	5.2
Light gasoline	33.0	12.9	7.9	8.8
Heavy naphtha	75.0	11.0	9.4	31.8
Jet fuel		89.0		
Diesel fuel			94.1	33.8



600°F + gas oil				35.0
H ₂ consump., scf/bbl	2,150	1,860	1,550	2,500

Economics: Example:

Investment, \$ per bpsd capacity 2,000–4,000

Utilities, typical per bbl feed:

Fuel, 10 ³ Btu	70–120
Electricity, kWh	7–10

Installation: Selected for 161 commercial units, including several converted from competing technologies. Total capacity exceeds 3.6 million bpsd.

Licensors: UOP LLC.

Hydrocracking, resid

Application: High-conversion catalytic hydrocracking of petroleum residua, heavy oil and bitumen, using a molecular-sized, dispersed catalyst. The $(\text{HC})_3$ dispersed catalyst may also be used as an additive in existing ebullated-bed resid hydrocrackers, to significantly reduce process fouling, and to increase feedstock flexibility and conversion.

Process description: The $(\text{HC})_3$ hydrocracking process battery limits include a unit for adding ppm levels of the proprietary liquid catalyst precursor in the resid feed, from which a molecular-sized catalyst is created in-situ. The battery limits also include hydrogen and feed heaters, one or two stages of gas-liquid, back-mixed reactors operating at constant catalyst activity throughout the liquid phase, a product separator for bottoms recycle, inline distillate hydrotreating and recycle gas cleaning. Liquid mixing and reactor temperature homogeneity are ensured via a recirculation pump at the bottom of the reactor. The process does not suffer from pressure drop or fouling, and produces a constant-quality hydrocracked product. Run lengths of five or more years between turnarounds are expected with the $(\text{HC})_3$ technology.

Operating conditions:

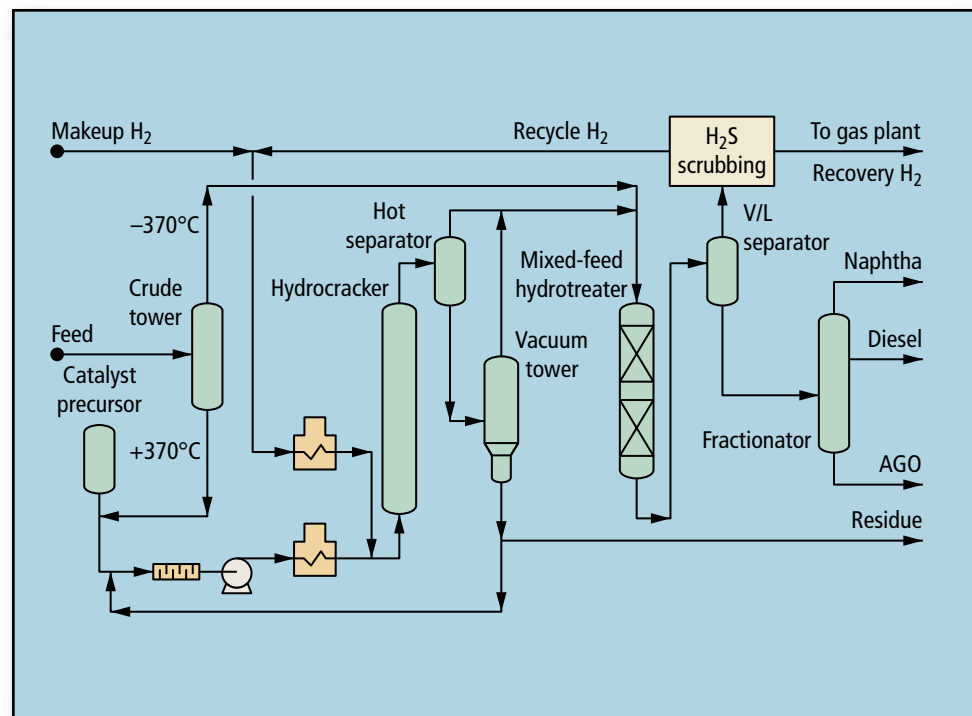
Temperature, °F	770–840
H ₂ partial pressure, psi	1,000–2000
LHSV, hr ⁻¹	0.4–2.0

Investment and operating costs: (2004 US Gulf Coast basis)

Capital investment: \$2,500–4,000 per bpsd [for $(\text{HC})_3$ standalone process]

Utilities: per bbl of feed

Fuel, 10 ³ Btu	30–90
Power, kWh	5–12
Water, cooling (20°F rise), gal	30–70
Catalyst makeup, \$	0.4–1.5 for standalone hydrocracker



For $(\text{HC})_3$ catalyst as an additive to improve ebullated bed operation: Capital cost is minimal; expect no increase in net, combined catalyst costs [that is, supported catalyst plus $(\text{HC})_3$ additive].

Installations: The $(\text{HC})_3$ additive is expected to be utilized in a commercial ebullated bed plant in 2004.

Licensors: Hydrocarbon Technologies, Inc.

Hydrocracking/hydrotreating— VGO/DAO

Application: The T-Star Process is an ebullated-bed process for the hydrotreatment/hydrocracking of vacuum gas oils. The T-Star Process is best suited for difficult feedstocks (coker VGO, DAO), high-severity operations and applications requiring a long run length.

Description: A T-Star process flow diagram, which includes integrated mid-distillate hydrotreating, is shown above. The typical T-Star battery limits include oil/hydrogen fired heaters, an advanced hot high-pressure design for product separation and for providing recycle to the ebullating pump, recycle gas scrubbing and product separation. Catalyst is replaced periodically from the reactor, without shutdown. This ensures the maintenance of constant, optimal catalyst activity and consistent product slate and quality. After high-pressure recovery of the effluent and recycle gas, the products are separated and stabilized through fractionation. A T-Star unit can operate for four-year run lengths with conversion in the 20–50% range and hydrodesulfurization in the 93–99% range.

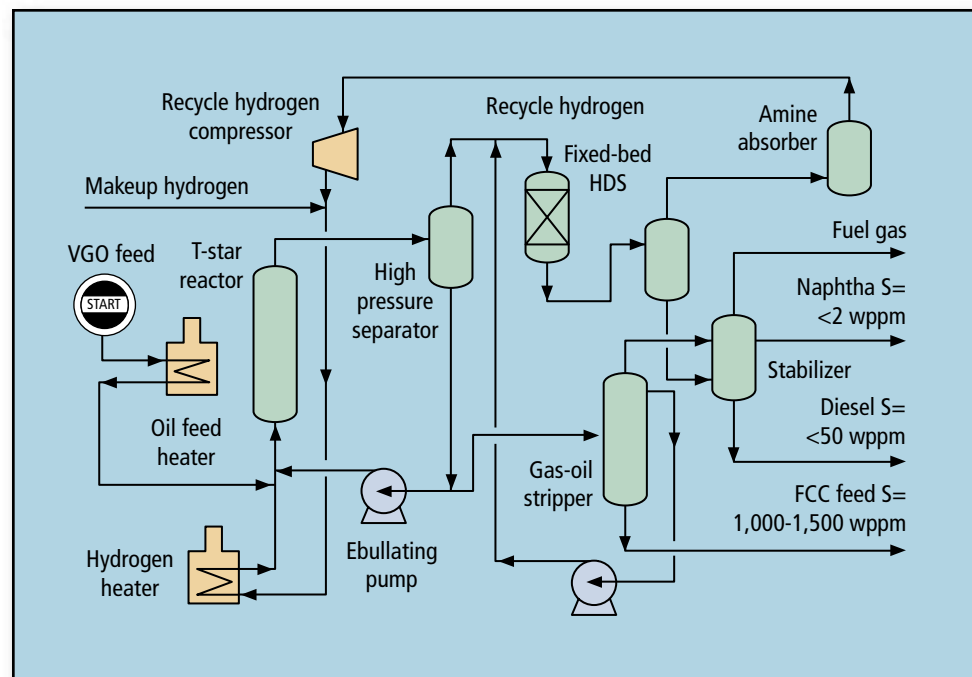
Operating conditions:

Temperature, °F	750–820
Hydrogen partial pressure, psi	600–1,500
LHSV, hr ⁻¹	0.5–3.0
VGO conversion, %	20–60

Examples: In Case 1, a deep-cut Arab heavy VGO is processed at 40 wt% conversion with objectives of mild conversion and preparing specification diesel and FCC unit feed. In Case 2, a VGO blend containing 20% coker material is processed at lower conversion to also obtain specification FCC unit feedstock and high-quality diesel.

Economics: Basis 2002 US Gulf Coast

Investment in \$ per bpsd	1,200–2,500
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Utilities, per bbl of feed

Fuel, 10 ³ Btu	60
Power, kWh	3
Catalyst makeup, \$	0.05–0.20

Installation: The T-Star process is commercially demonstrated based on the ebullated-bed reactor. Axens has licensed more than 1.5 MMbpsd of capacity in gas oil, VGO and residue. Axens has seven commercially operating ebullated-bed units and one start-up.

Reference: "A novel approach to attain new fuel specifications," *Petroleum Technology Quarterly*, Winter 1999/2000.

Licensors: Axens.

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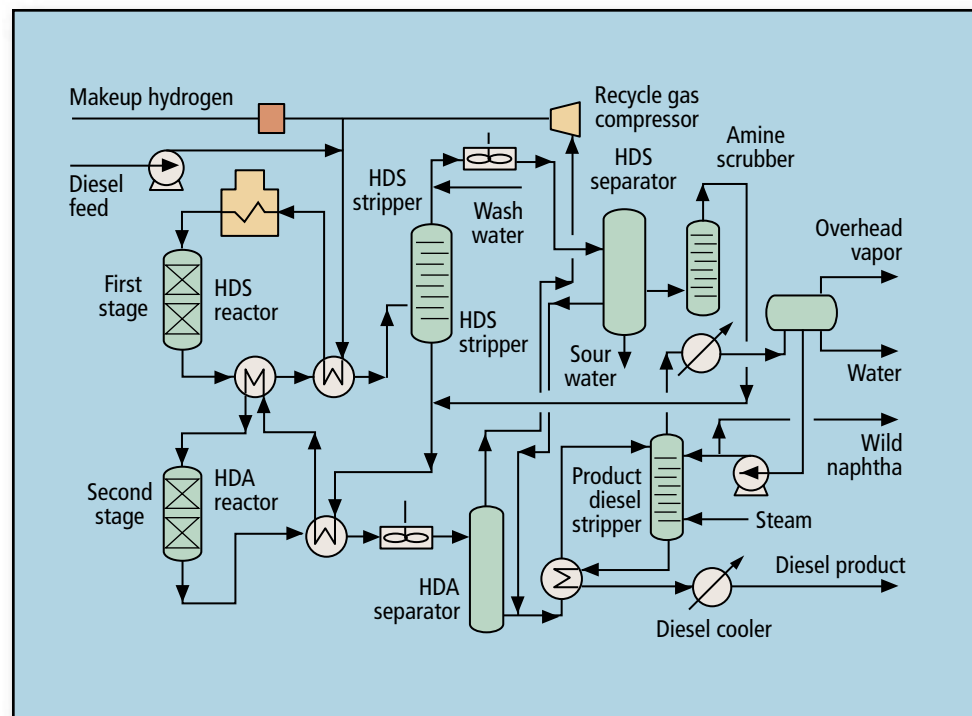
Hydrodearomatization

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-573 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 H_2S 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 H_2S , 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

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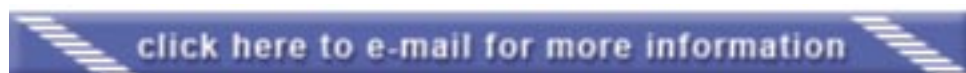
Hydrodearomatization, *continued*

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," Fourth ERTC, November 1999.

Installation: A total of five, two in Europe and three in North America.

Licensors: Haldor Topsøe A/S.



Hydrodesulfurization

Application: The ISAL process enables refiners to meet the world's most stringent specifications for gasoline sulfur while also controlling product octane.

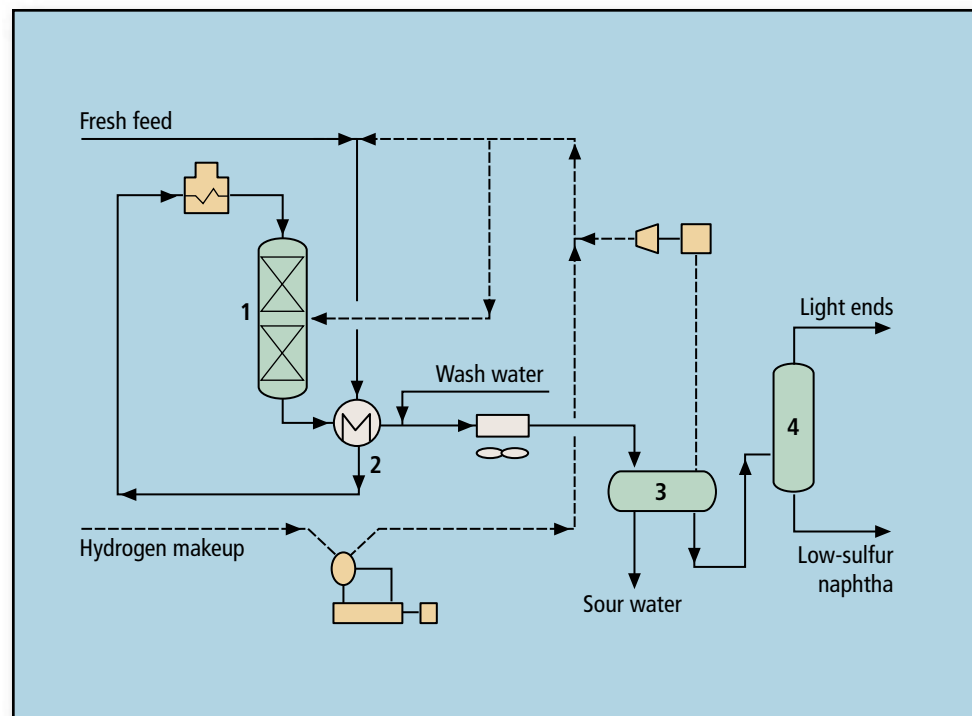
This moderate-pressure, fixed-bed hydroprocessing technology desulfurizes gasoline-range olefinic feedstocks and selectively reconfigures lower octane components to control product octane. This process can be applied as a stand-alone unit or as part of an overall integrated flow scheme for gasoline desulfurization.

Description: The flow scheme of the ISAL unit is very similar to that of a conventional hydrotreater. The naphtha feed is mixed with hydrogen-rich recycle gas and processed across fixed catalyst beds at moderate temperatures and pressures. Following heat exchange and separation, the reactor effluent is stabilized. The similarity of an ISAL unit to a conventional naphtha hydrotreating unit makes new unit and revamp implementation both simple and straightforward. In addition to new unit designs, the technology has been applied both to idle reforming and hydrotreating units.

Product quality: The ISAL unit's operation can be adjusted to achieve various combinations of octane recovery and yield. Yield/octane relationships for an integrated flow scheme processing an FBR FCC naphtha containing 420 wppm sulfur and 24 wt% olefins are:

Yield, vol%	99.5	97.2
Sulfur, wppm	10	10
(R + M)/2 change	-2	0

Economics: The capital and operating costs of an ISAL unit are slightly higher than those of a typical naphtha hydrotreating unit. With this process, refiners benefit from the ability to produce a higher-octane product at incremental additional operating cost primarily related to additional hydrogen consumption.



Installation: Four ISAL applications have been implemented in the US, with an additional three ISAL units currently in the process design stage.

Licensors: UOP LLC (in cooperation with PDVSA-INTEVEP).

Hydrodesulfurization—UDHDS

Application: A versatile family of premium distillates technologies is used to meet all current and possible future premium diesel upgrading requirements. Ultra-deep hydrodesulfurization (UDHDS) process can produce distillate products with sulfur levels below 10 wppm from a wide range of distillate feedstocks.

Products: High volume yield of ultra-low-sulfur distillate is produced. Cetane and API gravity uplift, together with the reduction of polyaromatics to less than 6 wt% or as low as 2 wt%, can be economically achieved.

Description: The UDHDS reactor and catalyst technology is offered through Akzo Nobel Catalysts bv. A single-stage, single-reactor process incorporates proprietary high-performance distribution and quench internals. Feed and combined recycle and makeup gas are preheated and contact the catalyst in a downflow, concurrent fixed-bed reactor. The reactor effluent is flashed in a high- and a low-pressure separator. An amine-absorber tower is used to remove H_2S from the recycle gas. In the example shown, a steam stripper is used for final product recovery. The UDHDS technology is equally applicable to revamp and grassroots applications.

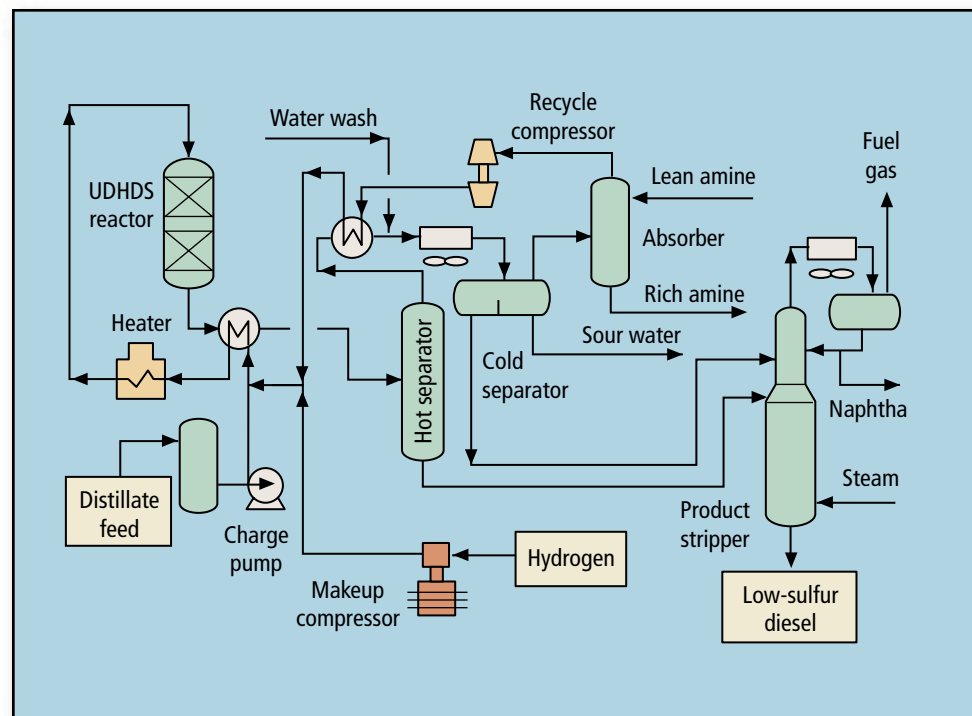
Economics:

Investment (Basis: 25,000–35,000 bpsd, 1Q 2000 US Gulf Coast)
New unit, \$ per bpsd 1,000 to 1,800

Installation: Over 60 distillate upgrading units have applied the Akzo Nobel ultra-deep HDS technology. Twenty-five of these applications produce, or will produce, <10ppm sulfur, using UDHDS technology.

Reference: "Technology for premium distillates," ERTC Low-Sulfur Fuels Workshop, February/March 2002, London.

Licensors: Akzo Nobel Catalysts bv.



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.

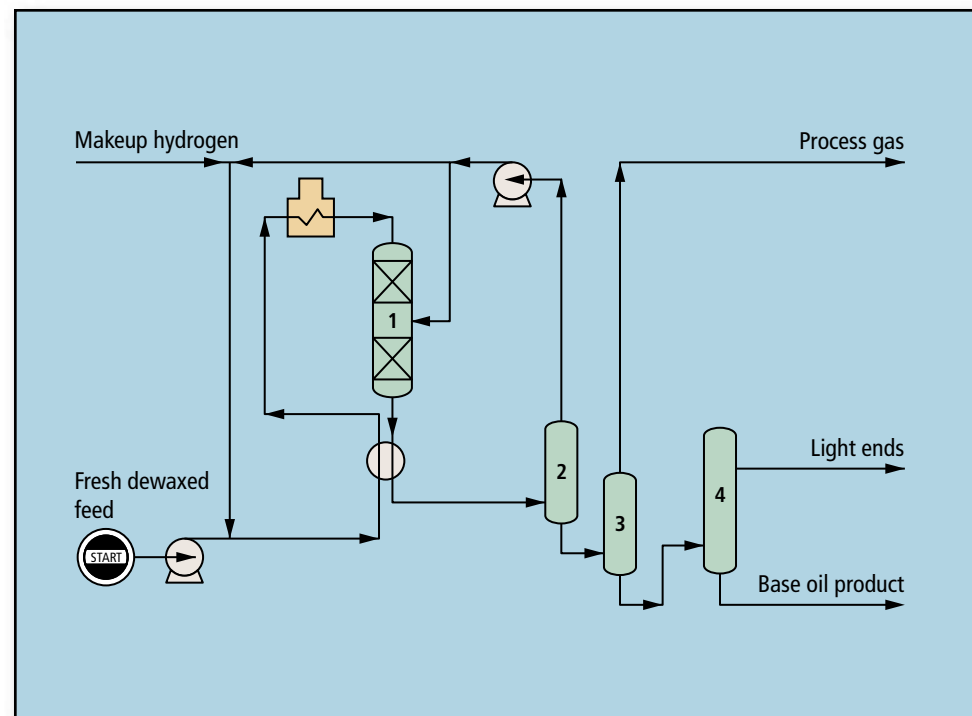
Economics:

Investment: For a stand-alone ISOFINISHING Unit, the ISBL capital is about 3,000–5,000 \$/bpsd, depending on the pressure level and size.

Utilities: Typical per bbl feed:

Power, kW	2.6
Fuel, kcal	3.4×10^3

Installation: Twenty units are in various stages of operation, construction or design.



Reference: NPRA Lubricants & Waxes Meeting, November 2002, Houston, Paper LW-02-128.

Licensors: Chevron Lummus Global LLC.

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.

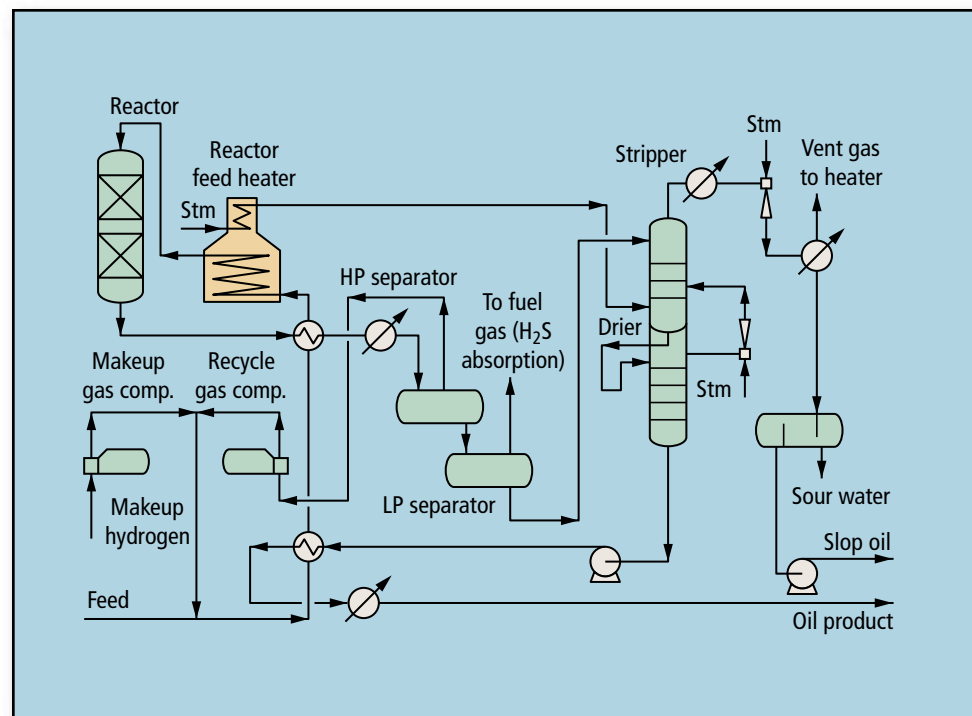
For lube-oil hydrofinishing, the catalytic hydrogenation process is operated at medium hydrogen pressure, moderate temperature and low hydrogen consumption. The catalyst is easily regenerated with steam and air.

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.



Licensors: Uhde GmbH.

Hydrogen

Application: To produce hydrogen from light hydrocarbons using steam-methane reforming.

Feedstock: Natural gas, refinery gas, LPG and naphtha.

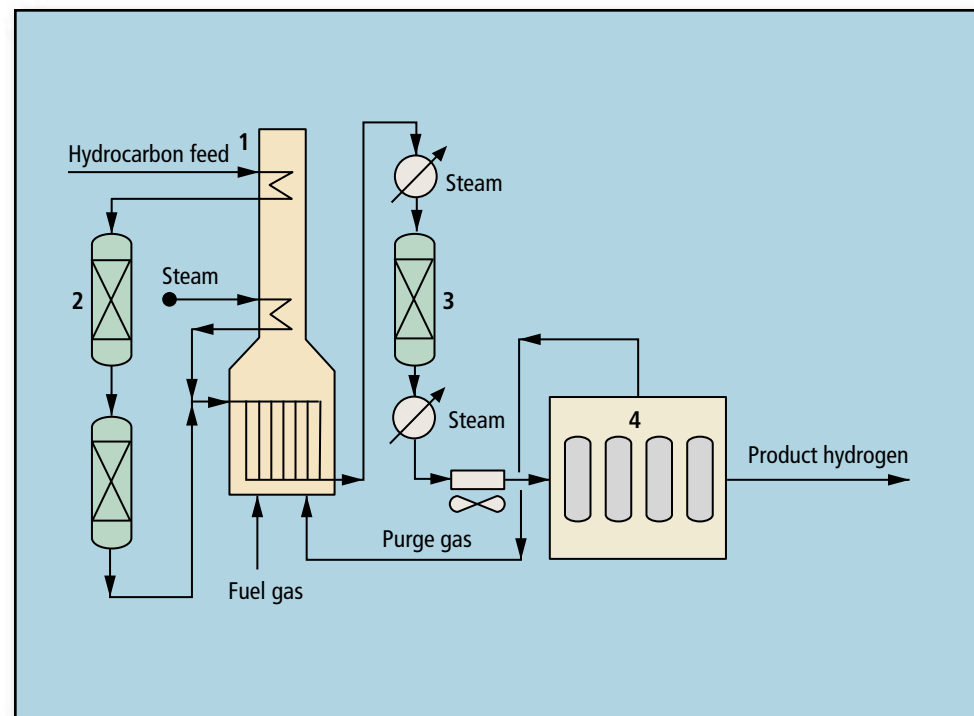
Product: High-purity hydrogen and steam.

Description: Light hydrocarbon feed (1) is heated prior to passing through two fixed-catalyst beds. Organic sulfur compounds present in feed gas (e.g., mercaptans) are converted to hydrogen sulfide (H_2S) and mono-olefins in the gas phase are hydrogenated in the first bed of cobalt molybdenum oxide catalyst (2). The second bed contains zinc oxide to remove H_2S by adsorption. This sulfur-removal stage is necessary to avoid poisoning of the reforming catalysts. Treated feed gas is mixed with steam and heated before passing to the reformer where the hydrocarbons and steam react to form synthesis gas (syngas).

Foster Wheeler supplies proprietary side-fired Terrace Wall reformers, with natural draft mode for increased reliability, compact plot layout with convection section mounted directly above the radiant section and modular fabrication option. Top-fired reformers are options for large capacity plants.

Syngas containing hydrogen, methane, carbon dioxide (CO_2), carbon monoxide (CO) and water leaves the reformer and passes through the waste-heat boiler to the shift reactor (3) where most of the CO is converted to CO_2 and hydrogen by reaction with steam. For heavier feedstocks, pre-reforming is used for conversion of feedstock upstream of the reformer.

The syngas is cooled through a series of heat-recovery exchangers before free water is recovered in a knockout drum. The resultant raw hydrogen stream passes to the pressure swing adsorption (PSA) unit for purification (4) to 99.9% hydrogen product quality. Tail gas from the PSA unit provides a substantial proportion of the firing duty for the



reformer. The remaining fuel is supplied from feed gas or other sources (e.g. refinery fuel gas).

Demineralized water make-up is deaerated, mixed with recovered condensate and preheated through a series of heat recovery exchangers, before passing to the steam drum. Saturated and superheated steam is raised by heat exchange with the reformed gas and flue gas in the convection section of the reformer. Steam export quantities can be varied between 1,250 to 5,750 lbs per MMscfd of hydrogen produced using air pre-heat and auxiliary firing options.

Economics: Plant design configurations are optimized to suit the clients' economic requirements, using discounted cash-flow modeling to establish the lowest lifecycle cost of hydrogen production.

Continued ▼

Hydrogen, *continued*

Investment: 10–100 MMscfd, 1st Q 2004, USGC \$7–55 million

Utilities, typical per MMscfd of hydrogen produced

(natural gas feedstock):

Feed + fuel, lb	960
Water, demineralized, lb	4,420
Steam, export, lb	3,320
Water, cooling, US gal	1,180
Electricity, kWh	12

Reference: Ward, R. D. and N. Sears, "Hydrogen plants for the new millennium," *Hydrocarbon Engineering*, Vol. 7, June 2002.

Installation: Over 100 plants, ranging from 1 MMscfd to 95 MMscfd in a single-train configuration and numerous multi-train configurations.

Licensors: Foster Wheeler.

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Hydrogen

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

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

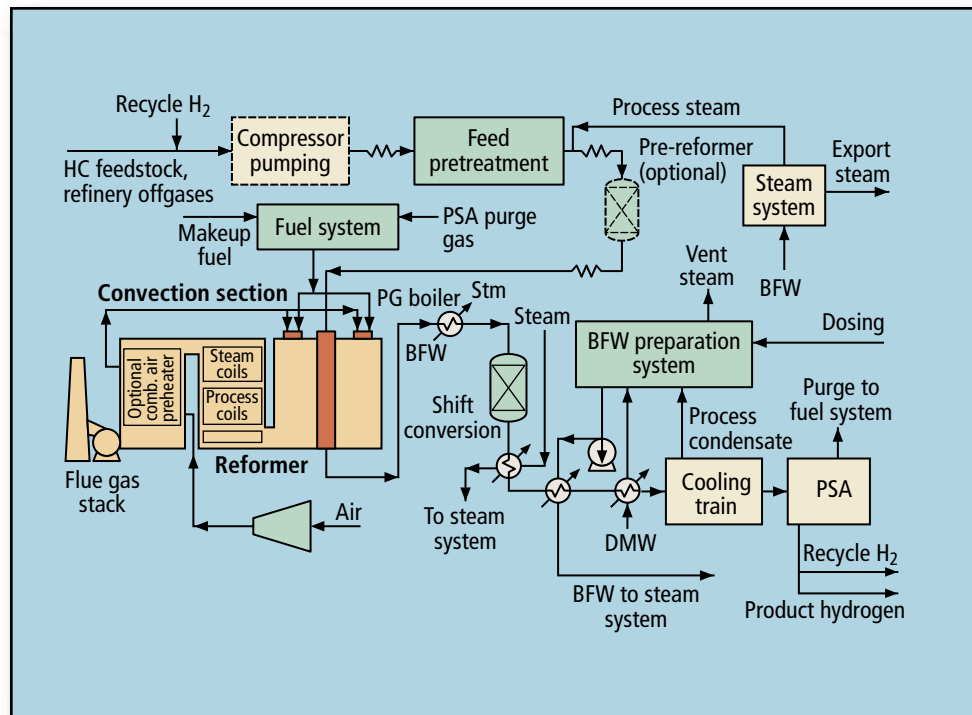
Description: The generic flowsheet consists of feed pretreatment, pre-reforming (optional), steam-HC reforming, shift conversion and hydrogen purification by pressure swing adsorption (PSA). However, it is often tailored to satisfy specific requirements.

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

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

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

Typical specific energy consumption based on feed + fuel – export steam ranges between 3.0 and 3.5 Gcal/KNm³ (330–370 Btu/scf) LHV, depending upon feedstock, plant capacity, optimization criteria and



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

Installations: TECHNIP has been involved in over 240 hydrogen plants worldwide, covering a wide range of capacities. Most installations are for refinery application with basic features for high reliability and optimized cost.

Licensors: Technip.

Hydrogen

Application: Produce hydrogen for refinery hydrotreating and hydrocracking or other refinery, petrochemical and industrial applications.

Feed: Natural gas, refinery offgas, LPG/butane, light naphtha and multiple feedstock.

Product: High-purity hydrogen (>99.9%). CO, CO₂ and/or electricity may also be produced separately for byproduct credit.

Description: The feedstock (natural gas, for example) is desulfurized (1), mixed with steam and converted to synthesis gas in the reformer (2) over nickel catalysts at 20–40 bar pressure and temperatures of 800–900°C.

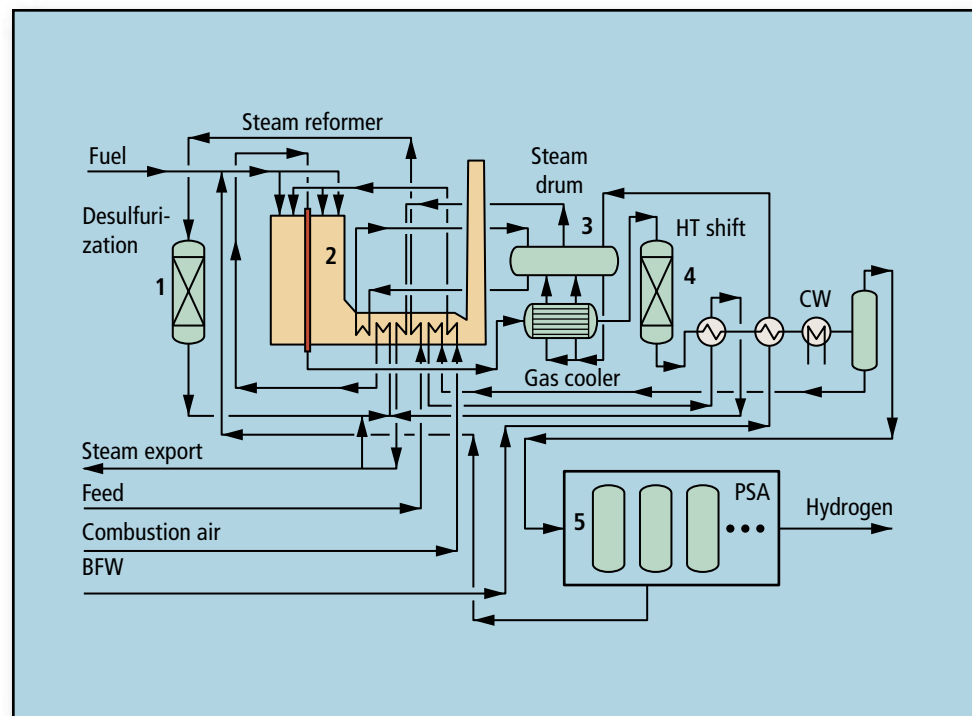
The Uhde steam reformer is a top-fired reformer, which has tubes made of centrifugally cast alloy steel and a proprietary “cold” outlet manifold system to enhance reliability. Subsequent high-pressure steam generation (3) and superheating permit maximum process heat recovery to achieve an optimized energy-efficient process.

The carbon monoxide (CO) shift occurs in a single-stage, adiabatic high-temperature reactor (4). Pressure swing adsorption (5) is a well-established purification step to obtain high-purity hydrogen (99.9 % and higher).

The Uhde reformer design with the unique proprietary cold outlet manifold system enables construction and operation of world-scale reformers with hydrogen capacities up to 220,000 Nm³/h (197 MMscfd) in single-train configuration.

Economics: Depending on the individual plant concept, the typical consumption figure (feed + fuel – steam) is approximately 3.15 Gcal/1,000 Nm³ (335 MMBtu/MMscf).

Installations: Uhde has recently commissioned two of the world's largest hydrogen plants for SINCOR C.A., Venezuela (2 x 98,000 Nm³/h or 2 x 88 MMscfd) and Shell Canada Ltd., Canada (2 x 130,000 Nm³/h or 2 x 116 MMscfd). More than 60 Uhde reformers have been constructed worldwide.



References: Larsen, J., M. Michel, J. Zschommler (Uhde), M. Whysall and S. Vanheertum (UOP), “Large-scale hydrogen plants, Uhde and UOP’s experience,” AIChE 2003 Spring Meeting, New Orleans, March 30–April 3, 2003.

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.

Licensors: Uhde GmbH.

Hydrogenation

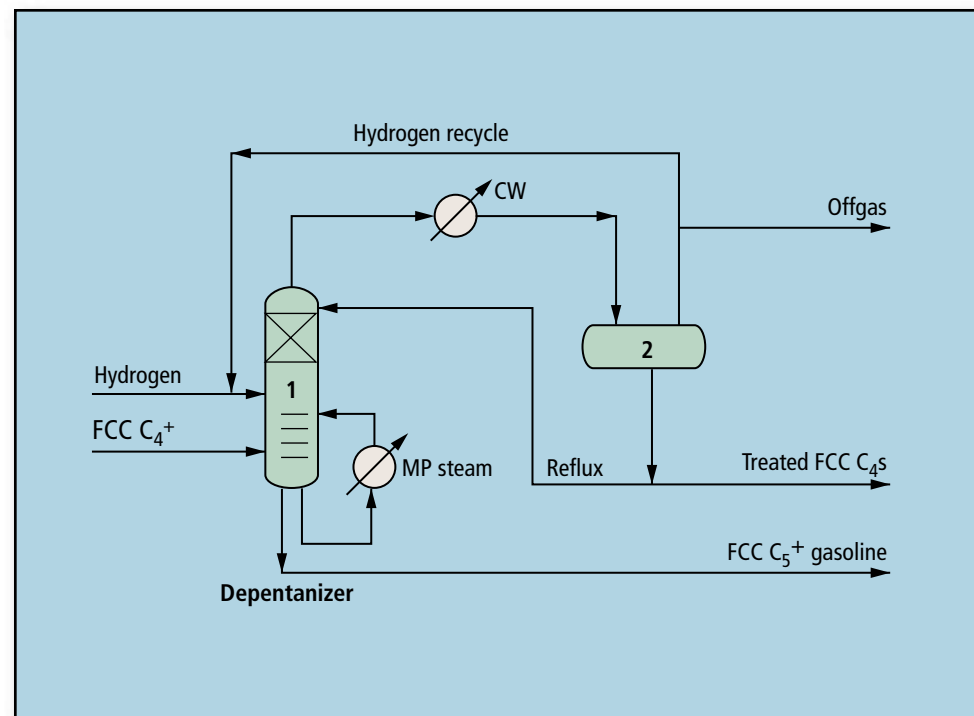
Application: CDHydro is used to selectively hydrogenate diolefins in the top section of a hydrocarbon distillation column. Additional applications—including mercaptan removal, hydroisomerization and hydrogenation of olefins and aromatics are also available.

Description: The patented process CDHydro 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 CDHydro process can operate at much lower pressure than conventional processes. Pressures for CDHydro 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 CDHydro with reformate and light-straight run for benzene saturation provides the refiner with increased flexibility to produce RFG. 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. CDHydro 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 CDHydro application. Elimination of the fixed-bed reactor and stripper can reduce capital cost by as much as 50%.

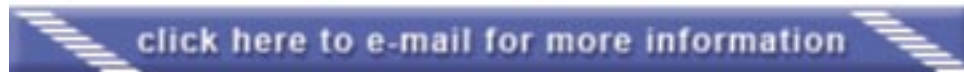
Installation: Twenty-seven CDHydro units are in commercial operation for C_4 , C_5 , C_6 and benzene hydrogenation applications. Fourteen units have been in operation for more than five years and total commercial

Continued ▼

Hydrogenation, *continued*

cial operating time now exceeds 100 years for CDHydro technologies.
Twelve additional units are currently in engineering / construction.

Licensors: CDTECH.



Hydrogen—HTCR-based

Application: Production of hydrogen from hydrocarbon feedstocks such as: natural gas, LPG, naphtha, refinery offgases, etc., using the **Haldor Topsøe Convective Reformer (HTCR)**. Plant capacities range up to 20,000 Nm³/h (20 MM scfd), and hydrogen purity from 99.5% to 99.999% is attainable. This is achieved without steam export.

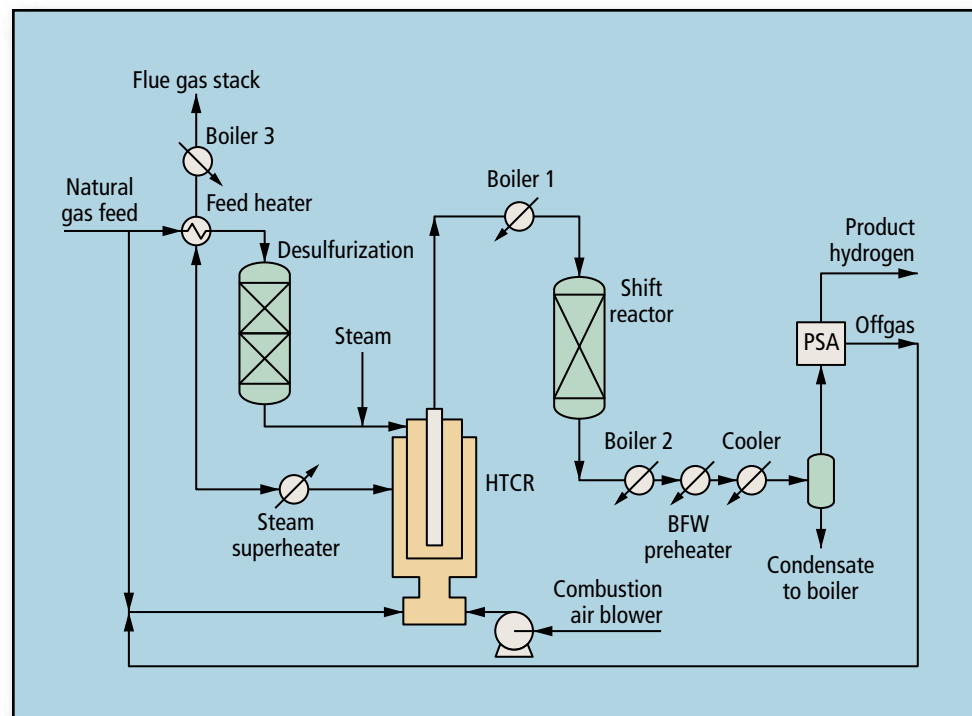
Description: The HTCR-based hydrogen plant can be tailor-made to suit the customer's needs with respect to feedstock flexibility. A typical plant comprises the following: The hydrocarbon feedstock is desulfurized. Subsequent, process steam is added, and the mixture is fed to the HTCR where the hydrocarbons are converted to CO, CO₂ and H₂ by steam reforming. Process gases are reacted in a CO shift converter and purified by pressure swing absorption (PSA) to obtain product-grade hydrogen. PSA offgases are consumed 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 its high thermal efficiency. Product gas and flue gas are both cooled to 600°C (1,100°F) by providing heat to the reforming reaction. The high-thermal efficiency is used to design energy-efficient hydrogen plants based on the HTCR without any steam export.

Economics: HTCR-based hydrogen plants provide the customer with a low investment and low operating cost option for hydrogen production. The plant can be supplied skid-mounted—providing a short erection time. The plants have high flexibility, reliability and safety. Fully automated operation, startup and shutdown allow minimum operator attendance. Net energy efficiency of 3.4 to 3.6 Gcal/KNm³ H₂ is achieved depending on size and feedstock (360–380 Btu/scf).

Installations: Twenty-seven HTCR units are in operation.

Licensors: Haldor Topsøe A/S.



Hydrogen—HTER-p based

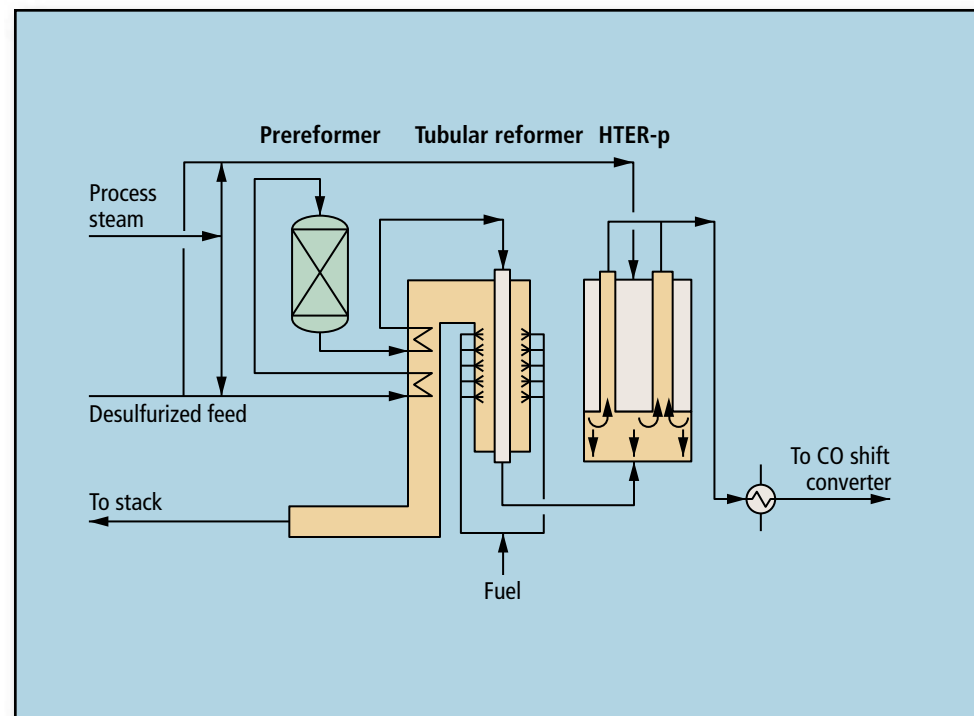
Application: Topsøe's proprietary and patented HTER-p (Haldor Topsøe Exchange Reformer—parallel installation) technology is a revamp option for production increase in a steam-reforming-based hydrogen plant. The technology allows hydrogen capacity increases of more than 25%. This option is especially 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-p is installed in parallel with the steam methane reformer (SMR) and fed independently with desulfurized feed taken upstream the reformer section. This enables individual adjustment of feed rate and steam-to-carbon ratio to obtain the desired conversion. The hydrocarbon feed is reformed over a catalyst bed installed in the HTER-p. Process effluent from the SMR is transferred to the HTER-p and mixed internally with the product gas from the HTER-p catalyst. The process gas supplies the required heat for the reforming reaction in the tubes of the HTER-p. Thus, no additional firing is required for the reforming reactions in the HTER-p.

Economics: An HTER-p 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/kNm³ 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

Licensors: Haldor Topsøe A/S.



Hydrogen—Methanol-to-Shift

Application: Topsøe's proprietary Methanol-to-Shift technology is a revamp option for hydrogen production increase for a reforming-based hydrogen plant. This technology can raise hydrogen production capacity by more than 25%. The capacity expansion is flexible and can be changed in very short time; the technology is suitable for capacity peak shaving and offers the refiner higher feedstock and product slate flexibility.

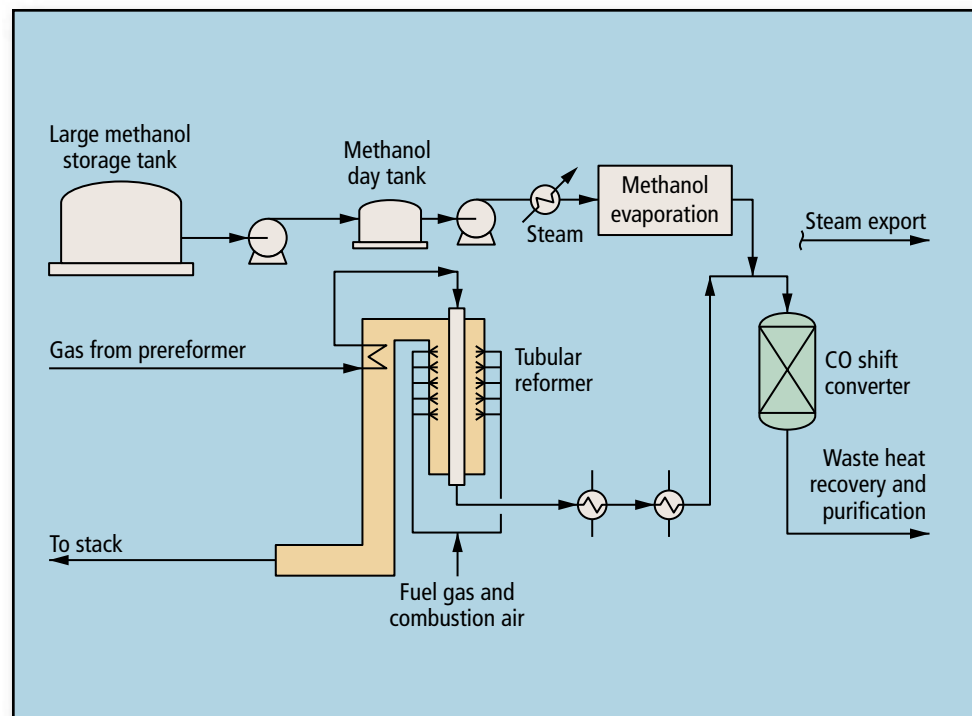
Description: Additional hydrogen is produced by reforming of methanol over Topsøe's novel dual-function catalyst—LK-510. When installed in the existing CO shift converter and fed simultaneously with methanol and reformed gas, the LK-510 catalyst promotes both the conversion of CO with steam to H_2 and CO_2 and the reforming of methanol to H_2 and CO_2 .

Methanol from a day tank is pumped to a steam-heated evaporator and fed as vapor to the existing CO shift converter, now loaded with the LK-510 catalyst. In most cases, it will be necessary to revamp the PSA unit for the additional capacity and to check the equipment downstream of the CO shift converter and modify as required.

Economics: The Methanol-to-Shift revamp technology is a low-investment option for hydrogen capacity increase and is rapid to install. The total investment cost is less than 40% of that of a new hydrogen plant. Methanol consumption is approximately 0.54 kg/Nm^3 hydrogen ($0.03 \text{ lb/scf } H_2$).

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.

Licensors: Haldor Topsøe A/S.



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.

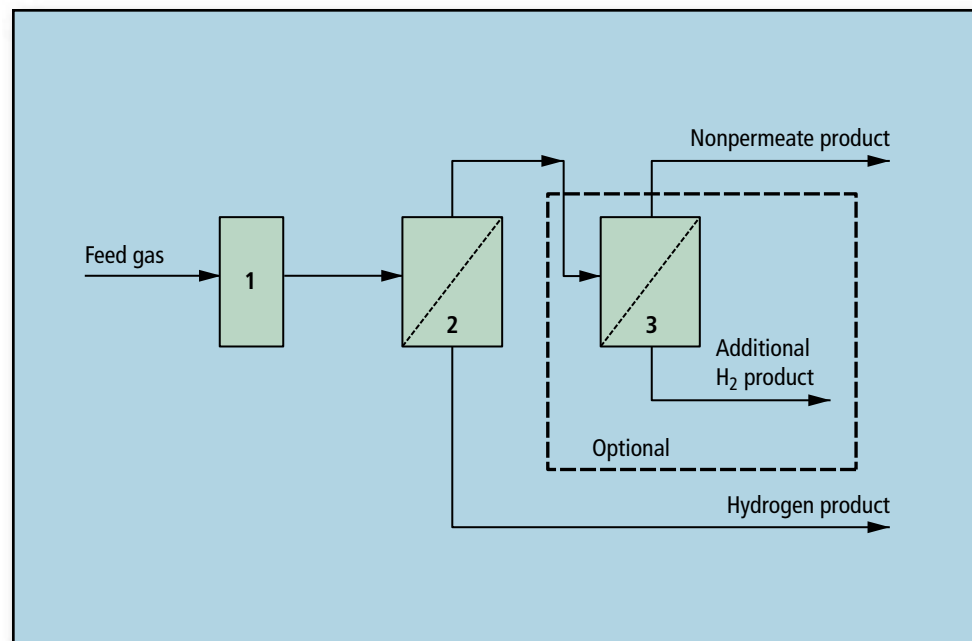
Product: Typical hydrogen (H_2) product purity is 90–98% and, in some cases, 99.9%. Product purity is dependent upon feed purity, available differential partial pressure and desired H_2 recovery level. Typical H_2 recovery is 80–95% or more.

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 270 PRISM H_2 membrane systems have been commissioned or are in design. These systems include over 54 systems in refinery applications, 124 in ammonia synthesis purge and 30 in synthesis gas applications.

Licensor: Air Products and Chemicals, Inc.

Hydrogen—steam methane reforming (SMR)

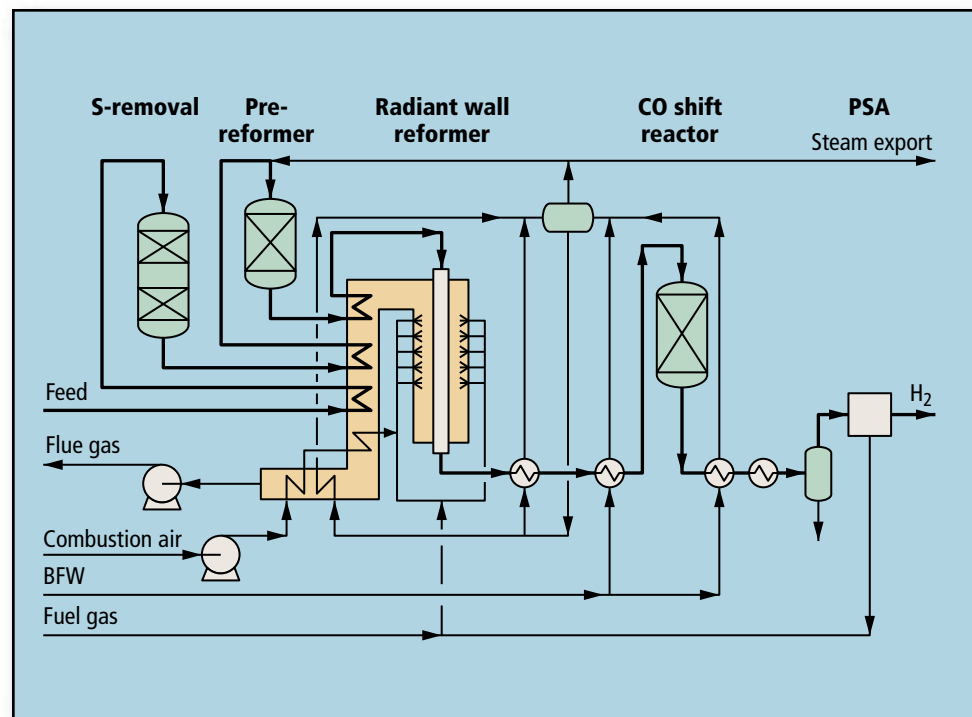
Application: Production of hydrogen from hydrocarbon feedstocks such as: natural gas, ethane, LPG, naphtha, refinery offgases, etc., using the Haldor Topsøe radiant-wall Steam Methane Reformer (SMR). Plant capacities range from 5,000 Nm³/h to more than 200,000 Nm³/h hydrogen (200+ MMscfd H₂) and hydrogen purity of up to 99.999+%.

Description: The Haldor Topsøe SMR-based hydrogen plant is tailor-made 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 medium-temperature 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/kNm³ hydrogen using natural gas feed (315 Btu/scf H₂).

Installations: More than 125 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.

Licensors: Haldor Topsøe A/S.

Hydroprocessing, residue

Application: Produces maximum distillates and low-sulfur fuel oil, or low-sulfur LR-CCU feedstock, with very tight sulfur, vanadium and CCR specifications, using moving bed “bunker” and fixed-bed technologies. Bunker units are available as a retrofit option to existing fixed-bed residue HDS units.

Description: At limited feed metal contents, the process typically uses all fixed-bed reactors. With increasing feed metal content, one or more moving-bed “bunker” reactors are added up-front of the fixed-bed reactors to ensure a fixed-bed catalyst life of at least one year. A steady state is developed by continuous catalyst addition and withdrawal: the catalyst aging is fully compensated by catalyst replacement, at typically 0.5 to 2 vol% of inventory per day.

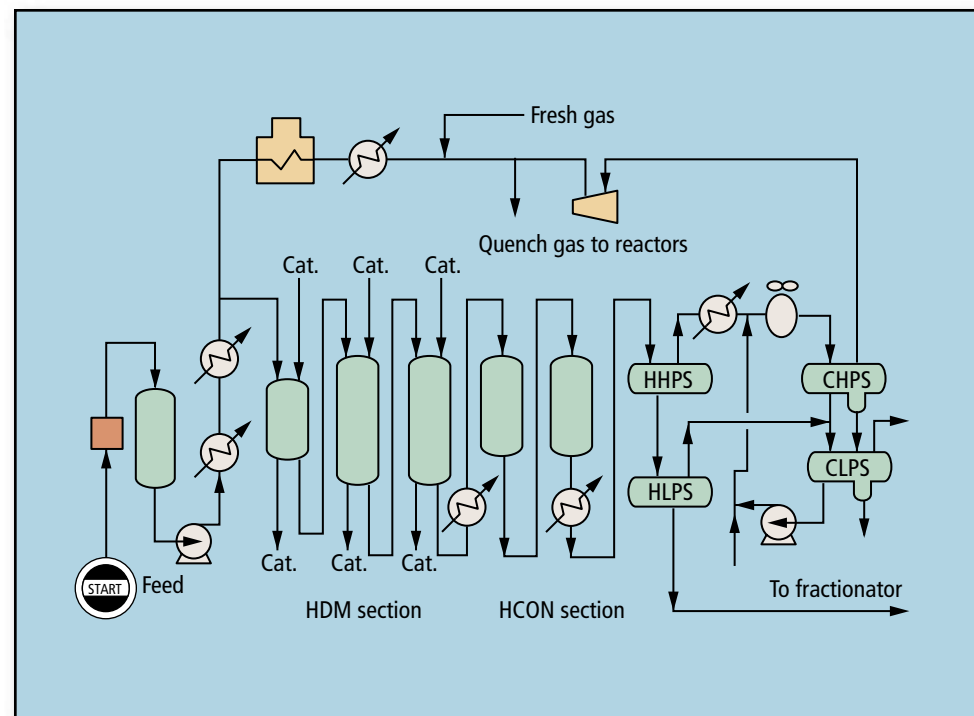
An all bunker option, which eliminates the need for catalyst change-out, is also available. A hydrocracking reactor, which converts the synthetic vacuum gasoil into distillates, can be efficiently integrated into the unit. A wide range of residue feeds, like atmospheric or vacuum residues and deasphalted oils, can be processed using Shell residue hydroprocessing technologies.

Operating conditions:

Reactor pressures:	100–200 bar	1,450–3,000 psi
Reactor temperatures:	370–420°C	700–790°F

Yields: Typical yields for an SR HYCON unit on Kuwait feed:

Feedstock		SR (95% 520C+) with integrated HCU	
Yields:		[%wof]	[%wof]
Gases	C ₁ –C ₄	3	5
Naphtha	C ₅ –165°C	4	18
Kero + gasoil	165–370°C	20	43
VGO	370–580°C	41	4
Residue	580°C+	29	29
H ₂ cons.		2	3



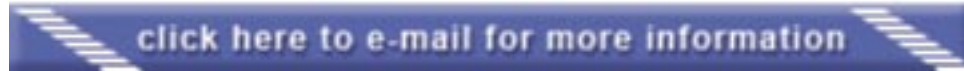
Economics: Investment costs for the various options depend strongly on feed properties and process objectives of the residue hydroprocessing unit. Investment costs for a typical new single string 5,000 tpsd SR-Hycon unit will range from 200 to 300 MM US\$; the higher figure includes an integrated hydrocracker.

Installation: There is one unit with both bunker reactors and fixed-bed reactors, operating on short residue (vacuum residue) at 4,300 tpd or 27 Mbpsd capacity, and two all-fixed bed units of 7,700 and 7,000 tpd (48 and 44 Mbpsd resp.), the latter one in one single string. Commercial experiences range from low-sulfur atmospheric residues to high-metal, high-sulfur vacuum residues with over 300-ppmw metals.

Hydroprocessing, residue, *continued*

Reference: Scheffer, B., et al, "The Shell Residue Hydroconversion Process: Development and achievements," The European Refining Technology Conference, London, November 1997.

Licensors: Shell Global Solutions International B.V.



Hydroprocessing, ULSD

Application: A versatile family of ExxonMobil Research and Engineering Co. (EMRE) process technologies and catalysts are used to meet all current and possible future premium diesel requirements.

ULSD HDS—Ultra-deep hydrodesulfurization process to produce distillate products with sulfur levels below 10 wppm.

HDHC—Heavy-distillate mild-hydrocracking process for the reduction of T90 and T95 boiling points, and high-level density reduction.

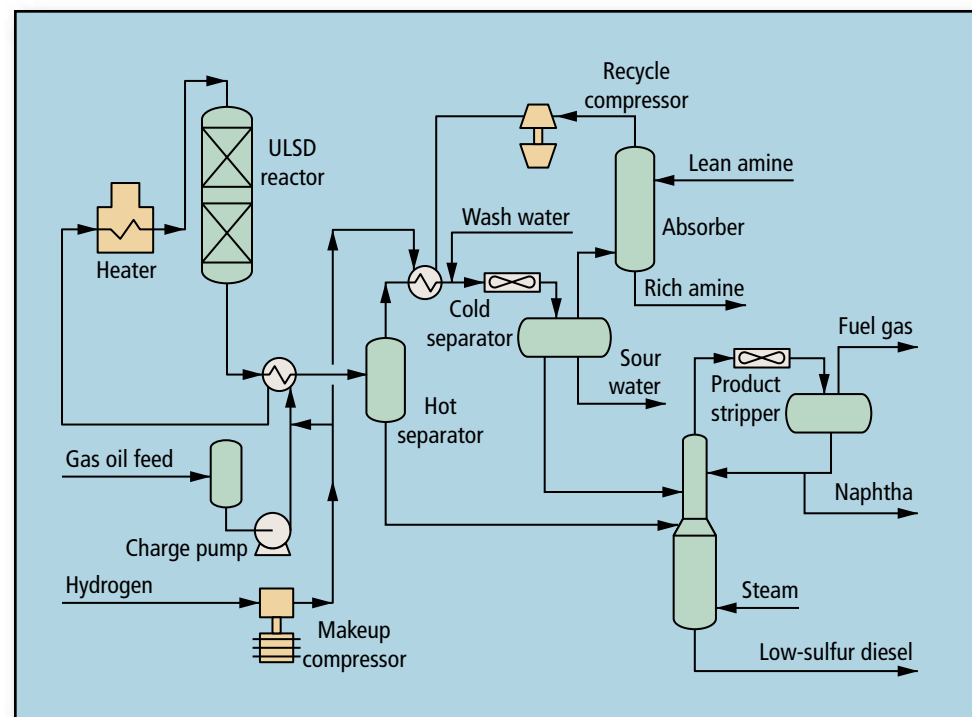
MAXSAT—High-activity aromatics saturation process for the selective reduction of polyaromatics under low pressure and temperature conditions.

CPI—Diesel cloud point improvement by selective normal paraffin hydrocracking (MDDW) or by paraffin isomerization dewaxing (MIDW).

Description: EMRE units combine the technologies listed above in low-cost integrated designs to achieve the necessary product uplift at minimum investment and operating cost. For ultra-low-sulfur-diesel hydrodesulfurization (ULSD HDS), a single-stage single-reactor process can be designed. A small cetane improvement, together with the reduction of polyaromatics to less than 11 wt. % or as low as 5 wt. %, can be economically achieved with proper specification of catalyst, hydrogen partial pressure, space velocity and the installation of high-performance Spider Vortex internals.

The addition of heavy-diesel hydrocracking (HDHC) function to the HDS reactor can achieve T95 boiling point reduction together with higher levels of density and aromatics reduction and greater cetane improvement.

When feedstock aromatics are very high, or very low aromatics in the product are desired, a second-stage aromatics saturation (MAXSAT) system is specified to avoid very high design pressures required for a single-step base-metal hydrotreating catalyst system. When the distil-



late product must also meet stringent fluidity specifications, EMRE can offer either paraffin isomerization dewaxing (MIDW) or selective normal paraffin cracking-based dewaxing technologies (MDDW). These can be closely integrated with ULSD HDS and other functions to achieve the full upgrading requirements.

The EMRE ULSD technologies are equally amenable to revamp or grassroots applications. EMRE has an alliance with Kellogg Brown & Root (KBR) to provide these technologies to refiners.

Economics:

Investment: (Basis: 20,000–35,000 bpsd, 1st quarter 2004 US Gulf Coast)
New unit, \$/bpsd

1,200–2,000

Continued ▼

Hydroprocessing, ULSD, *continued*

Installation: Nineteen distillate upgrading units have applied the EMRE ULSD technologies. Twelve of these applications are revamps.

Licensor: ExxonMobil Research and Engineering Co.



Hydrotreating

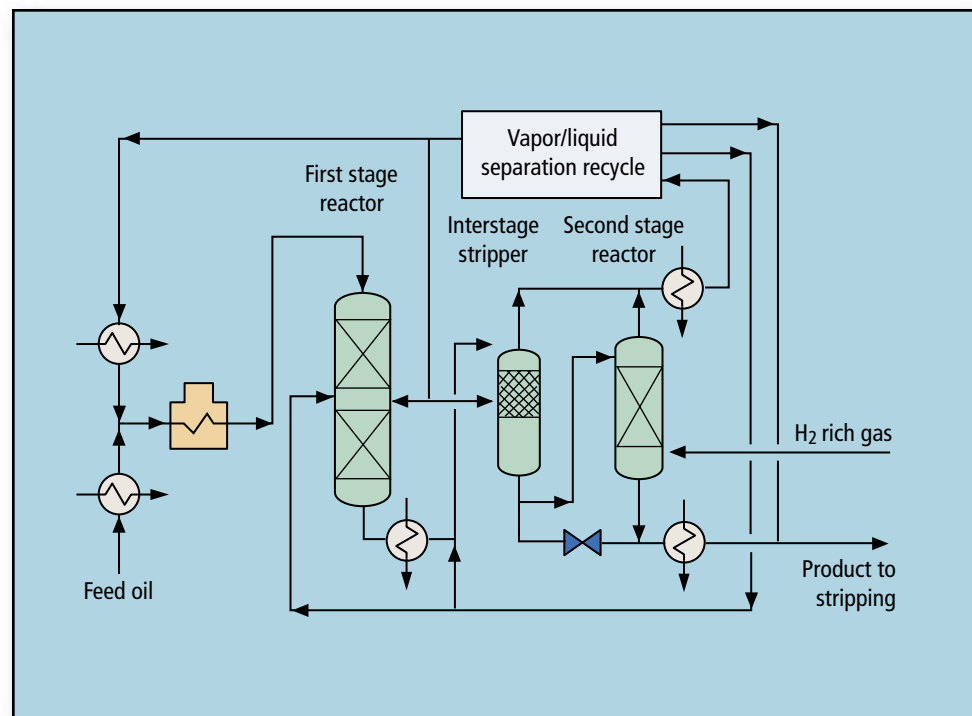
Application: Hydroprocessing of middle distillates, including cracked materials (coker/visbreaker gas oils and LCO), using SynTechnology maximizes distillate yield while producing ultra-low-sulfur diesel (ULSD) with improved cetane and API gain, reduced aromatics, T95 reduction and cold-flow improvement through selective ring opening, saturation and/or isomerization. Various process configurations are available for revamps and new unit design to stage investments to meet changing diesel specifications.

Products: Maximum yield of improved quality distillate while minimizing fuel gas and naphtha. Diesel properties include less than 10-ppm sulfur, with aromatics content (total and/or PNA), cetane, density and T95 dependent on product objectives and feedstock.

Description: SynTechnology includes SynHDS for ultra-deep desulfurization and SynShift/SynSat for cetane improvement, aromatics saturation and density/T95 reduction. SynFlow for cold flow improvement can be added as required. The process combines ABB Lummus Global's cocurrent and/or patented countercurrent reactor technology with special SynCat catalysts from Criterion Catalyst Co. LP. It incorporates design and operations experience from Shell Global Solutions to maximize reactor performance by using advanced reactor internals.

A single-stage or integrated two-stage reactor system provides various process configuration options and revamp opportunities. In a two-stage reactor system, the feed, makeup and recycle gas are heated and fed to a first-stage cocurrent reactor. Effluent from the first stage is stripped to remove impurities and light ends before being sent to the second-stage countercurrent reactor. When a countercurrent reactor is used, fresh makeup hydrogen can be introduced at the bottom of the catalyst bed to achieve optimum reaction conditions.

Operating conditions: Typical operating conditions range from 500–1,000 psig and 600°F–750°F. Feedstocks range from straight-run gas



oils to feed blends containing up to 70% cracked feedstocks that have been commercially processed. For example, the SynShift upgrading of a feed blend containing 72% LCO and LCGO gave these performance figures:

	Feed blend	Product
Gravity, °API	25	33.1
Sulfur, wt% (wppm)	1.52	(2)
Nitrogen, wppm	631	<1
Aromatics, vol%	64.7	34.3
Cetane index	34.2	43.7
Liquid yield on feed, vol%		107.5

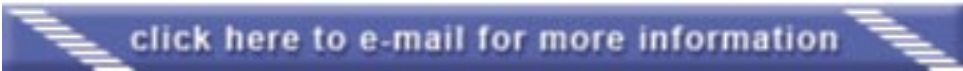
Hydrotreating, *continued*

Economics: SynTechnology encompasses a family of low-to-moderate pressure processes. Investment cost will be greatly dependent on feed quality and hydroprocessing objectives. For a 30,000 to 35,000-bpsd unit, the typical ISBL investment cost in US\$/bpsd (US Gulf Coast 2000) are:

Revamp existing unit	450–950
New unit for deep HDS	1,100–1,200
New unit for cetane improvement and HDA	1,500–1,600

Installation: SynTechnology has been selected for more than 30 units, with half of the projects being revamps. Seven units are in operation.

Licensors: ABB Lummus Global, on behalf of the SynAlliance, which includes Criterion Catalyst and Technologies Co., and Shell Global Solutions.



Hydrotreating

Application: Reduction of the sulfur, nitrogen and metals content of naphthas, kerosines, diesel or gas oil streams.

Products: Low-sulfur products for sale or additional processing.

Description: Single or multibed catalytic treatment of hydrocarbon liquids in the presence of hydrogen converts organic sulfur to hydrogen sulfide and organic nitrogen to ammonia. Naphtha treating normally occurs in the vapor phase, and heavier oils usually operate in mixed-phase. Multiple beds may be placed in a single reactor shell for purposes of redistribution and/or interbed quenching for heat removal. Hydrogen-rich gas is usually recycled to the reactor(s) (1) to maintain adequate hydrogen-to-feed ratio. Depending on the sulfur level in the feed, H_2S may be scrubbed from the recycle gas. Product stripping is done with either a reboiler or with steam. Catalysts are cobalt-molybdenum, nickel-molybdenum, nickel-tungsten or a combination of the three.

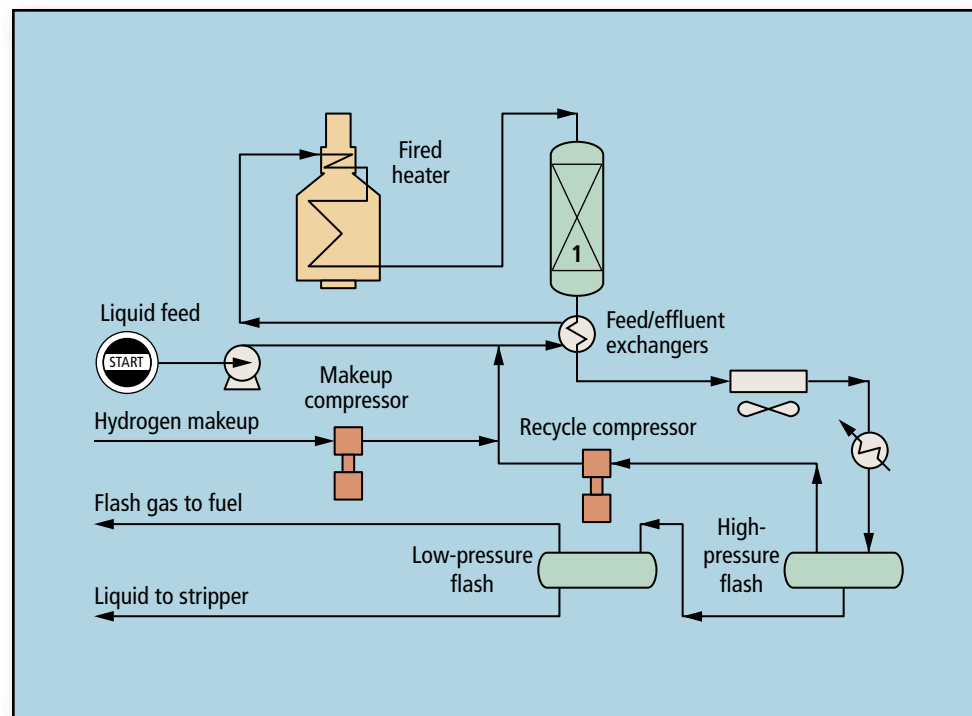
Operating conditions: 550°F to 750°F and 400 psig to 1,500 psig reactor conditions.

Yields: Depend on feed characteristics and product specifications. Recovery of desired product almost always exceeds 98.5 wt% and usually exceeds 99%.

Economics:

Utilities, (per bbl feed)	Naphtha	Diesel
Fuel, 10 ³ Btu release	48	59.5
Electricity, kWh	0.65	1.60
Water, cooling (20°F rise), gal	35	42

Licensors: CB&I Howe-Baker Process and Technology.



Hydrotreating

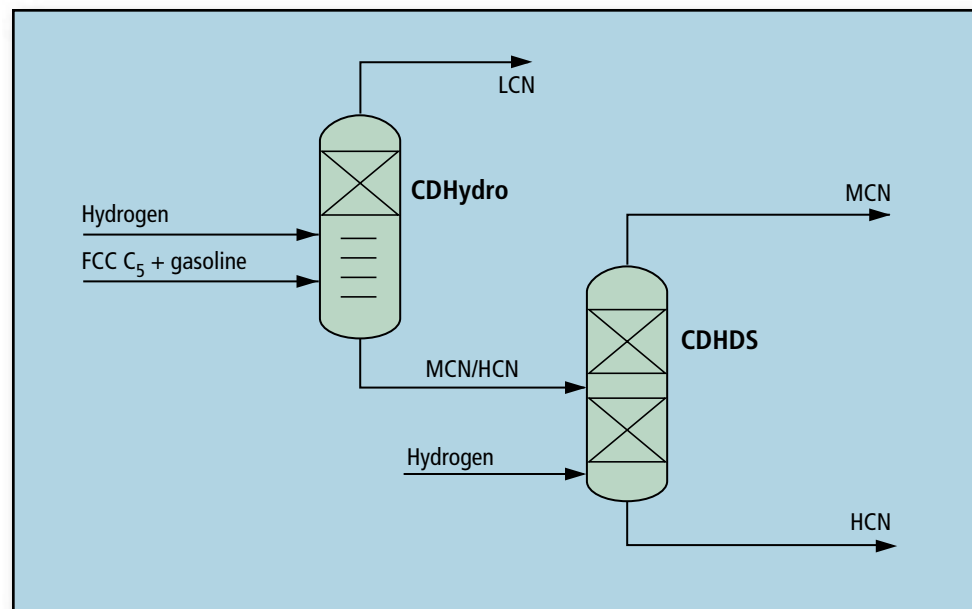
Application: CDHydro and CDHDS are used to selectively desulfurize FCC gasoline with minimum octane loss.

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 top of the column, where conditions are mild, while sulfur is 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 CDHydro/CDHDS units can operate throughout an FCC turn-around cycle up to five years without requiring a shutdown to regener-



ate 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 35,000-bpd CDHydro/CDHDS unit with 95% desulfurization is \$26 million (2000 US Gulf Coast). Direct operating costs—including utilities, catalyst, hydrogen and octane replacement—are estimated at \$0.04/gal of full-range FCC gasoline.

Installation: Fourteen CDHydro units are in operation treating FCC gasoline and 10 more units are currently in engineering/construction. Eight CDHDS units are in operation with 10 additional units currently in engineering/construction. Forty-six units have been awarded with a total capacity of one million bpsd.

Licensors: CDTECH.

Hydrotreating

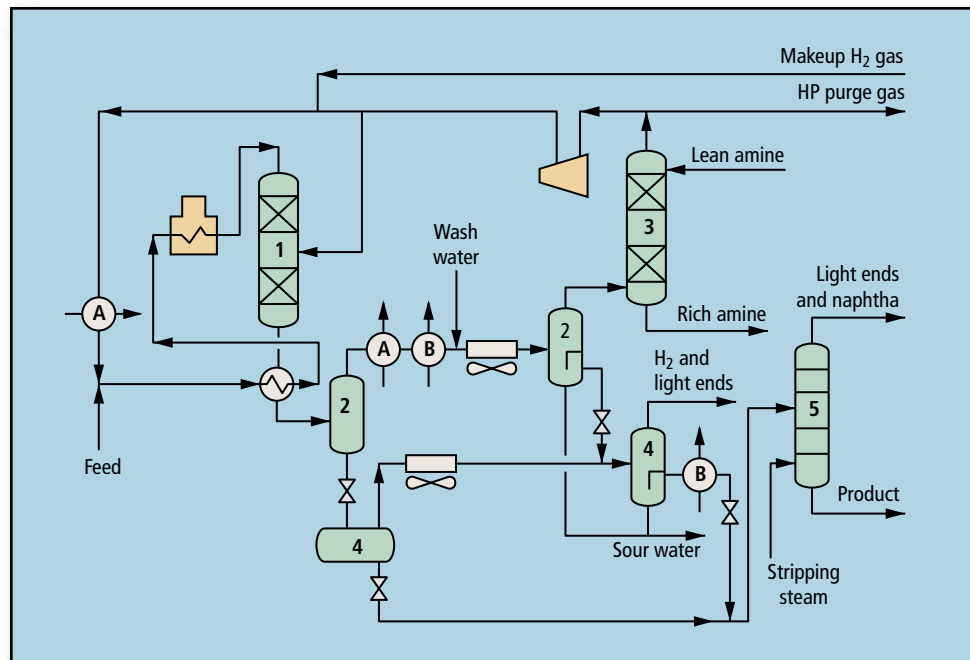
Application: Hydrotreating of light and middle distillates and various gas oils, including cracked feedstocks (coker naphtha, coker LGO and HGO, visbreaker gas oil, and LCO) using the ISOTREATING Process for deep desulfurization, denitrification and aromatics saturation and to produce low-sulfur naphtha, 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 H₂S 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, H₂S 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 600–1,800 psig and 550–750°F, 350–1,300 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 liquid product (350°F plus) yield can vary between 98 vol% from straight-



run 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 2004) is \$600–900/bpsd for a revamped unit and \$1,500–1,800/bpsd for a new unit.

Installation: Currently, there are more than 50 units operating based on ISOTREATING technology and an additional 14 units in various stages of engineering.

Licensors: Chevron Lummus Global LLC.

Hydrotreating

Application: The process was developed for the hydrotreatment for middle distillates to reduce sulfur and, with the appropriate catalysts, aromatics to meet the most stringent fuel specifications.

Products: Low-sulfur and aromatic middle distillate suitable for diesel.

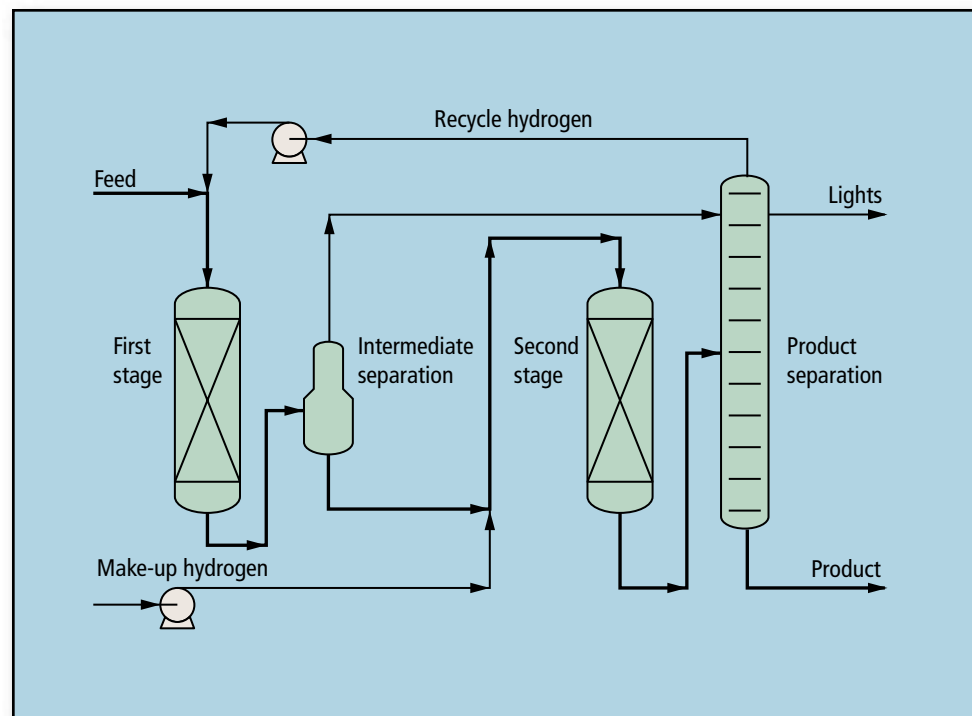
Description: The essential feature of the SuperTreet process is an interstage separation. The first-stage catalyst bed is generally filled with standard HDS catalyst to remove the less refractory sulfur compounds that accounts for a large part, 80%+, of the contained sulfur in a typical middle distillate. The hot, high-pressure separation enables removing H_2S before introduction of the treated stream to the second reactor. H_2S inhibits desulfurization reactions, and so this feature greatly enhances the effectiveness of the second-stage hydrotreating.

Fresh hydrogen is introduced to the second reactor to further remove more refractory sulfur compounds such as dibenzothiophenes. The advent of sulfur-tolerant HDA catalysts means that this final desulfurization and dearomatization can both occur in this second reactor. The intermediate removal of H_2S and the introduction of fresh hydrogen feed provides a much improved environment for the removal of the most difficult compounds.

Typical operating conditions: These are very dependent on the nature of the feed stream and product specification; typically the operating pressure is in the region of 40 bar. The system can be adapted to maximize the re-use of existing equipment in a revamp situation.

References: McKinley, D. H. and M. A. Wood, "Deep Desulfurization—An Insight into the Catalyst Bed," AIChE, Spring National Meeting 1995.

Lawrence, R. C., D. H. McKinley and M. A. Wood, "Process Developments in Gasoil Hydrotreating," OAPEC Seminar—"Refining Industry in the Arab Countries and the Challenges of the 21st Century," 1996.



Lawrence, R. C., D. H. McKinley and M. A. Wood, "Further Process Developments in Gasoil Hydrotreating," Japan Petroleum Institute Conference, Kyoto, 1998.

Licensors: Davy Process Technology Ltd.

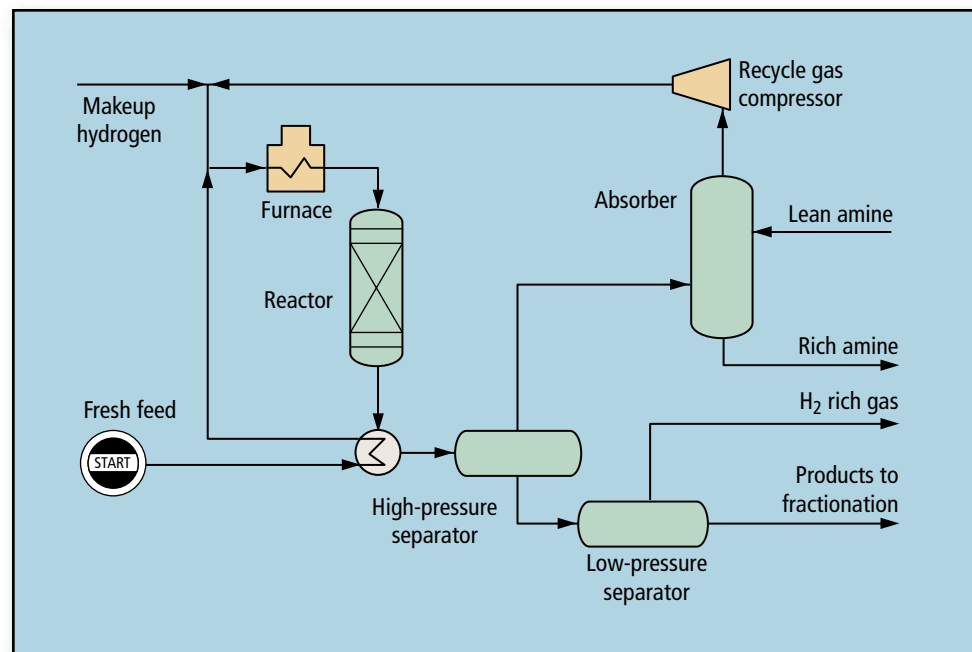
Hydrotreating

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 quench 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.

de la Fuente, E., P. Christensen and M. Johansen, "Options for meeting EU year 2005 fuel specifications," ERTC, November 1999.

Patel, R. and K. Knudsen, "How are refiners meeting the ultra-low-sulfur diesel challenge," NPRA Annual Meeting, March 2003.

Installation: More than 40 Topsøe hydrotreating units for the various applications above are in operation or in the design phase.

Licensors: Haldor Topsøe A/S.

Hydrotreating

Application: The IsoTherming process provides refiners an economical means to produce ultra-low-sulfur diesel (ULSD), low-sulfur and low-nitrogen FCC feedstocks, and other very low-sulfur hydrocarbon products. In addition, IsoTherming can provide a cost-effective approach to wax and petrolatum hydrogenation to produce food-grade or pharmaceutical-grade oil and wax products, and lubestock hydroprocessing for sulfur reduction and VI improvement.

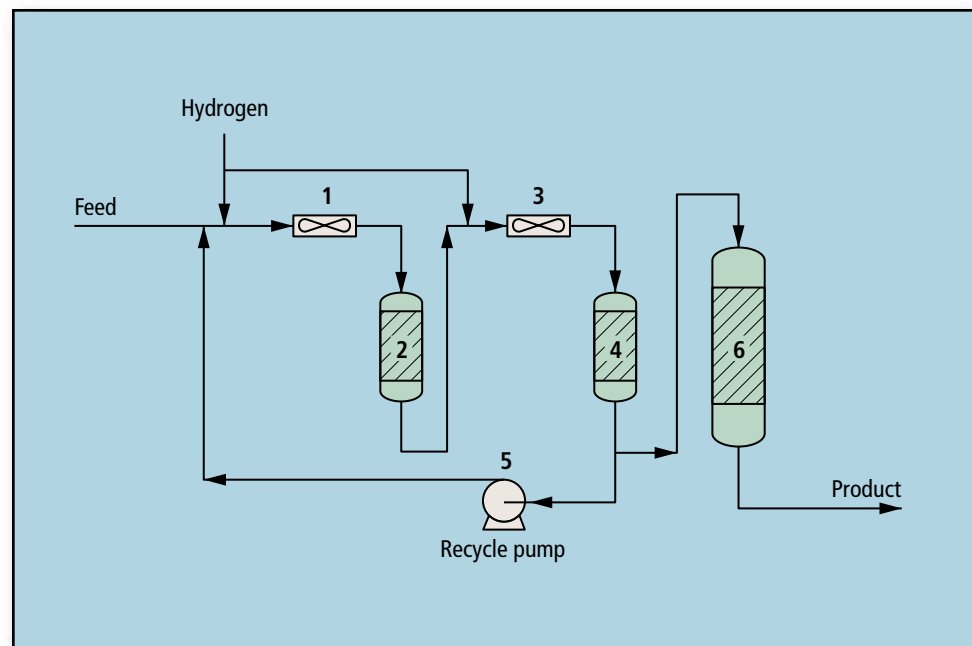
Products: ULSD, low-sulfur FCC feed, low-sulfur gasoline-kerosine type products. High-quality lube-oil stock and food- and pharmaceutical-grade oil and wax.

Description: This process uses a novel approach to introduce hydrogen into the reactor; it enables much higher space velocities than conventional hydrotreating reactors. The IsoTherming process removes the hydrogen mass transfer limitation and operates in a kinetically limited mode since hydrogen is delivered to the reactor in the liquid phase as soluble hydrogen.

The technology can be installed as a simple pre-treat unit ahead of an existing hydrotreater reactor or a new stand-alone process unit. Fresh feed, after heat exchange, is combined with hydrogen in Reactor One mixer (1). The feed liquid with soluble hydrogen is fed to IsoTherming Reactor One (2) where partial desulfurization occurs. The stream is combined with additional hydrogen in Reactor Two Mixer (3), and fed to IsoTherming Reactor Two (4) where further desulfurization takes place.

Treated oil is recycled (5) back to the inlet of Reactor One. This recycle stream delivers more hydrogen to the reactors and also acts as a heat sink; thus, a nearly isothermal reactor operation is achieved.

The treated oil from IsoTherming Reactor Two (4) may then be fed to additional IsoTherming reactors and/or to a trickle hydrotreating reactor (6) in the polishing mode to produce an ultra-low-sulfur product.



Operating conditions: Typical diesel IsoTherming conditions are:

	Diesel feed	IsoTherming pre-treat reactor	Treated product from existing conventional reactor
LCO, vol%	40		
SR, vol%	60		
Sulfur, ppm	7,500	900	5
Nitrogen, ppm	450	50	0
H ₂ consumption, scf/bbl		300	150
LHSV, Hr ⁻¹ *		5	2.5
Reactor ΔT		30	30
Reactor pressure, psig		1,110	900

*Based on fresh feedrate without recycle

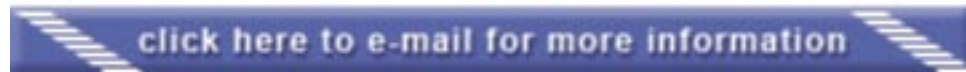
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Hydrotreating, *continued*

Economics: Revamp investment (basis 15,000–20,000 bpsd, 1Q 2004,
US Gulf Coast) \$400/bpsd diesel

Installation: First commercial diesel unit onstream October 2002.

Licensors: P. D. Licensing, LLC (Process Dynamics, Inc.).



Hydrotreating

Application: The IsoTherming process provides refiners an economical means to produce ultra-low-sulfur diesel (ULSD), low-sulfur and low-nitrogen FCC feedstocks, and other very low-sulfur hydrocarbon products. In addition, IsoTherming can provide a cost-effective approach to wax and petrolatum hydrogenation to produce food-grade or pharmaceutical-grade oil and wax products, and lubestock hydroprocessing for sulfur reduction and VI improvement.

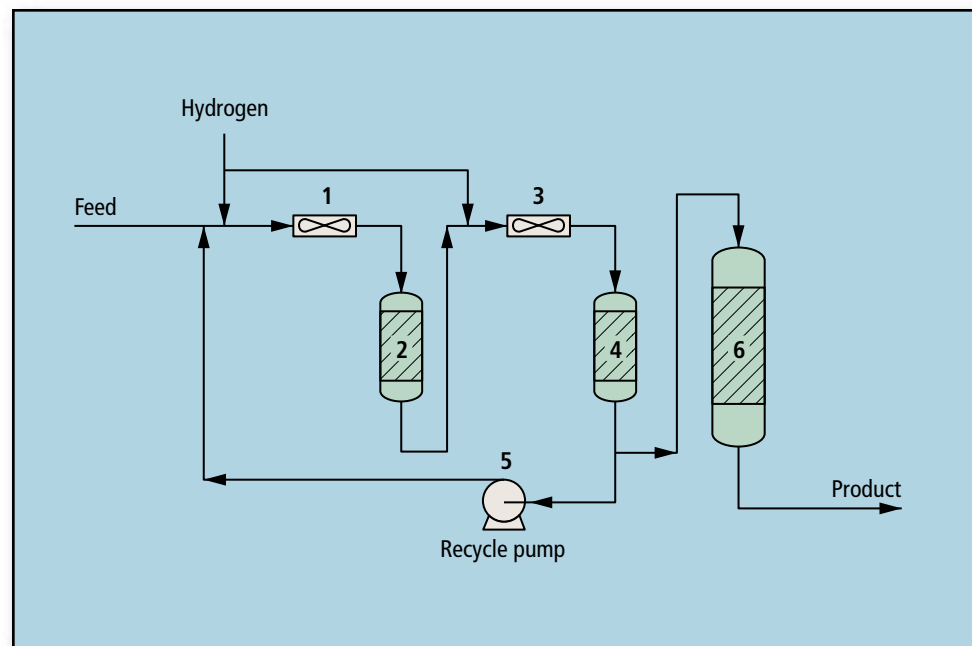
Products: ULSD, low-sulfur FCC feed, low-sulfur gasoline-kerosine type products. High-quality lube-oil stock and food- and pharmaceutical-grade oil and wax.

Description: This process uses a novel approach to introduce hydrogen into the reactor; it enables much higher space velocities than conventional hydrotreating reactors. The IsoTherming process removes the hydrogen mass transfer limitation and operates in a kinetically limited mode since hydrogen is delivered to the reactor in the liquid phase as soluble hydrogen.

The technology can be installed as a simple pre-treat unit ahead of an existing hydrotreater reactor or a new stand-alone process unit. Fresh feed, after heat exchange, is combined with hydrogen in Reactor One mixer (1). The feed liquid with soluble hydrogen is fed to IsoTherming Reactor One (2) where partial desulfurization occurs. The stream is combined with additional hydrogen in Reactor Two Mixer (3), and fed to IsoTherming Reactor Two (4) where further desulfurization takes place.

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Operating conditions: Typical diesel IsoTherming conditions are:

	Diesel feed	IsoTherming pre-treat reactor	Treated product from existing conventional reactor
LCO, vol%	40		
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Nitrogen, ppm	450	50	0
H ₂ consumption, scf/bbl		300	150
LHSV, Hr ⁻¹ *		5	2.5
Reactor ΔT		30	30
Reactor pressure, psig		1,110	900

*Based on fresh feedrate without recycle

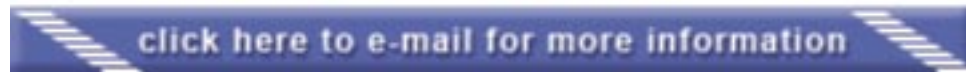
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Hydrotreating, *continued*

Economics: Revamp investment (basis 15,000–20,000 bpsd, 1Q 2004,
US Gulf Coast) \$400/bpsd diesel

Installation: First commercial diesel unit onstream October 2002.

Licensors: P. D. Licensing, LLC (Process Dynamics, Inc.).



Hydrotreating

Application: Hydrodesulfurization, hydrodenitrogenation and hydrogenation of petroleum and chemical feedstocks using the Unionfining and MQD Unionfining processes.

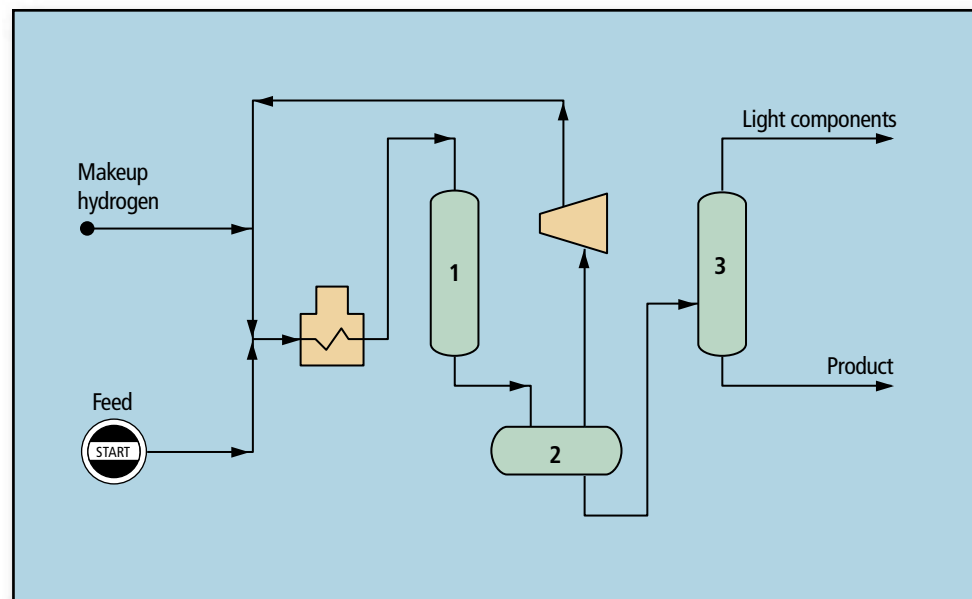
Products: Ultra-low-sulfur diesel fuel; feed for catalytic reforming, FCC pretreat; upgrading distillates (higher cetane, lower aromatics); desulfurization, denitrogenation and demetallization of vacuum and atmospheric gas oils, coker gas oils and chemical feedstocks.

Description: Feed and hydrogen-rich gas are mixed, heated and contacted with regenerable catalyst (1). Reactor effluent is cooled and separated (2). Hydrogen-rich gas is recycled or used elsewhere. Liquid is stripped (3) to remove light components and remaining hydrogen sulfide, or fractionated for splitting into multiple products.

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.

Yields:

Purpose	FCC feed	Desulf.	Desulf.	Desulf.
Feed, source	VGO + Coker	AGO	VGO	DSL
Gravity, °API	17.0	25.7	24.3	32.9
Boiling range, °F	400/1,000	310/660	540/1,085	380/700
Sulfur, wt%	1.37	1.40	3	1.1
Nitrogen, ppmw	6,050	400	1,670	102
Bromine number	—	26	—	—
Naphtha, vol%	4.8	4.2	3.9	1.6
Gravity, °API	45.0	50.0	54.0	51
Boiling range, °F	180/400	C ₄ /325	C ₄ /356	C ₅ /300
Sulfur, ppmw	50	<2	<2	<1
Nitrogen, ppmw	30	<1	<2	<0.5



Distillate, vol%	97.2	97.6	98.0	99.0
Gravity, °API	24.0	26.9	27.8	35.2
Boiling range, °F	400+	325/660	300+	300
Sulfur, wt%	0.025	0.001	0.002	0.001
H ₂ consump., scf/bbl	700	350	620	300

Economics:

Investment, \$ per bpsd	1,200–2,000
Utilities, typical per bbl feed:	
Fuel, 10 ³ Btu	40–100
Electricity, kWh	0.5–1.5

Installation: Several hundred units installed.

Licensors: UOP LLC.

Hydrotreating

Application: 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.

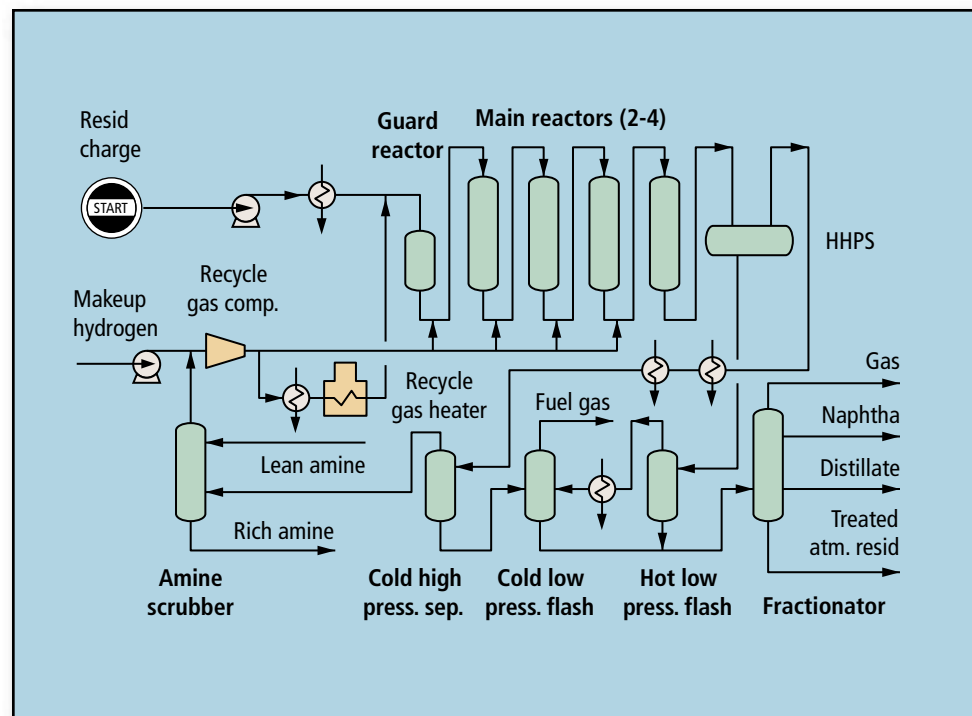
Fresh feed is combined with makeup hydrogen and recycled gas, and then heated by exchange and fired heaters before entering the unit's reactor section. Simple downflow reactors incorporating a graded bed catalyst system designed to accomplish the desired reactions while minimizing side reactions and 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 H_2S 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.

Economics:

Investment (basis: 15,000–20,000 bpsd, 2Q 2002, US Gulf Coast)
\$ per bpsd 2,000–3,500

Utilities, typical per barrel of fresh feed (20,000 bpsd basis)

Fuel, MMBtu/hr	46
Electricity, kWh	5,100



Steam, HP, lb/hr

8,900

Steam, LP, lb/hr

1,500

Installation: Twenty-six licensed units with a combined licensed capacity of approximately 900,000 bpsd. Commercial applications have included processing of atmospheric and vacuum residues and solvent-derived feedstocks.

Licensors: UOP LLC.

Hydrotreating—aromatic saturation

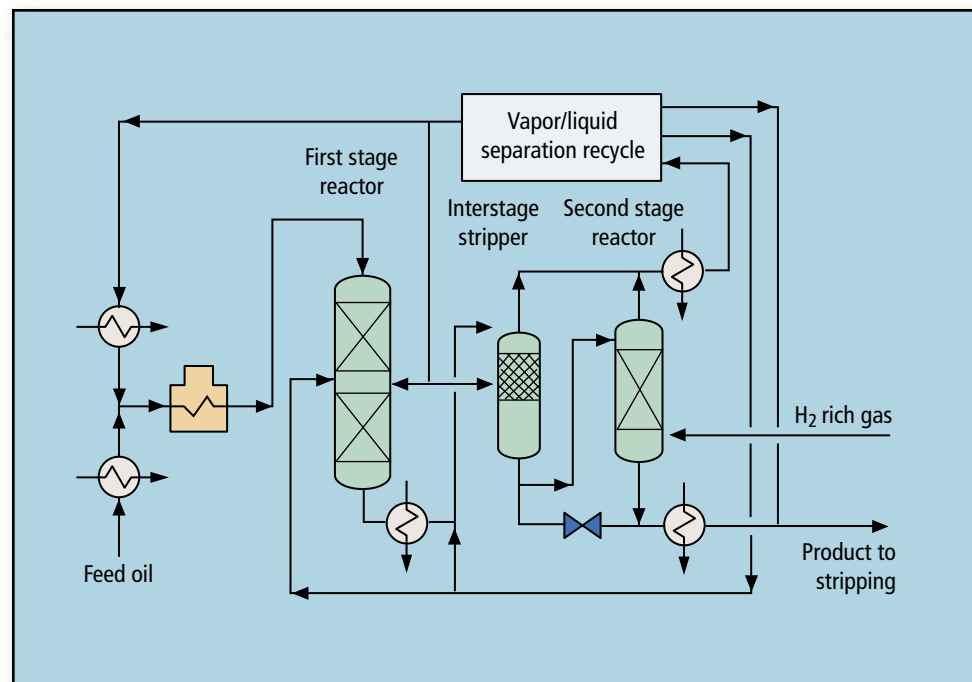
Application: Hydroprocessing of middle distillates, including cracked materials (coker/visbreaker gas oils and LCO), using SynTechnology maximizes distillate yield while producing ultra-low-sulfur diesel (ULSD) with improved cetane and API gain, reduced aromatics, T95 reduction and cold-flow improvement through selective ring opening, saturation and/or isomerization. Various process configurations are available for revamps and new unit design to stage investments to meet changing diesel specifications.

Products: Maximum yield of improved quality distillate while minimizing fuel gas and naphtha. Diesel properties include less than 10-ppm sulfur, with aromatics content (total and/or PNA), cetane, density and T95 dependent on product objectives and feedstock.

Description: SynTechnology includes SynHDS for ultra-deep desulfurization and SynShift/SynSat for cetane improvement, aromatics saturation and density/T95 reduction. SynFlow for cold flow improvement can be added as required. The process combines ABB Lummus Global's cocurrent and/or patented countercurrent reactor technology with special SynCat catalysts from Criterion Catalyst Co. LP. It incorporates design and operations experience from Shell Global Solutions to maximize reactor performance by using advanced reactor internals.

A single-stage or integrated two-stage reactor system provides various process configuration options and revamp opportunities. In a two-stage reactor system, the feed, makeup and recycle gas are heated and fed to a first-stage cocurrent reactor. Effluent from the first stage is stripped to remove impurities and light ends before being sent to the second-stage countercurrent reactor. When a countercurrent reactor is used, fresh makeup hydrogen can be introduced at the bottom of the catalyst bed to achieve optimum reaction conditions.

Operating conditions: Typical operating conditions range from 500–1,000 psig and 600°F–750°F. Feedstocks range from straight-run gas



oils to feed blends containing up to 70% cracked feedstocks that have been commercially processed. For example, the SynShift upgrading of a feed blend containing 72% LCO and LCGO gave these performance figures:

	Feed blend	Product
Gravity, °API	25	33.1
Sulfur, wt% (wppm)	1.52	(2)
Nitrogen, wppm	631	<1
Aromatics, vol%	64.7	34.3
Cetane index	34.2	43.7
Liquid yield on feed, vol%		107.5

Economics: SynTechnology encompasses a family of low-to-moderate pressure processes. Investment cost will be greatly dependent on feed
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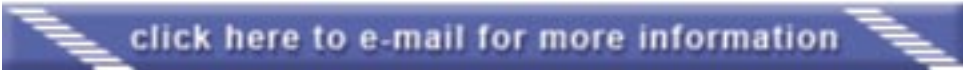
Hydrotreating—aromatic saturation, *continued*

quality and hydroprocessing objectives. For a 30,000 to 35,000-bpsd unit, the typical ISBL investment cost in US\$/bpsd (US Gulf Coast 2002) are:

Revamp existing unit	450–950
New unit for deep HDS	1,100–1,200
New unit for cetane improvement and HDA	1,500–1,600

Installation: Eleven SynTechnology units are in operation with an additional seven units in design and construction.

Licensors: ABB Lummus Global, on behalf of the SynAlliance, which includes Criterion Catalyst Co., LP, and Shell Global Solutions.



Hydrotreating—catalytic dewaxing

Application: A versatile family of premium distillates technologies is used to meet all current and possible future premium diesel upgrading requirements. The addition of selective normal paraffin hydrocracking (CFI) function to the deep hydrosulfurization (UDHDS) reactor will improve the diesel product cold flow properties for a wide range of waxy distillate feedstocks.

Products: Ultra-low-sulfur distillate is produced with modest amounts of lighter products. Low-cloud point, or pour point product quality diesel, can be achieved with the CFI processes.

Description: This Akzo-Fina CFI technology is offered through the alliance between Akzo Nobel Catalysts and Fina Research S.A. When the distillate product must meet stringent fluidity specifications, Akzo Nobel can offer this selective normal paraffin cracking based CFI dewaxing technology. Dewaxing is generally a higher-cost process but delivers higher total product quality. This technology can be closely integrated with UDHDS and other functions to achieve the full upgrading requirements in low-cost integrated designs. The CFI process uses a single-stage design even with high levels of heteroatoms in the feed. Akzo Fina CFI technology is equally applicable to revamp and grassroots applications.

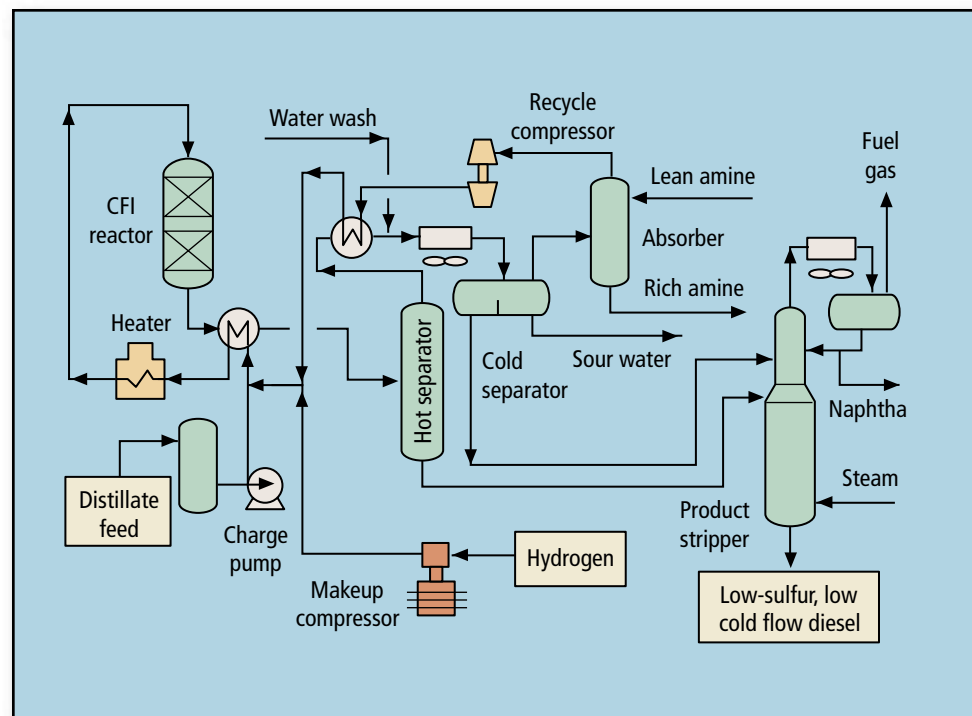
Economics:

Investment (Basis: 15,000–25,000 bpsd, 1Q 2000 US Gulf Coast)
Grassroots unit, \$ per bpsd 1,000 to 2,000

Installation: Over 17 distillate upgrading units have applied the Akzo Fina CFI technology.

Reference: “MAKFinig-Premium Distillates Technology: The future of distillate upgrading,” NPRA Annual Meeting, March 2000, San Antonio.

Licensors: Akzo Nobel Catalysts bv and Fina Research S.A.



Hydrotreating, diesel

Application: Produce ultra-low-sulfur diesel (ULSD) and high-quality diesel fuel (low aromatics, high cetane) via Prime-D toolbox of proven state-of-the-art technology, catalysts and services.

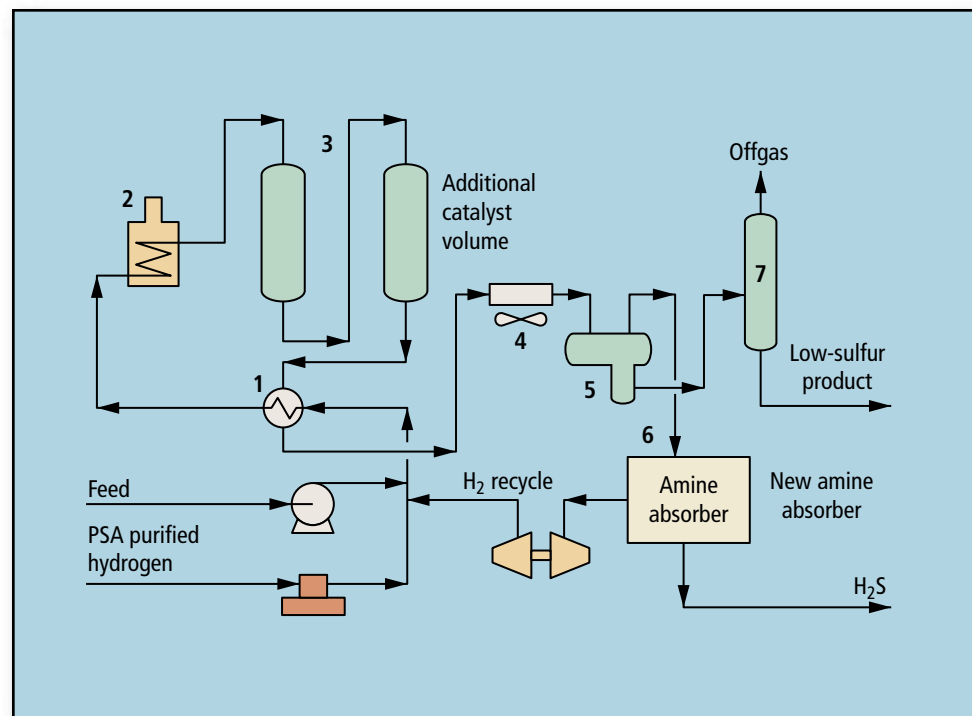
Description: In the basic process, as shown in the diagram, feed and hydrogen are heated in the feed-reactor effluent exchanger (1) and furnace (2) and enter the reaction section (3), with possible added volume for revamp cases. The reaction effluent is cooled by the exchanger (1) and air cooler (4) and separated in the separator (5). The hydrogen-rich 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 of solutions meets the challenge. Process objectives ranging from low-sulfur, ultra-low-sulfur, low-aromatics, and/or high cetane number are met with minimum cost by:

- Selection of the proper catalyst from the HR 400 series, based on the feed analysis and processing objectives. HR 400 catalysts cover the range of ULSD requirements with highly active and stable catalysts. HR 426 CoMo exhibits high desulfurization rates at low to medium pressures; HR 448 NiMo has higher hydrogenation activity at higher pressures; and HR 468 NiCoMo is very effective for ULSD in the case of moderate pressures.

- Use of proven, efficient reactor internals, EquiFlow, that allow near-perfect gas and liquid distribution and outstanding radial temperature profiles.

- Loading catalyst in the reactor(s) with the Catapac dense loading technique for up to 20% more reactor capacity. Over 8,000 tons of catalyst have been loaded quickly 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 100 middle distillate hydrotreaters have been licensed or revamped. They include 23 low- and ultra-low-sulfur diesel units (<50 ppm), as well as a number of cetane boosting units. Most of those units are equipped with EquiFlow internals.

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Hydrotreating, diesel, *continued*

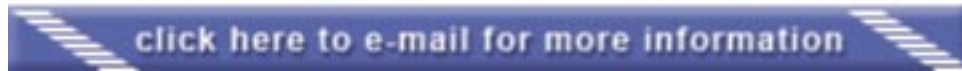
References: "Getting Total Performance with Hydrotreating," *Petroleum Technology Quarterly*, Spring 2002.

"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.

Licensors: Axens.



Hydrotreating—lube and wax

Application: The IsoTherming process provides refiners with a cost-effective approach to lube and wax hydrotreating to produce high-quality lube-base stocks and food-grade waxes.

Products: High-quality lube oils, food- or pharmaceutical-grade oil and wax products.

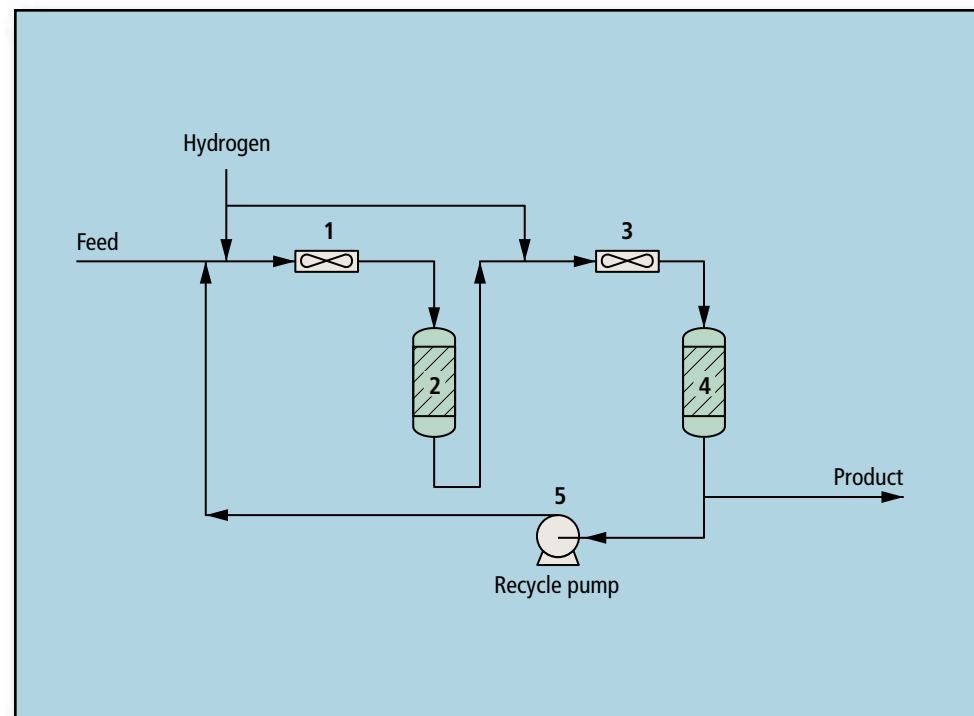
Description: This process uses a novel approach to introduce hydrogen into the reactor; it enables much higher LHSV than conventional hydrotreating reactors. The IsoTherming process removes the hydrogen mass transfer limitation and operates in a kinetically limited mode since hydrogen is delivered to the reactor in the liquid phase as soluble hydrogen.

The technology can be installed as a simple pre-treat unit ahead of an existing hydrotreater reactor or a new stand-alone process unit. Fresh feed, after heat exchange, is combined with hydrogen in Reactor One mixer (1). The liquid feed with soluble hydrogen is fed to IsoTherming Reactor One (2) where partial desulfurization, denitrofication and saturation occurs.

The stream is combined with additional hydrogen in Reactor Two mixer (3), and fed to IsoTherming Reactor Two (4) where further desulfurization, denitrofication and saturation take place. Treated oil is recycled (5) to the inlet of Reactor One. This recycle stream delivers more hydrogen to the reactors and also acts as a heat sink; thus, a nearly isothermal reactor operation is achieved.

Economics: Investment (basis 5,000 bpd)

Lube-base oil grassroots	\$7.5 million
Lube-base oil retrofit	\$3.1 million
Paraffin wax grassroots	\$6.0 million
Micro-wax grassroots	\$13.0 million
White oil	\$10.7 million



Licensor: P. D. Licensing, LLC (Process Dynamics, Inc.).

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).

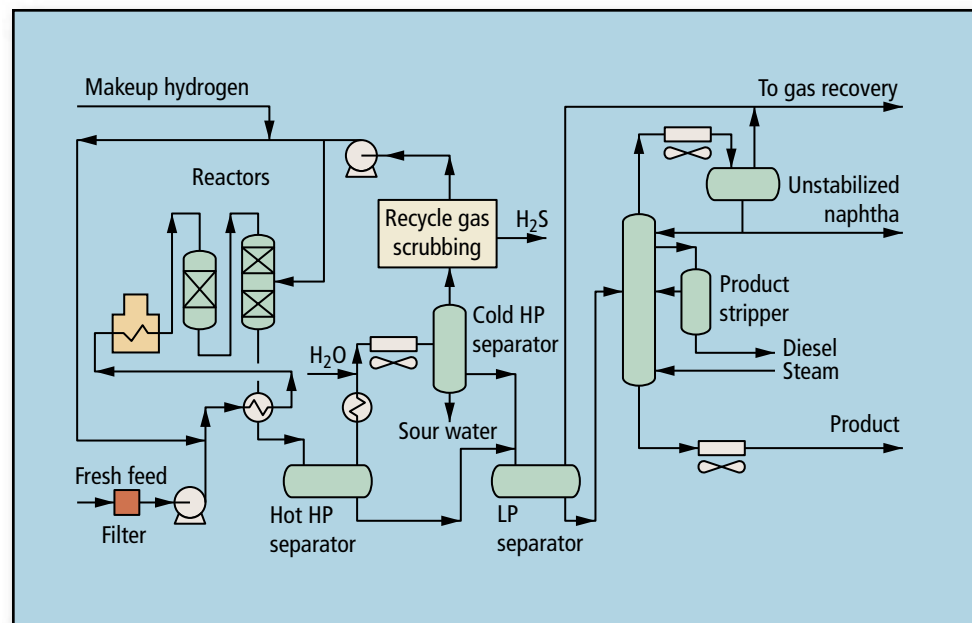
The process integrates well with residuum FCC units to minimize catalyst consumption, improve yields and reduce sulfur content of FCC products. RDS/VRDS also can be used to substantially improve the yields of downstream cokers and SDA units.

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 H₂S 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 up-flow 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 20 RDS/VRDS units are in operation. Six units have extensive experience with VR feedstocks. Twelve units prepare feedstock for RFCC units. Three OCR units and one UFR unit are in operation, with another two in engineering. Total current operating capacity is about 900,000 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.

Licensors: Chevron Lummus Global LLC.

Hydrotreating—resid

Application: Upgrade 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, 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.

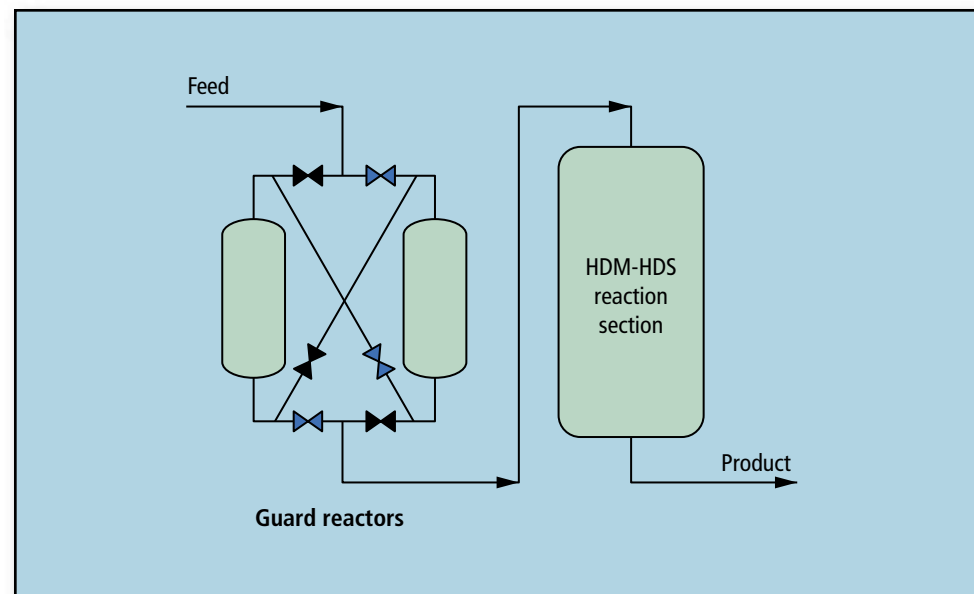
Following the guard reactors, the HDM section carries out the remaining demetallization and conversion functions. With most of the contaminants removed, the residue is sent to the HDS section where the sulfur level is reduced to the design specification.

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.

Economics:

Investments (Basis: 40,000 bpsd, AR to VR feeds,
2002 Gulf coast), US\$/ bpsd 3,500–5,500



Utilities, per bbl feed:

Fuel, equiv. fuel oil, kg	0.3
Power, kWhr	10
Steam production, MP, kg	25
Steam consumption, HP, kg	10
Water, cooling, m ³	1.1

Installation: Three units are in operation (one on atmospheric-residue feed, the other two on vacuum residue). The total installed capacity will reach 134,000 bpsd.

References: "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.

Licensors: Axens.

Isomerization

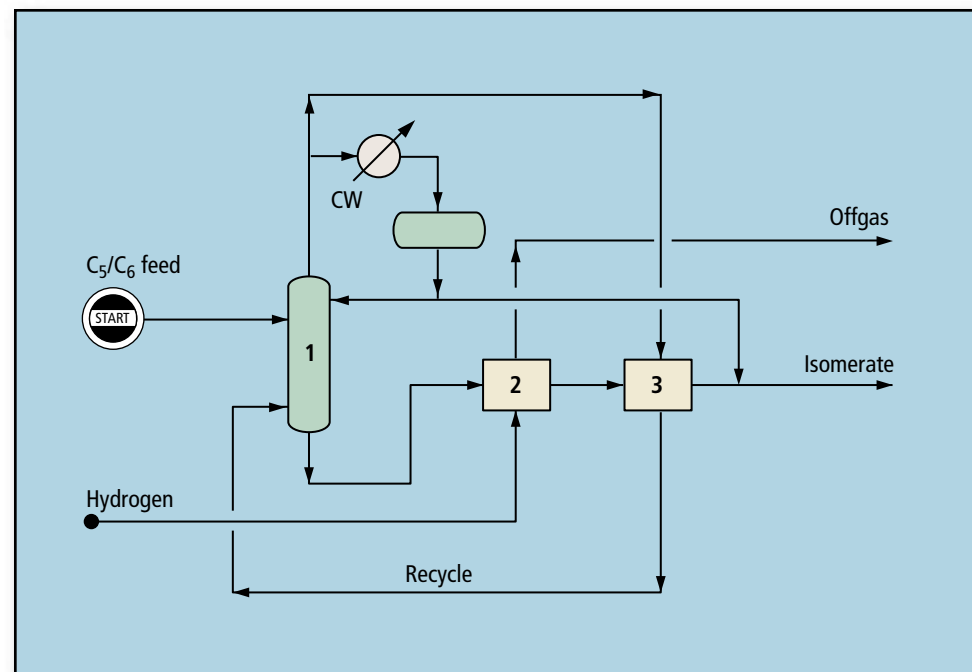
Application: C₅/C₆ paraffin-rich hydrocarbon streams are isomerized to produce high RON and MON product suitable for addition to the gasoline pool.

Description: Several variations of the C₅/C₆ isomerization process are available. With either a zeolite or chlorinated alumina catalyst, 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 catalyst), particularly with the Akzo Nobel/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.

Economics: (Basis: Ipsorb "A" Isomerization unit with a 5,000-bpsd 70 RONC feed needing a 20-point octane boost):

Investment* , million US\$	13
Utilities:	
Steam, HP, tph	1.0



Steam, MP, tph	8.5
Steam, LP, tph	6.8
Power, kWh/h	310
Cooling water, m ³ /h	100

* Mid-2002, Gulf coast, excluding cost of noble metals

Installation: Of 30 licenses issued for C₅/C₆ isomerization plants, 12 units are operating including one Ipsorb unit.

Reference: Axens/Akzo Nobel, "Advance solutions for paraffin isomerization," NPRA Annual Meeting, March 2004, San Antonio.

Licensors: Axens.

Isomerization

Application: Convert normal olefins to isoolefins.

Description:

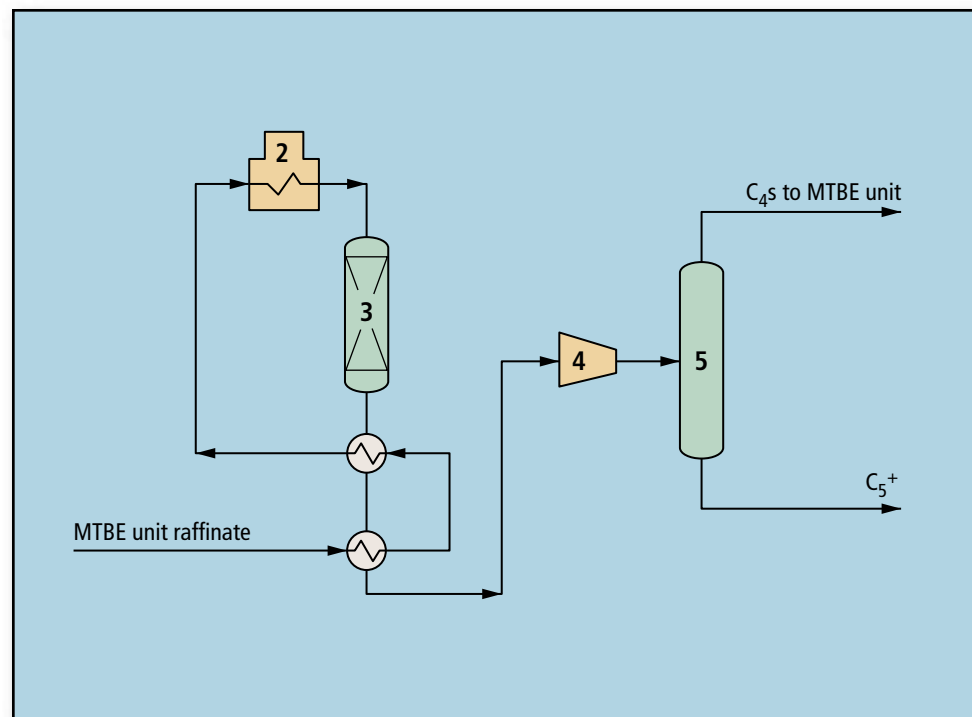
C₄ olefin skeletal isomerization (IsomPlus)

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 C₄ 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 isoamylenes at high selectivity and long process cycle times. Hydrocarbon feeds containing n-pentenes, such as C₅ 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. Also, the small quantity of heavy byproducts formed can easily be blend-



ed into the gasoline pool. Capital costs (equipment, labor and detailed engineering) for three different plant sizes are:

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

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

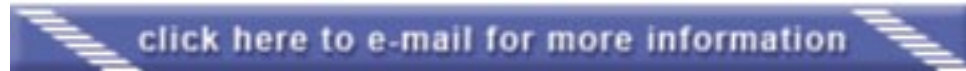
Power, kWh	3.2
Fuel gas, MMBtu	0.44
Steam, MP, MMBtu	0.002
Water, cooling, MMBtu	0.051
Nitrogen, scf	57–250

Continued ▼

Isomerization, *continued*

Installation: Two plants are in operation. Two licensed units are in various stages of design.

Licensors: CDTECH and Lyondell Chemical Co.



Isomerization

Application: Hydrisom is ConocoPhillips' selective diolefin hydrogenation process, with specific isomerization of butene-1 to butene-2 and 3-methyl-butene-1 to 2-methyl-butene-1 and 2-methyl-butene-2. The Hydrisom process uses a liquid-phase reaction over a commercially available catalyst in a fixed-bed reactor.

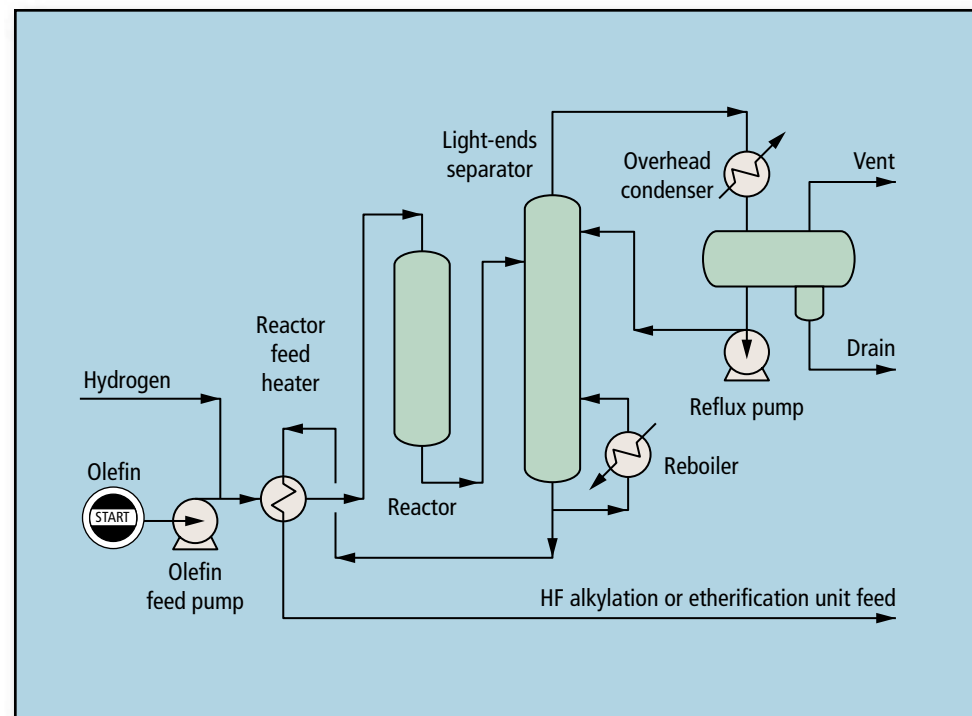
Description: ConocoPhillips' Hydrisom Process is a once-through reaction and, for typical cat cracker streams, requires no recycle or cooling. Hydrogen is added downstream of the olefin feed pump on ratio control and the feed mixture is preheated by exchange with the fractionator bottoms and/or low-pressure steam. The feed then flows downward over a fixed bed of commercial catalyst.

The reaction is liquid-phase, at a pressure just above the bubble point of the hydrocarbon/hydrogen mixture. The rise in reactor temperature is a function of the quantity of butadiene in the feed and the amount of butene saturation that occurs.

The Hydrisom process can also be configured using a proprietary catalyst to upgrade streams containing diolefins up to 50% or more, e.g., steam cracker C₄ streams, producing olefin-rich streams for use as chemical, etherification and/or alkylation feedstocks.

Installation of a Hydrisom unit upstream of an etherification and/or alkylation unit can result in a very quick payout of the investment due to:

- Improved etherification unit operations
- Increased ether production
- Increased alkylate octane number
- Increased alkylate yield
- Reduced chemical and HF acid costs
- Reduced ASO handling
- Reduced alkylation unit utilities
- Upgraded steam cracker or other high diolefin streams (30% to 50%) for further processing.



Installation: Ten units licensed worldwide, including an installation at ConocoPhillips' Sweeny, Texas, Refinery.

Licensors: Technology Solutions Division of ConocoPhillips.

Isomerization

Application: The widely used 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, low-vapor 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.

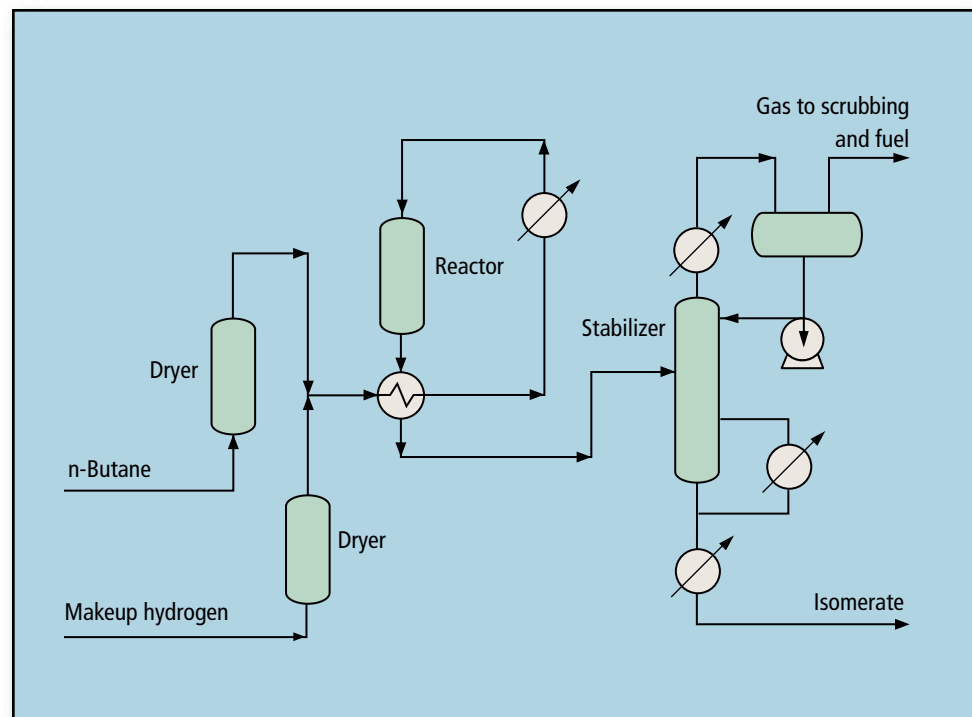
Typically, two reactors, in series flow, are used to achieve high onstream efficiency. The catalyst can be replaced in one reactor while operation continues in the other. The stabilizer separates the light gas from the reactor effluent.

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 light-ends yield from cracking is less than 1 wt-% of the butane feed.

Installation: More than 70 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).

Licensors: UOP LLC.

Isomerization

Application: The 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 charge heater, 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.

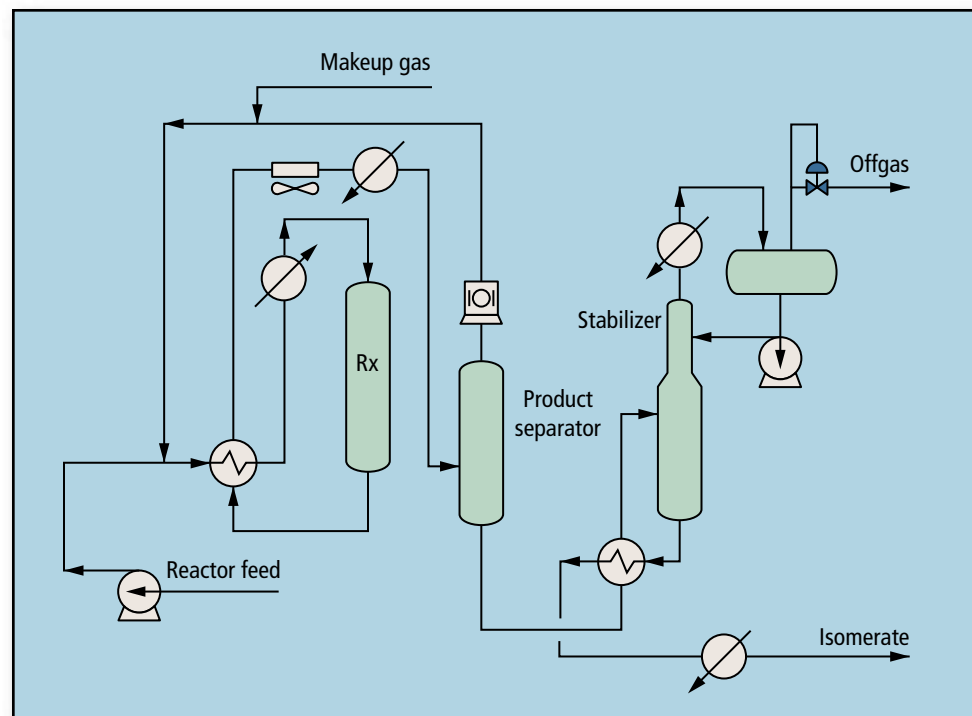
The reactor effluent is cooled and sent to a product separator where the recycle hydrogen is separated from the other products. Recovered recycle hydrogen is directed to the recycle compressor and back to the reaction section. Liquid product is sent to a stabilizer column where light ends and any dissolved 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 10 units in operation. The first



commercial application of PI-242 catalyst was in 2003, and the unit has demonstrated successful performance meeting all expectations.

Licensors: UOP LLC.

Isomerization

Application: Most of the implemented legislation requires limiting benzene concentration in the gasoline pool. This has increased the demand for high-performance C₅ and C₆ naphtha isomerization technology because of its ability to reduce the benzene concentration in the gasoline pool while maintaining or increasing the pool octane. The Penex process has served as the primary isomerization technology for upgrading C₅/C₆ light straight-run naphtha.

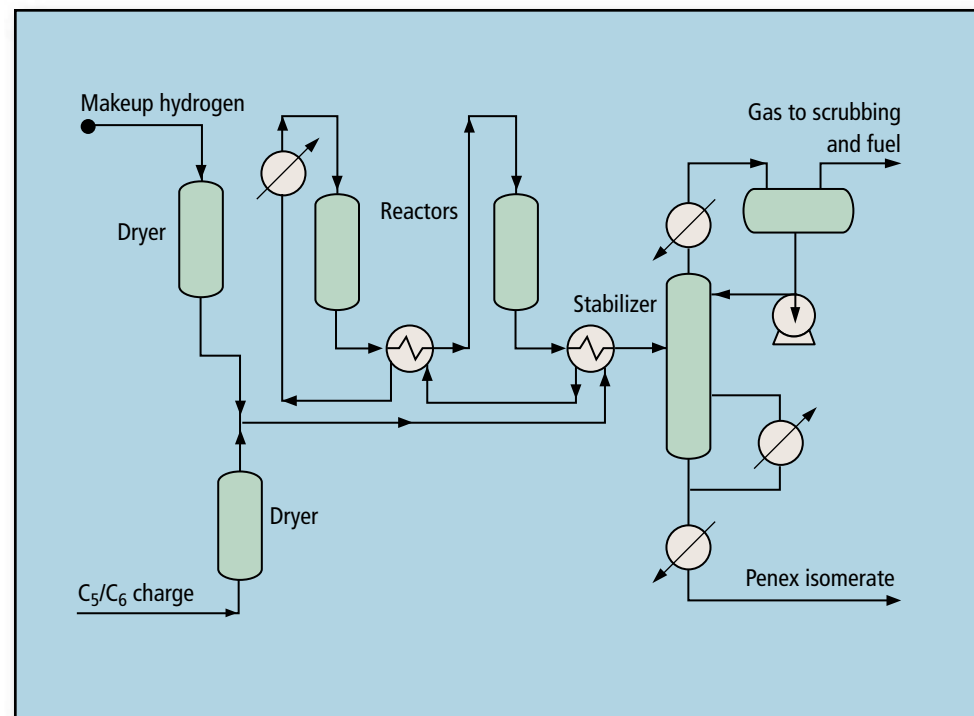
Description: UOP's innovative hydrogen-once-through (HOT) Penex process results in substantial savings in capital equipment and utility costs by eliminating the need for a product separator or recycle-gas compressor. The Penex process is a fixed-bed process that uses high-activity chloride-promoted catalysts to isomerize C₅/C₆ 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 C₅/C₆ 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.

Yields:

Penex process:	Octane 86
Penex process/DIH:	Octane 90
Penex process/Molex process:	Octane 91
DIP/Penex process/DIH:	Octane 93



Feed: Penex process can process feeds with high levels of C₆ cyclics and C₇ 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. Capacities range from 1,000 bpsd to more than 25,000 bpsd of fresh feed capacity.

Licensors: UOP LLC.

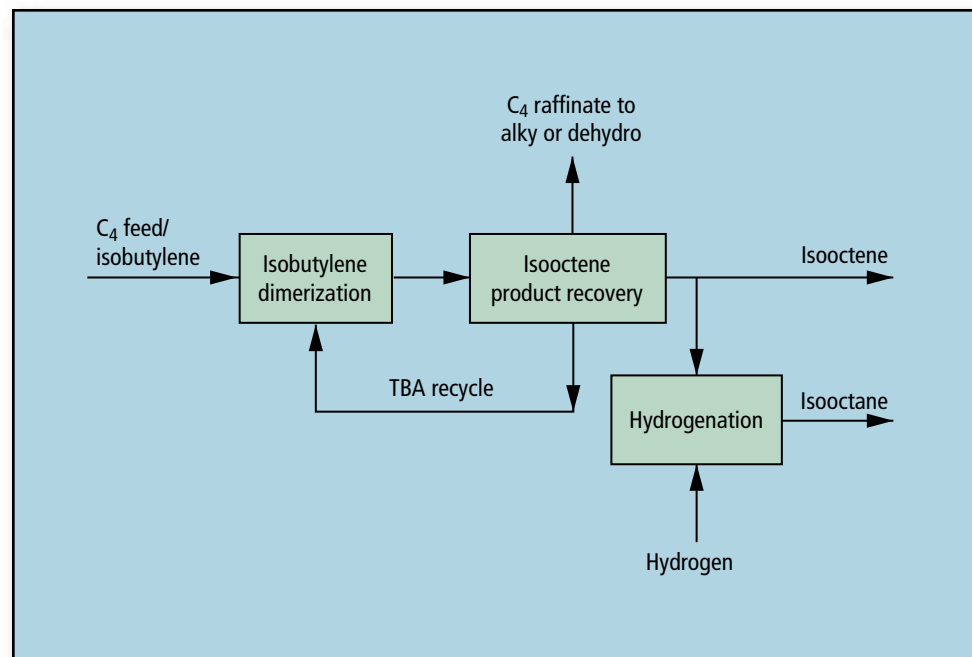
Isooctane

Application: Conversion of isobutylene contained in mixed-C₄ feeds to isooctane (2,2,4 tri-methyl pentane) to produce a high-quality gasoline blendstock. The full range of MTBE plant feeds can be processed—from refinery FCC, olefin-plant raffinate and isobutane dehydrogenation processes. The NExOCTANE process is specifically developed to minimize conversion costs of existing MTBE units and offers a cost-effective alternative to MTBE production.

Products: Isooctene and isooctane can be produced, depending on the refiner's gasoline pool. Typical product properties are:

	Isooctene	Isooctane
RONC	101–103	99–100
MONC	85–87	96–99
Specific gravity	0.701–0.704	0.726–0.729
Vapor pressure, psia	1.8	1.8
T50, °F	215	212
T90, °F	250	246
ASTM EP, °F	380–390	370–380

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



Economics:

Investment cost for revamps depend on the existing MTBE plant design, capacity and feedstock composition. Typical utility requirements per bbl product:

Steam, 150-psig, lb	700
Electricity, kWh	2.3
Water, cooling, ft ³	1.2

Installation: Process has been in commercial operation since 2002.

Licensor: Kellogg Brown & Root, Inc., and Fortum Oil and Gas OY.

Isooctane/isooctene

Application: CDIsoether is used for manufacture of high-octane, low-vapor pressure, "MTBE-free" isooctene and/or isooctane for gasoline blending. Coproduction of MTBE and isooctene/isooctane in the desired ratio is also possible.

Feed: Hydrocarbon streams containing reactive tertiary olefins such as: FCC C₄s, steamcracker C₄s or isobutane dehydrogenation product.

Products: Isooctene or isooctane stream containing at least 85% of C₈s, with less than 5,000 ppm oligomers higher than C₁₂s.

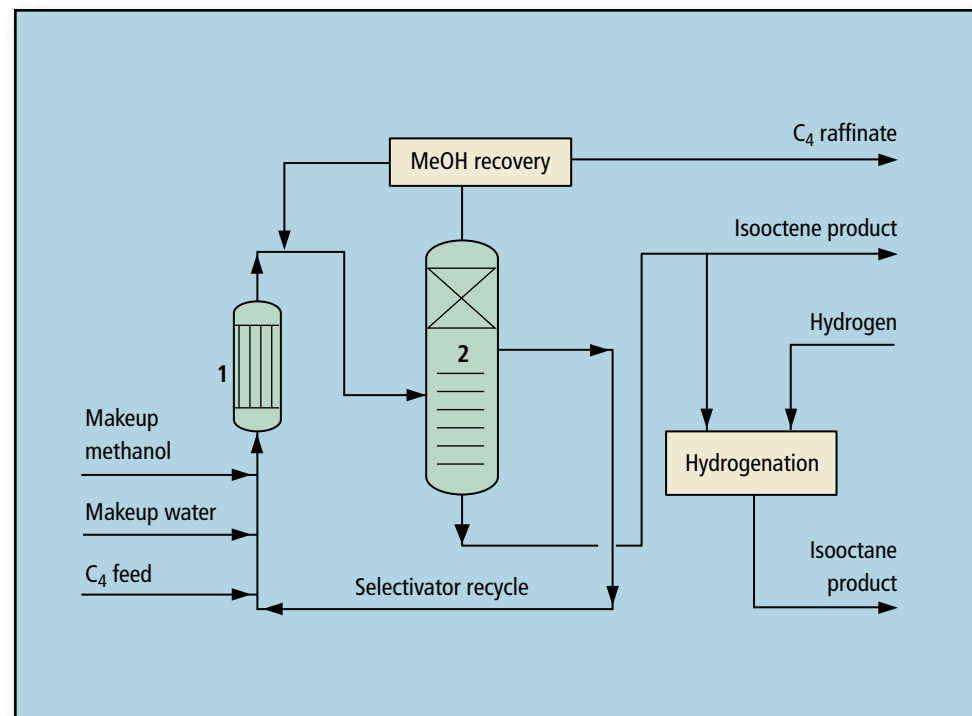
Description: Depending on conversion and investment requirements, various options are available. CDIsoether can provide isobutylene conversion of up to 99%. The C₄ feed is mixed with a recycle stream containing oxygenates (such as TBA and MTBE), used as "selectivator" and heated before entering the reactor. The reactor (1) is a water-cooled tubular reactor (WCTR) or a boiling-point reactor (BPR).

The heat of reaction is removed by circulating water through the shell of the WCTR, while the heat of reaction remains in the two-phase BPR effluent. There is no product recycle. The reactor effluent flows, along with the selectivator, to the reaction column (2), where isobutene conversion is maximized using catalytic distillation and isooctene product is fractionated as bottoms product.

Unreacted C₄s are taken as column overhead and the selectivator is drawn as a side stream for recycle together with some C₄ hydrocarbons. The isooctene product can be sent to storage or fed to the "hydrogenation unit" to produce saturated hydrocarbon—isoctane.

Economics:

Investment (Basis grassroots CDIsoethers unit, charging FCC C₄s)
US\$5,000–7,000 per bpsd of isooctene product



Investment for retrofitting an existing MTBE unit to isooctene production US\$500–750 per bpsd of isooctene produced

Utilities, per bbl of isooctene:

Steam, (300 psig), lb	200–250
Water, cooling, gal	1,500–2,000
Power, kWh	1.6–2.0

Licensors: Snamprogetti SpA.

Isooctene/Isooctane/ETBE

Application: To produce isooctene or isooctane from isobutylene both steps—via catalytic dimerization followed by hydrogenation; with intermediate and final fractionation as required to meet final product specifications. Ideally, it is a “drop-in” to an existing MTBE reactor with patented use of modifier to improve selectivity and prolong catalyst life.

The process can be easily modified to make ETBE from ethanol and isobutylene as well.

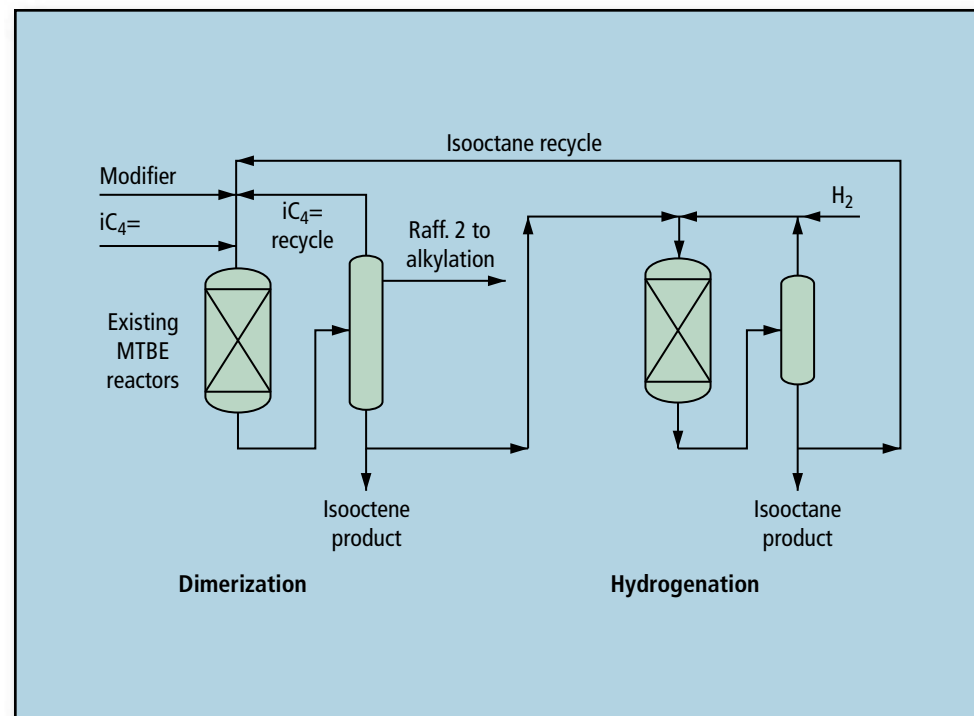
Description: The process produces an isooctene intermediate or final product starting with either a mixed C₄ feed or on-purpose isobutylene production. It is based on a highly selective conversion of isobutylene to isooctene followed by hydrogenation, which will convert over 99.5% of the isooctene to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

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

The unit can be designed to be inter-convertible between MTBE, isooctene/isooctane and/or ETBE operations. Thus, economics, as well as changes in regulations, can dictate changes in the mode of operation over time.

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

Licensors: Lyondell Chemical and Aker Kvaerner.



LPG recovery

Application: Recovery of propane and heavier components from various refinery offgas streams and from low-pressure associated natural gas. Propane recovery levels approaching 100% are typical.

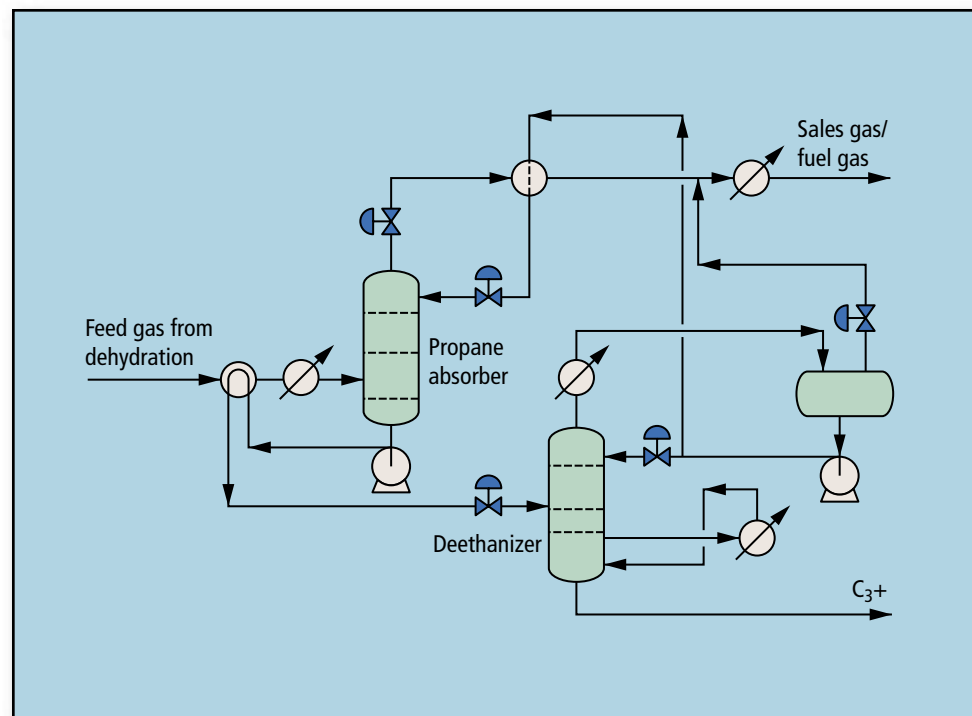
Description: Low-pressure hydrocarbon gas is compressed and dried before being chilled by cross-exchange and propane refrigerant. The chilled feed stream is then contacted with a recycled liquid ethane stream in the propane absorber. The absorber bottoms is pumped to the deethanizer, which operates at higher pressure than the absorber. The tower overhead is condensed with propane refrigerant to form a reflux stream composed primarily of ethane. A slip stream of the reflux is withdrawn and recycled back to the propane absorber. The deethanizer bottoms stream contains the valuable propane and heavier components which may be further processed as required by conventional fractionation.

Economics: Compared to other popular LPG recovery processes, PRO-MAX typically requires 10–25% less refrigeration horsepower.

Installation: First unit under construction for Pertamina.

Reference: US Patent 6,405,561 issued June 18, 2002.

Licensors: Black & Veatch Pritchard, Inc.



Lube and wax processing

Application: Vacuum gas oils (VGOs) are simultaneously extracted and dewaxed on a single unit to produce low-pour aromatic extracts and lube-base stocks having low-pour points. Low viscosity grades (60 SUS) to bright stocks can be produced. With additional stages of filtration, waxes can be deoiled to produce fully refined paraffin waxes.

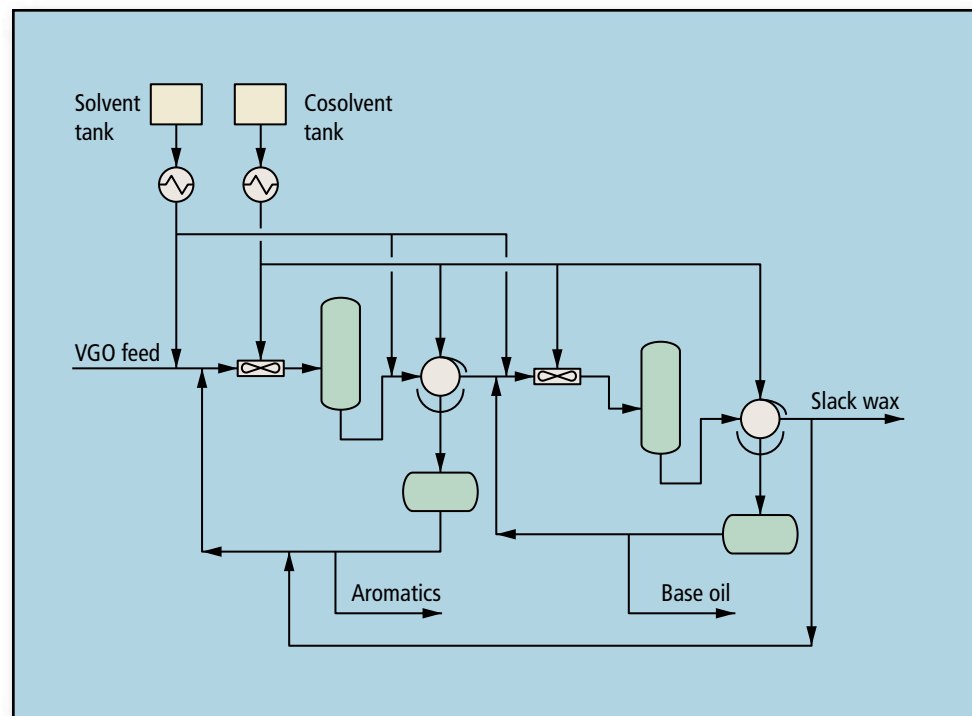
Products: Lube-base stocks having low pour points (-20°C). Very low pour point aromatic extracts. Slack waxes or low-oil content waxes.

Description: Process Dynamics' integrated extraction/dewaxing technology is a revolutionary process combining solvent extraction and solvent dewaxing onto a single unit, using a common solvent system, for extraction and dewaxing steps. This process offers the advantage of operating a single unit rather than separate extraction and dewaxing units; thus, reducing both capital and operating costs. The more selective solvent system produces lube-base stocks of higher quality and higher yields when compared to other technologies.

Primary solvent and warm feed are mixed together; temperature is controlled by adding the cosolvent solvent. Filtrate or wax may be recycled for solids adjustment. Cold cosolvent is added, and the slurry is filtered (or separated by other means). Solvents are recovered from the primary filtrate producing an aromatic extract. The wax cake is repulped with additional solvent/cosolvent mix and refiltered. Solvents are recovered from the filtrate producing a lube-base stock.

Extraction/dewaxing comparisons of 90 SUS stock

	Furfural/MEK	Process Dynamics	
		A	B
Raffinate yields, vol%	53	60	71
Dewaxed oil properties:			
Viscosity @40°C, cSt	16.5	18.7	20
Viscosity index	92	98	92
Pour pt., °F	5	5	5



Installation: Basic engineering package for the first commercial unit has been completed.

Licensors: P. D. Licensing, LLC (Process Dynamics, Inc.).

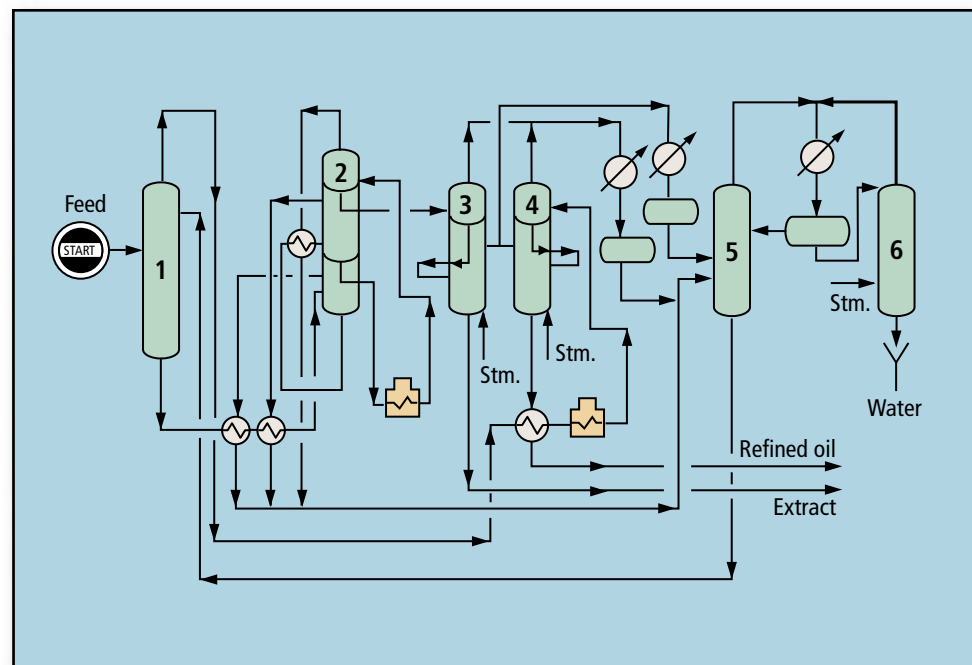
Lube extraction

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 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 feed rate capacity, 2004 US Gulf Coast), \$/bpsd	2,600
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 Corp.

[click here to e-mail for more information](#)

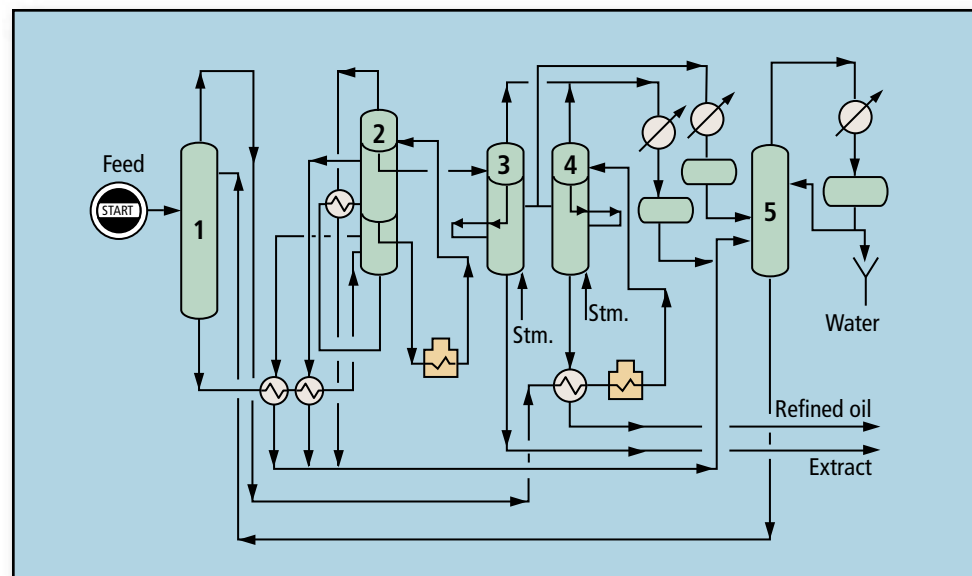
Lube extraction

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 processing 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.



Economics:

Investment (Basis: 10,000-bpsd feedrate capacity, 2004 US Gulf Coast), \$/bpsd	2,500
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 being planned for conversion.

Licensors: Bechtel Corp.

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.

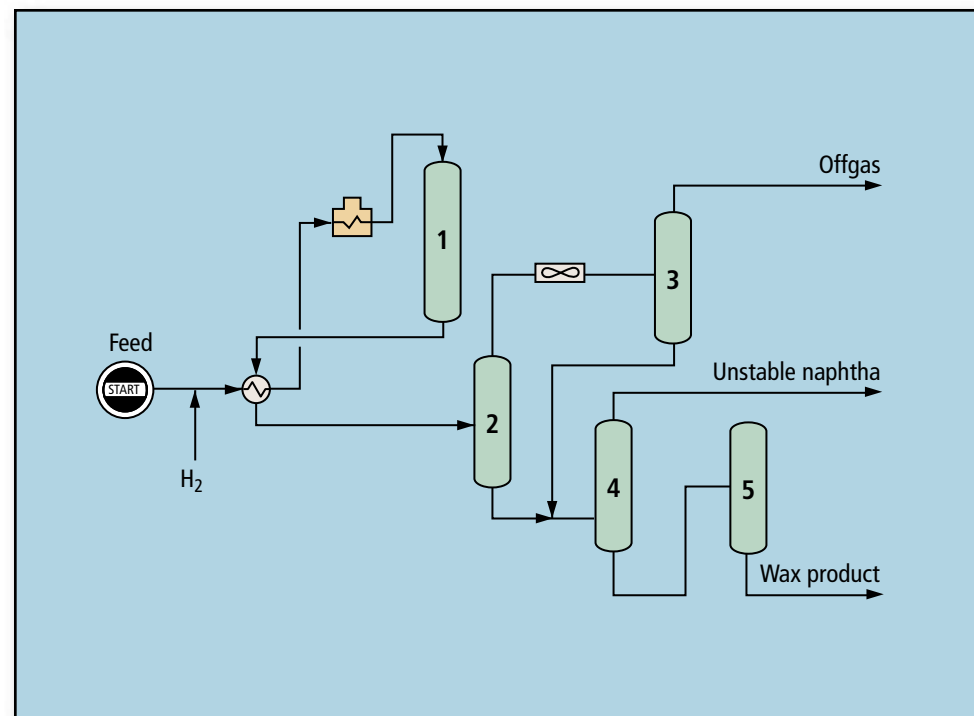
Description: Hydrocarbon feed is mixed with hydrogen (recycle plus makeup), preheated, and charged to a fixed-bed hydrotreating reactor (1). Reactor effluent is cooled in exchange with the mixed feed-hydrogen stream. Gas-liquid separation of the effluent occurs first in the hot separator (2) then in 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 H_2S before compression in the recycle hydrogen compressor (7).

Economics:

Investment (Basis 7,000-bpsd feedrate capacity,
2004 US Gulf Coast), \$/bpsd 4,200

Utilities, typical per bbl feed:

Fuel, 10^3 Btu (absorbed)	20
Electricity, kWh	5
Steam, lb	15
Water, cooling (25°F rise), gal	400



Licensors: Bechtel Corp.

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.

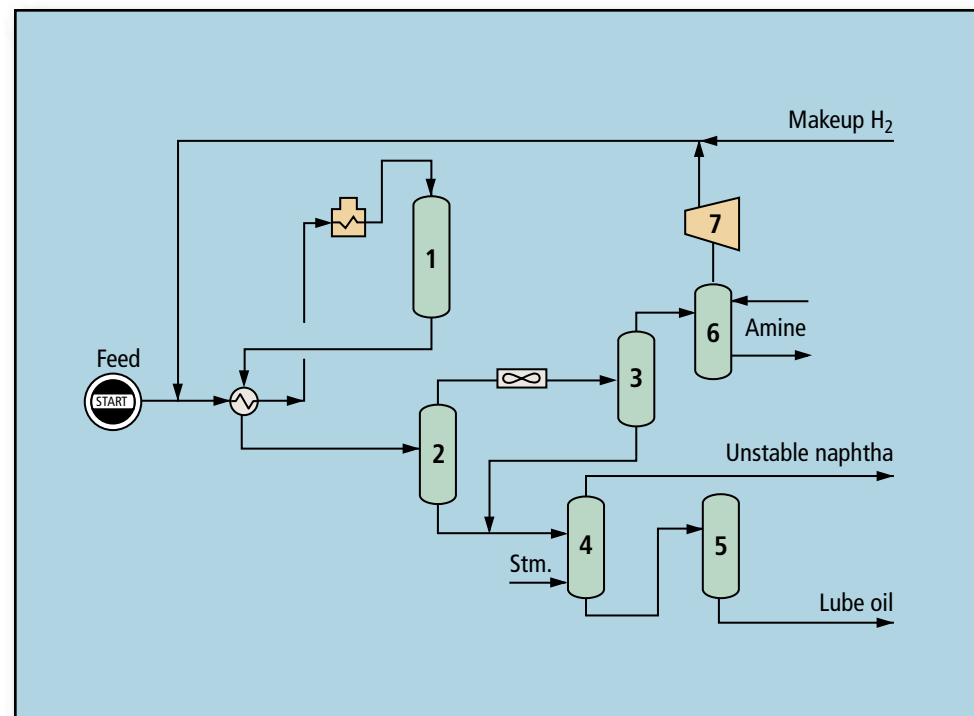
Description: Raffinate feed is mixed with hydrogen (recycle plus make-up), preheated, and charged to a fixed-bed hydrotreating reactor (1). The reactor effluent is cooled in exchange with the mixed feed-hydrogen stream. Gas-liquid separation of the effluent occurs first in the hot separator (2) then 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 H_2S before compression in the recycle-hydrogen compressor (7).

Economics:

Investment (Basis 7,000-bpsd feedrate capacity,
2004 U.S. Gulf Coast), \$/bpsd 5,900

Utilities, 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 Corp.

Lube oil refining, spent

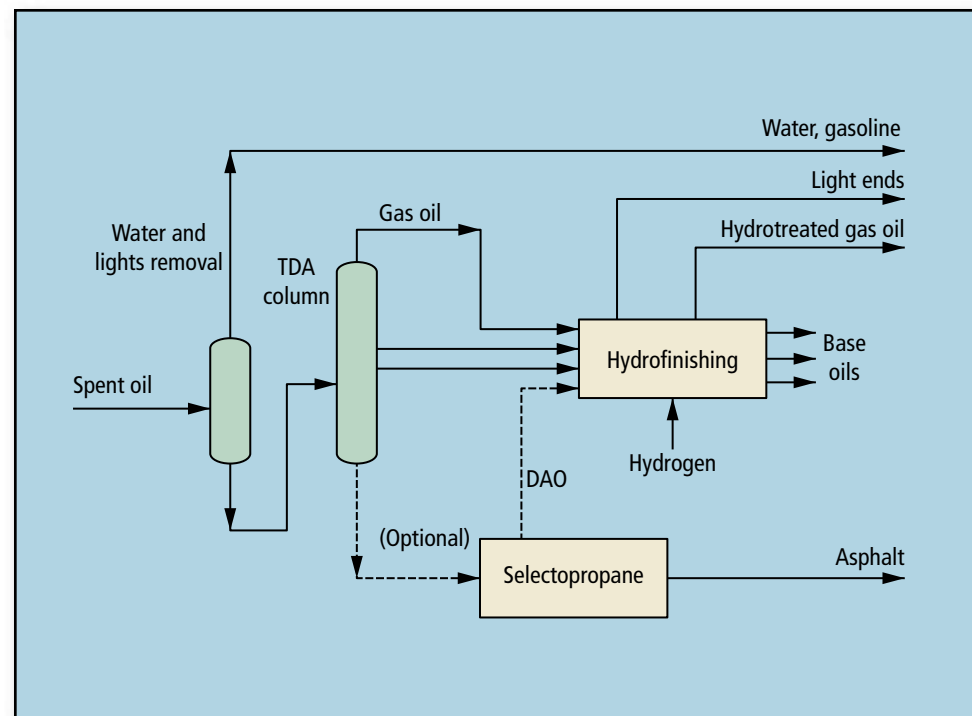
Application: The Revivoil process can be used to produce high yields of premium quality lube bases from spent motor oils. Requiring neither acid nor clay treatment steps, the process can eliminate environmental and logistical problems of waste handling and disposal associated with conventional re-refining 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 Selectopropene 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 com-



pounds 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 Selectopropene unit can be added at a later stage, to bring the oil recovery to the 95% level on dry basis. Economics below show that for two plants of equal capacity, payout times before taxes are two years in both cases.

Investment: Basis 100,000 metric tpy, water-free, ISBL 2004 Gulf Coast, million US\$

Configuration 1	(Atm. flash, TDA and Hydrofinishing units)	30
Configuration 2	(Same as above + Selectopropene unit)	35

Continued ▼

Lube oil refining, spent, *continued*

Utilities: Basis one metric ton of water-free feedstock

	Config. 1	Config. 2
Electrical power, kWh	45	55
Fuel, million kcal	0.62	0.72
Steam, LP, kg	—	23.2
Steam, MP, kg	872	890
Water, cooling, m ³	54	59

Installation: Ten units have been licensed using all or part of the Revivoil Technology.

Licensors: Viscolube SpA and Axens.



Lube treating

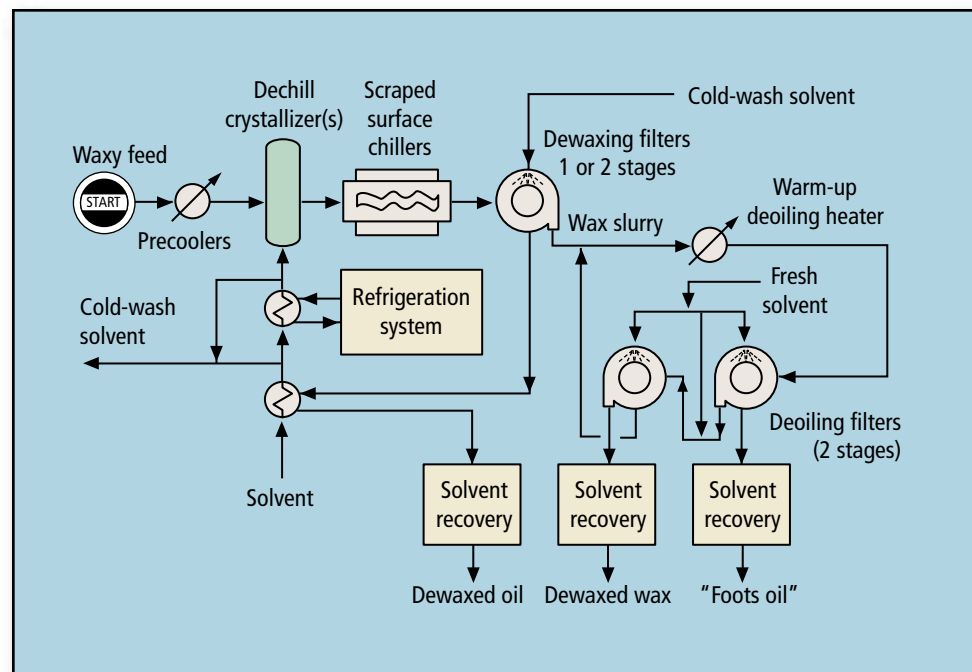
Application: Lube raffinates from extraction are dewaxed to provide basestocks having low pour points (as low as -35°C). Basestocks range from light stocks (60N) to higher viscosity grades (600N and bright stock). Byproduct waxes can also be upgraded for use in food applications.

Feeds: DILCHILL dewaxing can be used for a wide range of stocks that boil above 550°F , from 60N up through bright stock. In addition to raffinates from extraction, DILCHILL dewaxing can be applied to hydrocracked stocks and to other stocks from raffinate hydroconversion processes.

Processes: Lube basestocks have low pour points. Although slack waxes containing 2–10 wt% residual oil are the typical byproducts, lower-oil-content waxes can be produced by using additional dewaxing and/or “warm-up deoiling” stages.

Description: DILCHILL is a novel dewaxing technology in which wax crystals are formed by cooling waxy oil stocks, which have been diluted with ketone solvents, in a proprietary crystallizer tower that has a number of mixing stages. This nucleation environment provides crystals that filter more quickly and retain less oil. This technology has the following advantages over conventional incremental dilution dewaxing in scraped-surface exchangers: less filter area is required, less washing of the filter cake to achieve the same oil-in-wax content is required, refrigeration duty is lower, and only scraped surface chillers are required which means that unit maintenance costs are lower. No wax recrystallization is required for deoiling.

Warm waxy feed is cooled in a prechiller before it enters the DILCHILL crystallizer tower. Chilled solvent is then added in the crystallizer tower under highly agitated conditions. Most of the crystallization occurs in the crystallizer tower. The slurry of wax/oil/ketone is further cooled in scraped-surface chillers and the slurry is then filtered in rotary vacuum filters. Flashing and stripping of products recover solvent. Additional filtration stages can be added to recover additional oil or/to produce low-oil content saleable waxes.



Economics: Depend on the slate of stocks to be dewaxed, the pour point targets and the required oil-in-wax content.

Utilities: Depend on the slate of stocks to be dewaxed, the pour point targets and the required oil-in-wax content.

Installation: The first application of DILCHILL dewaxing was the conversion of an ExxonMobil affiliate unit on the U.S. Gulf Coast in 1972. Since that time, 10 other applications have been constructed. These applications include both grassroots units and conversions of incremental dilution plants. Six applications use “warm-up deoiling.”

Licensors: ExxonMobil Research and Engineering Co.

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.

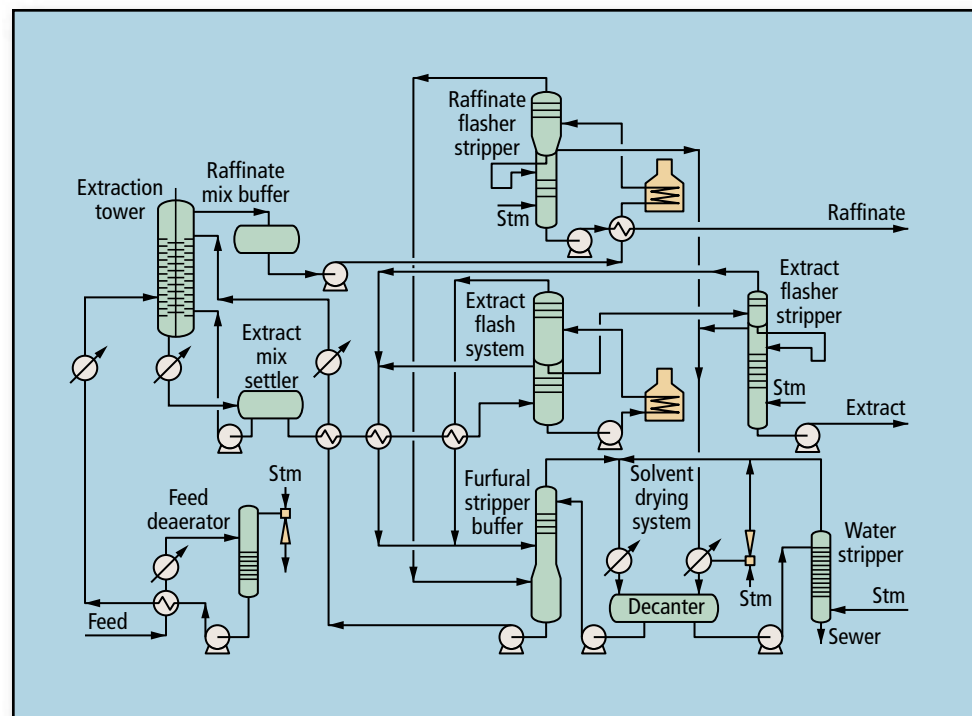
Products: Lube oil raffinates of high viscosity indices. The raffinates contain substantially all of the desirable lubricating oil components present in the feedstock. The extract contains a concentrate of aromatics that may be utilized as rubber oil or cracker feed.

Description: This liquid-liquid extraction process uses furfural as the selective solvent to remove aromatics and other impurities present in the distillates and deasphalted oils. Furfural has 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. Multi-stage 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.

Mercaptan removal

Application: Extraction of mercaptans from gases, LPG, lower boiling fractions and gasolines, or sweetening of gasoline, jet fuel and diesel by in situ conversion of mercaptans into disulfides.

Products: Essentially mercaptan sulfur-free, i.e., less than 5 ppmw, and concomitant reduced total sulfur content when treated by Merox extraction technique.

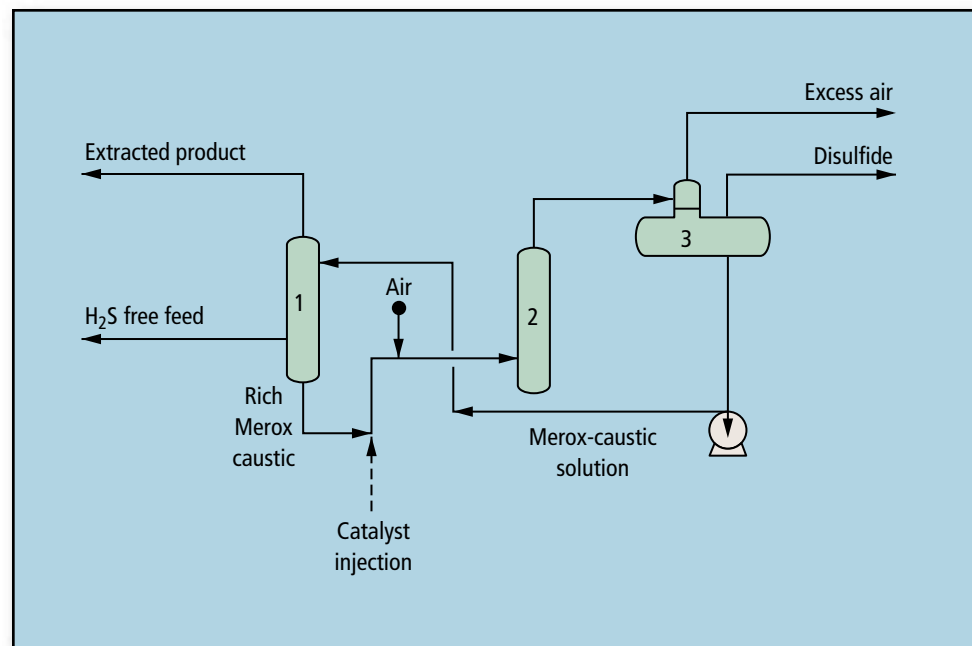
Description: Merox units are designed in several flow configurations, depending on feedstock type and processing objectives. All are characterized by low capital and operating costs, ease of operation and minimal operator attention.

Extraction: Gases, LPG and light naphtha are countercurrently extracted (1) with caustic containing Merox catalyst. Mercaptans in the rich caustic are oxidized (2) with air to disulfides that are decanted (3) before the regenerated caustic is recycled.

Sweetening: Minalk is now the most prevalent Merox gasoline sweetening scheme. Conversion of mercaptans into disulfides is accomplished with a fixed bed of Merox catalyst that uses air and a continuous injection of only minute amounts of alkali. Sweetened gasoline from the reactor typically contains less than one ppm sodium.

Heavy gasoline, condensate, kerosine/jet fuel and diesel can be sweetened in a fixed-bed unit that closely resembles Minalk, except that a larger amount of more concentrated caustic is recirculated intermittently over the catalyst bed. A new additive, Merox Plus catalyst activator, can be used to greatly extend catalyst life.

Economics: Typical capital investment and operating costs of some Merox process schemes are given based on 2004 dollars for a 10,000-bpsd capacity liquid unit and 10 million-scf/d gas unit with modular design and construction.



Product	Gas	LPG	Gasoline	Heavy naphtha fixed bed
Scheme	Ext.	Ext.	Minalk	
Est. plant capital, modular \$10 ³	2,600	2,000	1,100	1,500
Direct operating cost, ¢/bbl (¢/10 ⁶ scf)	(1.5)	0.4	0.2	1.0

Installations: Capacity installed and under construction exceeds 13 million bpsd. More than 1,600 units have been commissioned to date, with capacities between 40 and 140,000 bpsd. UOP has licensed gas Merox extraction units with capacities as high as 2.9-billion-scf/d for mercaptan control.

Licensors: UOP LLC.

NO_x abatement

Application: Flue gases are treated with ammonia via ExxonMobil's proprietary selective noncatalytic NO_x reduction technology—THERMAL DeNO_x. NO_x plus ammonia (NH₃) are converted to elemental nitrogen and water if temperature and residence time are appropriate. The technology has been widely applied since it was first commercialized in 1974.

Products: If conditions are appropriate, the flue gas is treated to achieve NO_x reductions of 40% to 70%+ with minimal NH₃ slip or leakage.

Description: The technology involves the gas-phase reaction of NO with NH₃ (either aqueous or anhydrous) to produce elemental nitrogen if conditions are favorable. Ammonia is injected into the flue gas using steam or air as a carrier gas into a zone where the temperature is 1,600°F to 2,000°F. This range can be extended down to 1,300°F with a small amount of hydrogen added to the injected gas. For most applications, wall injectors are used for simplicity of operation.

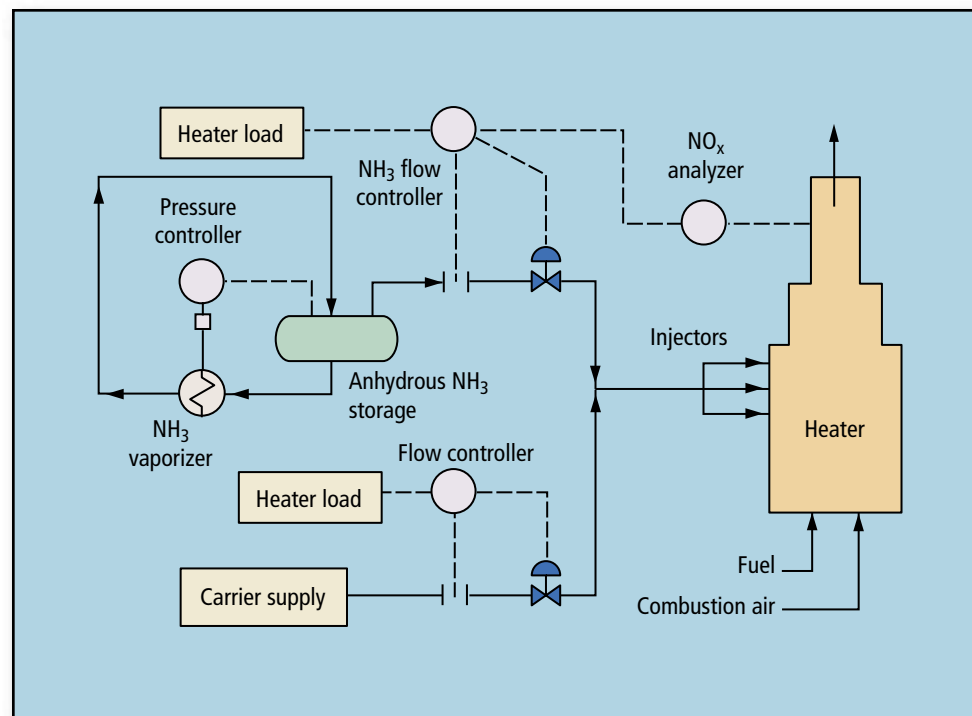
Yield: Cleaned flue gas with 40% to 70%+ NO_x reduction and less than 10-ppm NH₃ slip.

Economics: Considerably less costly than catalytic systems but relatively variable depending on scale and site specifics. Third-party studies have estimated the all-in cost at about 600 US\$/ton of NO_x removed.

Installation: Over 135 applications on all types of fired heaters, boilers and incinerators with a wide variety of fuels (gas, oil, coal, coke, wood and waste). The technology can also be applied to full-burn FCCU regenerators.

Reference: McIntyre, A. D., "Applications of the THERMAL DeNO_x process to utility and independent power production boilers," ASME Joint International Power Generation Conference, Phoenix, 1994.

McIntyre, A. D., "The THERMAL DeNO_x process: Liquid fuels appli-



cations," International Flame Research Foundation's 11th Topic Oriented Technical Meeting, Biarritz, France, 1995.

McIntyre, A. D., "Applications of the THERMAL DeNO_x process to FBC boilers," CIBO 13th Annual Fluidized Bed Conference, Lake Charles, Louisiana, 1997.

Licensors: ExxonMobil Research and Engineering Co., via an alliance with Engineers India Ltd. (for India) and Hamon Research-Cottrell (for the rest of the world).

NO_x reduction, low-temperature

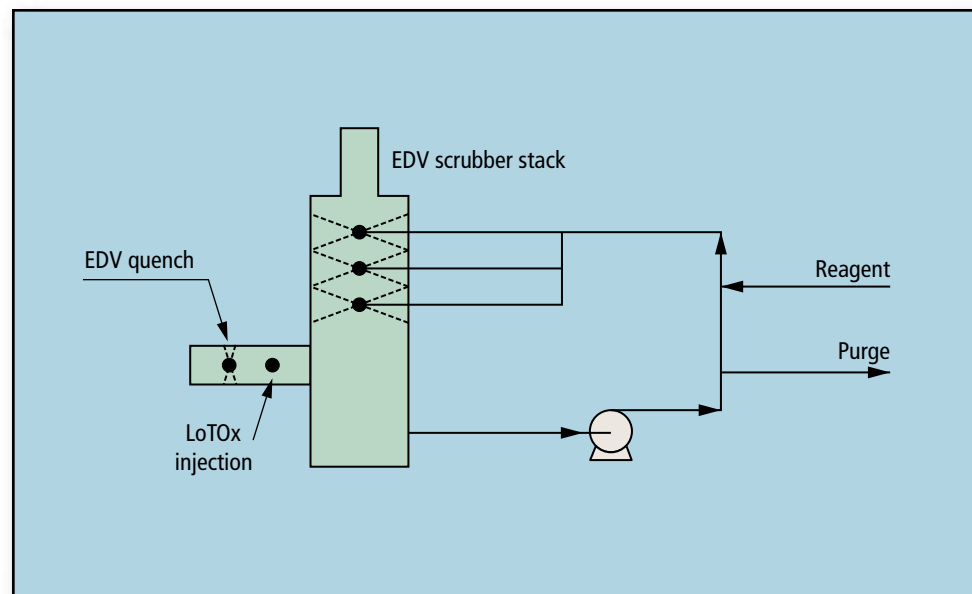
Application: The LoTOx low-temperature oxidation process removes NO_x from flue gases in conjunction with BELCO's EDV wet scrubbing system. Ozone is a very selective oxidizing agent; it converts relatively insoluble NO and NO₂ to higher, more soluble nitrogen oxides. These oxides are easily captured in a wet scrubber that is controlling sulfur compounds and/or particulates simultaneously.

Description: In the LoTOx 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 LoTOx system.



Installation: The technology has been developed and commercialized over the past seven years, winning the prestigious 2001 Kirkpatrick Chemical Engineering Technology Award. As of early 2002, four full-scale commercial installations are operating successfully. Pilot-scale demonstrations have been completed on coal- and petroleum-coke fired boilers, as well as refinery FCC units.

Reference: Confuorto, et al., "LoTOx technology demonstration at Marathon Ashland Petroleum LLC's refinery at Texas City, Texas," NPRA Annual Meeting, March 2004, San Antonio.

Licensors: Belco Technologies Corp., as a sub-licensor for The BOC Group, Inc.

Olefin recovery

Application: Recovery of olefins from refinery and/or petrochemical offgas streams that may otherwise be burned as fuel or flared.

Description: Well-proven low-temperature technology that achieves high olefin recoveries, often with minimal power consumption or rotating equipment.

The process flowsheet can be optimized based on feed and product pressures and the value of recovered olefins. All necessary refrigeration may be produced by turbo-expansion of feed gases to a low-pressure fuel gas header. Plate-fin heat exchangers are used to give high-energy efficiency and to maximize olefin recovery.

Reflux heat exchanger technology is used for very high olefin recovery, whereby a plate-fin heat exchanger separates the desired olefins in a similar way to an absorption column.

Olefin recovery units are normally supplied as a number of pre-assembled modules for ease of installation and commissioning.

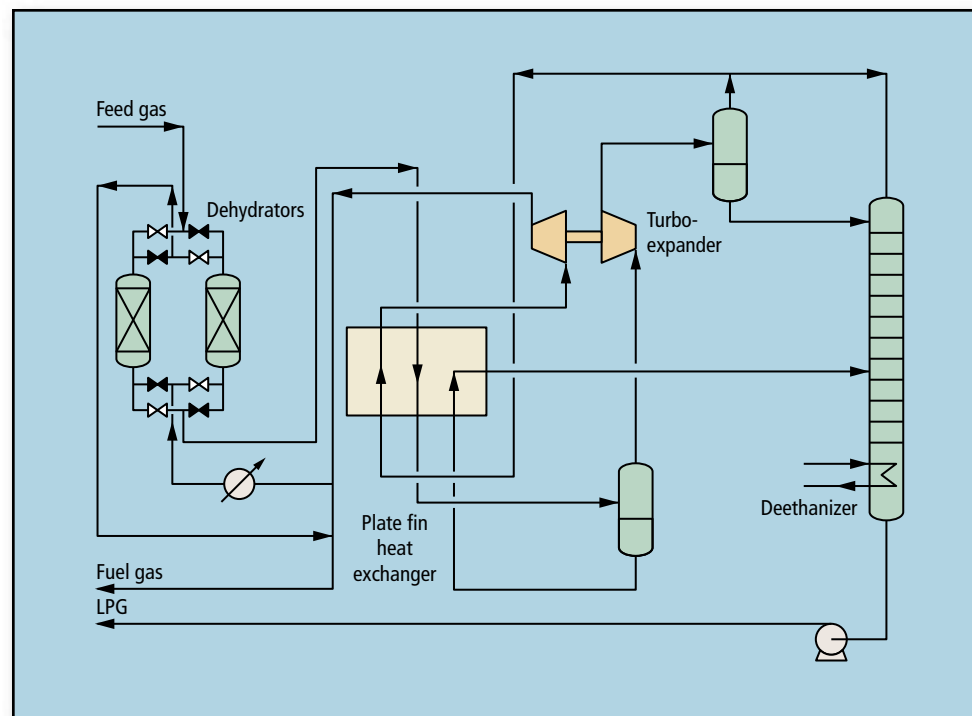
Economics: Olefin recoveries in excess of 98% can be economically achieved yielding payback times of typically less than 30 months.

Installation: Costain Oil, Gas & Process Ltd. has supplied approximately 15 units for recovery of propylene and butylenes from refinery offgases and dehydrogenation plant effluent, with numerous further installations for recovery of ethylene, LPG and hydrogen.

Reference: Johnson, G. L., et al., "Low temperature separation of hydrocarbon gas," US patent no. 6581410.

Tomlinson, T. R., "Improved operating margins with ethylene recovery," *Petroleum Technology Quarterly*, Spring 2002, p. 125.

Licensor: Costain Oil, Gas & Process Ltd.



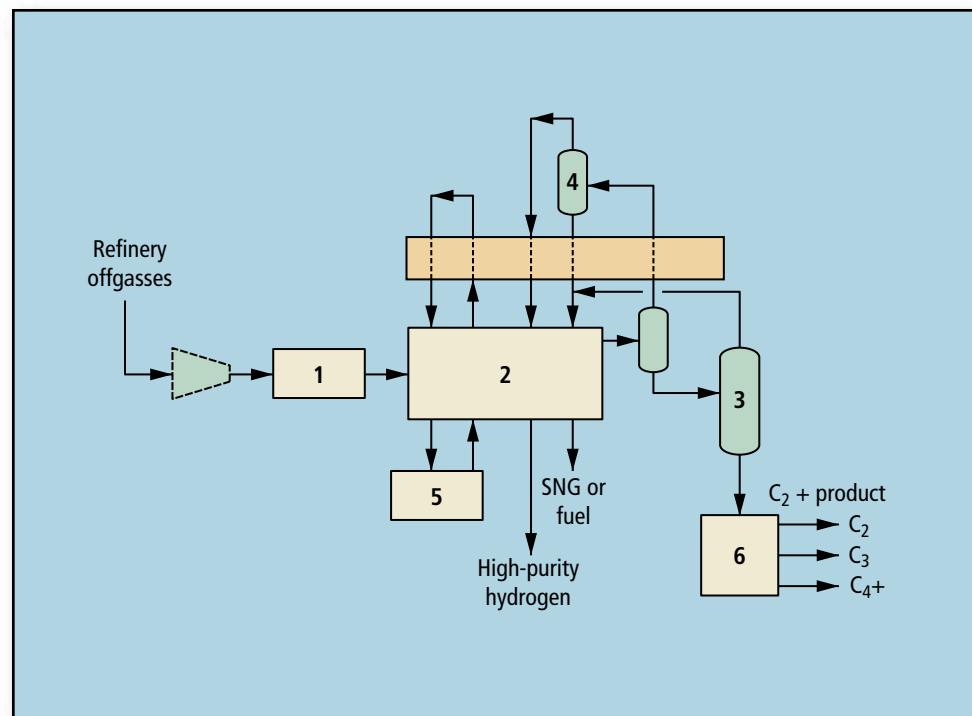
Olefins recovery

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% H_2 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 (CO_2), H_2O and other trace impurities. Treated feed is partially condensed in an integrated multi-pass exchange 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 C_2^+ 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.

Olefins recovery

Application: Linde BOC Process Plants Cryo-Plus process recovers ethylene or propylene and heavier components from refinery offgas streams. Typical applications are on cat crackers, cokers or reformers downstream of the existing gas-recovery systems. Incremental valuable hydrocarbons that are currently being lost to the refinery fuel system can now be economically recovered.

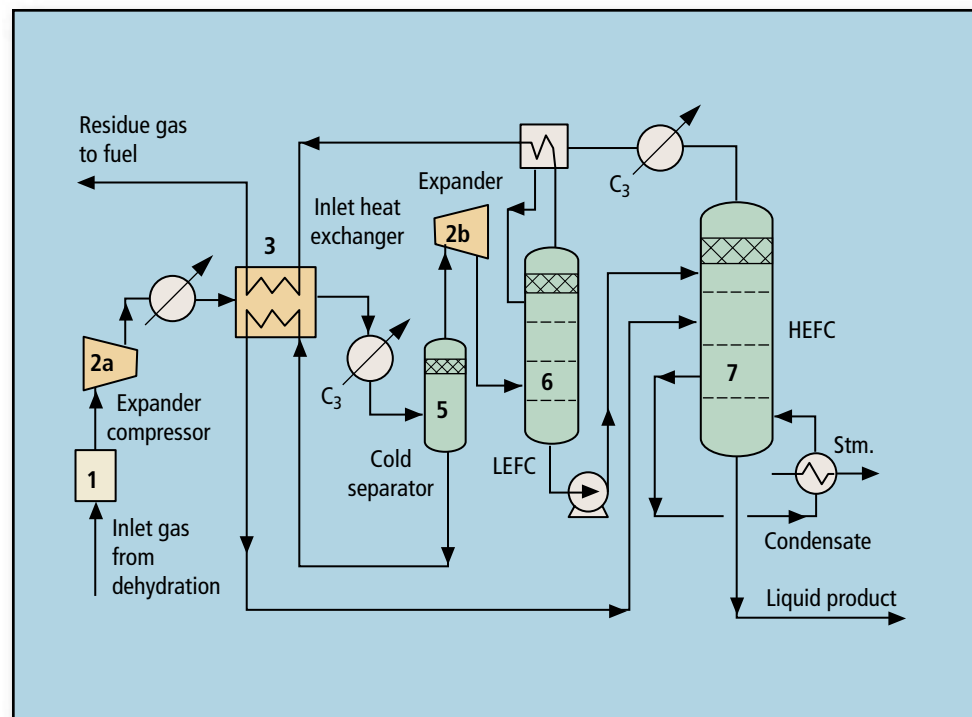
Description: Refinery offgases from cat crackers, cokers or other sources are first dehydrated by molecular sieve (1). The expander/compressor (2a) compresses the gas stream, which is then cooled by heat exchange with internal process streams (3). Depending on the richness of the feed gas, supplemental refrigeration (4) may be used to further cool the gas stream prior to primary vapor/liquid separation (5). Light gases are fed to a turboexpander (2b) where the pressure is reduced resulting in a low discharge temperature. The expander discharge is fed to the bottom of the LEFC (6). The HEFC (7) overhead is cooled and fed to the top of the LEFC. The recovered ethylene or propylene and heavier liquid stream exit the bottom of the HEFC (7). Process advantages include:

- Low capital cost
- High propylene or high ethylene recovery (up to 99%)
- Low energy usage
- Small footprint—can be modularized
- Simple to operate
- Wide range of turndown capability.

Economics: Typically, the payback time for plant investment is one to two years.

Installation: Sixteen plants operating in US refineries, with two under construction. The first plant was installed in 1984.

References: Buck, L., "Separating hydrocarbon gases," US Patent No. 4,617,039, Oct. 14, 1986.



Key, R., and Z. Malik, "Technology advances improve liquid recovery from refinery offgases," NPRA Annual Meeting, San Antonio, March 26–28, 2000.

Licensors: Linde BOC Process Plants LLC, a member of Linde Engineering Division.

Olefins-butenes extractive distillation

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

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

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

Economics:

Consumption per metric ton of FCC C₄ fraction feedstock:

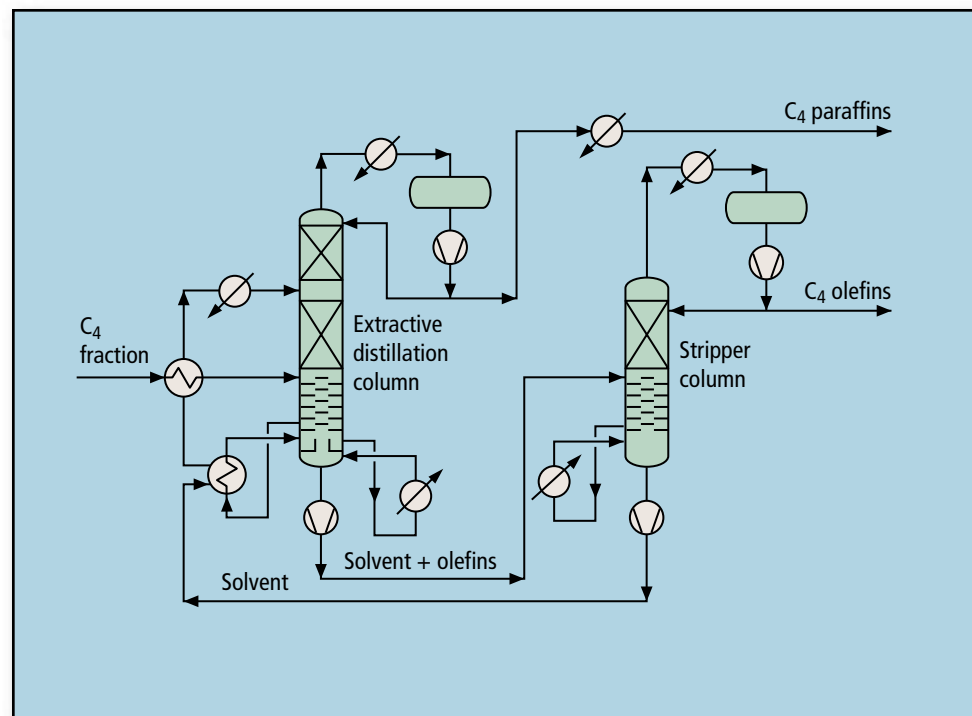
Steam, t/t	0.5–0.8
Water, cooling ($\Delta T = 10^{\circ}\text{C}$), m ³ /t	15.0
Electric power, kWh/t	25.0

Product purity:

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

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

Licensors: Uhde GmbH.



Olefins-dehydrogenation

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

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

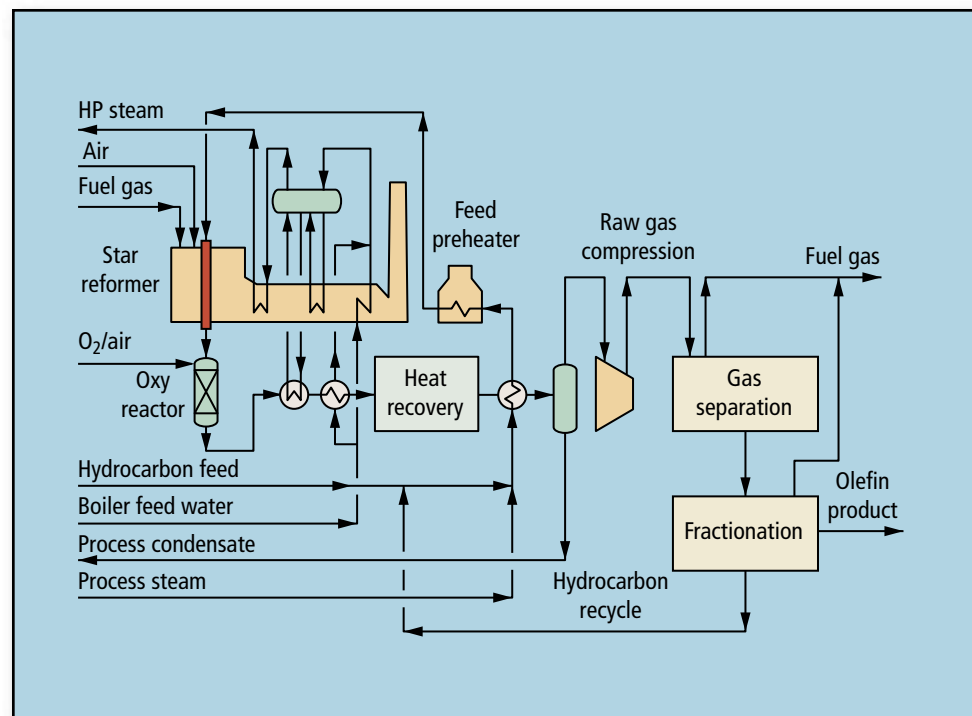
Product: Propylene (polymer- or chemical-grade); isobutylene; n-butylenes; high-purity hydrogen (H_2) may also be produced as a byproduct.

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

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

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

After cooling and condensate separation, the product is subsequently compressed, light-ends are separated and the olefin product is separated from unconverted paraffins in the fractionation section.



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

Economics: Typical specific consumption figures (for polymer-grade propylene production) are shown (per metric ton of propylene product):

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

Installations: Two commercial plants using the STAR process for dehy-

Continued ▼

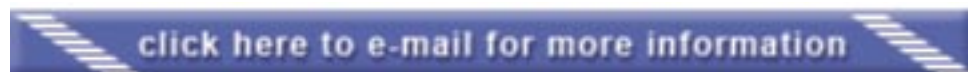
Olefins-dehydrogenation, *continued*

drogenation of isobutane to isobutylene have been commissioned (in the US and Argentina). More than 60 Uhde reformers and 25 Uhde secondary reformers have been constructed worldwide.

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

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

Licensors: Uhde GmbH.



Oligomerization of C₃C₄ cuts

Application: To dimerize light olefins such as ethylene, propylene and butylenes using the Dimersol process. The main applications are:

- Dimerization of propylene, producing a high-octane, low-boiling point gasoline called Dimate
- Dimerization of n-butylene producing C₈ olefins for plasticizer synthesis.

The C₃ feeds are generally the propylene cuts from catalytic cracking units. The C₄ cut source is mainly the raffinate from butadiene and isobutylene extraction.

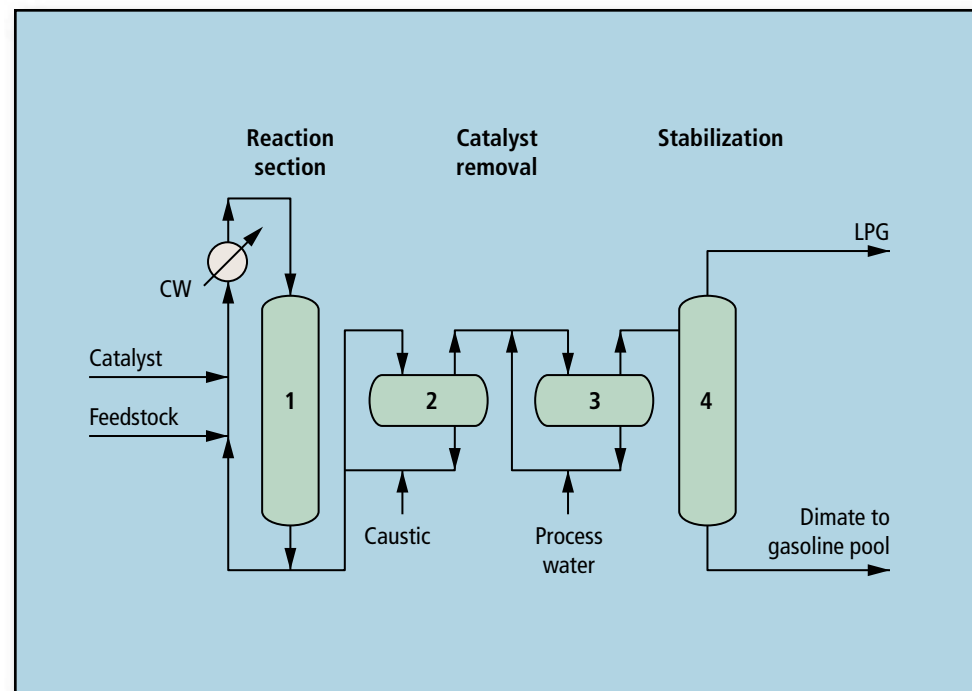
Description: Dimerization is achieved in the liquid phase at ambient temperature by means of a soluble catalytic complex. One or several reactors (1) in series are used. After elimination of catalyst (2, 3), the products are separated in an appropriate distillation section (4).

Product quality: For gasoline production, typical properties of the Dimate are:

Specific gravity, @15°C	0.70
End point, °C	205
70% vaporized, °C	80
Rvp, bar	0.5
RONC	96
MONC	81
RON blending value, avg.	103

Economics: For a plant charging 100,000 tpy of C₃ cut (% propylene) and producing 71,000 tpy of Dimate gasoline:

Investment for a 2002 ISBL Gulf Coast erected cost,
excluding engineering fees, US \$7 million



Utilities per ton of feed

Electric power, kWh	10.8
Steam, HP, t	0.14
Water, cooling, t	28.5
Catalyst + chemicals, US\$	9.3

Installation: Twenty-seven units have been built or are under construction.

Reference: "Olefin oligomerization with homogeneous catalysis," 1999 Dewitt Petrochemical Conference, Houston.

Licensors: Axens.

Oligomerization—polynaphtha

Application: To produce C_6+ isoolefin fractions that can be used as high-octane blending stocks for the gasoline pool and high-smoke-point blending stocks for kerosine and jet fuel. The Polynaphtha and Selectopol processes achieve high conversions of light olefinic fractions into higher value gasoline and kerosine from propylene and mixed-butene fractions such as C_3 and C_4 cuts from cracking processes.

Description: Propylene or mixed butenes (or both) are oligomerized catalytically in a series of fixed-bed reactors (1). Conversion and selectivity are controlled by reactor temperature adjustment while the heat of reaction is removed by intercooling (2). The reactor section effluent is fractionated (3), producing raffinate, gasoline and kerosine.

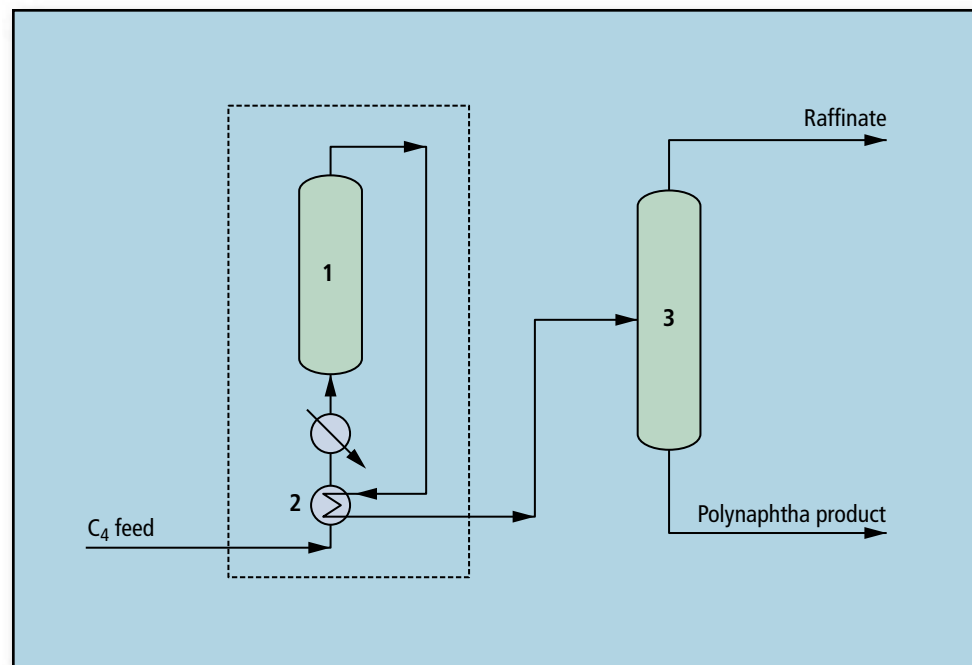
The Selectopol process is a variant of the polynaphtha process where the operating conditions are adjusted to convert selectively the isobutene portion of an olefinic C_4 fraction to high-octane, low-Rvp gasoline blending stock. It provides a low-cost means of debottlenecking existing alkylation units by converting all of the isobutene and a small percentage of the n-butenes, without additional isobutane.

Polynaphtha and Selectopol processes have the following features: low investment, regenerable solid catalyst, no catalyst disposal problems, long catalyst life, mild operating conditions, versatile product range, good-quality motor fuels and kerosine following a simple hydrogenation step and the possibility of retrofitting old phosphoric acid units.

The polygasoline RON and MON obtained from FCC C_4 cuts are significantly higher than those of FCC gasoline and, in addition, are sulfur-free. Hydrogenation improves the MON, whereas the RON remains high and close to that of C_4 alkylate.

Kerosine product characteristics such as oxidation stability, freezing point and smoke point are excellent after hydrogenation of the polynaphtha product. The kerosine is also sulfur-free and low in aromatics.

The Polynaphtha process has operating conditions very close to those of phosphoric acid poly units. Therefore, an existing unit's major equip-



ment items can be retained with only minor changes to piping and instrumentation. Some pretreatment may be needed if sulfur, nitrogen or water contents in the feed warrant; however, the equipment cost is low.

Economics: Typical ISBL Gulf Coast investments for 5,000-bpd of FCC C_4 cut for polynaphtha (of maximum flexibility) and Selectopol (for maximum gasoline) units are US\$8.5 million and US\$3.0 million, respectively. Respective utility costs are US\$4.4 and US\$1.8 per ton of feed while catalyst costs are US\$0.2 per ton of feed for both processes.

Installations: Seven Selectopol and polynaphtha units have been licensed (five in operation), with a cumulative operating experience exceeding 40 years.

Licensors: Axens.

Oxygen enrichment for Claus units

Application: Increase the capacity of Claus plants and decompose 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 efficient 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:

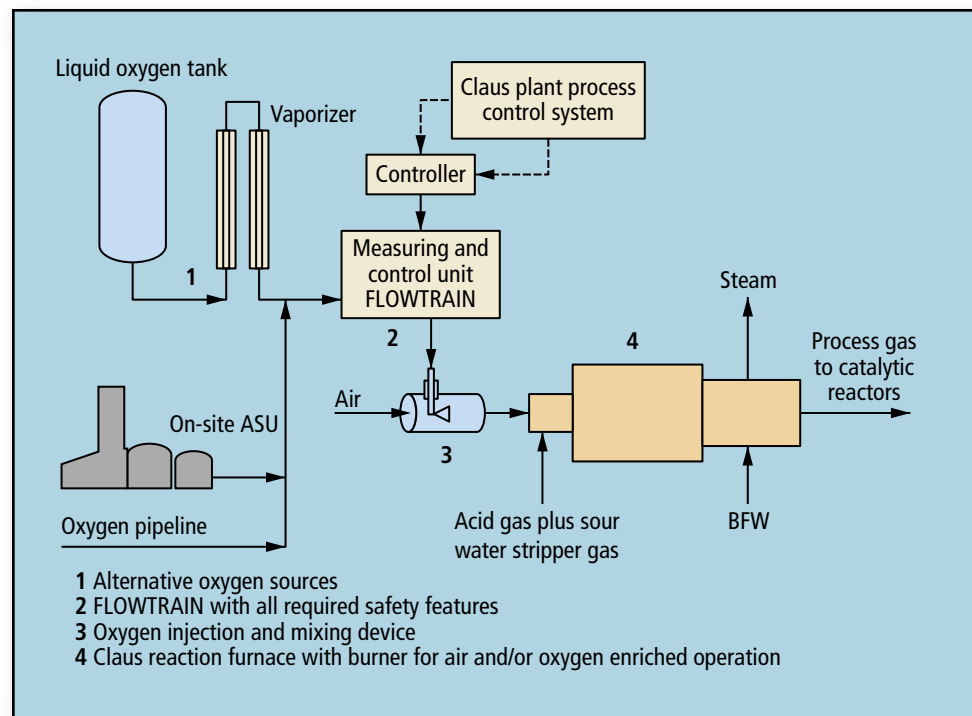
1. *Up to approximately 28% oxygen.* Oxygen is simply added to the Claus furnace air. This can raise sulfur capacity up to 30%.

2. *Up to approximately 40% oxygen.* The burner of the Claus furnace must be replaced. Up to 50% additional sulfur capacity can be achieved by this method.

3. *Beyond 40% oxygen.* The temperature in the Claus furnace is elevated so high that the product gas must be recycled to maintain temperature control. This process is expensive and, therefore, rarely applied.

Oxygen sources can be liquid oxygen tanks, onsite 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 efficient 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. 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 cost for a Claus plant, providing the same additional sulfur capacity.

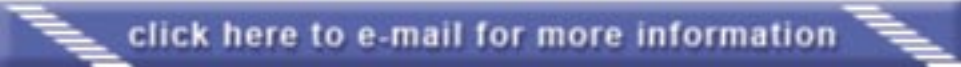
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Oxygen enrichment for Claus units, *continued*

Installations: Over 10, plus numerous test installations to quantify the effects of capacity increase and ammonia decomposition

Reference: Reinhardt, H. J. and P. M. Heisel, "Increasing the capacity of Claus plants with oxygen," *Reports on Science and Technology*, No. 61 (1999), p. 2 ff.

Contributor: Linde AG, Gas Division.



[click here to e-mail for more information](#)

Oxygen enrichment for FCC units

Application: Increase the throughput capacity by up to 50% and/or conversion in FCC units; process heavier feeds

Description: "Clean fuels" regulations are being implemented. Plus, the demand for transport fuels continually shifts toward more kerosine and diesel. The reason is that the regulations and the change in demand are totally independent developments. But both contribute to the requirement of more flexibility in the 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.

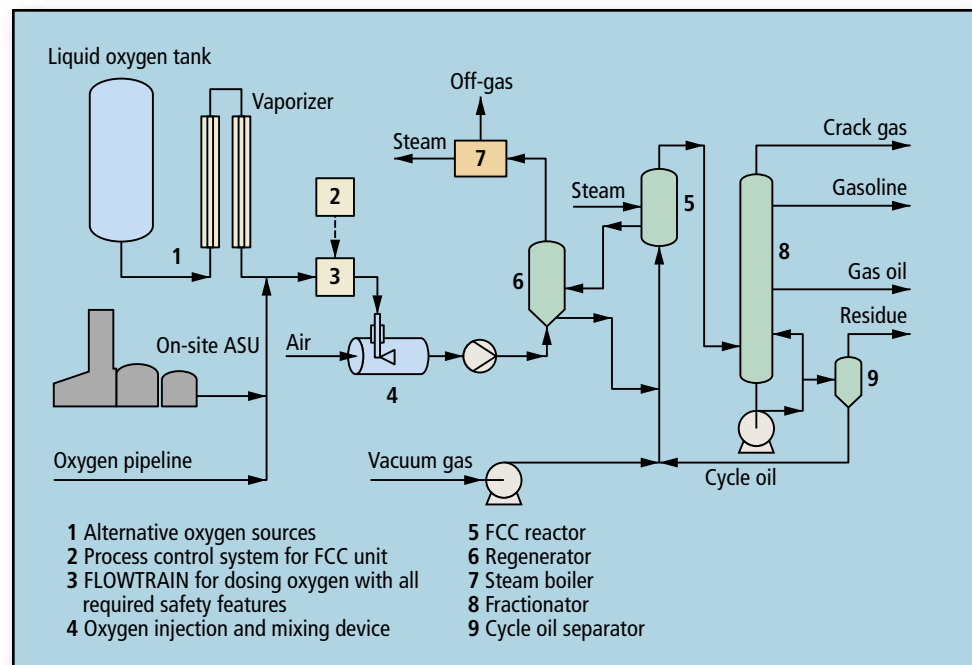
In the FCC reactor, long-chain hydrocarbons are cleaved into shorter chains in a fluidized-bed reactor at 450–550°C. This reaction produces coke as a byproduct that deposits on the catalyst. To remove the coke from the catalyst, it is burned off at 650–750°C in the regenerator. The regenerated catalyst is returned to the reactor.

Oxygen enrichment, typically 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 through-



put 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, two units are in operation, plus test installations to quantify the effects of higher capacity and conversion levels.

Reference: Heisel, M. P., C. Morén, A. Reichhold, A. Krause, A. Berlanga, "Cracking with Oxygen," to be published in *Linde Technology 1*, 2004.

Contributor: Linde AG, Gas Division.

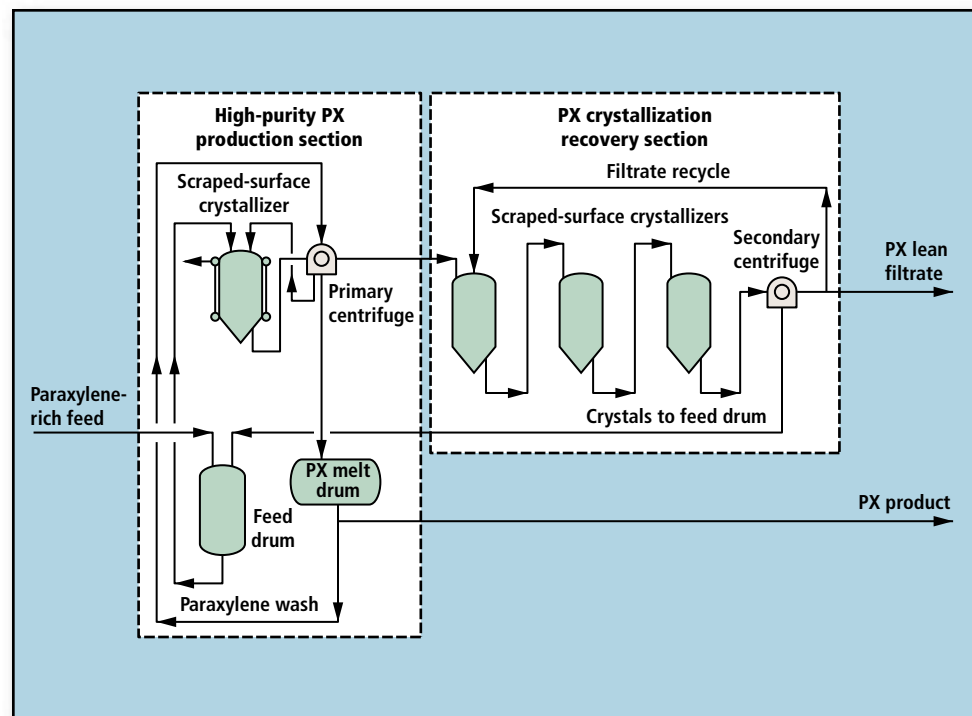
Paraxylene

Application: CrystPX is a modern crystallization technology to produce high-purity paraxylene (PX). This process offers lower capital cost and applies a simpler process scheme when compared to other technologies. CrystPX can be used in grassroots designs as a more economical alternative to adsorption processes, or applied in various revamp configurations to improve product purity, increase capacity or lower operating costs.

Description: CrystPX uses reliable suspension crystallization as the method to produce PX from a mixture of C₈ aromatics. The technology incorporates an optimized arrangement of equipment to conserve the cooling energy and reduce recycle rates. A pusher-type centrifuge separates PX crystals from the mother liquor, which is recycled to another stage, or xylene isomerization unit. The number of stages required is set by the feedstock composition and recovery required. The PX crystals are washed with paraxylene product, avoiding the use of other components that must subsequently be separated.

This process is economical to use with equilibrium xylene feedstock (20–25% PX); or with more concentrated feeds, such as originating from selective toluene conversion processes. In these cases, the process technology is even more economical to produce high-purity PX product. This technology takes advantage of recent advances in crystallization techniques and advancements in equipment to create this economically attractive method for PX recovery and purification.

The design uses only crystallizers and centrifuges in the primary operation. This simplicity of equipment promotes low maintenance costs, easy incremental expansions and controlled flexibility. For the case with concentrated feedstock, high-purity PX is produced in the front section of the process at warm temperatures, taking advantage of the high concentration of PX present in the feed. At the back end of the process, additional PX recovery is obtained through a series of crystallizers operated successively at colder temperatures. This scheme minimizes the need for recycling excessive amounts of filtrate, thus reducing total energy requirements.



Process advantages include:

- High PX purity and recovery (99.8+ wt.% purity at up to 95% recovery)
 - Crystallization equipment is simple, easy to procure and operationally trouble free
 - Compact design requires small plot size, and lowest capital investment
 - Operation is flexible to meet market requirements for PX purity
 - System is easily amenable to future requirement for incremental capacity increases
 - Feed concentration of PX is used efficiently
 - Technology is flexible to process a range of feed concentrations (20–95 wt.% PX) using a single or multistage system.
 - Aromatics complex using CrystPX technology is cost competitive with adsorption-based systems for PX recovery
- Continued ▼

Paraxylene, *continued*

Economics: Table 1 lists the benefits of the CrystPX process.

TABLE 1. Techno-economic comparison of CrystPX to conventional technologies

Basis: 90% PX feed purity, 400,000 tpy of 99.9 wt% PX		
	CrystPX	Other crystallization technologies
Investment cost, \$MM	26.0	40.0
Paraxylene recovery, %	95	95
Electricity consumption, kWh/ ton PX	50	80
Operation mode	Continuous	Batch

Licensor: GTC Technology Inc.

Note: CrystPX is a proprietary process technology marketed and licensed by GTC Technology Inc., in alliance with Lyondell Chemical Co.



Prereforming with feed ultra purification

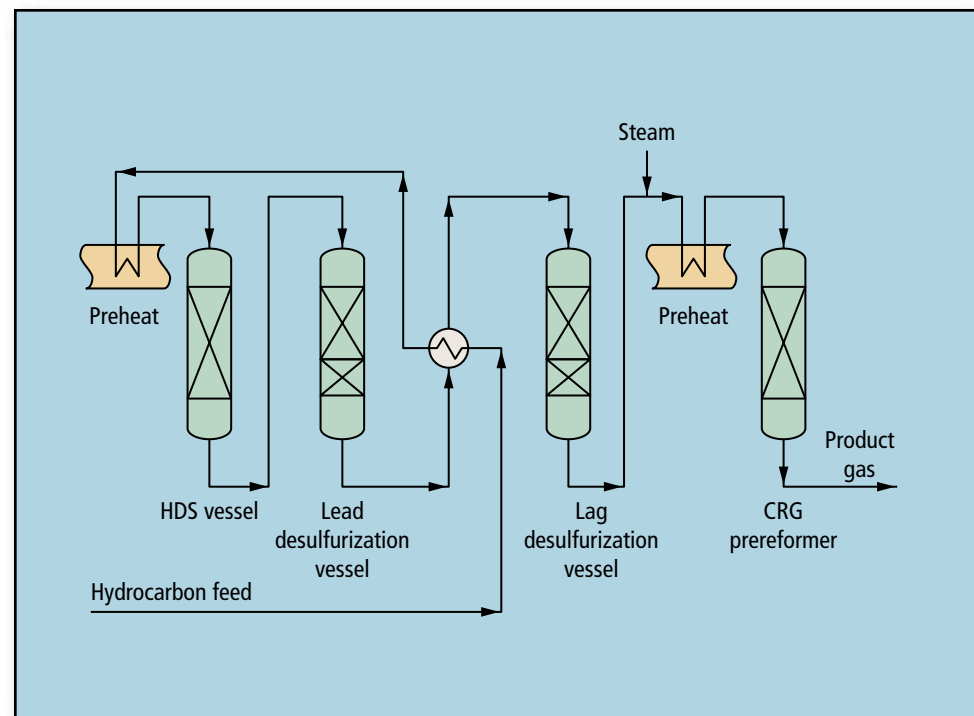
Application: Ultra-desulfurization and adiabatic-steam reforming of hydrocarbon feed from refinery offgas or natural gas through LPG to naphtha feeds as a prereforming step in the route to hydrogen production.

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 , CO_2 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 40 years of experience with over 150 plants built and operated. Ongoing development of the catalyst has lead to almost 50 such units since 1990.

Catalyst: The CRG catalyst is manufactured under license by Syntex.

Licensors: The process and CRG catalyst are licensed by Davy Process Technology.

Resid catalytic cracking

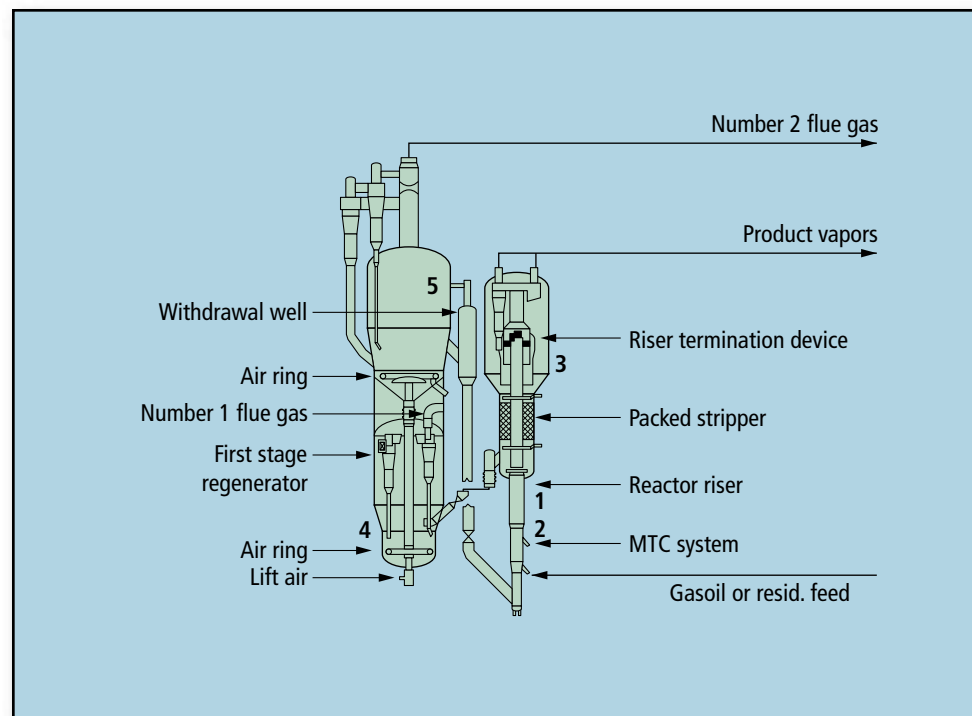
Application: Selective conversion of gas oil and heavy residual feedstocks.

Products: High-octane gasoline, distillate and C_3 – C_4 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 (1) 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 (2).

Reaction products exit the riser-reactor through a high-efficiency, close-coupled, proprietary riser termination device RS² (riser separator stripper) (3). Spent catalyst is pre-stripped followed by an advanced high-efficiency packed stripper prior to regeneration. The reaction product vapor may be quenched using BP's proprietary technology to give the lowest 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 two independent stages (4, 5) 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 24 units and is licensed exclusively by Stone & Webster/Axens.



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, flue-gas treatment and slurry filtration.

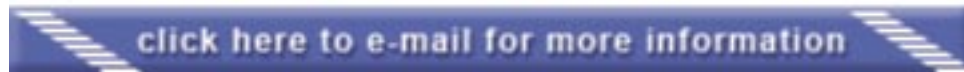
Existing gas oil units can be easily retrofitted to this technology. Re-vamps incorporating proprietary feed injection and riser termination devices and vapor quench result in substantial improvements in capacity, yields and feedstock flexibility within the mechanical limits of the existing unit.

Resid catalytic cracking, *continued*

Installation: Stone & Webster and Axens have licensed 27 full-technology R2R units and performed more than 150 revamp projects.

Reference: Letzsch, W. S., "Commercial performance of the latest FCC technology advances," NPRA Annual Meeting, March 2000.

Licensors: Stone & Webster Inc., a Shaw Group Co., and Axens, IFP Group Technologies.



SBS SO₃ removal process

Application: SBS is a patented process used for high level of SO₃ reduction with either wet scrubbing systems or dry systems such as an ESP. When used in conjunction with BELCO's wet scrubbing system, and the LoTox* process, one can achieve simultaneously very high reduction of particulate, SO₂, SO₃ and NO_x in a single scrubber vessel.

Description: SBS injection technology uses sodium bisulfite (SBS) as the reagent. A clear solution of sodium bisulfite is injected into the hot flue gas stream upstream of the emission control devices used to remove particulate and SO₂ from the flue gas. SO₃ in the flue gas reacts with the injected SBS to produce dry sodium sulfate and sodium bisulfate particles, which are removed downstream along with the other particulate.

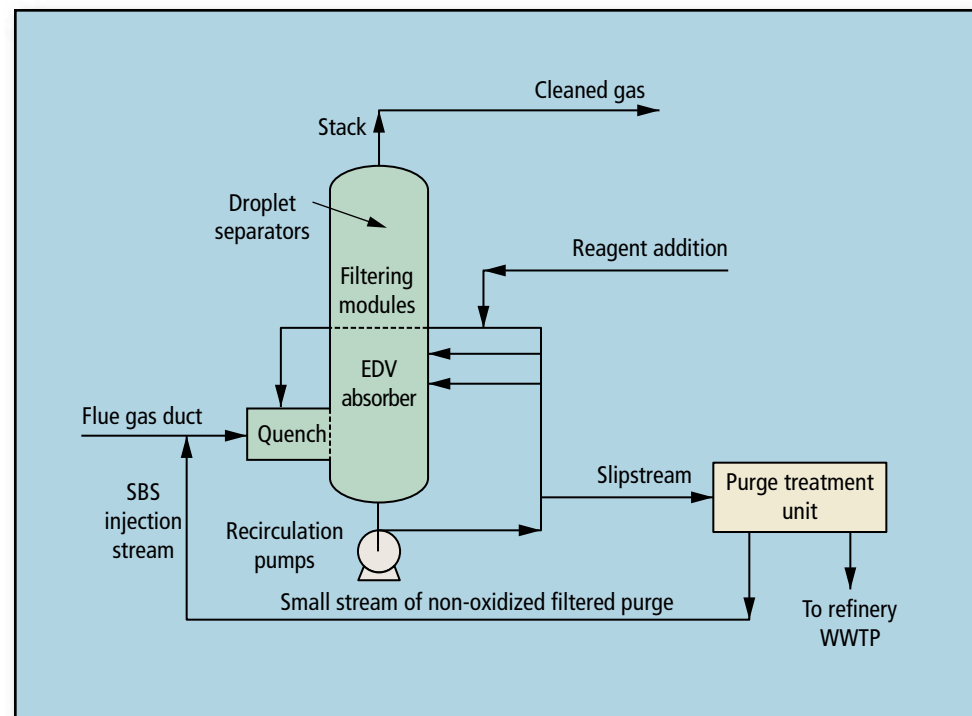
The reaction rates are fast; so, only short residence times are required between reagent injection and the downstream particulate collection device. Both sodium bisulfite (NaHSO₃) and sodium sulfite (Na₂SO₃) make up the reagent feed. Because the reactions are specific to SO₃, very little reagent is injected.

Operating conditions: SBS injection occurs in the flue-gas duct upstream of the scrubber or ESP, at atmospheric pressure and typical flue-gas temperatures. High particulate and sulfur levels do not cause problems for this process.

Economics: When very high levels of SO₃ reduction are required, the SBS process is extremely competitive against alternate processes and equipment.

Development status: Full-scale applications of the process have been operating successfully at several large power station applications in the US.

* LoTox is a trademark of The BOC Group.



Reference: Weaver, Barrasso and Jarvis, "An update of wet scrubbing control technology for FCCU-multiple pollutant control," NPRA Annual Meeting, San Antonio, March 2003.

Licensors: Belco Technologies Corp., as a sub-licensor for Codan Development LLC.

SO₂ removal, regenerative

Application: Regenerative scrubbing system to recover SO₂ from flue gas containing high SO₂ levels such as gas from FCC regenerator or incinerated SRU tail gas and other high SO₂ 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.

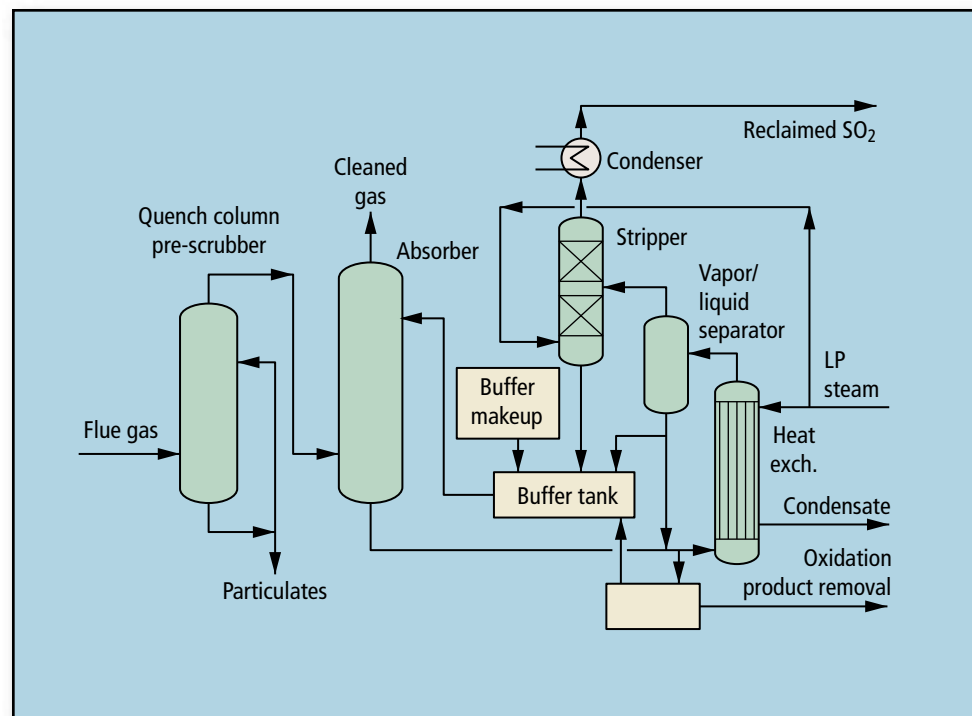
Products: The product from the LABSORB process is a concentrated SO₂ stream consisting of approximately 90% SO₂ and 10% moisture. This stream can be sent to the front of the SRU to be mixed with H₂S and form sulfur, or it can be concentrated for other marketable uses.

Description: Hot dirty flue gas is cooled in a flue-gas cooler or waste-heat 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°C–75°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.

Installations: 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.

Licensors: Belco Technologies Corp.

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 420°C in a waste heat boiler. The gas then enters the SO_2 converter containing one or several beds of SO_2 oxidation catalyst to convert SO_2 to SO_3 . The gas is cooled in the gas cooler whereby SO_3 hydrates to H_2SO_4 (gas), which is finally condensed as concentrated sulfuric acid (typically 98% w/w).

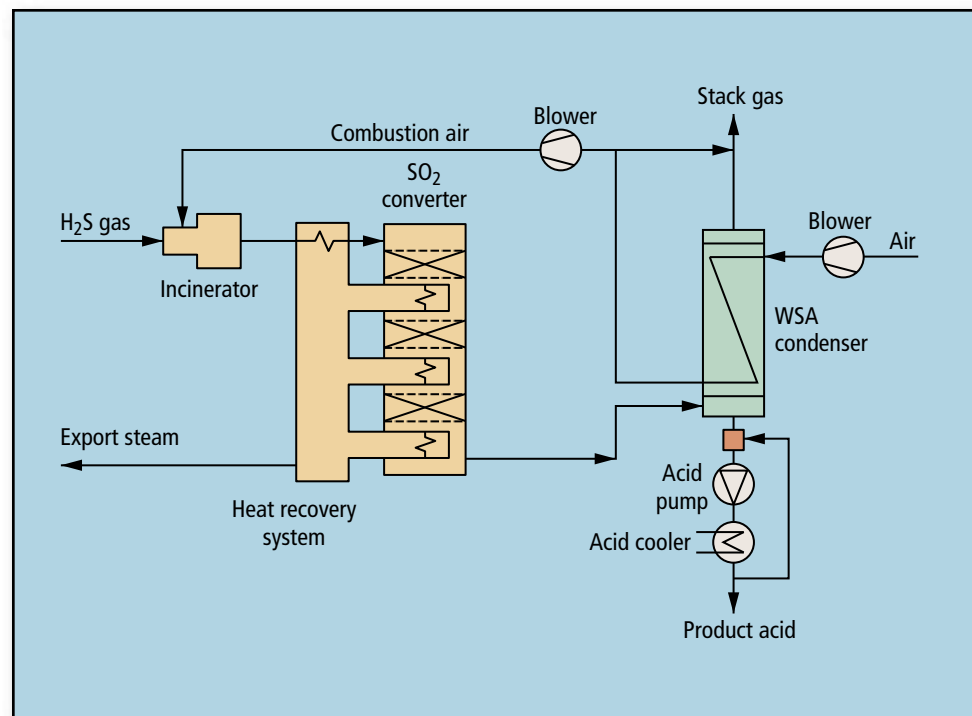
The WSA condenser is cooled by ambient air, and heated air may be used as combustion air in the burner for increased thermal efficiency. The heat released by incineration and SO_2 oxidation is recovered as steam. The process operates without removing water from the gas. Therefore, the number of equipment 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:

- More than 99% 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 45 units worldwide.

Licensors: Haldor Topsøe A/S.



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 coke 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 H_2S and removal of SO_x .

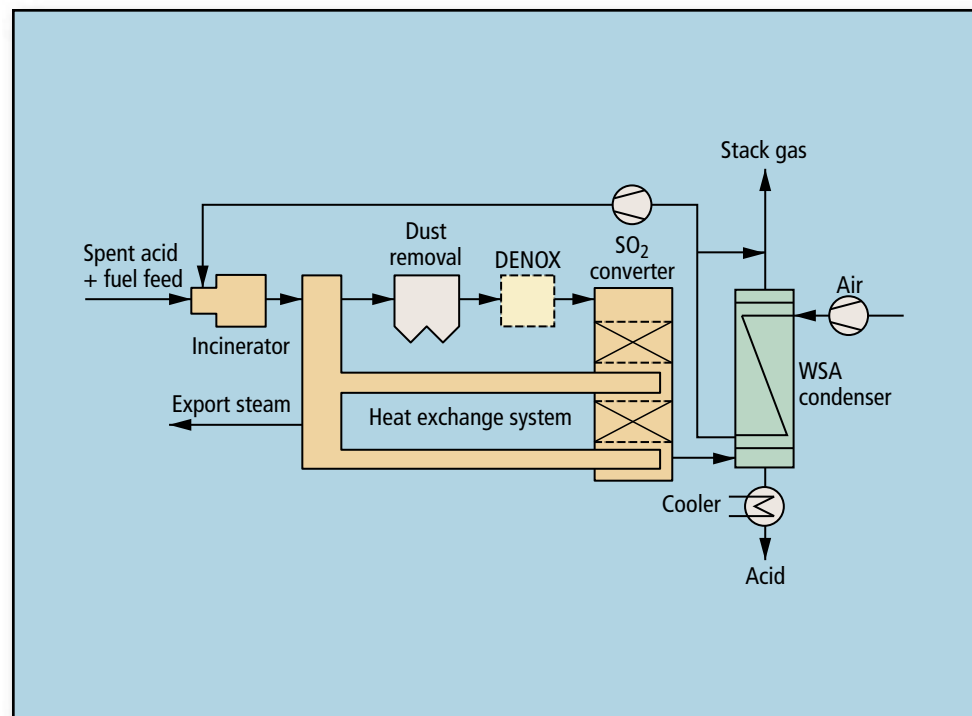
Description: Spent acid is decomposed to SO_2 and water in a burner using amine regenerator offgas or refinery gas as fuel. The SO_2 containing flue gas is cooled in a waste-heat boiler and solid matter originating from the acid feed is separated in an electrostatic precipitator. By adding preheated air, the process gas temperature and oxygen content are adjusted before the catalytic converter when 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 in the burner for increased thermal efficiency. The heat released by incineration 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:

- More than 99% recovery of 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 flow and composition.



Installation: More than 45 WSA units worldwide, including 8 for spent acid regeneration.

Licensors: Haldor Topsøe A/S.

Spent lube oil re-refining

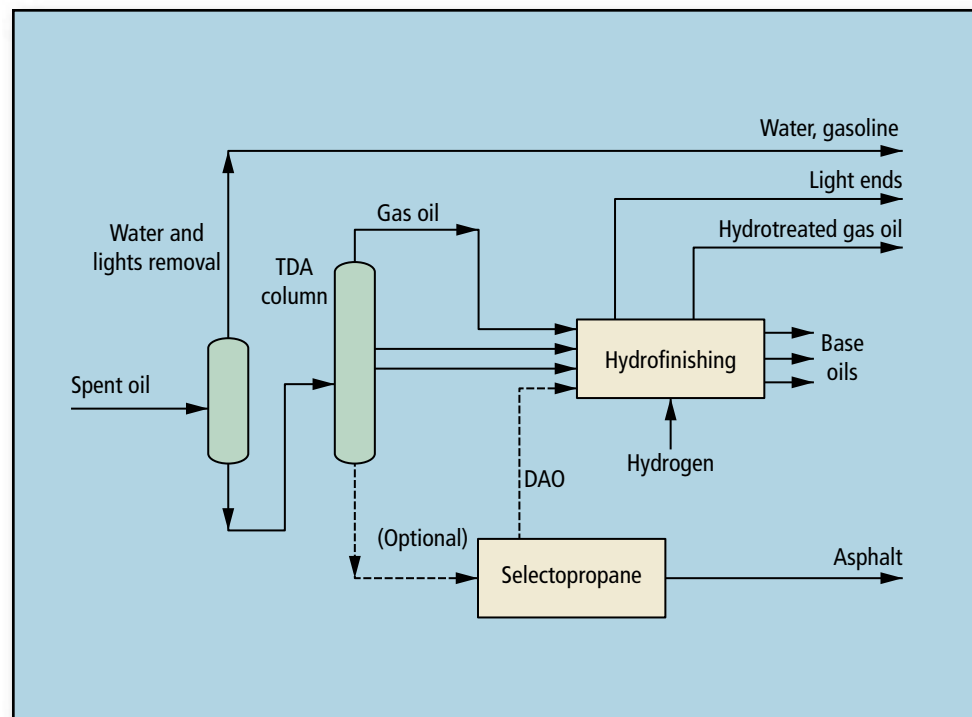
Application: The Revivoil process can be used to produce high yields of premium quality lube bases from spent motor oils. Requiring neither acid nor clay treatment steps, the process can eliminate environmental and logistical problems of waste handling and disposal associated with conventional re-refining 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 Selectopropylene 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 com-



pounds 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 Selectopropylene unit can be added at a later stage, to bring the oil recovery to the 95% level on dry basis. Economics below show that for two plants of equal capacity, payout times before taxes are two years in both cases.

Investment: Basis 100,000 metric tpy, water-free, ISBL 2004 Gulf Coast, million US\$

Configuration 1	(Atm. flash, TDA and Hydrofinishing units)	30
Configuration 2	(Same as above + Selectopropylene unit)	35

Continued ▼

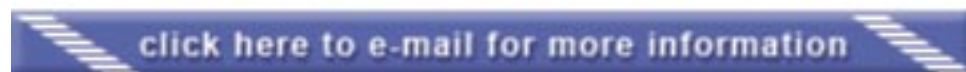
Spent oil lube re-refining, *continued*

Utilities: Basis one metric ton of water-free feedstock

	Config. 1	Config. 2
Electrical power, kWh	45	55
Fuel, million kcal	0.62	0.72
Steam, LP, kg	—	23.2
Steam, MP, kg	872	890
Water, cooling, m ³	54	59

Installation: Ten units have been licensed using all or part of the Revivoil Technology.

Licensors: Axens and Viscolube SpA.



Sulfur degassing

Application: Hydrogen sulfide (H_2S) removal from sulfur.

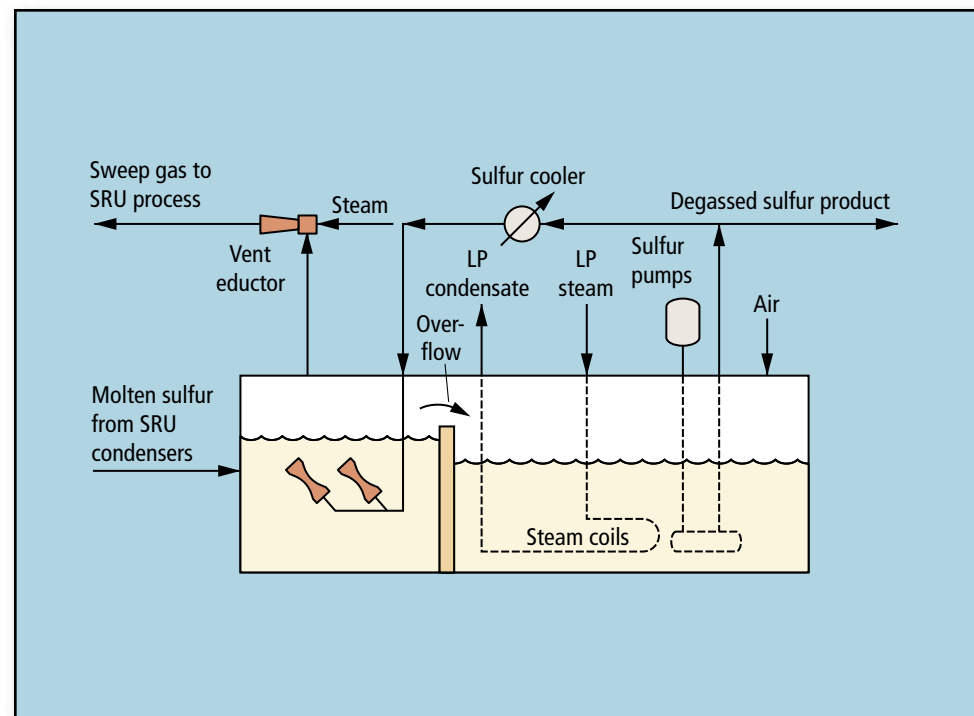
Description: Sulfur, as produced by the Claus process, typically contains from about 200 ppmw to 500 ppmw H_2S . The H_2S may be contained in the molten sulfur as H_2S or as hydrogen polysulfides (H_2S_x). The dissolved H_2S separates from the molten sulfur readily, but the H_2S_x does not.

The sulfur degassing process accelerates the decomposition of hydrogen polysulfides to H_2S and elemental sulfur (S). The dissolved H_2S gas is released in a controlled manner. Sulfur temperature, residence time and the degree of agitation all influence the degassing process. Chemical catalysts, including oxygen (air) that accelerate the rate of H_2S_x decomposition are known to improve the degassing characteristics.

In fact, the majority of successful commercial degassing processes use compressed air, in some fashion, as the degassing medium. Research performed by Alberta Sulphur Research Ltd. has demonstrated that air is a superior degassing agent when compared to nitrogen, steam or other inert gases. Oxygen present in air promotes a level of direct oxidation of H_2S to elemental S , which reduces the gaseous H_2S partial pressure and increases the driving force for H_2S_x decomposition to the more easily removed gaseous phase H_2S .

The MAG degassing system concept was developed to use the benefits of degassing in the presence of air without relying on a costly compressed air source. With the MAG system, motive pressure from a recirculated degassed sulfur stream is converted to energy in a mixing assembly within the undegassed sulfur. The energy of the recirculated sulfur creates a high air-to-sulfur interfacial area by generating intense turbulence within the jet plume turning over the contents many times, thus exposing the molten sulfur to the sweep air. Intimate mixing is achieved along with turbulence to promote degassing. This sulfur degassing system can readily meet a 10 ppmw total H_2S ($\text{H}_2\text{S} + \text{H}_2\text{S}_x$) specification.

Tests show degassing rate constants nearly identical to traditional air



sparging for well-mixed, air-swept degassing systems. Thus, comparable degassing to air sparging can be achieved without using a compressed air source. The assemblies are designed to be self-draining of molten sulfur and to be easily slipped in and out for maintenance through the pit nozzles provided. The mixing assemblies require no moving parts or ancillary equipment other than the typical sulfur-product-transfer pump that maximizes unit reliability and simplifies operations.

The process is straightforward; it is inherently safer than systems using spray nozzles and/or impingement plates because no free fall of sulfur is allowed.

Economics: Typically does not require changes to existing sulfur processing infrastructure.

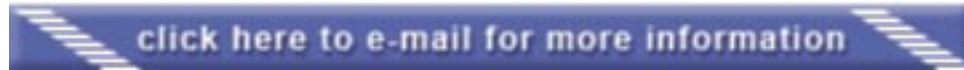
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Sulfur degassing, *continued*

Installation: Several units are in design.

Reference: US Patent 5935548 issued Aug. 10, 1999.

Licensors: Black & Veatch Pritchard, Inc.



Sulfur recovery

Application: The COPE process for O_2 enrichment is utilized to increase capacity and recovery of existing Claus sulfur recovery/tail gas cleanup units, provide redundant sulfur processing capacity, and improve combustion performance of units processing lean acid gas.

Description: The sulfur processing capacity of typical Claus sulfur recovery units can be increased to more than 200% of the base capacity through partial to complete replacement of combustion air with pure O_2 . SRU capacity is typically limited by hydraulic pressure drop. As O_2 replaces combustion air, the quantity of inert nitrogen is reduced, allowing additional acid gas to be processed. The process can be implemented in two stages.

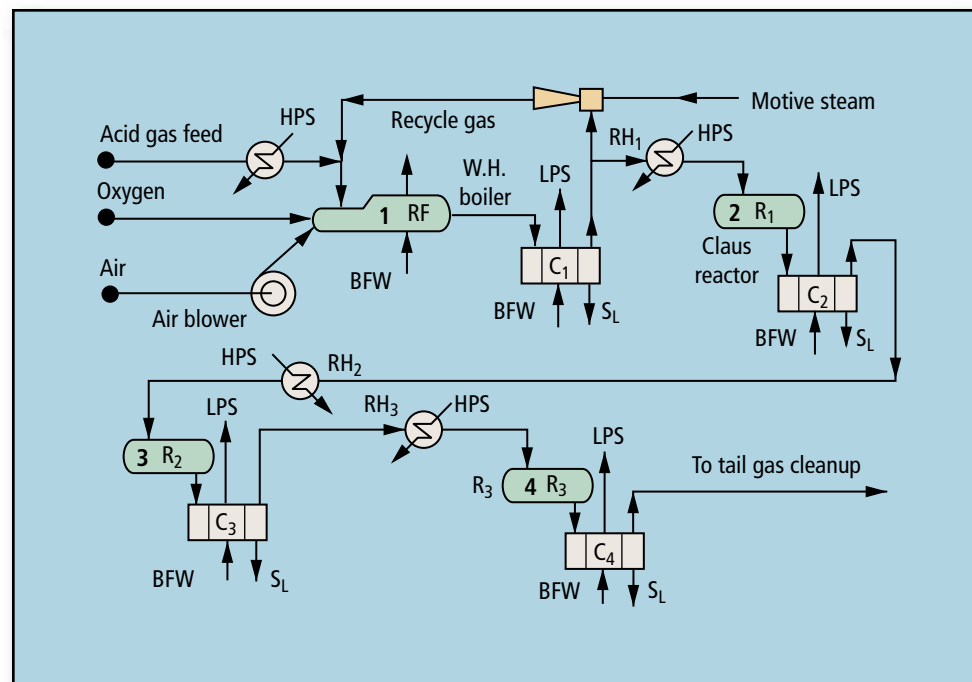
As the O_2 enrichment level increases, the combustion temperature (1) increases. COPE Phase I, which does not use a recycle stream, can often achieve 50% capacity increase through O_2 enrichment to the maximum reaction furnace refractory temperature limit of about 2,700–2,800°F.

Higher O_2 enrichment levels are possible with COPE Phase II which uses an internal process recycle stream to moderate the combustion temperature allowing enrichment up to 100% O_2 . Flow through the remainder of the SRU (2, 3, & 4) and the tail gas cleanup unit is greatly reduced.

Ammonia and hydrocarbon acid gas impurity destruction and thermal stage conversion are improved at the higher O_2 enriched combustion temperatures. Total SRU sulfur recovery is increased by 0.5 to 1%. A single proprietary COPE burner handles acid gas, recycle gas, air and oxygen.

Operating conditions: Combustion pressure from 6 to 12 psig; combustion temperature up to 2,800°F. Oxygen concentration from 21% to 100%. SRU sulfur recovery is 95–98%.

Economics: Expanded SRU and tail gas unit retrofit sulfur processing capacity at capital cost of 15–25% of new plant cost. New plant savings of up to 25%, and redundant capacity at 15% of base capital cost. Operating costs are a function of oxygen cost, reduced incinerator fuel, and reduced operating and maintenance labor costs.



Installations: Twenty-one COPE trains in operation at twelve locations.

Reference: US Patents 4,552,747 and 6,508,998.

Sala, L., W. P. Ferrell, and P. Morris, "The COPE process—increase sulfur recovery capacity to meet changing needs," European Fuels Week Conference, Giardini Naxos, Taormina, Italy, April 2000.

Nasato, E., and T. A. Allison, "COPE Ejector—Proven Technology," *Sulphur 2002*, Vienna, Austria, October 2002.

Licensors: Goar, Allison & Associates, Inc. and Air Products and Chemicals, Inc.

Sulfur recovery

Application: Removal of dissolved H_2S and H_2S_x from produced liquid sulfur by the D'GAASS process. Undegassed sulfur can create odor problems and poses toxic and explosive hazards during the storage and transport of liquid sulfur.

Description: Degasification is accomplished in a pressurized vertical vessel where undegassed sulfur is efficiently contacted with pressurized process air (instrument or clean utility air). The contactor vessel may be located at any convenient location. The undegassed sulfur is pumped to the vessel and intimately contacted with air across special fixed vessel internals.

Operation at elevated pressure and a controlled temperature accelerates the oxidation of H_2S and polysulfides (H_2S_x) to sulfur.

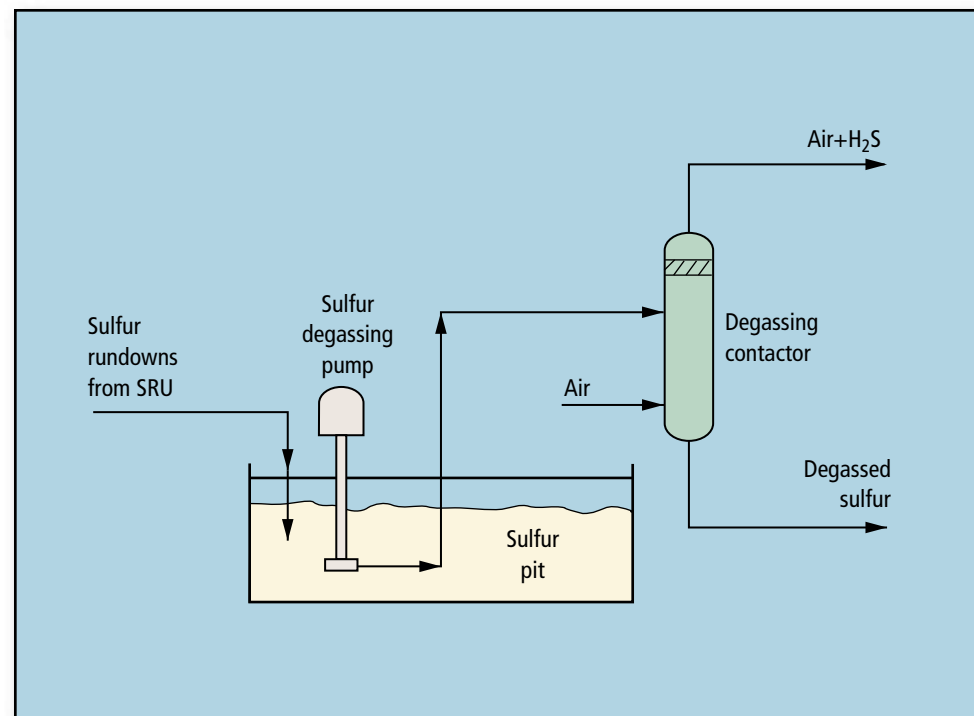
The degassed sulfur can be sent to storage or directly to loading without additional pumping. Operation at elevated pressure allows the overhead vapor stream to be routed to the traditional incinerator location, or to the SRU main burner or TGTU line burner—thus eliminating the degassing unit as an SO_2 emission source.

Economics: D'GAASS achieves 10 ppmw combined $\text{H}_2\text{S}/\text{H}_2\text{S}_x$ in product sulfur. Elevated pressure results in the following benefits: low capital investment, very small footprint, low operating cost and low air requirement. Operation is simple, requiring minimal operator and maintenance time. No chemicals or catalysts are required.

Installations: Sixteen units in operation. Eighteen additional trains in engineering and construction phase with total capacity over 19,000 ltpd.

Reference: US Patent 5,632,967.

Nasato, E., and T. A. Allison, "Sulfur Degasification—The D'GAASS Process," Proceedings of the 1998 Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, March 1998.



Fenderson, S., "Continued development of the D'GAASS sulfur degasification process," Brimstone Sulfur Recovery Symposium, Canmore, Alberta, May 2001.

Licensors: Goar, Allison & Associates, Inc.

Thermal gasoil process

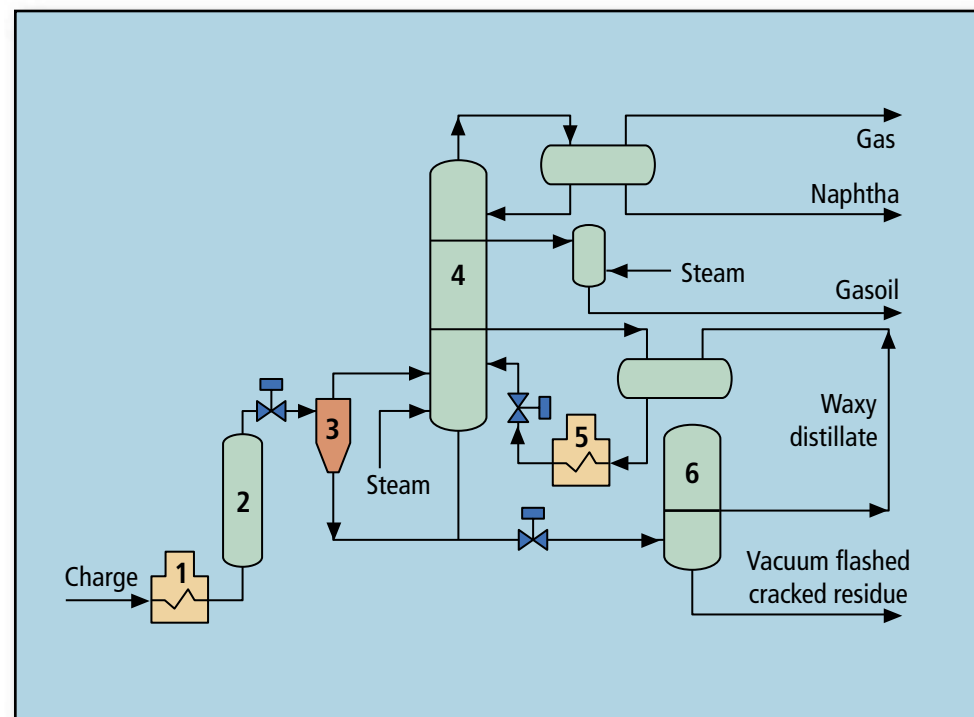
Application: The Shell Thermal Gasoil process is a combined residue and waxy distillate conversion unit. The process is an attractive low-cost conversion option for hydroskimming refineries in gasoil-driven markets or for complex refineries with constrained waxy distillate conversion capacity. The typical feedstock is atmospheric residue, which eliminates the need for an upstream vacuum flasher. This process features Shell Soaker Visbreaking technology for residue conversion and an integrated recycle heater system for the conversion of waxy distillate.

Description: The preheated atmospheric (or 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 soaker and is controlled by 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 including a light waxy distillate. The cyclone and fractionator bottoms are routed to a vacuum flasher (6), where waxy distillate is recovered. The combined waxy distillates are fully converted in the distillate heater (5) at elevated pressure.

Yields: Depend on feed type and product specifications.

Feed atmospheric residue	Middle East
Viscosity, cSt @ 100°C	31
Products, % wt.	
Gas	6.4
Gasoline ECP 165°C	12.9
Gasoil ECP 350°C	38.6
Residue ECP 520°C+	42.1
Viscosity 165°C plus, cSt @100°C	7.7

Economics: The investment amounts to 1,400–1,600 US\$/bbl installed excluding treating facilities and depending on capacity and configuration (basis: 1998).



Utilities, typical consumption per bbl of feed @ 180°C:

Fuel, 10 ³ cal	34
Electricity, kWh	0.8
Steam, net production, kg	29
Water, cooling, m ³	0.17

Installation: Thirteen Shell thermal gasoil units have been built or are under construction. Post startup services and technical services on existing units are available from Shell.

Reference: "Thermal Conversion Technology in Modern Power Integrated Refinery Schemes," 1999 NPRA Annual Meeting.

Thermal gasoil process, *continued*

Licensors: Shell Global Solutions International B.V., and ABB Lummus Global B.V.



Treating—gases

Application: AMINEX and THIOLEX systems extract H_2S , COS and CO_2 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. Hydrocarbon also flows through the contactor parallel to the amine-wetted fibers where the H_2S , COS and/or CO_2 are extracted into the aqueous phase. The two phases disengage in the separator vessel with the rich amine flowing to the amine regeneration unit and the treated gas flowing to storage.

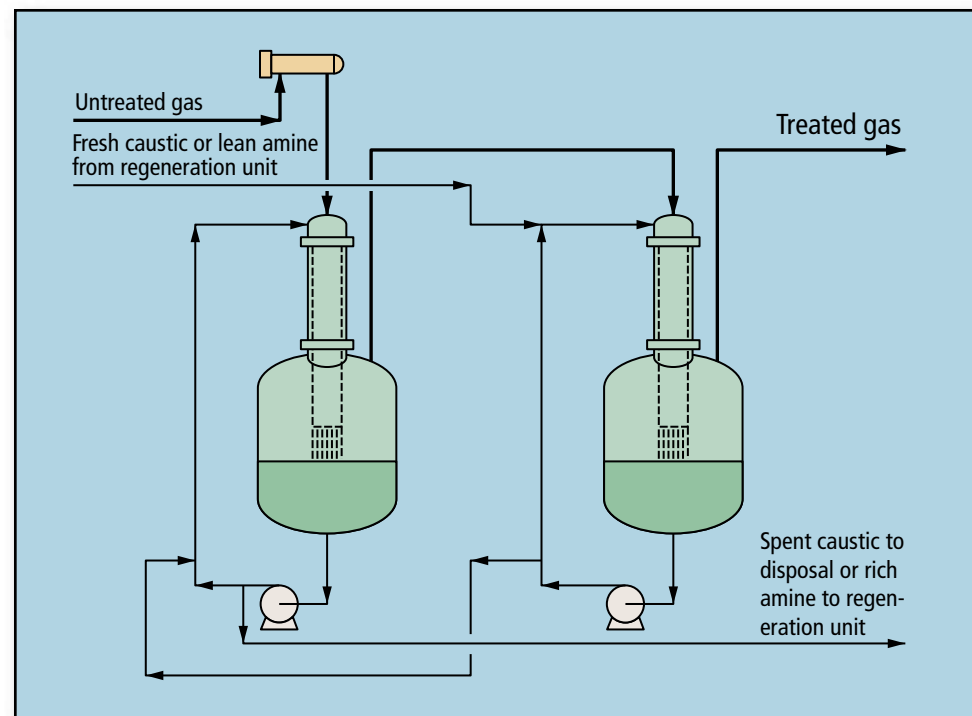
Similarly, a THIOLEX system uses the same process utilizing caustic to preferentially wet the fibers where the H_2S , COS and CO_2 are extracted into the caustic phase. The rich caustic flows to sulfidic caustic storage, and treated gas flows to storage. MEA can be added to the fresh caustic to catalyze the hydrolysis of COS into H_2S and CO_2 which are subsequently removed by the caustic phase.

Competitive advantages: FIBER-FILM Contactor technology requires smaller processing vessels, allowing for shorter separation times and less sulfidic treating solution generation. Result: Saving valuable plant space and reducing capital expenditures.

Installations: Three installations worldwide in THIOLEX service.

Reference: *Hydrocarbon Processing*, Vol. 63, No. 4, April 1984, p. 87.

Licensors: Merichem Chemicals & Refinery Services LLC.



Treating—gasoline

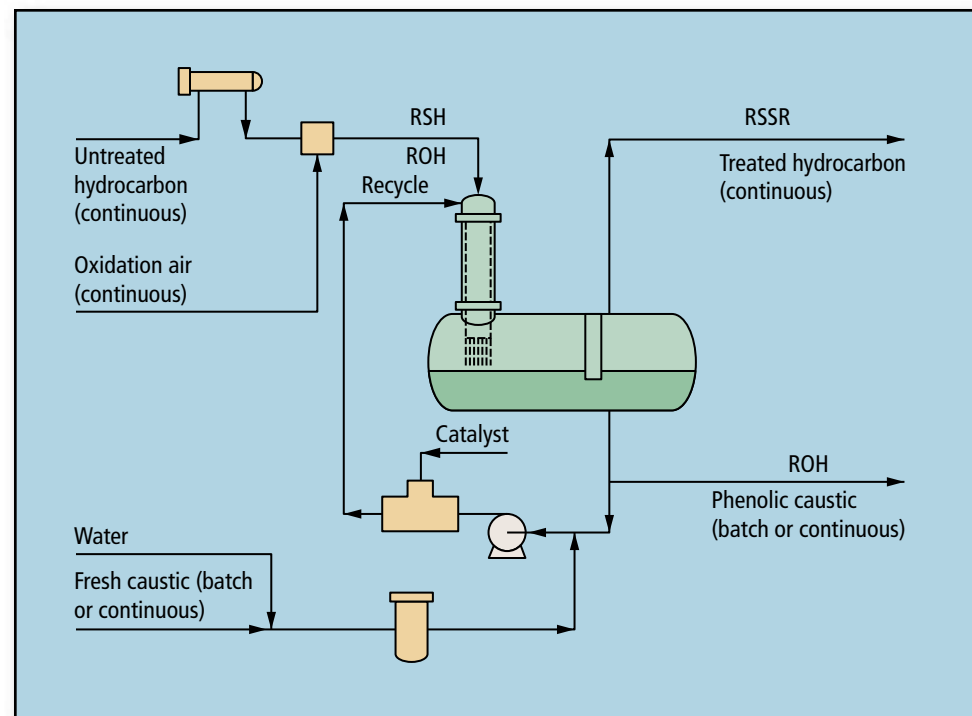
Application: MERICAT systems oxidize mercaptans to disulfides in gasoline or condensate by reacting mercaptans with air and caustic in the presence of catalyst using FIBER-FILM Contactor technology.

Description: In a MERICAT system, the caustic phase flows along the fibers of the FIBER-FILM Contactor as it preferentially wets the fibers. The hydrocarbon mixes with air through a proprietary air sparger and flows through the caustic-wetted fibers where the mercaptans are converted to disulfides in the caustic phase and are absorbed back into the hydrocarbon phase. The two phases disengage and the phenolic caustic flows to storage or can be shipped to Merichem as a product.

Competitive advantages: FIBER-FILM Contactor technology requires smaller processing vessels, allowing for shorter separation times and less waste generation. Result: Saving valuable plant space and reducing capital expenditures.

Installations: 121 installations worldwide.

Licensors: Merichem Chemicals & Refinery Services LLC.



Treating—gasoline and light hydrocarbon liquids

Application: THIOLEX/REGEN systems extract H_2S and mercaptans from gases and light liquid streams, including gasoline, with caustic using FIBER-FILM Contactor technology. It can also be used to hydrolyze COS contained in LPG.

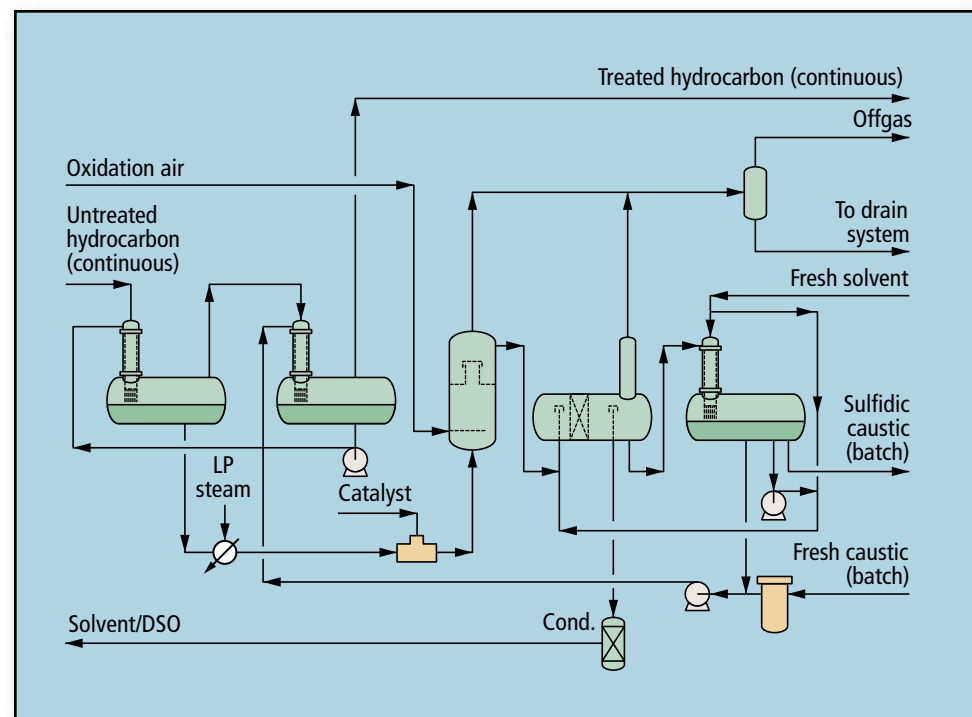
Description: In a THIOLEX system, the caustic phase flows along the fibers of the FIBER-FILM Contactor as it preferentially wets the fibers. Hydrocarbon also flows through the caustic-wetted fibers where the H_2S and mercaptans are extracted into the caustic phase. The two phases disengage and the caustic flows to the REGEN where the sulfidic caustic is regenerated using 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.

Competitive advantages: FIBER-FILM Contactor technology requires smaller processing vessels, allowing for shorter separation times and less sulfidic caustic generation. Result: Saving valuable plant space and reducing capital expenditures.

Installations: 270 installations worldwide.

Reference: *Oil & Gas Journal*, August 12, 1985, p. 78.

Licensor: Merichem Chemicals & Refinery Services LLC.



Treating—gasoline desulfurization, ultra deep

Application: EXOMER extracts recombinant mercaptan sulfur from selectively hydrotreated FCC gasoline streams with a proprietary treating solution. This is done using FIBER-FILM Contactor technology to reduce 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.

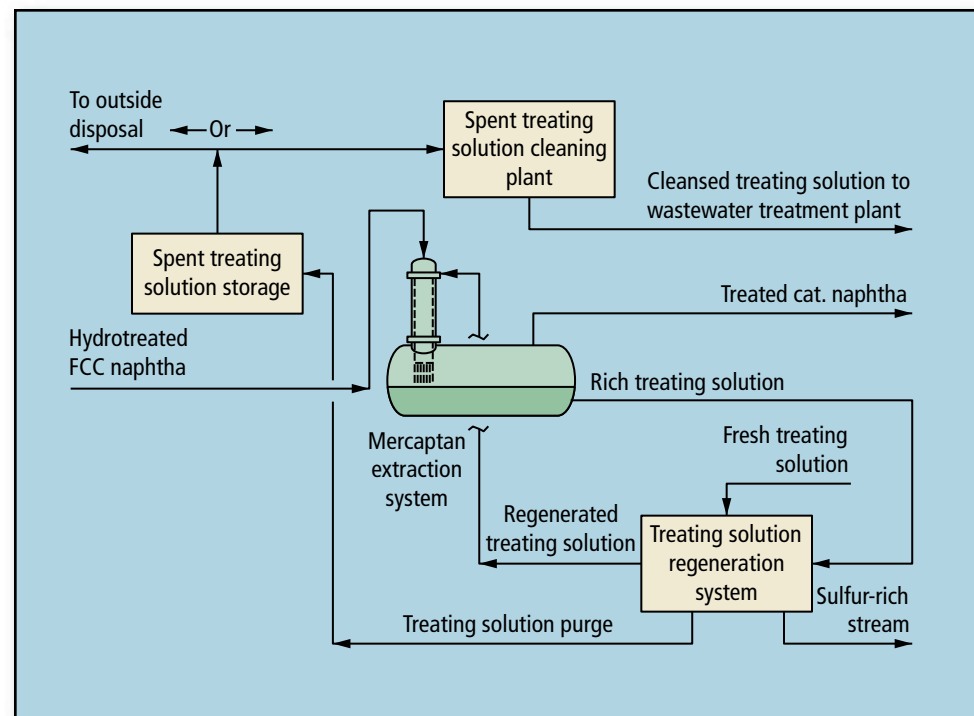
The separated rich treating solution phase is sent to the regeneration unit where sulfur-bearing components are removed. The removed sulfur is sent to another refinery unit for further processing. After polishing, the lean treating solution is returned to the extraction step for further use.

Economics: EXOMER allows refiners to meet new stricter sulfur specifications while preserving octane. The capital expenditure for a grass roots EXOMER solution is 35–50% of the cost of most incremental conventional hydrotreating solutions. Operating costs per barrel can be more than 60–70% less than conventional hydrotreating.

FIBER-FILM Contactor technology requires smaller processing vessels; thus, allowing for shorter separation times and less spent treating solution generation. Result: Saving valuable plant space and reducing capital expenditures.

Installations: Three installations worldwide.

Reference: *Hydrocarbon Processing*, February 2002, p. 45.



Licensors: Merichem Chemicals & Refinery Services LLC.

Treating—jet fuel/kerosine

Application: NAPFINING/MERICATII/AQUAFINING systems remove naphthenic acids and/or mercaptans from kerosine with caustic, air and catalyst using FIBER-FILM Contactor technology followed by an upflow catalyst impregnated carbon bed.

Description: In the NAPFINING system, the caustic phase flows along the fibers of the FIBER-FILM Contactor as it preferentially wets the fibers. Kerosine simultaneously flows through the caustic-wetted fibers where naphthenic acids react with the caustic phase to form sodium naphthenate. The two phases disengage and the kerosine flows to the MERICAT II where the mercaptans react with caustic, air and catalyst in the FIBER-FILM Contactor and are subsequently converted to disulfides. The two phases disengage and the kerosine flows upward through a catalyst-impregnated carbon bed where any remaining mercaptans are converted to disulfides.

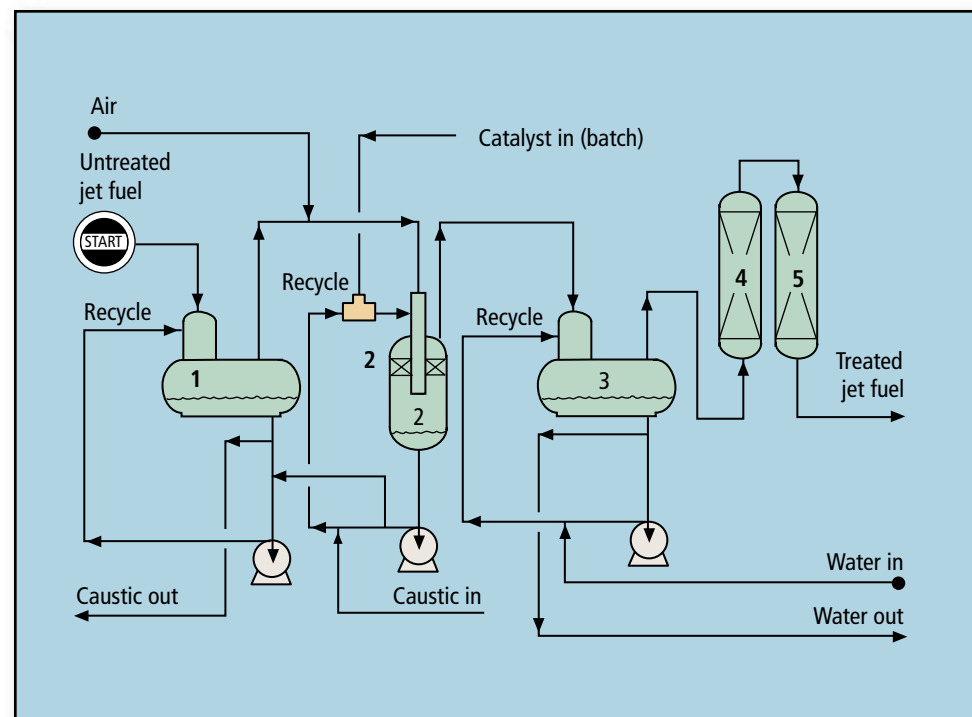
An AQUAFINING system is then used to wash any sodium entrained in the kerosine leaving the MERICAT II vessel. Salt driers and clay filters may be used to remove additional water, surfactants and particulates to ensure a completely clean stream.

Competitive advantages: FIBER-FILM Contactor technology requires smaller processing vessels, allowing for shorter separation times and less waste generation. Result: Saving valuable plant space and reducing capital expenditures.

Installations: 153 installations worldwide.

Reference: *Hydrocarbon Technology International*, 1993.

Licensor: Merichem Chemicals & Refinery Services LLC.



Treating—light liquids

Application: AMINEX extracts H_2S , COS and CO_2 from light-liquid streams with an amine solution using FIBER-FILM Contactor technology.

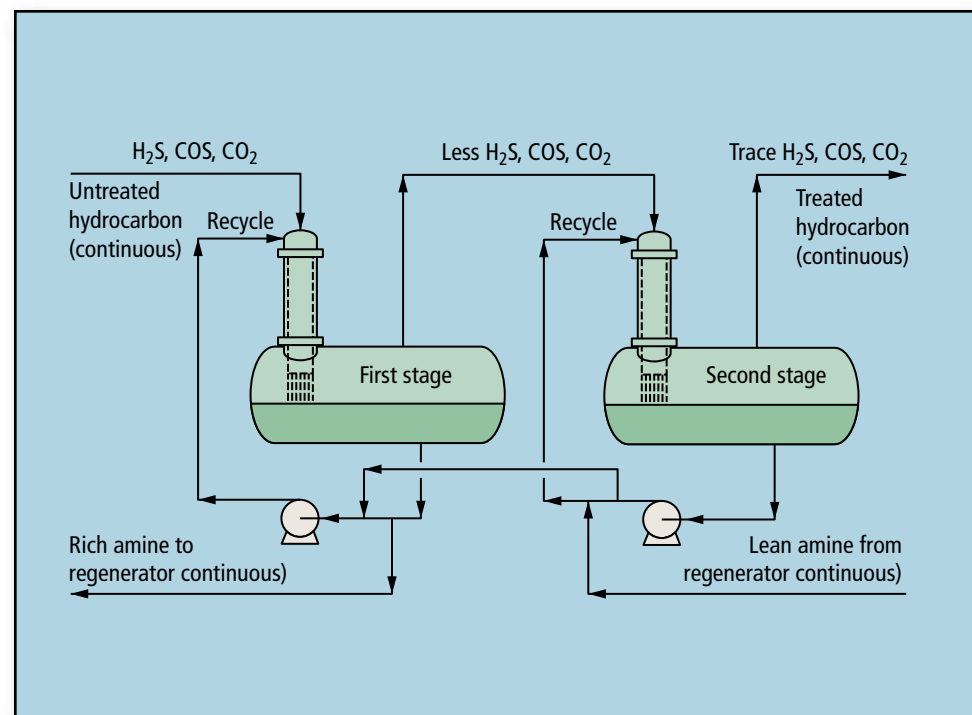
Description: In an AMINEX system, the amine phase flows along the fibers of the FIBER-FILM Contactor as it preferentially wets the fibers. Hydrocarbon also flows through the amine-wetted fibers where the H_2S , COS and/or CO_2 are extracted into the amine phase. The two phases disengage in the separator vessel with the rich amine flowing to the amine regeneration unit and the treated light liquids flowing to storage.

Competitive advantages: FIBER-FILM Contactor technology requires smaller processing vessels, allowing for shorter separation times and less sulfidic treating solution generation. Result: Saving valuable plant space and reducing capital expenditures.

Installations: Twelve installations worldwide.

Reference: *Hydrocarbon Processing*, Vol. 63, No. 4, April 1984, p. 87.

Licensors: Merichem Chemicals & Refinery Services LLC.



Treating—Phenolic caustic

Application: ECOMERICAT removes phenols from phenolic caustics using a FIBER-FILM Contactor while neutralizing the free caustic content.

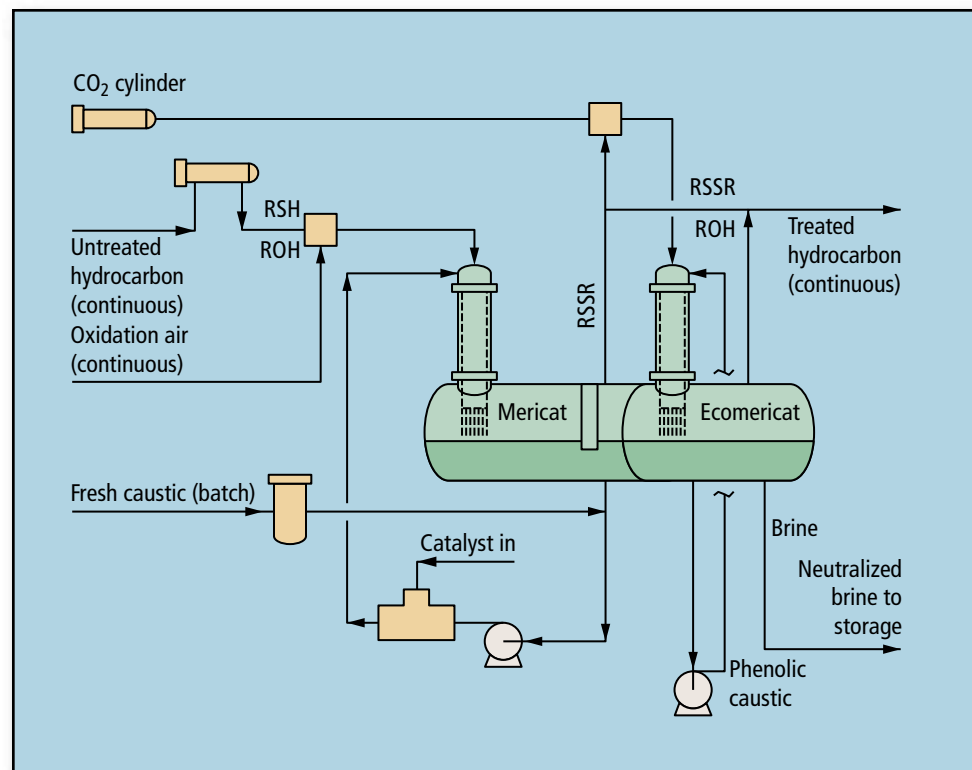
Description: In an ECOMERICAT system, the spent caustic is contacted with a slipstream of sweetened gasoline and CO₂ whereby the sprung phenols are extracted into the gasoline and the free caustic is neutralized, yielding neutral brine with minimal COD.

Competitive advantages are:

- Minimizes disposal cost at existing effluent caustic processing facilities.
- Reduces phenol content of spent caustic and returns value to the gasoline product.
- Operates over a wide pH range.
- Simple to operate.

Installations: One installation worldwide.

Licensors: Merichem Chemicals & Refinery Services LLC.



Treating—reformer products

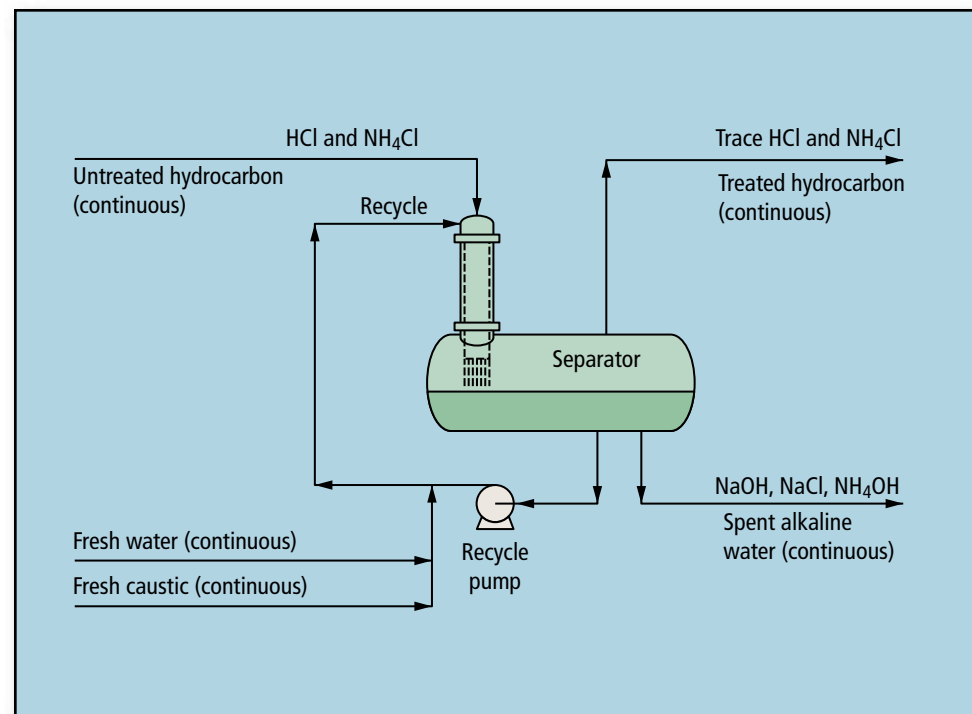
Application: CHLOREX removes inorganic chloride compounds from liquid and gas reformer products using a FIBER-FILM Contactor and an alkaline water treating solution.

Description: The CHLOREX system uses an alkaline water solution to react chloride impurities contained in the reformate feeding the stabilizer or the overhead product with sodium hydroxide. Fresh caustic and fresh process water are added to the system to maintain the pH of the recycle solution. Water makeup is set to maintain the total sodium of the recycled solution within a specified range.

Competitive advantages: FIBER-FILM Contactor technology requires smaller processing vessels, allowing for shorter separation times and less waste generation. Result: Saving valuable plant space and reducing capital expenditures.

Installations: Four installations worldwide.

Licensors: Merichem Chemicals & Refinery Services LLC.



Treating—spent caustic deep neutralization

Application: MERICON systems neutralize spent caustics containing sulfides, mercaptans, naphthenic acids and phenols.

Description: In a MERICON system, spent caustic is neutralized with acid to a low pH. The sprung acid oils are separated from the low pH brine. The resulting acid gases (H_2S and mercaptans) flow to a sulfur plant. Any acid oils produced in the neutralization reaction are returned to the refinery for processing. The acidified brine is further stripped with fuel gas to remove traces of H_2S and mercaptans. The brine is mixed with caustic to return it to a neutral pH.

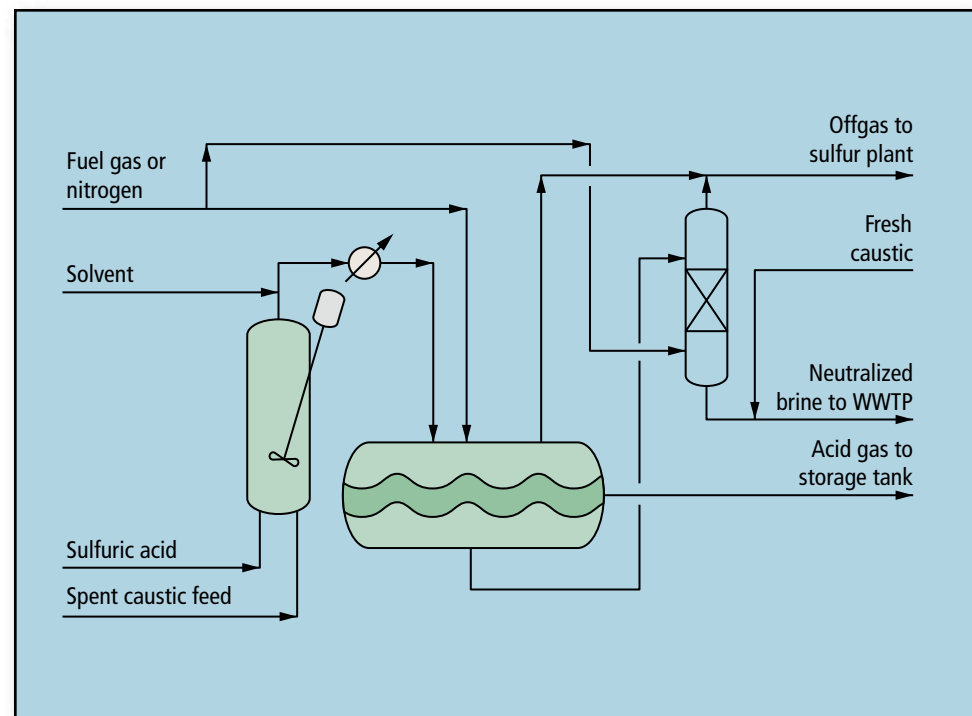
Competitive advantages are:

- Minimal operator attention and 100% onstream factor between turnarounds
- Minimal capital investment with over 70 years of knowhow
- Maximum COD reduction
- Non-odorous neutralized brine product.

Installations: Nineteen installations worldwide.

Reference: *Petroleum Technology Quarterly*, Spring 2001, p. 55.

Licensors: Merichem Chemicals & Refinery Services LLC.



Treating—sweetening

Application: MERICAT II oxidizes mercaptan sulfur components to disulfides to reduce product corrosivity and odor. The streams treated are jet fuel, kerosine, natural gasoline and selectively hydrotreated FCC gasolines.

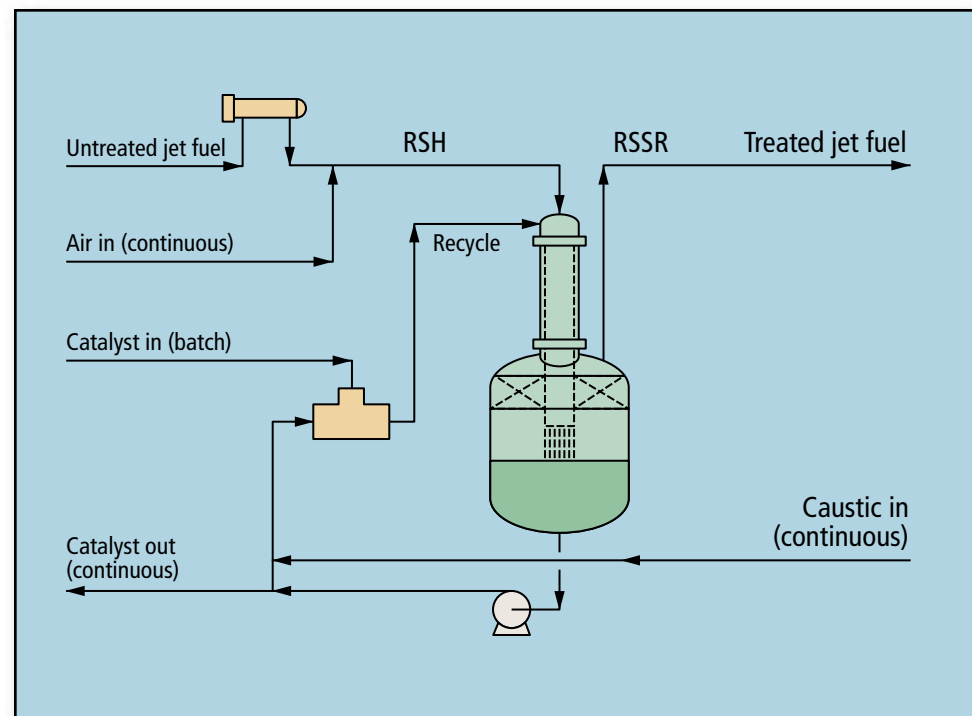
Description: A MERICAT II system removes mercaptans with a FIBER-FILM Contactor, air, oxidation catalyst and caustic solution followed by an upflow catalyst-impregnated carbon bed reactor for removal of high-boiling mercaptans.

Competitive advantages are:

- Minimal caustic and catalyst consumption
- Operating simplicity
- Minimal capital investment
- Online recausticizing
- Liquid sweetening step keeps out organic acids that can plug fixed beds.

Installations: Thirty-two installations worldwide.

Licensors: Merichem Chemicals & Refinery Services LLC.



Vacuum distillation

Application: Process to produce vacuum distillates that are suitable for lubricating oil production by downstream units, as well as feedstocks to FCC and hydrocracker units.

Feeds: Atmospheric bottoms from crude oils (atmospheric residue) or hydrocracker bottoms.

Products: Vacuum distillates of precisely defined viscosities and flash points as well as vacuum residue with specified softening point, penetration and flash point.

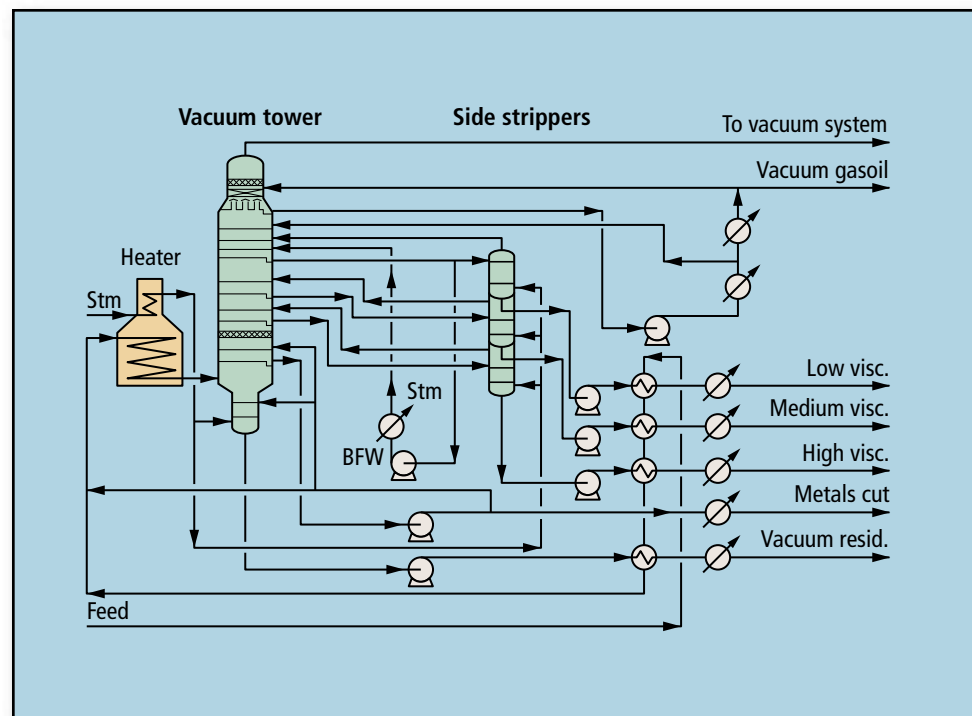
Description: Feed is preheated in a heat-exchanger train and fed to the fired heater. The heater-coil temperature is controlled to produce the required quality of vacuum distillates and residue. Uhde (Edeleanu)-designed units ensure that vaporization occurs in the furnace coils to minimize superheating the residue. Circulating reflux streams enable maximum heat recovery and reduced column diameter.

Wash trays minimize the metals content in the heaviest vacuum distillate to avoid difficulties in downstream lubricating oil production plants. 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, Middle East Crude), units per m³ of feed:

Electricity, kWh	7
Steam, MP, kg	30
Steam production, LP, kg	35
Fuel oil, kg	15
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.

Licensors: Uhde GmbH.

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 "coil" type visbreaking processes.

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).

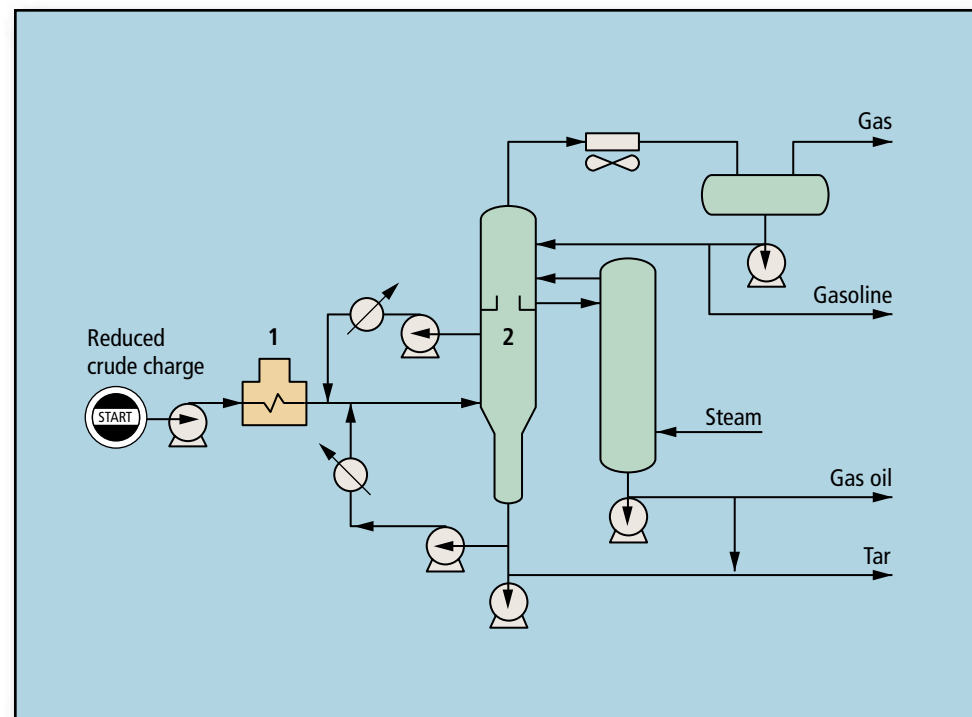
Operating conditions: Typical ranges are:

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.

Yields:

Feed, source	Light Arabian	Light Arabian
Type	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
Gas oil (330–600°F)	14.5	15.5 ⁽¹⁾
Visbroken resid (600°F+)	74.5	76.1 ⁽²⁾



⁽¹⁾ 330–662°F cut for Light Arabian vacuum residue.

⁽²⁾ 662°F+ cut for Light Arabian vacuum residue.

Economics:

Investment (basis: 40,000–10,000 bpsd, 2Q 2004, US Gulf), \$ per bpsd	800–1,600
Utilities , typical per bbl feed:	
Fuel, MMBtu	0.1195
Power, kW/bpsd	0.0358
Steam, MP, lb	6.4
Water, cooling, gal	71.0

Installation: Over 50 units worldwide.

Continued ▼

Visbreaking, *continued*

Reference: *Handbook of Petroleum Refining Processes*, 2nd Ed., McGraw-Hill, 1997, pp. 12.83–12.97.

Licensors: Foster Wheeler/ UOP LLC.

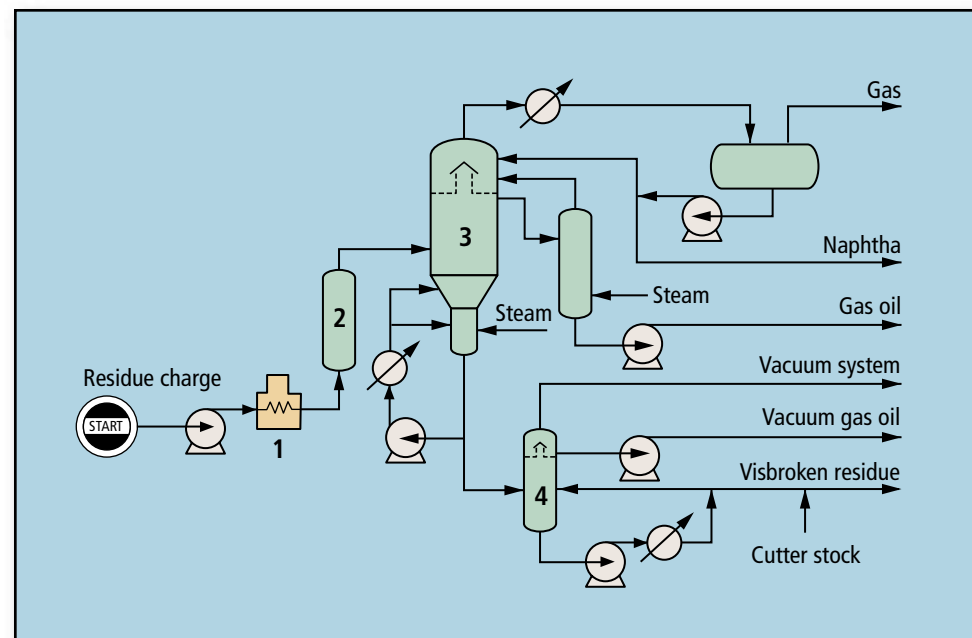


Visbreaking

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 gas oil and waxy distillates 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, gas oil, waxy distillates and cracked residue. If a vacuum flasher is installed, additional gas oil and waxy distillates are recovered from the cracked residue.

Yields: Vary with feed type and product specifications.



Utilities, typical consumption per bbl feed @180°C:

Fuel, 10 ³ kcal	16
Electricity, kWh	0.5
Steam, net production, kg	18
Water, cooling, m ³	0.1

Installation: Eighty-six Shell Soaker Visbreaking units have been built or are under construction. Post startup services and technical services for existing units are available from Shell.

Reference: *Visbreaking Technology*, Erdöl und Kohle, January 1986.

Licensors: Shell Global Solutions International B.V. and ABB Lummus Global B.V.

Feed, vacuum residue	Middle East
Viscosity, cSt @100°C	770
Products, wt%	
Gas	2.3
Gasoline, 165°C EP	4.7
Gas oil, 350°C EP	14.0
Waxy distillate, 520°C EP	20.0
Residue, 520°C+	59.0
Viscosity, 165°C plus, cSt @100°C	97

Economics: The investment amounts to 1,000 to 1,400 US\$/bbl installed excluding treating facilities and depending on capacity and the presence of a vacuum flasher (basis: 1998).

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.

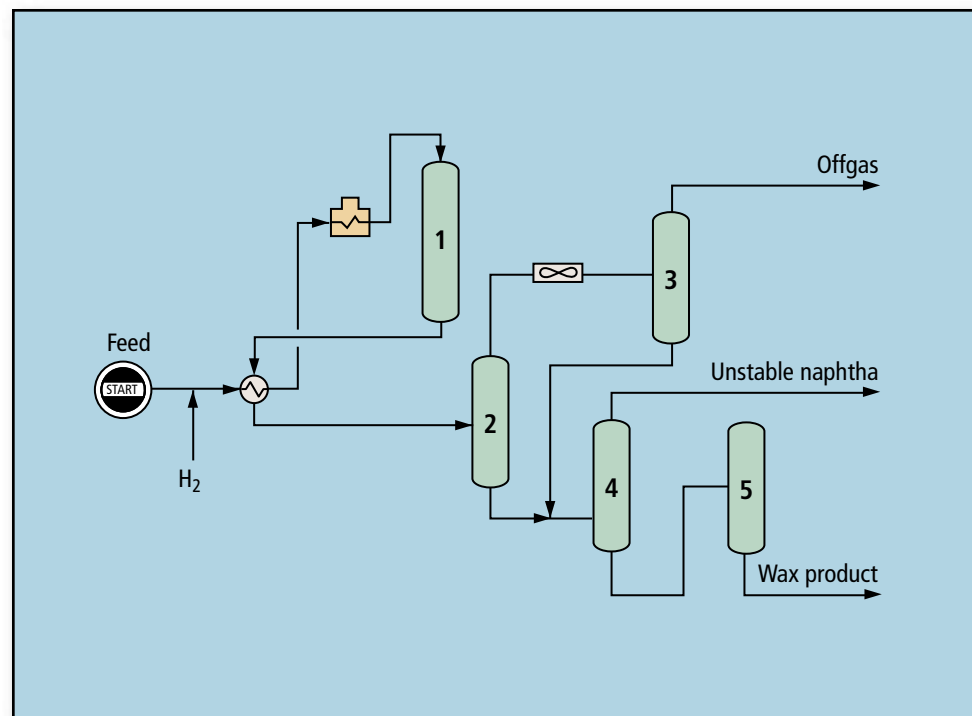
Bechtel has been offering for license the Wax Hy-Finishing process. Bechtel now is marketing a line of modular, standard hydrogen finishing units for wax treatment. Standard sizes are 500, 1,000, 2,000 and 3,000-bpsd feedrate.

The core of the unit is standardized; however, individual modules are modified as needed for specific client needs. This unit will be fabricated to industry standards in a shop environment and delivered to the plant site as an essentially complete unit. Cost and schedule reductions of at least 20% over conventional stick-built units are expected. The standard licensor's process guarantees and contractor's performance guarantees (hydraulic and mechanical) come with the modules.

Description: Hard-wax feed is mixed with hydrogen (recycle plus make-up), 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,
2004 US Gulf Coast), \$/bpsd 6,000



Utilities, typical per bbl feed:

Fuel, 10 ³ Btu (absorbed)	30
Electricity, kWh	5
Steam, lb	25
Water, cooling (25°F rise), gal	300

Licensor: Bechtel Corp.

Wet gas scrubbing (WGS)

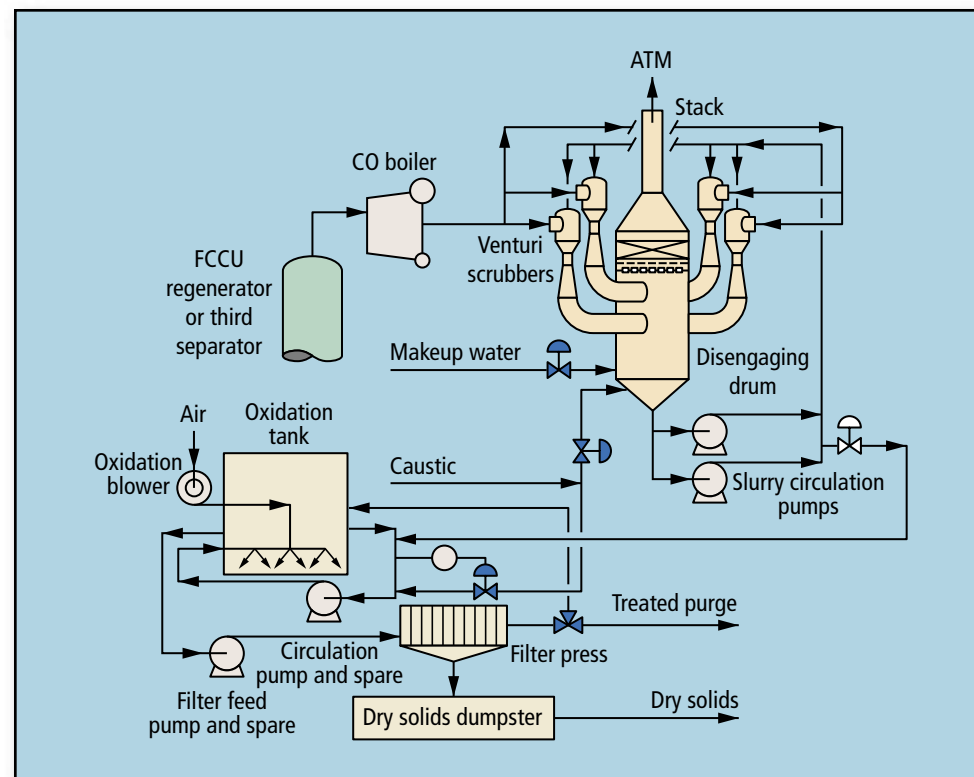
Application: To reduce fluid catalytic cracking unit (FCCU) particulate (catalyst) and sulfur oxides (SO_x) emissions to achieve compliance with environmental regulations—generally NSPS (New Source Performance Standards) and consent decrees (in the US). The technology can also be adapted for other refinery applications, e.g., coke calciners when flue gases must be treated to reduce SO_x and particulate emissions.

Description: The WGS process takes dirty gas from FCCUs and simultaneously removes particulate matter and SO_x via direct contact with a buffered liquid. Particulate removal is accomplished via inertial impaction of the particulate with the scrubbing liquid. SO_2 removal is accomplished via absorption into and reaction with the buffered scrubbing liquid. SO_3 removal is accomplished via a combination of nucleate condensation, absorption and inertial impaction. All of this can be accomplished with low- (3-in. of water column) or no pressure drop. This is important when aged heat recovery systems are involved.

The liquid purge from the WGS system is further treated in either the refinery wastewater system or in a segregated system, either of which will remove solids for landfill disposal and will reduce the chemical oxygen demand (COD) of the stream to meet local discharge requirements. Operation of WGS systems demonstrates:

- Flexible/"forgiving" performance under a wide range of FCCU operations/upsets
- Service factors equal to or better than FCCUs with runs exceeding 10 years
- Low/zero pressure drop
- Ability to meet stringent emission regulations, e.g., consent decree requirements.

Performance: All WGS facilities are in compliance with their permitted values. Compliance has been achieved for the current consent decree particulate limits that can require emission of less than ½-lb of particulates/1,000 lb of coke burned. They are also in compliance with consent



decree SO_2 requirements of 25 vppmd @ 0% O_2 and SO_3 consent decree emission requirements of less than 10 vppmd. In addition, the WGS has recorded run lengths in excess of 10 years without affecting FCCU throughput.

Installation: Seventeen operating plants have over 400 years of operating experience. Four additional units are in various stages of engineering.

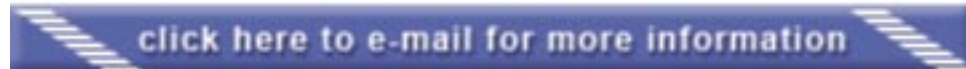
Reference: 1991 AIChE Spring National Meeting, Paper No. 62c.
1990 National Petroleum Refiners Association Annual Meeting, Paper No. AM-90-45, March 1990.

Wet gas scrubbing (WGS), *continued*

1996 National Petroleum Refiners Association Annual Meeting, Paper No. AM-96-47, March 1996.

Technology owner: ExxonMobil Research and Engineering Co.

Licensors: Hamon Research-Cottrell, GN-Hamon, LLC.



Wet scrubbing system, EDV

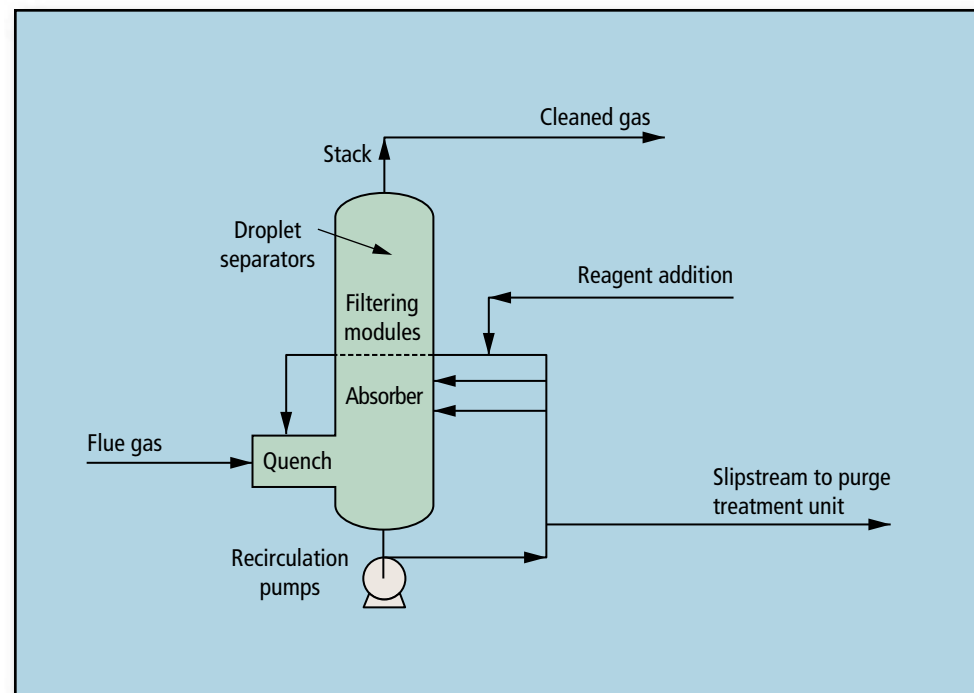
Application: EDV Technology is a low pressure drop scrubbing system, to scrub particulate matter (including PM2.5), SO₂ and SO₃ from flue gases. It is especially well suited where the application requires high reliability, flexibility and the ability to operate for 4–7 years continuously without maintenance 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 used 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 SO₃. 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-



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 37 FCCU applications, 3 CDU applications and 1 fluidized coker application to date.

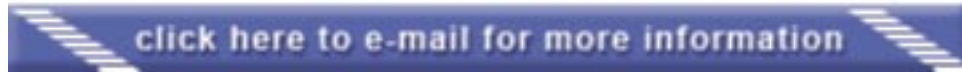
Reference: Confuorto and Weaver, "Flue gas scrubbing of FCCU regenerator flue gas—performance, reliability, and flexibility—a case history," *Hydrocarbon Engineering*, 1999.

Continued ▼

Wet scrubbing system, EDV, *continued*

Eagleson and Dharia, "Controlling FCCU emissions," 11th Refining Technology Meeting, HPCL, Hyderabad, 2000.

Licensors: Belco Technologies Corp.



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.

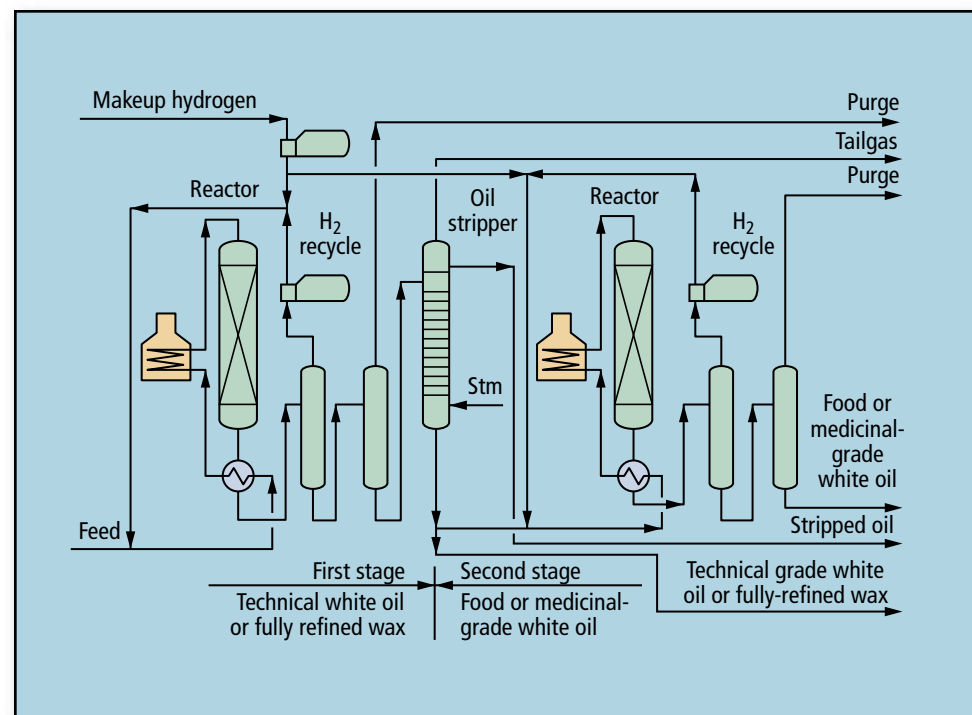
Products: Technical- and medical-grade white oils and waxes for plasticizer, textile, cosmetic, pharmaceutical and food industries. Products are in accordance with the US Food and Drug Administration (FDA) regulations and the German Pharmacopoeia (DAB 8 and DAB 9) specifications.

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 techn. white oil	2nd stage for med. white oil	Food-grade 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.

Licensors: Uhde GmbH and through sublicense agreement with BASF.

Refining Articles

ConocoPhillips S Zorb Gasoline Sulfur Removal Technology

by Jeff Vander Laan, ConocoPhillips

The State of Liquid Redox

by Gary J. Nagl, Gas Technology Products

Suncor's Optimization of a Sulfur Recovery Facility

by Dean Freeman, Suncor; Jackie Barnette and Gary Nagl, Gas Technology Products

ATCO Midstream's Gas Sweetening Experience Using Iron-Redox Technology

by Gary Gialet, Curtis Sexsmith, Rob Girard, Neil McCagherty, Neil Carnegie, Spencer Yelland, and Dave Graubard, Gas Technology Products

Sulfur reduction: What are the options?

by C. Fredrick, Merichem Chemicals & Refinery Services

Pluses and minuses of caustic treating

by F. J. Suarez, Merichem Co.

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Executives:

Sales Manager (Chemical Industry) Mr. Lothar Grutesen

Sales Manager (Power Plants) Mr. Johannes Fliegen

The principle of the company is to develop, produce and sell control valves and the corresponding pneumatic, electro-pneumatic and the recently introduced second generation intelligent positioners.

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Axens

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Description: Axens is a refining, petrochemical and natural gas market focused supplier of process technology, catalysts, adsorbents and services, backed by nearly fifty years of commercial success. Axens is a world leader in several areas, such as: Petroleum hydrotreating & hydroconversion, FCC gasoline desulfurization, Catalytic Reforming, BTX (benzene, toluene, xylenes) production & purification, Selective Hydrogenation of olefin cuts, Sulfur recovery catalysts. Axens is a fully-owned subsidiary of IFP.

Executives: Jean Sentenac, Chairman & CEO
Jean-Pierre Franck, Chief Operating Officer
Michel Dugert, Managing Director & Process Licensing
Francis Nativel, Managing Director & Performance Programs
Christian Vaute, Managing Director & Procatalyse Catalysts and Adsorbents

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www.burckhardtcompression.com

Executives:

Vice President Marketing Peter Huber

Vice President Sales Martin Heller

Company Description:

Burckhardt Compression is a world leader in reciprocating compressor technology and the only manufacturer of a complete series of labyrinth (Laby circle r), process gas and hyper compressors for numerous applications. Their compressors are used in the field of oil refining, chemical and petrochemical industries, air separation, as well as gas transport and storage. Burckhardt Compression has a worldwide service network.

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DMC Clad Metal Div.

Dynamic Materials Corp.

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Fax:	303-604-1839
E-mail:	sales@dynamicmaterials.com
Website:	www.dynamicmaterials.com
Executives:	
Sales	Jose Olivas
Sales	Jim Gray

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Engelhard Corporation

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Executives:

Barry W. Perry, Chairman & Chief Executive Officer

Victor Sprenger, Group Vice-President – Process Technologies

Engelhard Corporation is a surface and materials science company that develops technologies to improve customers' products and processes. A Fortune 500 company, Engelhard is a world-leading provider of technologies offering a comprehensive range of FCC catalysts, environmental and performance additives for the petroleum refining industry. For more information, visit Engelhard on the Internet at www.engelhard.com.

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Emerson Process Management, Fisher Valve Division

301 S. 1st Ave.

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USA

Tel: 641-754-3011

<http://www.fisher.com>

The Fisher Valve Division of Emerson Process Management delivers time-tested and innovative control valve solutions designed to help reduce plant maintenance costs, reduce capital requirements, reduce the cost of regulatory compliance, and increase process availability.

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**Gas Technology Products LLC,
A Member of the Merichem Family of Companies**

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<http://www.gtp-merichem.com>

Description: Devising a comprehensive, flexible hydrogen sulfide (H₂S) removal/recovery solution requires more than a systems, media and equipment – it requires expertise. With more than twenty-five years of experience in H₂S removal, Gas Technology Products LLC understands the needs of every operator and every plant.

Products: Gas Technology Products provides a full line of complementary hydrogen sulfide oxidation products: LO-CAT® and LO-CAT® II, Sulfur-Rite® and The Eliminator™ processes, along with its ARI®-100 mercaptan oxidation products and engineering services.

GTP offers both liquid and solid media desulfurization technologies to sweeten gas streams and ventilation air containing virtually any levels of hydrogen sulfide or mercaptans – for systems of widely ranging capacities. For any size or type application, GTP offers complete turnkey systems and can take total system responsibility.

As a wholly owned subsidiary of Merichem Chemicals & Refinery Services LLC, Gas Technology Products LLC is a part of a fully integrated organization with unmatched technical knowledge, applications expertise, and worldwide service coverage.

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SAMSON AG Mess- und Regeltechnik

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Tel: +49 69 4009-0
Fax: +49 69 4009-1507
E-mail: samson@samson.de
www.samson.de

SAMSON produces control valves and butterfly valves in all commonly used materials and in accordance with the DIN, ANSI, and JIS standards. The valves are suitable for use in all areas of process engineering. SAMSON also manufactures self-operated regulators for simple control systems. Sophisticated transmitters, controllers, and automated systems round off our product line.

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SNC-Lavalin GDS, Inc.

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Executives:

President James M. Walters, P.E.

Vice President, Engineering Gary L. Gibson, P.E.

SNC-Lavalin GDS specializes in full service engineering, procurement and construction management services, particularly for the petrochemical and refining industries. As part of the SNC-Lavalin Group we are a leading engineering and construction firm in the world. The Group has offices in 30 countries and is doing work in some 100 countries.

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Thermo Electron Corporation

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Executives:

Director of Sales John Schwin

Director of Marketing Karen Minyard

Thermo Electron Corporation is a world leader in instrumentation. We enable our customers to **analyze, detect, measure, and control** with increasingly advanced precision. The Process Instruments Division offers a variety of gas flow computers, data acquisition systems, liquid flowmeters, data management solutions, gas analyzers, level sensors, and much more to the petroleum industry.

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UOP LLC

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847 391 2000

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UOP LLC is a leading international supplier and licensor of process technology, catalysts, adsorbents, process plants, equipment and consulting services to the petroleum refining, petrochemical, and gas processing industries. UOP's expertise extends from R&D to the manufacture and sale of adsorbents, catalysts, and specialty chemicals. We focus on delivering solutions to improve our customers' competitiveness.

President & CEO: Carlos Guimaraes

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US Filter

**301 West Military Road
Rothschild, WI 54474
USA**

Tel: 713-359-7211
Fax: 713-355-3219
E-mail: hpi@usfilter.com
www.usfilter.com

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KBC Advanced Technologies, Inc.

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Houston, TX 77079 USA**

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Fax: 281-293-8290

Web: www.kbcat.com

E-mail: kbc@kbcat.com

KBC Advanced Technologies is a leading independent consulting and services group, delivering improvements in business performance and asset value to owners and operators in the oil refining, petrochemical and processing industries worldwide. KBC analyses plant operations and business processes, and recommends changes that deliver material and measurable improvements in profitability.

Executives:

Peter J. Close, Chief Executive Officer

Nicholas J. Stone, Finance Director

W. George Bright, Chief Operating Officer



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- Selective Hydrogenation of olefin cuts
- Sulfur recovery catalysts.

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Processes

[Alkylation—feed preparation](#)

[Benzene reduction](#)

[Catalytic reforming](#)

[Diesel hydrotreating](#)

[Ethers](#)

[Gasoline desulfurization, ultra-deep](#)

[Hydrocracking](#)

[Hydrocracking/hydrotreating—VGO/DAO](#)

[Hydrotreating—resid](#)

[Isomerization](#)

[Lube oil refining, spent](#)

[Oligomerization of C₃C₄ cuts](#)

[Oligomerization—polynaphtha](#)

[Spent oil lube re-refining](#)

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Articles

ConocoPhillips S Zorb Gasoline Sulfur Removal Technology

by Jeff Vander Laan, ConocoPhillips

Processes

Alkylation

Coking

Gasoline desulfurization

Isomerization



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Using Iron-Redox Technology

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Processes

H_2S removal (LO-CAT)

H_2S removal (Sulfur-Rite)



A leader in processing refinery spent caustic streams at its USA processing plants for chemicals recovery for over 50 years, **Merichem Company** has more recently been recognized worldwide for its expertise and technology for processing spent caustics within the refinery.

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Articles

Sulfur reduction: What are the options?

by C. Fredrick, Merichem Chemicals & Refinery Services

Pluses and minuses of caustic treating

by F. J. Suarez, Merichem Co.

Processes

H₂S removal (LO-CAT)

H₂S removal (Sulfur-Rite)

Treating—gases

Treating—gasoline

Treating—gasoline and light hydrocarbon liquids

Treating—gasoline desulfurization, ultra deep

Treating—jet fuel/kerosine

Treating—light liquids

Treating—Phenolic caustic

Treating—reformer products

Treating—spent caustic deep neutralization

Treating—sweetening