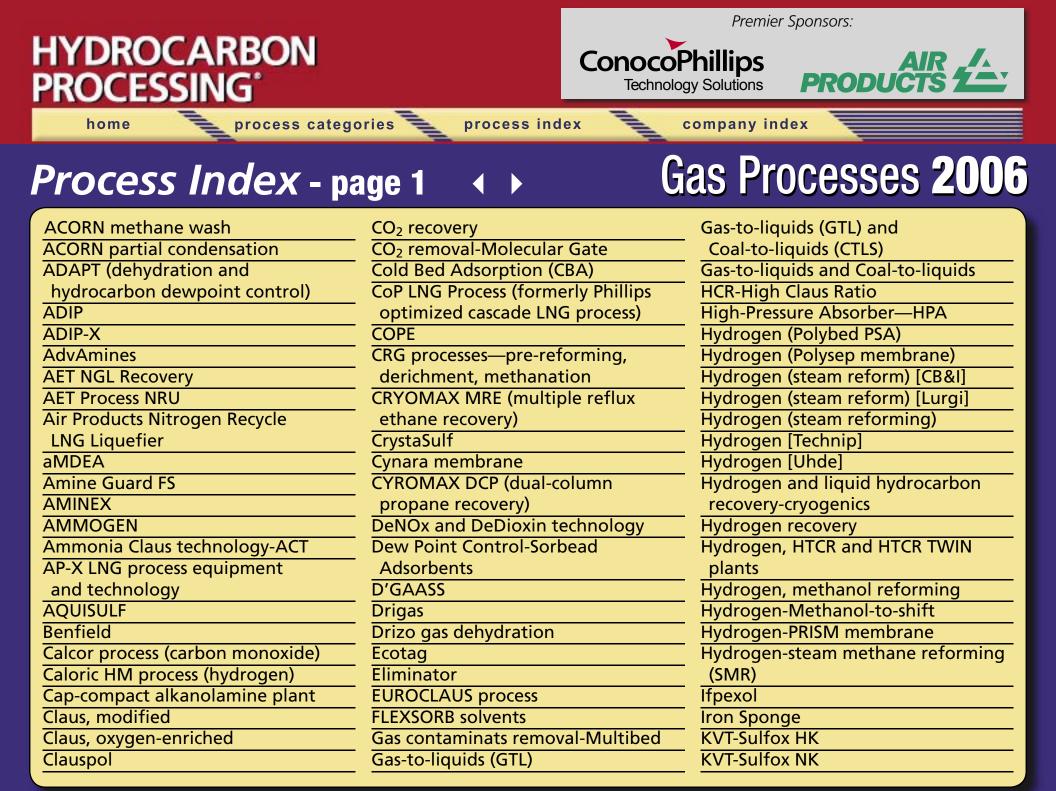


Hydrocarbon Processing's Gas Processes Handbooks have helped to provide the natural gas industry with process technology for more than 30 years. The technology that is covered in the Handbook includes drying, treating, NGL, LNG, liquid treating and sulfur removal. In a further expansion of the technology presented, we also provide hydrogen generation, gas effluent cleanup, synthesis gas and flue gas treatment. In the interest of maintaining as complete listings as possible, the Gas Processes 2006 Handbook is available on CD-ROM and at our website, *www.HydrocarbonProcessing.com*.

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Dehydrogenation Drying Effluent cleanup Flue gas treatment Hydrogen Liquid treating NGL and LNG Pre-reforming Sulfur Synthesis gas Treating



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Process Index - page 2 () Gas Processes 2006				
Liquefin LNG Dual Expander Cycle LNG end flash MLP (maxi LNG production) LNG plants LNG vaporization LNG-Pro LPG recovery LRS10 – CO ₂ Removal LTGT (Lurgi tail-gas treatment process) MCR process equipment and technology MEDAL membrane (hydrogen) MEDAL membrane—Simplified Biogas System MegaSyn MERICAT II Merox Morphysorb (acid gas removal from natural gas) Multipurpose gasification N ₂ removal NATCO Shell-Paques	NGL recoveryNGL-MaxNGL-ProNitrogen recycle LNG lidNitrogen rejectionNitrogen removal (rejection)Nitrogen removal (rejection)OmniSulfOxyClausPRICO (LNG)PURASPECPurisolRectisolResulf—Tail gas treatingSCOTSELEXOLSeparex Membrane SystemShell HCN/COS HydrolyseShell Sulfur Degassing FShell-Paques ProcessSlexsorbSour water stripper (SWSPREX—(sulfur pre-extroprocess)SRU	Sulferd Sulfind Sulfind Sulfint SULFR SULFU SULFU SULFU SULFU Sultim Super SUPER Super Syngas	ol HP EEN degassing R-RITE ate Hy-Pro CLAUS process	
Natural gas liquids (NGL) recovery NGL from LNG	SulfaTreat—DO SulfaTreat—Gas or air H	₂ S removal		



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ABB Lummus Global Inc., **Randall Gas Technologies Division** Advanced Extraction technologies Advantica Air Liquide Air Products and Chemicals, Inc. Axens **BASE AG** Black & Veatch Inc. BOC BP Caloric Anlagenbau GmbH **CB&I Howe-Baker CB&I TPA Comprimo Sulfur Solutions** Connelly GPM, Inc. **ConocoPhillips** Costain Oil, Gas & Process Ltd. CrystaTech, Inc. **Davy Process Technology** Englehard ExxonMobil Research and Engineering Co. **Foster Wheeler** Gas Technology Products, LLC Goar, Allison & Associates, Inc. Haldor Topsøe A/S

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Gas Processes 2006

Uhde STAR process (dehydrogenation of light paraffins to olefins)

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

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

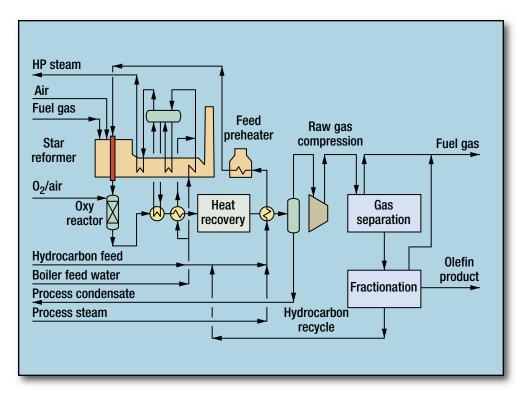
Product: Propylene (polymer- or chemical-grade); isobutylene; n-butylenes; high-purity hydrogen (H₂) may also be produced as a byproduct.

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

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

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

After cooling and condensate separation, the product is subse-



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quently compressed, light-ends are separated and the olefin product is separated from unconverted paraffins in the fractionation section.

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

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

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

Commercial plants: Two commercial plants using the STAR process for dehydrogenation of isobutane to isobutylene have been commissioned

Uhde STAR process (dehydrogenation of light paraffins to olefins), *continued*

(in the US and Argentina). More than 60 Uhde reformers and 25 Uhde secondary reformers have been constructed worldwide.

References: Heinritz-Adrian, M., "Advanced technology for C_3/C_4 dehydrogenation, "First Russian & CIS GasTechnology Conference, Moscow, Russia, September 2004.

Heinritz-Adrian, M., N. Thiagarajan, S. Wenzel and H. Gehrke, "STAR—Uhde's dehydrogenation technology (an alternative route to C_3 - and C_4 -olefins)," ERTC Petrochemical 2003, Paris, France, March 2003.

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

Licensor: Uhde GmbH.



ADAPT (Gas dehydration and hydrocarbon dewpointing)

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Application: Dehydration, hydrocarbon dewpointing, aromatics, methanol, mercaptan and carbon dioxide removal from high-pressure gases. ADAPT can be used at natural gas reception terminals, underground gas storage facilities (i.e., salt cavities, aquifers and depleted fields) and prior to LNG production. The process is suitable for prepurification and protection facilities for gas membrane systems.

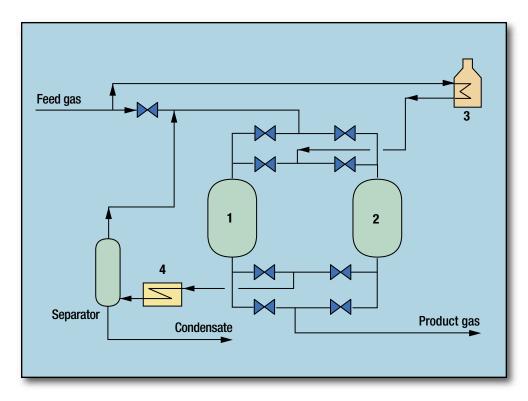
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Description: Undesirable components in high-pressure natural gases are simultaneously removed within a solid adsorbent bed (1). Tailored adsorbents selectively remove gas-phase components and control the slippage rate to the export gas, thus meeting required production specification. Once saturated, the adsorbing bed is switched to regeneration mode and a fresh bed (2) is brought online. Process flexibility enables multiple bed systems that allow very high throughputs. Using pre-heated (3) feed or product gas regenerates the saturated bed, which depends on the application requirements and economics. Regeneration temperature depends on the components being removed, but typically range from 200°C to 300°C. The rich-regeneration gas is cooled, producing a saleable hydrocarbon condensate (4). Cooler system flash gas is recycled back to the adsorbing bed for further processing. Some advantages of ADAPT over competing processes are:

- Compact process plant
- Rapid startup and shutdown
- No hot standby required
- Turndown to 10% of design flow
- High reliability and low maintenance
- Long adsorbent life.

Operating conditions: Typical operating pressures range from 30 bar to 120 bar, and feed gas temperatures up to 45°C. Plants can be skid mounted or modular enabling phased asset development. Typical feed gas flows from 10 MMscfd to over 1,500 MMscfd.



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Economics: Costs vary with scale and application but typically range from £2 million for a 200 MMscfd plant to £9 million for a 1,500-MMscfd plant.

Installations: Plants in operation or construction across Europe, Africa and Asia. Total throughput for current ADAPT designs is approximately 9,000 MMscfd.

Reference: Metters, S. D., "An adaptable solution," *Hydrocarbon Engineering*, March 2000.

Licensor: Advantica Ltd.



Drigas

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Application: Drigas is used to dehydrate natural gas to very low dew points by glycol absorption, without using vacuum regeneration, no solvents and no consumption of stripping gas.

process categories

Description: Drigas process recycles the glycol regenerator's overhead vapors, cooled and dried, to the stripping tower.

The vent gas off of a conventional regenerator with a stripping tower is cooled in an overhead condenser (1) and condensed water is separated in the overhead knockout drum (2). The wet gas coming from (2) is reused as stripping gas, feeding it to the bottom of the stripping tower by means of a blower (3).

Spent glycol is used to dry the recirculated gas to the stripping tower by means of a random packed atmospheric absorber (4) and a glycol pump (5) to move rich glycol from the bottom of the atmospheric absorber to the still tower.

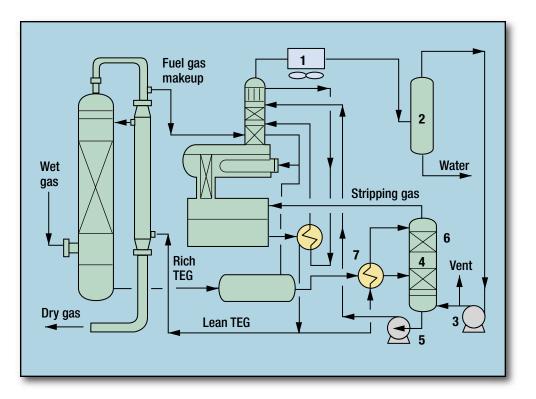
If higher concentrations are required, a second stage of absorption (6) can be incorporated into the same atmospheric column fed by a small fraction of the regenerated, lean TEG. This arrangement gives TEG purity up to 99.99 wt%.

Main advantages of the Drigas process are:

- Very low dew points
- Stripping gas is not required
- Low operating cost
- Low pollution.

Operating conditions: Glycol flowrates up to 1,000 m³/d, with TEG purity up to 99.99 wt%. Gas flowrate up to 15 million scmd for each train, wet gas temperature up to 60° C and pressure up to 150 bar.

Economics: A Drigas regenerator costs marginally more than a traditional plant with stripping gas, but without any consumption of stripping gas.



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Installations: One Drigas unit, with a capacity of 200 m³/d DEG.

Reference: Franci, P. F., "New glycol regenerator adaptable to offshore use," *World Oil*, July 1993.

Licensor: SIIRTEC NIGI.

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Drizo gas dehydration

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Application: Low water dew points, typical water dew point depressions up to 180°F (depressions greater than 200°F achievable with Drizo HP), 95%+ recovery of BTEX vapor components.

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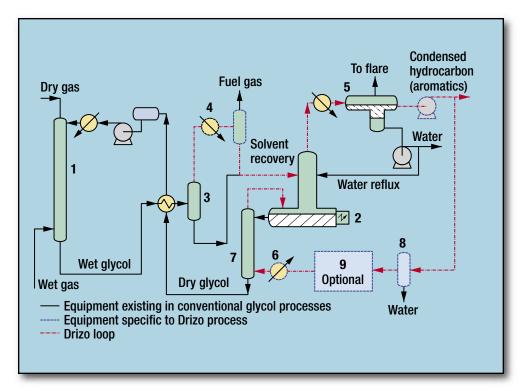
Description: Water is absorbed (1) from natural gas by glycol (DEG, TEG or tetraethylene glycol). The glycol is then thermally regenerated in reboiler (2). The main differences with conventional glycol processes are: glycol is flashed after preheating (3) to allow high recovery of liquid hydrocarbons (4). After heteroazeotropic distillation, these liquid hydrocarbons are recovered from the still column condenser (5), vaporized (6) and used to strip the hot glycol (7). Water, still present in the liquid hydrocarbons, can be removed by a coalescer (8) and by an optional solvent dehydration package (9) (Drizo + and Drizo HP versions). Glycol purities above 99.99 wt% and up to 99.998+ wt% (Drizo HP) are obtained, thus enabling residual water content in the treated gas down to below 0.1 ppm.

Economics: Combining very low dewpoints with low CO_2 and BTEX emissions, Drizo is an environmentally friendly process compared with the other glycol processes. Drizo is very competitive with all dehydration processes at water dewpoints below -30° C. A Drizo unit would be roughly 20% cheaper than an equivalent glycol stripping unit with recompression of the stripping gas (in addition to the fact that Drizo is able to reach much lower water dewpoints), and can be 50% cheaper than a mol sieve unit.

Installations: More than 45 units.

References: Rigaill, C., "Solving Aromatic and CO₂ emissions with the Drizo gas/glycol dehydration process," GPA Europe Meeting, February 23, 2001.

Smith, R. S., "Enhancement of Drizo gas dehydration," 47th Laurance Reid Gas Conditioning Conference, March 2–5, 1997.



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Smith, R. S. and S. E. Humphrey, "High-Purity Glycol Design Parameters and Operating Experience," 45th Laurance Reid Gas Conditioning Conference, 1995.

Aarskog, A., T. Fontaine, C. Rigaill and C. Streicher, "Drizo revamping of TEG unit improves NGL recovery: The Ekofisk Challenge," 82nd GPA Convention, San Antonio, March 9–12, 2003.

Licensors: Prosernat IFP Group Technologies.



Ecoteg

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Application: Ecoteg is a process that uses triethyleneglycol (TEG) to dehydrate gases rich in aromatic compounds (BTEX) where effluent control is critical. Its aromatics emission into the environment is negligible.

process categories

Description: When TEG is used to dehydrate natural gas, it absorbs selectively not only water but also part of the BTEX that may be present. BTEX are released with all the outgoing streams of the regenerator.

The vent gas off a still column is cooled in an overhead condenser (1) and condensed water and BTEX are separated in the overhead knockout drum (2). The wet gas coming from knockout drum (2) is reused as stripping gas and is fed to the bottom of the stripping tower by means of a blower (3).

The spent glycol is used to dry the gas recirculated to the stripping tower by means of a random-packed atmospheric absorber (4) and a glycol pump (5) to move the rich glycol from the bottom of the atmospheric absorber to the still tower.

The liquid BTEX are recovered as oil if an oil product is already present in the plant; otherwise, they are returned to dried gas by means of a pump (6) or recycled to presaturate the lean TEG.

Condensed water, before disposal, is stripped through a stripping tower (7) by means of combustion air.

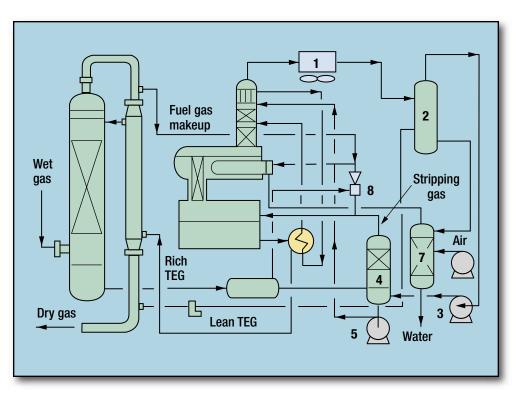
Main advantages of the Ecoteg process are:

• Meets more stringent regulations for disposal without additional facilities

- Low operating cost
- Low gas dew point.

Operating conditions: Gas flowrates up to 15 million scmd for each train, wet gas temperature up to 60°C and pressure up to 150 bar.

Economics: Ecoteg is an ecological and cost-effective dehydration process that does not require additional external facilities to meet regulations for effluents. This simplifies the first installation and/or additions to



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an existing plant. Savings in stripping gas helps the economics and may be a determinant when low gas dew points are required.

Reference: Franci, P. F. and J. W. Clarke, "Emission-free, high-purity TEG regenerator," 1994 GRI Glycol Dehydrator/Gas Processing Air Toxic Conference, San Antonio.

Licensor: SIIRTEC NIGI.

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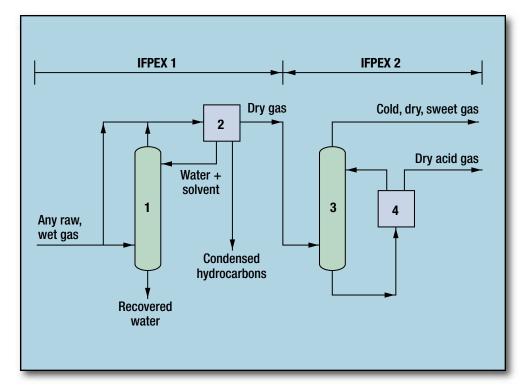
Ifpexol

Application: Treat any gas for dehydration, hydrate protection, dewpoint control and acid-gas removal, using a single, low-freezing point solvent—methanol. Ifpexol is a two-step process; each step can be used independently or in combination:

- Ifpex-1—simultaneous water and hydrocarbon dew pointing (down to -100°C)
- Ifpex-2—removal of acid gases and sulfur compounds (to sales gas specifications).

Description: *Ifpex-1:* A partial stream from the feed gas is loaded with methanol by stripping in a contactor (1). The methanol/water mixture is recycled from the cold process (2). Pure water is obtained from the bottom of the contactor (1). Overhead gas is mixed with the main gas stream and contains enough methanol to prevent freezing during the cold process (2). During this process, the gas is cooled to the required dewpoint temperature by any appropriate means (J-T expansion, turbo expander or external refrigeration). The treated dry gas is recovered from the low-temperature separator along with condensed hydrocarbons and the methanol/water mixture. This methanol/water mixture is recovered as a separate liquid phase and recycled to the contactor (1).

Ifpex-2: The gas from Ifpex-1 (or any other feed gas) is contacted with refrigerated methanol-based solvent in the contactor (3). Acid gases (CO₂, H_2S) are absorbed, along with other sulfur compounds (mercaptans, COS), and a dry sweet gas is obtained on top of the contactor (3). The solvent loaded with acid gases is regenerated by a simple flash and, in some cases, by thermal regeneration. Hydrocarbon co-absorption is controlled by the solvent composition and a multi-flash regeneration recovers most of the co-absorbed hydrocarbons in a separate gas stream. Acid gases are recovered dry and under pressure (typically around 10 bar); thus, this process is particularly suitable for acid-gas reinjection applications.



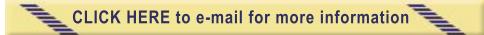
Economics: For dewpoints below –30°C, Ifpex-1 can compete with glycol processes and offers much reduced (about 30% lower) CAPEX. Ifpex-2 offers significant savings compared to other processes for bulk acid-gas removal with acid-gas reinjection.

Installations: Fifteen Ifpex-1 units with capacities up to 350 MMscfd.

References: "Methanol treating schemes offer economics, versatility," *Oil & Gas Journal,* June 1, 1992, p. 65.

Minkkinen, A., et al., "Technological developments in sour gas processing," *Gas Cycling*, Les Entretiens IFP, May 14, 1998, Technip.

Licensors: Prosernat IFP Group Technologies and Titan SNC Lavalin.



AMMOGEN

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Application: AMMOGEN provides gaseous ammonia to fossil-fuel-burning plants to operate pollution-control systems such as $DeNO_x/DeSO_x$ SCR, SNCR and flue-gas treatment units. This process produces gaseous ammonia onsite and on demand with harmless and easy-to-handle feedstocks—urea and water. It eliminates the hazard of transporting and storing toxic compounds such as anhydrous or aqueous ammonia.

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Products: The gaseous stream of ammonia (15–35%vol.), carbon dioxide and water vapor.

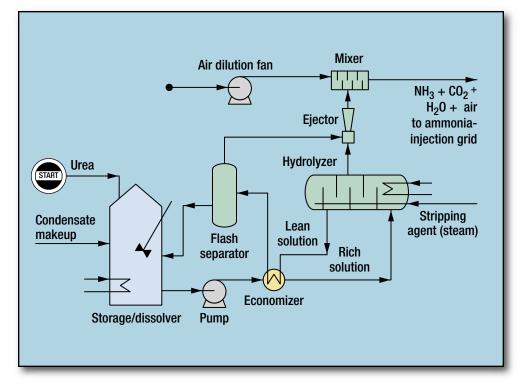
Description: Dry urea enters the dissolver/storage tank where it is dissolved using lean-recycle solution and condensate. The stirrer reduces mixing time, and the rich-urea solution (20-60% wt) is pumped to the hydrolyzer through the economizer where the lean solution sensible heat is recovered. A multistage hydrolysis, at $180-250^{\circ}C$ and 15-30 bar, is done in the baffled hydrolyzer, while the reaction products, i.e., ammonia and carbon dioxide, are removed by a stripping fluid (typically steam). The heat of reaction is supplied by an internal heater and stripping fluid. After the urea decomposition, the lean solution is flashed at atmospheric pressure in the flash separator, from where almost pure water is recycled to the dissolver. The flashed vapor, rich in NH₃, joins the main stream produced by the hydrolyzer and both are sent to the static mixer and diluted with air before delivery to the ammonia-injection grid of the flue-gas treatment system.

Main advantages include:

• Gaseous ammonia produced onsite and on demand

• Utmost safety (no governmental reportable amounts or contingency plans)

- Urea feedstock is harmless, easy-to-handle and widely available
- Simple and safe noncatalytic process
- No carryover of compounds that can damage SCR systems
- Very rapid response time and maximum turndown availability



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- Quick startup, shutdown and standby
- Automatic operation and low maintenance

• Limited plant footprint for easier installation; also can be skid-mounted or module

- Low capital and operating cost
- Capacity from several to thousands kg/h of ammonia.

Installations: Four plants in the US with design capacity from 270 kg/h to 1,600 kg/h. One plant in Europe with design capacity of 900 kg/h.

Licensors: SIIRTEC NIGI and HERA LLC.



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Clauspol

Application: Claus tail-gas treatment with total sulfur recoveries up to 99.9+%. Liquid-phase conversion of H_2S and SO_2 into liquid elemental sulfur (S).

Description: Claus tail gas is contacted counter-currently with an organic solvent in a low-pressure drop-packed column (1). Hydrogen sulfide (H_2S) and SO_2 are absorbed in the solvent and react to form liquid elemental S according to the Claus reaction, which is promoted by an inexpensive dissolved catalyst. The solvent is pumped around the contactor (1), and the heat of reaction is removed through a heat exchanger (3) to maintain a constant temperature slightly above the sulfur melting point. Due to the limited solubility of S in the solvent, pure liquid S separates from the solvent and is recovered from a settling section (2) at the bottom of the contactor (1). This standard Clauspol II flow scheme allows S recovery up to 99.8% (Claus + Clauspol). The recovery level can be customized by adapting the size of the contactor (1).

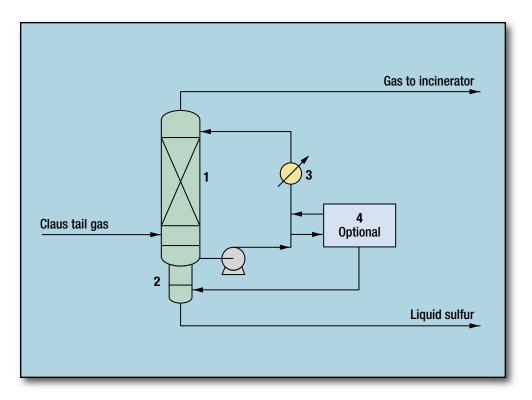
The latest development is the optional solvent desaturation section (4). By removing the dissolved sulfur from the circulating solvent, the overall sulfur recovery can be raised up to 99.9+%.

Economics: For a Clauspol unit treating a typical Claus tail gas, in the 99.7–99.9% recovery, the CAPEX are typically 60–80% and OPEX 40–60% of those for a conventional hydrogenation/amine plant. Contrarily to the hydrogenation/amine process, Clauspol does not recycle any H_2S to the Claus unit, thus saving Claus plant capacity.

Installations: More than 40 units.

References: Barrère-Tricca, C., et al., "Thirty Years of Operating Experience with a Wet Subdewpoint TGT Process," GPA Europe Annual Conference, Amsterdam, September 26–28, 2001.

Ballaguet, J. P., C. Barrère-Tricca and C. Streicher, "Latest developments of the Clauspol TGT process," AIChE Spring Meeting, New Orleans, March 30–April 3, 2003.



Licensor: Prosernat IFP Group Technologies.



LTGT (Lurgi tail gas treatment process)

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Application: Wet-scrubbing process purifies Claus tail gas for total sulfur recovery ranging from 99.8% to 99.9+%.

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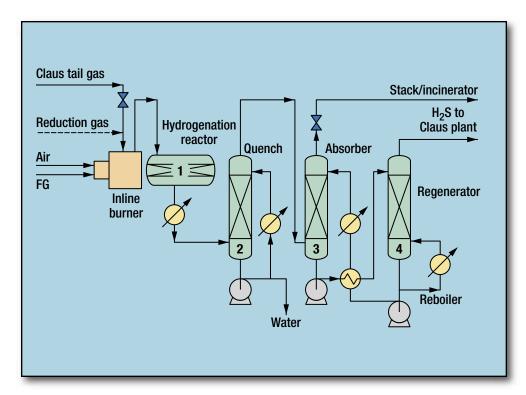
Description: The optimum Claus tail gas treatment converts sulfur species to H_2S and recovers it in a wet-scrubbing process. The Lurgi tail gas treatment process (LTGT) is an amine treating system with generic MDEA solvent, structured packing and plate heat exchangers when possible. This process enables using smaller-diameter columns, plot size, worldwide treating solution availability, proven technology and high selectivity. Installing smaller equipment lowers total investment costs.

Different sulfur species from the incoming Claus tail gas are converted (1) to H_2S . Process water formed by the Claus reaction is removed in a direct cooler (2), and H_2S is expunged by MDEA solution in an absorber column (3). The amine solution is regenerated in a steam-heated stripper column (4) and produces an H_2S gas stream that is recycled back to the Claus section. Due to hydrogenation in the tail gas treatment, both acid gases— H_2S and CO_2 —are produced and routed to the absorber column.

Tertiary amines like MDEA, which are used in the LTGT, have the ability to selectively absorb H_2S due to chemical structure and do not coabsorb CO_2 . Primary (MEA) and secondary amines (DEA) will absorb H_2S along with most of the CO_2 . In tertiary amine solutions, CO_2 can only be absorbed by an indirect acid/base reaction forming bicarbonates; this is a very slow reaction.

Economics: Investment amounts are approximately 85–95% of the Claus unit cost. Using a common regeneration along with the upstream amine unit, investments are approximately 65–75% of the Claus unit cost.

Installations: Eight LTGT units for processing Claus tail gases are in operation or under design.



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Reference: Connock, L., "Emerging sulphur recovery technologies," *Sulphur,* March/April 2001.

Licensor: Lurgi AG.

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Resulf—Tail gas treating

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Application: Purification of sulfur recovery unit (SRU) tail gas for incineration. Resulf, Resulf-10 and Resulf-MM units are easily retrofitted to existing SRU complexes. They feature a low unit pressure drop and can use the latest specialty solvents to lower energy consumption and maximize flexibility.

process categories

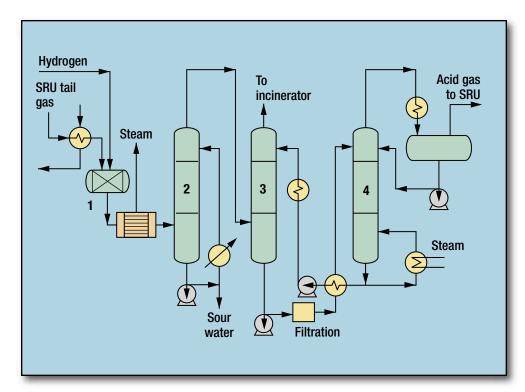
Products: Treated vent gas from a Resulf-MM unit typically contains 1,000 ppm H_2S and must be incinerated. Treated vent gas from a Resulf unit typically contains less than 150 ppmv H_2S and is oxidized in an incinerator before venting to the atmosphere. Vent gas from a Resulf-10 unit has a maximum of 10 ppmv H_2S and may not require incineration.

Description: SRU tail gas is heated in the feed heater, then mixed with a reducing gas containing H_2 . The heated stream passes through the reactor (1), where the SO₂, elemental sulfur and other sulfur-containing compounds, such as COS and CS₂, are converted to H_2S . Hot gas leaving the reactor is cooled in a waste-heat steam generator. The gas is further cooled in a direct contact water cooler (2). The overhead gas stream is fed to the absorber (3).

Lean solvent is also fed to the absorber. The downward flowing solvent contacts the upward flowing gas and absorbs nearly all the H_2S and only part of the CO_2 . Rich solvent is sent to the regenerator (4) where the H_2S and CO_2 are removed by steam stripping. Acid gas from the regenerator is recycled to the SRU. Lean solvent from the regenerator is cooled and returned to the absorber.

Operating conditions: Resulf units use generic MDEA or formulated MDEA as a solvent. Resulf-10 units are designed using specialty amines such as formulated MDEA. Resulf-MM units use amine from the primary amine unit (MEA, DEA or MDEA).

Economics: Plate and frame heat exchangers have been used to reduce capital costs. Modular designs can also be used to reduce capital costs while maintaining critical project schedules. The cost for Resulf-MM is



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significantly lower than for Resulf or Resulf-10 due to the lower recovery. Key features of the Resulf-MM and Resulf technologies are that they can be inexpensively upgraded.

Installations: CB&I TPA has licensed and designed worldwide:

Resulf units:	45
Resulf-10 units:	3
Resulf-MM units:	2

Supplier: CB&I TPA.

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SCOT

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Application: A low-pressure drop, high-sulfur recovery efficiency process to recover sulfur components from tail gas of sulfur plants. The SCOT process is insensitive to variations in the upstream SRU, such as in the H_2S/SO_2 ratio, hydrocarbon or ammonia breakthrough.

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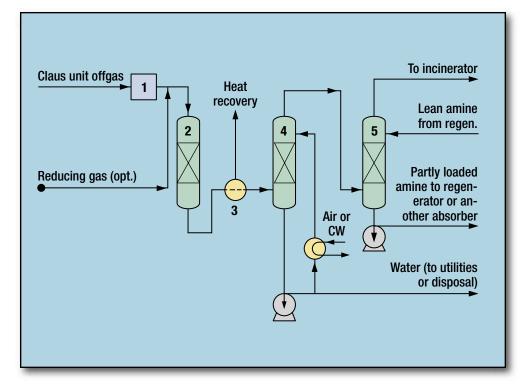
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Products: Offgas from a SCOT unit contains a total sulfur content less than 120 ppmv; offgas from a Super SCOT unit contains maximum 50 ppmv total sulfur content, and the offgas from Low Sulfur SCOT contains less than 10 ppm.

Description: The Claus tail gas feed to the SCOT unit is heated to 220°C to 280°C using an inline burner or heat exchanger (1) with optionally added H₂ or a mixture of H₂/CO. If reducing gas, H₂ or CO is not available, an inline burner (1) is operated in an air-deficient mode to produce reducing gas. The heated gas then flows through a catalyst bed (2) where sulfur components, SO₂, elemental sulfur (S), COS and CS₂ are practically completely converted to H₂S. The gas is cooled to 40°C in an optional heat-recovery system (3) and a water-quench tower (4), followed by selective H₂S removal in an amine absorber (5) to typically 30 ppmv to 100 ppmv H₂S. The semi-loaded amine is often further loaded in another absorber. The H₂S absorbed in the SCOT, Super SCOT or Low Sulfur SCOT process is recycled to the Claus unit via the amine regenerator. The absorber offgas is incinerated.

The process is continuous, has a pressure drop of 4 psi or lower, provides excellent sulfur recovery and can be operated at high reliability with less than 1% unscheduled downtime.

Economics: The total sulfur recovery efficiency of the SCOT process combined with the upstream Claus unit, typically guarantees a sulfur recovery of at least 99.8%. In the case of a Super SCOT unit, an overall sulfur recovery efficiency of 99.95% can be guaranteed. An integrated and cascaded SCOT unit has capital and operational expenditures comparable to other tail gas treating technologies, but has higher total sulfur recovery efficiency.



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References: Kees van den Brand, "Shell's Low Cost SCOT Process," Sulphur Recovery Symposium, Vail, September 2002.

Hoksberg, et al., "Sulfur recovery for the new millennium," *Hydrocarbon Engineering*, November 1999.

Verhulst, "Recent developments in SCOT tail gas technology," Bovar/Western Research Sulfur Seminar, Istanbul, 1994.

Kuypers, *Ten years SCOT experience,* Erdol and Kohle, January 1985.

Licensor: Shell Global Solutions International B.V.



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SULFREEN

Application: Catalytic purification of Claus tail gas or lean H_2S waste gas for an overall sulfur recovery ranging from 99% to 99.9%. Different versions of the SULFREEN process are available.

Description: The SULFREEN process is based on the well-known Claus reaction in which the components— H_2S and SO_2 in tail gas—are catalytically converted into elemental sulfur. The process occurs in the gas phase; the operating conditions being those at which the tail gas leaves the upstream Claus plant. The catalyst, which is arranged in fixed beds, consists of impregnated activated alumina, the properties of which are similar to those of Claus catalysts.

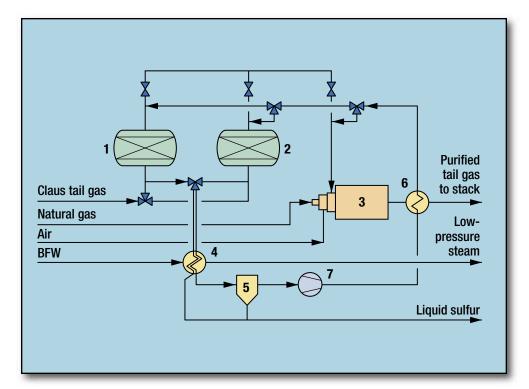
Tail gas leaving the Claus plant at temperatures of 120°C to 140°C passes through one of the two reactors (1) (2), where most of the H_2S and SO_2 are converted into elemental sulfur and adsorbed on the catalyst.

The sulfur-laden catalyst is regenerated by using part of the Claus plant tail gas. The regeneration gas is heated in a gas/gas-heat exchanger (6), using the heat in the hot offgases from the incineration unit (3). A gas-fired heat exchanger, a direct-fired heater or an electrical heater can also be used for heating purposes.

The desorbed sulfur contained in the hot regeneration gas is recovered in the sulfur condenser (4) (5). The regeneration-gas blower (7) serves for overcoming the pressure drop of the closed regeneration loop. After subsequent cooling of the catalyst bed with purified tailgas, the reactor (1) (2), is again ready to be switched to adsorption.

If high COS and CS_2 concentrations are expected to be present in the tail gas, a modified version of the process, named HYDROSULFREEN, is available. The HYDROSULFREEN process includes a pretreatment of the tail gas in an hydrolysis and oxidation reactor, located upstream of the SULFREEN reactors. For sulfur recoveries up to 99.9%, the DOXO-SULFREEN process can be applied. This process includes an additional direct oxidation step downstream of the SULFREEN reactors.

Economics: SULFREEN investment amounts to 30-45% of the Claus



unit cost for the conventional version, and 50–85% for the improved versions. Operating costs are much lower than for solvent-based processes.

Installations: More than 75 SULFREEN units—for processing tail gases of Claus plants, ranging from 5 tpd to 2,200 tpd of sulfur—are in operation or under design.

Reference: Willing, W. and T. Lindner, "Lurgi's TGT processes and new operational results from SULFREEN plants," presented at the SULPHUR '94 Conference, Tampa, Florida, Nov. 6–9, 1994.

Licensor: Lurgi AG.



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Gas Processes 2006

DeNO_x and **DeDioxin** technology

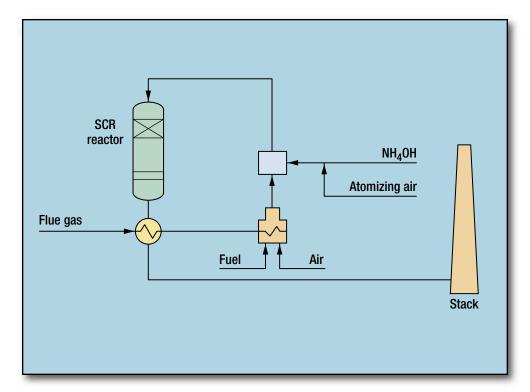
Application: Nitrogen Oxides (NO_x) and Dioxin removal contained in flue-gas leaving combustion processes, to meet the most stringent environment regulations concerning atmospheric pollution.

Description: The De NO_x and DeDioxin process technologies consist of the selective catalytic reduction (SCR) of NO, NO_2 and dioxin to elemental components like nitrogen and water (H₂O) vapor. The reducing agent is ammonia (NH₃), which is available from anhydrous NH₃, H₂O diluted or produced from urea via hydrolysis.

The reaction takes place over a regenerable catalyst based on titanium dioxide (TiO_2) as a carrier with vanadium pentoxide (V_2O_5) and tungsten trioxide (WO_3) as active elements. The catalyst can have either a honeycomb structure with homogeneous pore size distribution and a very active surface or plate structure with a low-pressure drop.

The gas entering the SCR system is heated up to reaction temperature by an inline fuel gas burner. The reducing agent is injected upstream of the SCR reactor by a multiple spray nozzle system or by an injection grid. NH_3 is uniformly distributed and led to intimate contact with the contaminants by a static mixer. Typically, downstream of the SCR reactor, a gas-gas heat exchanger is used to preheat gas entering the DeNO_x system by cooling down the outlet gas from the reactor routed to the stack.

Operating conditions: The SCR system pressure drop ranges from 0.20 bar to 0.30 bar and operating pressure is slightly under atmospheric pressure. Operating temperature can vary between 150°C and 450°C depending on gas composition. Lower-limit temperature is dictated by the need to avoid condensation leading to a catalyst deactivation, while the upper limit is to avoid TiO₂ sintering. Catalyst regeneration is performed onsite with a proprietary technology (ReCat). The SCR system can reduce both NO_x up to 90–95% and dioxin levels down to 0.1ng/Nm³. NH₃ slip in the flue gas to the stack is generally kept below 5 ppm vol.



Economics: Technology is based on standard equipment and most are fabricated in carbon steel. Capital cost can range from \$1 million for 50,000 Nm³/h to \$10 million for 800,000 Nm³/h.

Commercial plants: More than 40 units are already in operation worldwide. Recently, three plants in Italy and two in France have been built by SIIRTEC NIGI under IUT license. Capacity of $DeNO_x$ and DeDioxin plants can range from thousands to millions Nm^3/h of flue gas.

Licensor: SIIRTEC NIGI - Milan, Italy is the exclusive sub-licensor for Italy and other territories of Integral Umwelt Unlagentechnik - Wien (Austria).



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Gas Processes 2006

Shell-Paques process

Application: Biological desulfurization of high-pressure natural gas, synthesis gas and Claus tail gas.

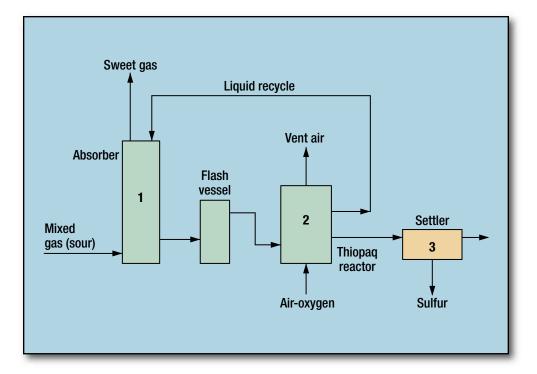
Products: The Shell-Paques unit can be designed such that the treated gas stream contains less than 5-ppmv hydrogen sulfide (H₂S); the resulting sulfur recovery is consequently over 99.99%, based on gas streams. The biosulfur produced can be used directly as fertilizer, since it has a hydrophilic character. Thus, the sulfur is more accessible in soil for oxidation and subsequent uptake by plants. Alternatively, the bio-sulfur can be washed and remelted to produce a final liquid sulfur product that will meet industrial specifications. The hydrophilic character of the bio-sulfur is lost after remelting.

Description: In the Shell-Paques process, H_2S is directly oxidized to elemental sulfur (S) using colorless sulfur bacteria (Thiobacilli). These naturally occurring bacteria are not genetically modified. Feed gas is sent to a caustic scrubber (1) in which the H_2S reacts to sulfide. The sulfide is converted to elemental S and caustic by the bacteria when air is supplied in the bioreactor (2). Sulfur particles are covered with a (bio-) macropolymer layer, which keeps the sulfur in a milk-like suspension that does not cause fouling or plugging.

In this process, a sulfur slurry is produced, which can be concentrated to a cake containing 60% dry matter. This cake can be used directly for agricultural purposes, or as feedstock for sulfuric acid manufacturing. Alternatively, the biological sulfur slurry can be purified further by melting to high-quality sulfur to meet international Claus sulfur specifications.

Economics: The Shell Paques/Thiopaq process achieves a very low H_2S content in the treated gas; a very high-sulfur recovery efficiency of 99.99% is achievable. This process can thus replace the combination of an amine/ Claus/TGTU or, for smaller applications, liquid redox processes.

Installations: There are four Shell-Paques units in operation with two more licenses sold. It compares favorably in terms of capital expendi-



ture with practically all liquid redox applications, and with the traditional amine/Claus/TGTU for sulfur capacities, up to around 50 tpd. The capital and operating costs for this biological process decrease with decreasing CO_2/H_2S ratios.

References: Cameron Cline, et al., "Biological process for H₂S removal from gas streams. The Shell-Paques/THIOPAQ gas desulfurization process" Laurence Reid, February 2003.

Janssen, A. J. H., et al, "Biological process for H_2S removal from high-pressure gas: The Shell-Paques/THIOPAQ gas desulfurization process," *Sulphur*, 2001.

Licensors: Shell Paques: Paques B.V. and Shell Global Solutions International B.V.



Thiopaq DeSO_x

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Application: The Thiopaq $DeSO_x$ biological process selectively removes and converts SO_x in the flue gases to elemental sulfur or H_2S .

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Product: The sulfur produced is hydrophilic; thus, it prevents equipment from fouling or blocking. Moreover, this characteristic makes the product sulfur suitable for agricultural use as fertilizer or as an insecticide. Alternatively, the sulfur can be melted to a high-purity product and meet international Claus sulfur specifications. Alternatively, H_2S can be produced and the gas can be sent to the sulfur treatment unit (amine/ Claus).

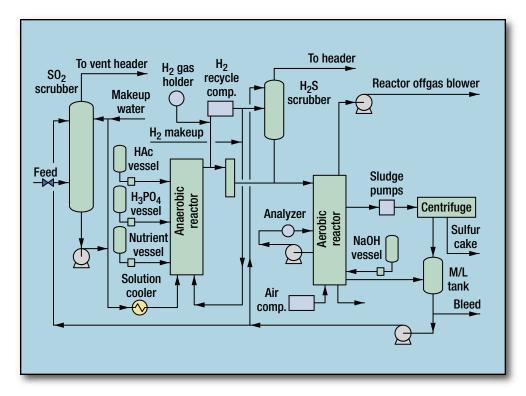
Description: The Thiopaq $DeSO_x$ is a commercial, two-step biological process. It can convert sulfite and sulfate to elemental sulfur or H_2S . A sodium biphosphate solution quenches and removes particulates and absorbs SO_x from the flue gas. The scrubbing liquid is regenerated and recycled to the scrubber.

The heart of the Thiopaq process is the proprietary anaerobic and aerobic bioreactors. In these air-lift-loop reactors, the absorbed sulfite is reduced to sulfide (HS⁻) inside the anaerobic reactor in the presence of microorganism with hydrogen and could be removed as H_2S alternatively.

The sulfide is oxidized under controlled conditions to elemental sulfur via the microorganisms. The produced elemental sulfur has a hydrophilic nature and is separated from the aqueous effluent in a proprietary three-phase separator.

Operating conditions: The scrubber operates close to the atmospheric pressure and at saturation temperature of the scrubbing liquid. The anaerobic bioreactor can be operated at pressures of up to 6 bar and 35°C. The aerobic bioreactor operates at atmospheric pressure and 35°C.

Installations: Thirty-one Thiopaq units operating worldwide to remove sulfur from gas and liquid streams for a variety of industries.



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Licensors: UOP LLC, Monsanto Environchem System Inc., and Paques B.V.



Thiopaq—H₂S Removal

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Application: The biological Thiopaq process selectively removes and converts H_2S and light mercaptans from gas streams, aqueous streams and/or light hydrocarbons to elemental sulfur or sulfate.

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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 melted to a high-purity product meeting international Claus sulfur specifications.

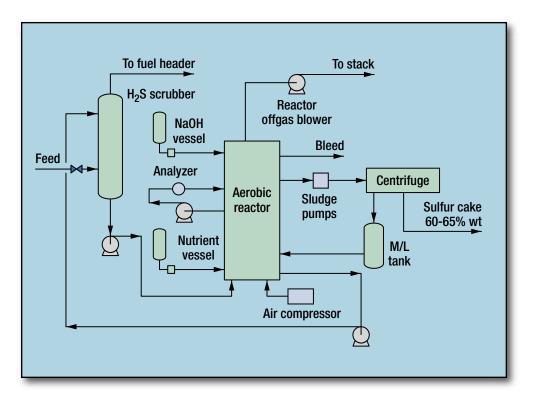
Description: The Thiopaq process consists of three integrated process sections: an absorption section to remove the H_2S from the gas stream, bioreactor(s) and a sulfur-separation section.

The heart of this process is the proprietary bioreactor. In this airlift-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 H_2S 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 H_2S is compensated by the oxidation of H_2S 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.

Other applications: The Thiopaq process may also be used to treat spent sulfidic caustic by converting the sulfide to sulfate.



company index

Installations: Thirty-one units are operating worldwide to remove sulfur from gas and liquid streams in a variety of industries.

Licensors: UOP LLC, Shell Global Solutions B.V. and Paques B.V.



Caloric HM process (hydrogen)

Application: To produce hydrogen (H_2) from methanol (MEOH) using steam reforming.

process categories

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Description: The HM process uses MEOH reforming combined with a pressure swing absorption (PSA) purification step to produce high-purity H_2 . MEOH and demineralized water (H_2O) are mixed in a tank (1). This is vaporized and superheated in heat exchangers by hot synthesis gas leaving the reformer (2) and vent gas heated by a high-velocity burner (3). The superheated MEOH/ H_2O vapor mixture is then distributed into the reformer tubes, which are filled with catalyst. The reformer is heated by hot vent gas recycled by a fan.

Passing the catalyst, the MEOH/H₂O vapor mixture is converted into synthesis gas consisting of H₂, CO, CO₂, methane (CH₄) and H₂O vapor. In the cooler, the synthesis gas is cooled to ambient temperatures, while, simultaneously, H₂O vapor is condensed and recycled to the storage tank.

The synthesis gas now passes the molecular sieve PSA purification unit where the H_2 is isolated to the specified purity. The tail gas from the PSA purification unit is sent to the buffer tank (4). From the buffer tank, the tail gas is used as fuel for the high-velocity burner. Using vent gas instead of thermal oil for heating the reformer, handling and inspection is much easier due to discharging thermal oil.

Economics: To produce 1,000 Nm³/h H₂, the following utilities are required:

• 650 kg/h MEOH

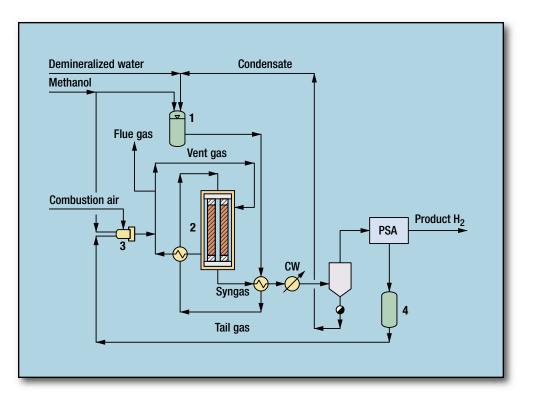
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- 360 kg/h demineralized H₂O
- 55 kW electric power
- 13 m³/h cooling H_2O

Installations: 17 plants are built worldwide, ranging in capacity up to 1,500 Nm³/h of pure H_2 .



company index

Reference: Neumann, P. and F. von Linde, "Opportunities for an economical H₂ supply," *Inform,* Vol. 14, No. 5, May 2003.

Licensor: Caloric Anlagenbau GmbH.



Hydrogen

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

process categories

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

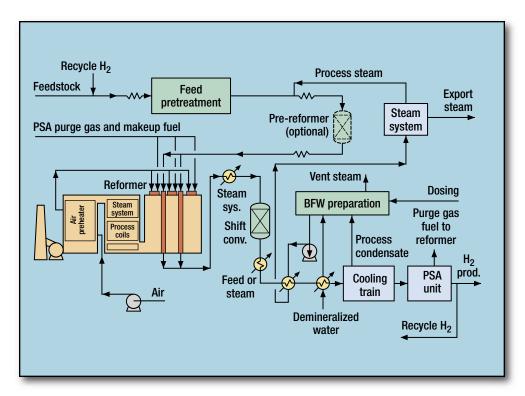
Description: The generic flowsheet consists of feed pretreatment, prereforming (optional), steam-HC reforming, shift conversion and hydrogen purification by pressure swing adsorption (PSA). However, it is often tailored to satisfy specific requirements.

Feed pretreatment normally involves removal of sulfur, chlorine and other catalyst poisons after preheating to appropriate level.

The treated feed gas mixed with process steam is reformed in a fired reformer (with adiadatic 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 in the shift reactor. 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 Gcal/KNm³ and 3.5 Gcal/KNm³ of H_2 (330–370 Btu/scf) on LHV basis, depending upon feedstock, plant ca-



pacity, optimization criteria and steam-export requirements.

Recent advances include integration of hydrogen recovery and generation, 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.

Licensor: Technip.

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Hydrogen

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Application: Produce hydrogen (H_2) for refinery applications (e.g., hydrotreating and hydrocracking) as well as for petrochemical and other industrial uses.

process categories

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Feed: Natural gas, refinery offgases, LPG, naphtha or mixtures thereof.

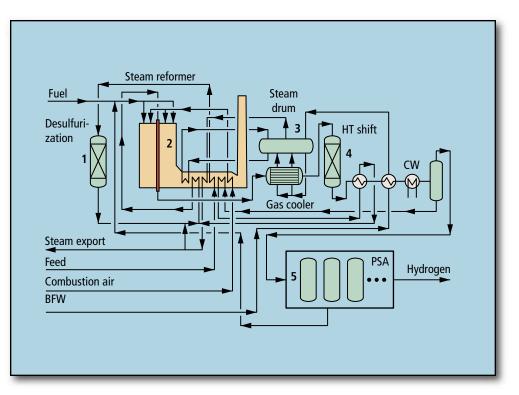
Product: High-purity H_2 (typically >99.9%), carbon monoxide (CO), carbon dioxide (CO₂), high-pressure steam and/or electricity may be produced as separate creditable by-product.

Description: The feed is desulfurized (1), mixed with steam and converted to synthesis gas in steam reformer (2) over a nickel-containing catalyst at 20–40 bar pressure and outlet temperatures of 800–900°C. The Uhde steam reformer features a well-proven top-fired design with tubes made of centrifugally cast alloy steel and a unique proprietary "cold" outlet manifold system for enhanced reliability.

A further speciality of Uhde's H_2 plant design is an optional bi-sectional steam system for the environmentally friendly full recovery of process condensate and production of high-pressure export steam (3) with a proven process gas cooler design. The Uhde steam reformer concept also includes a fully pre-fabricated and modularized shop-tested convection bank design to further enhance the plant quality and minimize construction risks. The final process stages are the adiabatic CO shift (4) and a pressure swing adsorption unit (5) to obtain high-purity H_2 .

Process options include feed evaporation; adiabatic feed pre-reforming and/or HT/LT shift to process, for example, heavier feeds and/or to optimize feed/fuel consumption and steam production. Uhde's design allows combining maximized process heat recovery and optimized energy efficiency with operational safety and reliability.

The Uhde reformer design is particularly advantageous for the construction and reliable operation of large-scale reformers with H_2 capacities up to 220,000 Nm³/h (197 MMscfd) in single-train configurations. Uhde offers either standard or tailor-made designs and applies either



customer or own design standards.

Economics: Depending on the individual plant concept, the typical consumption figure for natural gas-based plants (feed + fuel – steam) can be as low as 3.13 Gcal /1,000 Nm³ (333 MMBtu/MMscf) or 3.09 (329) with pre-reforming.

Installations: Recently, Uhde has successfully commissioned large-scale H_2 plants for SINCOR C.A., Venezuela (2 x 100,000 Nm³/h or 2 x 90 MMscfd), and Shell Canada Ltd., Canada (2 x 130,000 Nm³/h or 2 x 115 MMscfd), and is presently executing four H_2 projects, including H_2 plants for Neste Oil Oyj (formerly Fortum Oil Oy), Finland (1 x 155,000 Nm³/h or 140 MMscfd) and Shell Canada Ltd., Canada, (1 x 150,000 Nm³/h or 135 MMscfd). More than 60 Uhde reformers have been designed and constructed worldwide.

Hydrogen, continued

References: Michel, M., "Design and engineering experience with largescale hydrogen plants," *Oil Gas European Magazine,* Vol. 30 (2004) No. 2 in: *Erdöl Erdgas Kohle,* Vol. 120 (2004) No. 6, pp. OG 85–88 Larsen, J., M. Michel, J. Zschommler (Uhde), M. Whysall and S. Vanheertum (UOP), "Large-scale H₂ plants, Uhde and UOP's experience," AIChE 2003 Spring Meeting, New Orleans, March 30–April 3, 2003..

Licensor: Uhde GmbH.



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Hydrogen (Polybed PSA)

Application: Production of any purity hydrogen, typically 90% to +99.9999 mole%. Impurities efficiently removed include: N₂, CO, CH₄, CO₂, H₂O, Ar, O₂, C₂–C₈+, CH₃OH, NH₃, H₂S and organic sulfur compounds. The technology can also be used to: purify CH₄, CO₂, He, N₂ and Cl; remove CO₂; adjust synthesis gas stream composition ratios and separate nitrogen from hydrocarbons.

process categories

Feed: Steam reformer (at any point after the reformer), catalytic reformer net gas, other refinery purge streams, gasification offgases, ammonia plant purge gases (before or after the NH₃ waterwash), demethanizer or other ethylene plant offgases, partial oxidation gases, styrene plant offgases, methanol plant purge gases, coke-oven gas, cryogenic purification offgases or other H₂ sources. Feed pressures up to 1,000 psig have been commercially demonstrated.

Product: Recovery of H_2 varies between 60% and 90%, depending on composition, pressure levels and product requirements. Typical temperatures are 60°F to 120°F. Purity can be +99.9999 mole%.

Description: Purification is based on advanced pressure swing adsorption (PSA) technology. Purified H_2 is delivered at essentially feed pressure, and impurities are removed at a lower pressure.

Polybed PSA units contain 4 to +16 adsorber vessels. One or more vessels are on the adsorption step, while the others are in various stages of regeneration. Single-train Polybed PSA units can have product capacities over 200 million scfd.

All systems use advanced proprietary adsorbents and patented voidgas recovery techniques to provide maximum product recovery. Other than entrained liquid removal, no feed pretreatment is required. In addition, all impurities are removed in a single step, and purities exceeding 90% are obtained irrespective of impurities. Many units presently produce streams with less than one ppmv impurity from feed concentrations of +40 mole%.

Operation is automatic with pushbutton startup and shutdown. After startup, the unit will produce H_2 in two to four hours. Onstream fac-

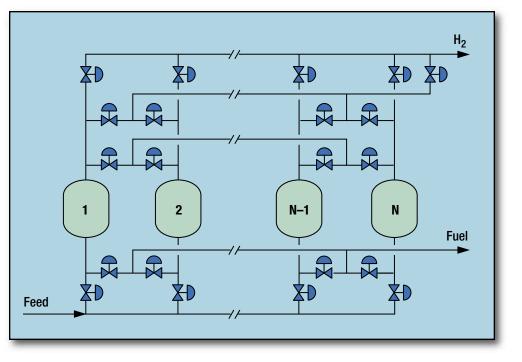
tors in excess of 99.8% relative to unplanned shutdowns are typical.

Turndown capability is typically 50% but can be even lower where required. The units are built compactly with plot plans ranging from 12 ft x 25 ft to 60 ft x 120 ft. Units are skid-mounted and modular to minimize installation costs. Material for piping and vessels is carbon steel. Control can be via a local or remote-mounted control panel or by integration into the refinery's computer control system. Units are designed for outdoor, unattended operation and require no utilities other than small quantities of instrument air and power for instrumentation.

Installations: More than 700 units are in operation or under construction, including the world's first 16-bed system, and the world's largest single-train system.

Licensor: UOP LLC.





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Hydrogen (Polysep membrane)

Application: Hydrogen recovery and purification or rejection from various refining, petrochemical and chemical process gas streams. Other examples are synthesis gas ratio adjustment and carbon monoxide (CO) recovery.

Feed: Refinery streams include catalytic reformer offgas, hydrotreater and hydrocracker purge, and fluid catalytic cracking offgas. Chemical and petrochemical feed streams are: ethylene offgases, ammonia plant purges, methanol plant offgases, synthesis gas streams from steam reforming, partial oxidation or other gasification technologies.

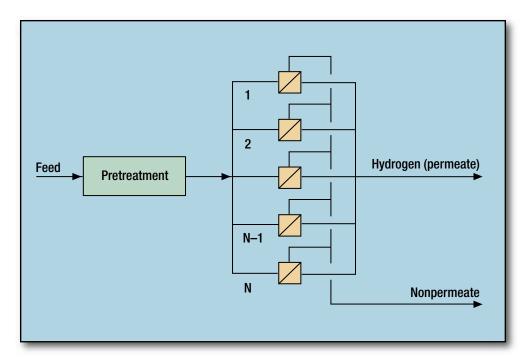
Product: For typical hydrogen purification applications, recovery varies between 70% and 95+%, and purity ranges from 70 mol% to 99 mol%, depending on feed composition, pressure levels and product requirements.

Polysep membrane systems are also designed to produce high-purity CO for petrochemical products such as polyurethanes and polycarbonates, and to ratio adjust synthesis gas streams in methanol and oxoalcohol plants. Also, a new application is hydrogen recovery from IGCC power generation systems.

Description: The Polysep separation system is based on state-of-the-art, composite, hollow-fiber polymer membrane technology. The hollow fibers are packaged in a proprietary countercurrent-flow bundle configuration that maximizes the separation driving force and minimizes required membrane area.

The Polysep separation is a pressure-driven process. It requires a minimum of moving parts, utilities and operator attention. The systems are compact, shop-fabricated, modular units allowing reduced delivery schedules and simple inexpensive installation. Feed pretreatment equipment typically includes: a knockout drum for bulk liquid removal, a coalescing filter for particulate and entrained liquid removal, and a preheater to optimize the membranes' performance.

Operation features include: automatic startup, capacity control,



product-purity control, auto depressurization and turnup/turndown. Turndown capability is typically 30% using a patented control strategy. Membrane system control is typically via integration into the refinery's control system. Once installed, a membrane system can reach steady-state operation from cold startup in a few hours with onstream factors over 99.8% relative to unplanned shutdowns.

Economics: Polysep membrane systems can be efficiently and economically scaled, from just a few modules to over 100 modules, depending on the application. Membrane-separation systems have low capital costs and plot area, and offer a rapid return on investment.

Installations: Over 50 units are in operation or under construction. Largest unit processes over 320 million scfd of synthesis gas.

Licensor: UOP LLC.



Hydrogen (steam reform)

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Application: Production of hydrogen for refinery hydrotreating and hydrocracking or other refinery, petrochemical, metallurgical, and food-processing uses.

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Feedstock: Light hydrocarbons such as natural gas, refinery fuel gas, LPG/butane mixed pentanes and light naphtha.

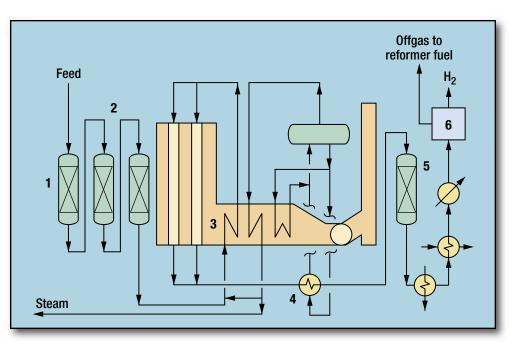
Product: High-purity hydrogen (99.9+%) at any required pressure.

Description: The feed is heated in the feed preheater and passed through the hydrotreater (1). The hydrotreater converts sulfur compounds to H_2S and saturates any unsaturated hydrocarbons in the feed. The gas is then sent to the desulfurizers (2). These adsorb the H_2S from the gas. The desulfurizers are arranged in series and designed so that the adsorbent can be changed while the plant is running.

The desulfurized feed gas is mixed with steam and superheated in the feed preheat coil. The feed mixture then passes through catalyst-filled tubes in the reformer (3). In the presence of nickel catalyst, the feed reacts with steam to produce hydrogen and carbon oxides. Heat for the endothermic reforming reaction is provided by carefully controlled external firing in the reformer.

Gas leaving the reformer is cooled by the process steam generator (4). Gas is then fed to the shift converter (5), which contains a bed of copper-promoted iron-chromium catalyst. This converts CO and water vapor to additional H_2 and CO_2 . Shift converter effluent gas is cooled in a feed preheater, a BFW preheater and a DA feed water preheater. Hot condensate is separated out. Process gas is then cooled in a gas air cooler and a gas trim cooler. The cooled stream flows to a cold condensate separator where the remaining condensate is separated and the gas is sent to a PSA hydrogen purification system (6).

The PSA system is automatic, thus requiring minimal operator attention. It operates on a repeated cycle having two basic steps: adsorption and regeneration. PSA offgas is sent to the reformer, where it provides most of the fuel requirement. Hydrogen from the PSA unit is sent off plot. A small hydrogen stream is then split off and recycled to the front of the plant for hydrotreating.



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The thermal efficiency of the plant is optimized by recovery of heat from the reformer flue gas stream and from the reformer effluent process gas stream. This energy is utilized to preheat reformer feed gas and generate steam for reforming and export. Hot flue gas from the reformer is sent through the waste-heat recovery convection section and is discharged by an induced-draft fan to the stack. The boiler feed water deaerator and preheat circuits are integrated to maximize heat recovery. A common steam drum serves the steam generation coils and process steam generator for steam production via natural circulation.

Installations: Over 175 plants worldwide—ranging in size from less than 1 million scfd to over 100 MMSCFD capacities. Plant designs for capacities from 1 million scfd to 280 MMSCFD.

Supplier: CB&I Howe Baker.



Hydrogen (steam reform)

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Application: Hydrogen production from natural gas, refinery gas, associated gas, naphtha, LPG or any mixture of these. Appropriate purity product (up to 99.999%) can be used in refinery upgrade processes, chemical production and metallurgy (direct reduction). Possible byproducts are export steam or electricity, depending on cost and/or efficiency optimization targets.

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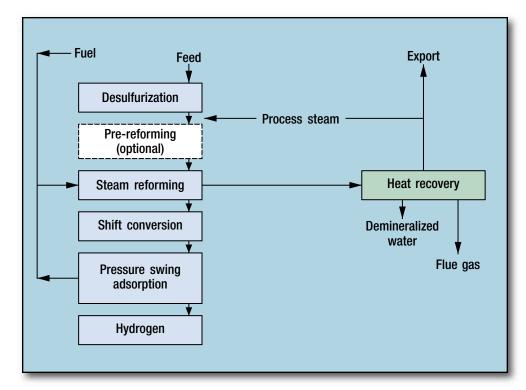
Description: The hydrocarbon feedstock is admixed with some recycle hydrogen and preheated to 350-380°C. Sulfur components are totally converted to H₂S at CoMo catalyst and then adsorbed on zinc oxide by conversion to ZnS. The desulfurized feed is mixed with process steam at an optimized steam/carbon ratio.

The desulfurized feed is mixed with process steam at an optimized steam/carbon ratio, superheated to 500–650°C and fed to the Lurgi Reformer. The feed/steam mixture passing the reformer tubes is converted at 800–900°C by presence of a nickel catalyst to a reformed gas containing H_2 , CO_2 , CO, CH_4 and undecomposed steam. The reformed gas is cooled to approximately 33°C in a reformed gas boiler.

The Lurgi Reformer is a top-fired reformer with a low number of burners and low heat losses, almost uniform wall temperature over the entire heated tube length and low NO_x formation by very accurate fuel and combustion air equipartition to the burners.

An adiabatic pre-reformer operating at an inlet temperature of 400– 500°C (dependent on feedstock) may be inserted upstream of the feed superheater as a process option. Feedgas is partly converted to H₂, CO and CO₂ with high-activity catalyst; all hydrocarbons are totally converted to methane. The pre-reformer limits steam export to maximize heat recovery from the process and increases feedstock flexibility.

The CO in the reformed gas is shift-converted with an iron-chromium catalyst, increasing hydrogen yield and reducing CO content to below 3-vol.%. The shift gas is cooled to 40°C and any process condensate is separated and recycled to the process. The gas is then routed



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to the PSA unit, where pure hydrogen is separated from the shift-gas stream. Offgas is used as fuel for steam reforming.

Recovered waste heat from the reformed and flue gases generates steam, which is used as process steam with the excess exported to battery limits.

Turndown rates of 30% or even less are achievable. The control concept allows fully automatic operation with load changes typically 3% of full capacity/minute.

Economics: Consumption figures based on light natural gas feedstock/1 millon scfd of H_2 :

Feed + fuel, million scfd	0.4
Demineralized water, t	1.25
Cooling water, m ³	3.0
Electricity, kWh	19
Export steam, t	0.7

Hydrogen (steam reform), continued

Installations: More than 119 gas reforming plants, 28 being hydrogen plants, with single-train capacities ranging from 1 million scfd to 200 million scfd.

Licensor: Lurgi AG.



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Gas Processes 2006

Hydrogen (steam reforming)

Application: Manufacture hydrogen (H_2) for hydrotreating, hydrocracking or other refinery or chemical use.

Feedstock: Light saturated hydrocarbons: refinery gas or natural gas, LPG or light naphtha.

Product: Typical purity 99.9%; pressure 300 psig, with steam or carbon dioxide (CO_2) as byproducts.

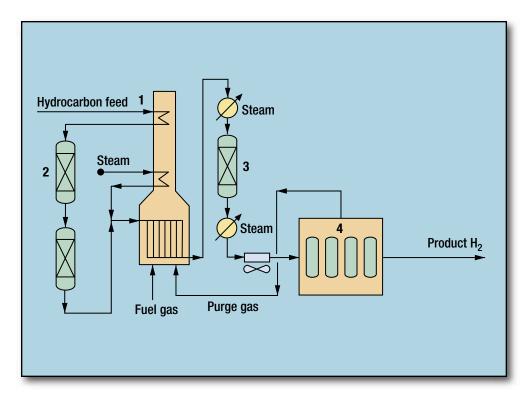
Process description: H_2 is produced by steam reforming of hydrocarbons with purification by pressure swing adsorption (PSA). Feed is heated (1) and then hydrogenated (2) and purified with zinc oxide to remove sulfur. The purified feed is mixed with steam and preheated further, then reformed over nickel catalyst in the tubes of the reforming furnace (1).

Foster Wheeler's Terrace Wall reformer combines high efficiency with ease of operation and reliability. Depending on size or site requirements, Foster Wheeler can also provide a downfired furnace. Combustion air preheat can be used to reduce fuel comsumption and steam export.

Pre-reforming can be used upstream of the reformer if a mixture of naphtha and light feeds will be used, or if steam export must be minimized. Syngas from the reformer is cooled by generating steam, then reacted with steam in the shift converter to convert carbon monoxide (CO) to additional H_2 and CO_2 .

In the PSA section (4), impurities are removed by solid adsorbent, and the adsorbent beds are regenerated by depressurizing. Purge gas from the PSA section, containing CO_2 , methane (CH₄), CO and some H₂, is used as fuel in the reforming furnace. Heat recovery from reformer flue gas may be via combustion air preheat or additional steam generation. Variations include a scrubbing system to recover CO_2 .

Installations: Over 100 plants, ranging from less than 1 MMscfd to 95 MMscfd in a single train, with numerous multi-train installations.



Utility Requirements (50 MMscfd plant):

	Air preheat	Steam generation
Natural gas (feed plus fuel)	780 MMBtu/hr	885 MMBtu/hr
Export steam (600 psig/700°F)	35,000 lb/hr	130,000 lb/hr
Boiler feedwater	70,000 lb/hr	170,000 lb/hr
Electricity	670 kW	170 kW
Cooling water (18°F rise)	350 gal/min	350 gal/min

Reference: Fleshman, J. and R. Myers, eds., *Handbook of Petroleum Refining Processes*, McGraw Hill 2003.

Contributor: Foster Wheeler.



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Gas Processes 2006

Hydrogen and liquid hydrocarbon recovery—cryogenics

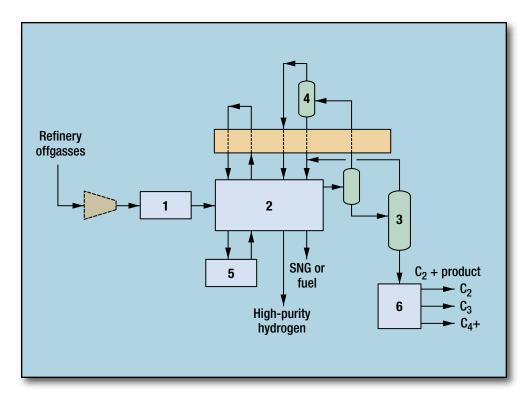
Application: Recover high-purity hydrogen and C_2 + liquid products from refinery offgases.

Description: Cryogenic separation of refinery offgases and purges containing from 10% to 80% hydrogen (H₂) and 15% to 40% hydrocarbon liquids such as ethylene, ethane, propylene, propane and butanes. Refinery offgases are optionally compressed and then pretreated (1) to remove sulfur, carbon dioxide (CO₂), H₂O and other trace impurities. Treated feed is partially condensed in an integrated multi-passage exchanger system (2) against returning products and refrigerant.

Separated liquids are sent to a demethanizer (3) for stabilization while hydrogen is concentrated (4) to 90% to +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 million scfd 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 employed 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, Louisiana, March 14, 2002, Paper 102d.

Licensor: Air Products & Chemicals Inc.



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Gas Processes 2006

Hydrogen recovery (cryogenic)

Application: Recovery of relatively pure hydrogen from refinery and petrochemical offgas streams such as from thermal hydrodealkylation (THDA), catalytic reformers, hydrotreaters and fluid catalytic crackers. Cryogenic processing is the optimal route to produce carbon monoxide (CO) from syngas.

Products: 90% to 98% pure hydrogen. Valuable product streams, such as LPG, may also be recovered.

Description: A typical autorefrigerated cryogenic unit for recovery of hydrogen consists of two stages of cooling and partial condensation. Suitably pretreated feed gas is cooled and partially condensed against hydrogen product and fuel in the plate-fin heat exchanger (1). The hydrocarbon rich condensate is separated in the two-phase separator (2), and the vapor is further cooled and partially condensed in the second plate-fin heat exchanger (3). The methane-rich condensate is separated in the second two-phase separator (4) giving relatively pure hydrogen product, which is reheated through both exchangers.

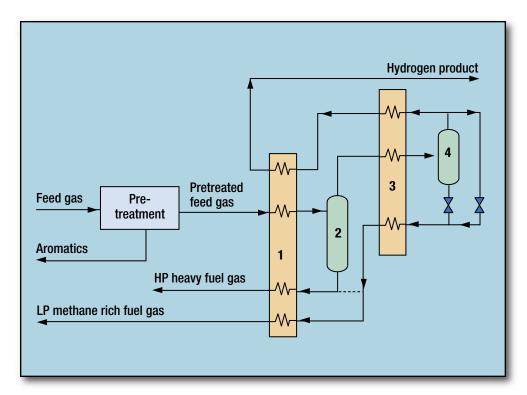
Autorefrigerated cryogenic units use refrigeration from Joule-Thomson expansion of the condensate streams and can generate hydrogen purities up to 96%.

Pretreatment ensures that the feed gas to the cryogenic unit is dry and contains no components that would freeze in the cold section. Depending on the pretreatment scheme, additional products can be obtained.

Depending on feed gas conditions and hydrogen product requirements, one, two or three stages of separation may be optimal.

Operating conditions: Typical hydrogen recoveries are 90% to 96%.

Economics: Cryogenic recovery of hydrogen is economically favored by the ability to recover other valuable products, e.g., olefins and LPG. Compared with alternative technologies, cryogenic processing is the



most efficient and has the lowest utilities cost. Cryogenic recovery has been used to treat gases with hydrogen feed concentrations as high as 80% and pressures up to 80 barg.

Installations: Fourteen.

Reference: Allen, P., "Managing hydrogen recovery," *Hydrocarbon Engineering*, April 1999, p. 71.

Licensor: Costain Oil, Gas & Process Ltd.



Hydrogen, HTCR and HTCR TWIN plants

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Application: Produce hydrogen from a hydrocarbon feedstock such as: natural gas, LPG, naphtha, refinery offgases, using the Haldor Topsøe Convective Reformer (HTCR). Plant capacities range from 2,000 Nm³/h to +25,000 Nm³/h (2 Mscfd to +25 MMscfd) and hydrogen purity from 99.5% to 99.999+%.

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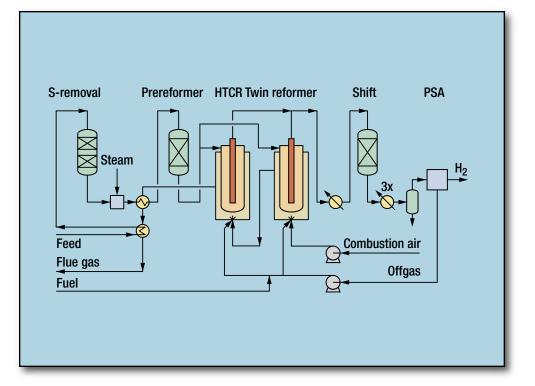
Description: The HTCR-based hydrogen plant can be tailor-made to suit customer needs with respect to feedstock flexibility. Typical plants comprise of feedstock desulfurization, prereforming, HTCR reforming, shift conversion and PSA purification to obtain product-grade hydrogen. PSA offgasis used as fuel in the HTCR. Excess heat in the plant is efficiently used for process heating and steam generation.

A unique feature of the HTCR is the high thermal efficiency. Product gas and flue gas are both cooled by providing heat to the reforming reaction. The high thermal efficiency allows design of energy-efficient hydrogen plants without steam export. In the larger plants, the reforming section consists of two HTCR reformers in a novel layout: HTCR TWIN, which provides optimal utilization of the combustion air and an even lower energy consumption.

Economics: HTCR-based hydrogen plants provide low investment and low operating costs 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 about 3.2 to 3.4 Gcal/1,000 Nm³ (340 to 360 Btu/scf) is achieved depending on size and feedstock.

Installations: Twenty-seven licensed units.

Licensor: Haldor Topsøe A/S.



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Hydrogen, methanol reforming

Application: Produce hydrogen, typically in the capacity range of 300–600 Nm³/h of hydrogen for usage in the oil hardening, manufacture of electronics or in the chemical industry.

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Description: Feed methanol and water are mixed, evaporated and superheated before being introduced into the methanol reforming reactor. In this reactor, the methanol is reacted to form H_2 , CO and CO₂.

The raw gas from the reactor is cooled. The process condensate is separated, after which the gas is further purified by means of a pressure swing absorption (PSA) unit. Fully automatic startup, operation and shutdown are process features.

Features: Utility requirements per Nm³ of hydrogen are:

Methanol, kg	0.63
Fuel, kcal	320
Demineralizaed water, kg	0.37
Electricity, kWh	0.06
Additional utilities required	Cooling water, instrument air and nitrogen

The compactness of the hydrogen plant allows for skid-mounted supply.

Economics: Key process features include:

• Low investment

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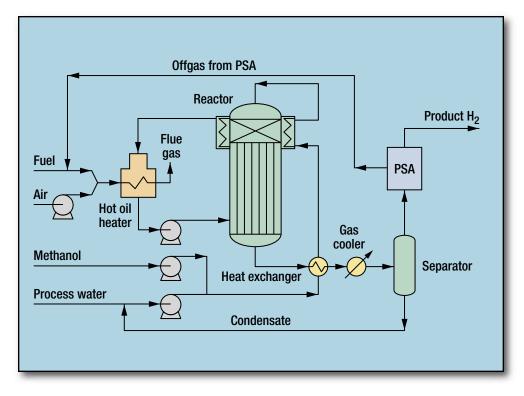
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- Low operating costs
- Low maintenance expenses
- Short delivery time
- Fast installation of the skid-mounted unit
- Fully automated operation.

Installations: Ten plants in operation worldwide.

Licensor: Haldor Topsøe A/S.



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Hydrogen-Methanol-to-Shift

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

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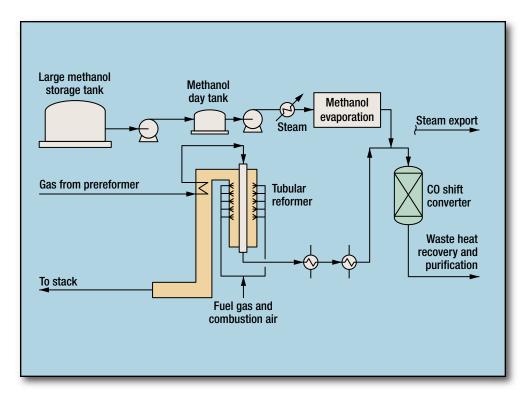
Description: Additional hydrogen is produced by the reforming of methanol over Topsøe's novel dual-function catalyst—LK-510. When installed in the existing CO shift converter and fed simultaneously with methanol and reformed gas, the LK-510 catalyst promotes both the conversion of CO with steam to H_2 and CO₂ and the reforming of methanol to H_2 and CO₂.

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 with a short installation time. The total investment cost is less than 40% of that of a new hydrogen plant. Methanol consumption is approximately 0.54 kg/Nm³ hydrogen (0.03 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.

Licensor: Haldor Topsøe A/S.





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Gas Processes 2006

Hydrogen—PRISM membrane

Application: To recover and purify hydrogen or to reject hydrogen from refinery, petrochemical or gas processing streams. Refinery streams include hydrotreating or hydrocracking purge, catalytic reformer offgas, fluid catalytic cracker offgas or fuel gas. Petrochemical process streams include ammonia synthesis purge, methanol synthesis purge or ethylene offgas. Synthesis gas includes those generated from steam reforming or partial oxidation.

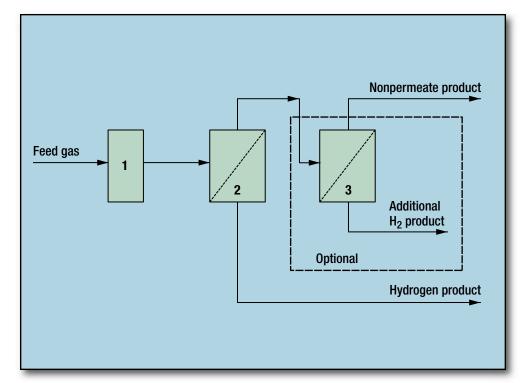
Product: Typical hydrogen (H₂) product purity is 90% to 98% and, in some cases, 99.9%. Product purity is dependent upon feed purity, available differential partial pressure and desired H₂ recovery level. Typical H₂ recovery is 80% to 95% or more.

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 fac-



tory tested for ease of installation and commissioning.

Economics: Economic benefits are derived from high-product recoveries and purities, and 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)

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Application: Produce hydrogen (H₂) from hydrocarbon feedstocks such as: natural gas, LPG, naphtha, refinery offgases, etc., using the Haldor Topsøe radiant wall steam-methane reformer (SMR) process. Plant capacities range from 5,000 Nm³/h to 200,000+ Nm³/h (4.5 MMscfd to 200+ MMscfd), and hydrogen purity ranges from 99.5% to 99.999+%.

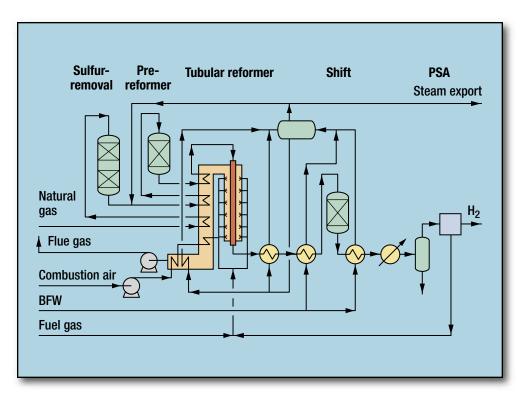
Description: Haldor Topsøe SMR-based hydrogen plants can be tailor-made to suit the customer's needs with respect to feedstock flexibility and steam export. In a typical low-steam export plant, the hydrocarbon feedstock is desulfurized. Subsequently, process steam is added, and the mixture is fed to a pre-reformer. Further reforming is done in the Topsøe radiant wall SMR. Subsequently, process gases are reacted in a water-gas shift reactor and purified by the pressure swing absorption (PSA) unit to obtain product-grade H₂. PSA offgases are used as fuel in the SMR. Excess heat in the plant is efficiently used for process heating and steam generation.

The SMR operates at high outlet temperatures [up to about 950°C (1,740°F)] while the Topsøe reforming catalysts enable low steam-tocarbon ratios. Both conditions (advanced steam reforming) are necessary for high-energy efficiency and low hydrogen production costs. Topsøe's reforming technology is in operation in more than 200 industrial plants worldwide.

Economics: The Advanced Steam Reforming conditions described can achieve a net energy consumption as low as about 2.96 Gcal/1,000 Nm³ hydrogen using natural gas feed (315 Btu/scf).

References: Dybkjær, I. and S. W. Madsen, "Advanced reforming technologies for hydrogen production," *Hydrocarbon Engineering*, December/January 1997/1998.

Gøl, J. N., et al., "Options for hydrogen production," *HTI Quarterly*, Summer 1995.



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Rostrup-Nielsen, J. R. and T. Rostrup-Nielsen, "Large-scale hydrogen production," *CatTech*, Vol. 6, No. 4.

Rostrup-Nielsen, T., "Manufacture of hydrogen," *Catalysis Today,* Vol. 105, 2005, p. 293.

Licensor: Haldor Topsøe A/S.



MEDAL membrane (hydrogen)

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Application: Hydrogen recovery and purification from refinery, petrochemical and ammonia plant gas streams.

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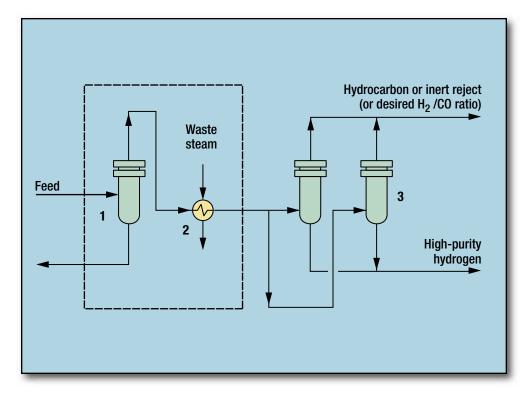
Feed: Refinery streams include hydroprocessing unit purge streams, catalytic reformer offgas, fuel gas streams and steam reformer (feed preparation/product purification). Petrochemical streams include: olefin plant process and recycle streams, polypropylene recycle streams, methanol plant purge, syngas streams from steam reforming and gasification processes for hydrogen (H₂)/carbon monoxide (CO) ratio adjustment and/or process efficiency improvement.

Product: Hydrogen purity of 90–99% is typical of most applications. Hydrogen recovery range is from 80% to 95+% depending on operating conditions and customer requirements. In refining applications, the hydrocarbon by-product, non-permeate stream leaves the unit at feed pressure with up to 99% recovery.

Description: Purification is based on polyaramide or polyimide hollowfiber membrane modules with high resistance to typical hydrocarbon stream contaminants. The hollow fibers are assembled in a patented radial cross flow permeator module. Modules are combined in pressure vessels to provide maximum system performance and to minimize space requirements.

Hydrogen membrane systems typically include a coalescing filter (1), a preheat exchanger (2) and membrane separators (3). The membrane system's modular nature allows for maximum flexibility in system capacity and permits future expansion.

Consistent H_2 recovery and product purity can be maintained through wide fluctuations in feed composition, operating pressures and feed flow rates. The systems are skid-mounted for compactness and minimal installation costs, and are designed for unattended outdoor operation. A small amount of low-pressure steam, instrument air and power for instrumentation are the only utilities required.



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Economics: MEDAL hydrogen membrane systems are characterized by low capital and operating costs, and a high return on capital.

Installations: Over 100 installations are in operation or under construction. MEDAL hydrogen membrane systems have been in operation since 1987.

Licensor: Air Liquide S.A. (MEDAL, L.P.)



AMINEX

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Application: Extract H_2S , COS and CO₂ from gases and light liquid streams with amine solution using FIBER-FILM contactor technology.

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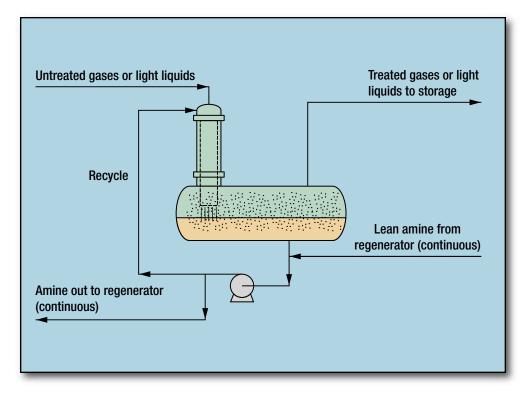
Description: The amine phase flows along the FIBER-FILM contactor fibers, which are continuously renewed, as the wet fibers are preferentially wetted by the amine phase in the AMINEX process. Hydrocarbons flow through the shroud parallel to the amine-wetted fibers where the H_2S , COS and/or CO₂ are extracted into the amine phase. The two phases disengage in the separator vessel where the rich amine flows to the amine regeneration unit and the treated gas or light liquids go to storage.

Economics: FIBER-FILM contactor technology requires smaller processing vessels, allowing shorter separation times and less waste generation. This saves plant space and reduces capital expenditures.

Installations: Ten worldwide.

Reference: "Gas Processing Handbook," *Hydrocarbon Processing*, April 1984, p. 87.

Licensor: Merichem Chemicals & Refinery Services LLC.





MERICAT II

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Application: Oxidize mercaptans to disulfides for gas condensates and natural gasoline with air, caustic and catalyst using FIBER-FILM contactor technology. This is followed by an upflow catalyst impregnated carbon bed.

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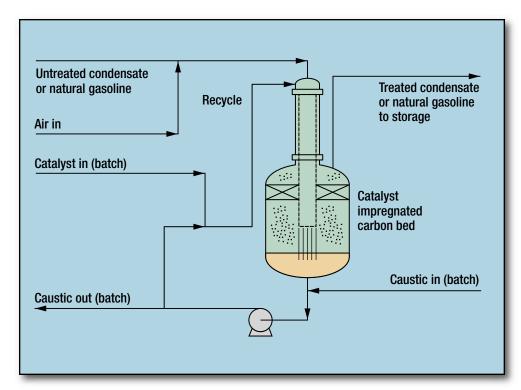
Description: The caustic phase flows along the FIBER-FILM contactor fibers, which is continuously renewed, as the fibers are preferentially wetted by the caustic phase in the MERICAT II process. Hydrocarbon flows through the shroud parallel to the caustic phase where mercaptans are extracted into the caustic phase. It is converted to disulfides by air and catalyst at the hydrocarbon-caustic interface. The two phases disengage and the hydrocarbon flows upward through a catalyst-impregnated carbon bed where the remaining mercaptans are converted to disulfides.

Economics: FIBER-FILM contactor technology requires smaller processing vessels allowing shorter separation times and less waste generation. This saves plant space and reduces capital expenditures.

Installations: Twenty-eight worldwide.

Reference: Hydrocarbon Technology International, 1993.

Licensor: Merichem Chemicals & Refinery Services LLC.





THIOLEX/REGEN

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Application: Extract H_2S , COS and mercaptans from gases and light liquid streams, including gasoline, with caustic using FIBER-FILM contactor technology. It can also be used to hydrolize COS contained in LPG.

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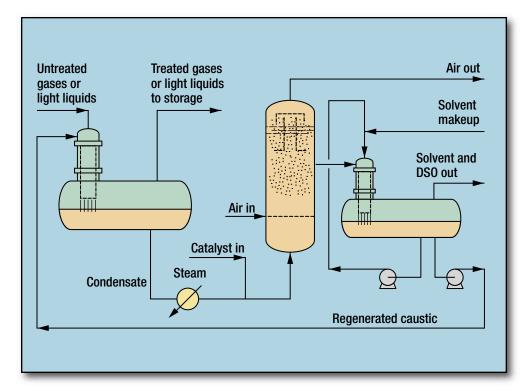
Description: The caustic phase flows along the FIBER-FILM contactor fibers, which is continuously renewed, as the wet fibers are preferentially wetted by the caustic phase in the THIOLEX process. Hydrocarbons flow through the shroud parallel to the caustic phase where the H_2S and mercaptans are extracted into the caustic phase. The two phases disengage and the caustic flows to the REGEN system. The spent caustic is regenerated using air and catalyst in the oxidizer for reuse, which converts the extracted mercaptans to disulfides. The disulfides are removed from the caustic by a FIBER-FILM contactor solvent wash system.

Economics: FIBER-FILM contactor technology requires smaller processing vessels, allowing shorter separation times and less waste generation. This saves plant space and reduces capital expenditures.

Installations: Over 200 worldwide.

Reference: Oil & Gas Journal, Aug. 12, 1985, p. 78.

Licensor: Merichem Chemicals & Refinery Services LLC.





AET NGL recovery

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Application: The patented AET Process NGL Recovery Unit technology utilizes propane-refrigeration-based absorption to recover C_2 + or C_3 + NGLs from natural gas streams.

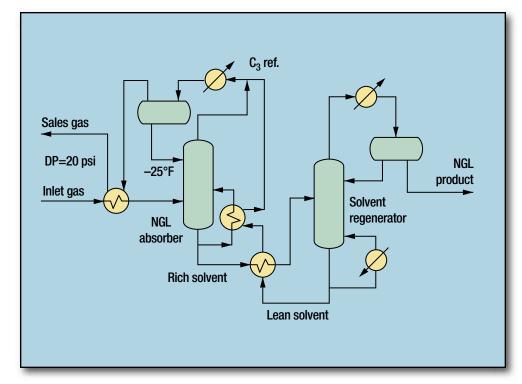
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Description: The absorbed NGLs in the rich solvent from the bottom of the NGL absorber column are fractionated in the solvent regenerator column, which separates NGLs overhead and lean solvent at the bottom. After heat recuperation, the lean solvent is presaturated with absorber overhead gases. The chilled solvent flows into the top of the absorber column. The separated gases from the presaturator separator form the pipeline sales gas.

Operating conditions: Wide operating pressure range: 200 psig to 1,200 psig feeds without inlet gas compression. Inexpensive metallurgy: Lowest temperature, limited by C_3 refrigeration, permits the use of predominantly carbon steel metallurgy. Feed pretreatment: CO_2 removal is not necessary, and glycol injection for dehydration is adequate. The AET NGL plant uses lighter (70 MW to 90 MW) lean oils. For most applications, there are no solvent makeup requirements.

Economics: Low capital and operating costs: The initial and on-going costs are lower when flexibility for ethane recovery or rejection is important. High ethane recoveries: One pass ethane recovery typically exceeds 96+%. NGL component flexibility: Online switching, from 96+% C_2 and 99+% C_3 to <2% C_2 and 98+% C_3 , with simple controls. Upgrading simple refrigeration plants: Add-on unit enhances propane recoveries, from typical 30–55% to 96+%, by processing cold separator gases. Depending upon the economics of ethane recovery, the operation of the AET NGL plant can be switched online from ethane plus recovery to propane plus recovery without affecting the propane recovery levels.



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References: *Oil & Gas Journal,* Vol. 95, No. 39, September 29, 1997, pp. 86–91.

"Upgrading Straight Refrigeration Plants for NGL Enhancement—A Follow-Up," Gas Processors Association 77th Annual Convention, Dallas, Texas, March 1998.

US Patent No. 5,561,988; US Patent No. 5,687,584.

Licensor: Advanced Extraction Technologies.



AET Process NRU

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Application: The patented AET Process Nitrogen Rejection Unit utilizes noncryogenic absorption to separate methane and heavier hydrocarbons from nitrogen containing natural gases. If desired, propane plus NGL product can also be produced.

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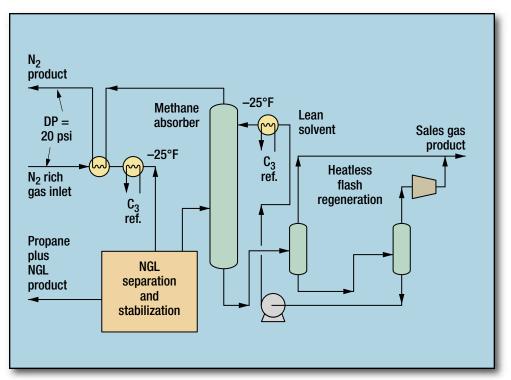
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Description: The absorbed methane and heavier hydrocarbons are flashed off from the solvent by reducing the pressure of the absorber bottoms stream in multiple steps to minimize gas compression. The separated gases leave as the sales gas product. The liquid from the proven, heatless flash regeneration step is returned to the top of the methane absorber as lean solvent. If helium is present, the overhead stream from the methane absorber is further processed in a membrane/PSA unit to produce Grade A helium, and nitrogen product is available at high pressure. For most applications, there are no solvent makeup requirements.

Operating conditions: Wide operating pressure range: 240 psig to 1,200 psig feeds without inlet gas compression. Low pressure drop for N₂: 15–30 psi is typical and suitable for noncryogenic helium production and N₂ reinjection. Inexpensive metallurgy: Lowest temperature, limited by C₃ refrigeration, permits use of predominantly carbon steel metallurgy. Feed pretreatment: CO₂ removal is not necessary; glycol injection for dehydration is adequate.

Economics: Low, capital operating costs: When high flexibility for inlet gas flow and composition is desired, the initial and ongoing costs are lower. High methane recoveries: One pass methane recovery typically exceeds 98+%. Low nitrogen content sales gas: Sales gas product at <2 mol% N₂. Wide feedstock flexibility: For constant inlet gas flow, inlet composition can vary between 15 mol% and 50 mol% N₂ without impacting sales gas. Short construction schedule: Excluding the compressor and membrane/ PSA delivery, expected to be 4–8 months based on unit capacity.

Installations: Two commercial.



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References: "Noncryogenic N₂-rejection process gets Hugoton field test," *Oil & Gas Journal,* May 24, 1993.

Gas Research Institute Topical Report GRI-93/0448, "Field Test Performance Evaluation of the Mehra Process for Nitrogen Rejection from Natural Gas," February 1994.

US Patent Nos. 4,623,371; 4,680,042; 4,832,718; 4,883,514; 5,224,350; 5,462,583; 5,551,972.

Licensor: Advanced Extraction Technologies.



Nitrogen recycle LNG liquefier

HYDROCARBON

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Application: Liquefaction of natural gas for mid-range capacities of 5 million to 30 million scfd (~5,500 Nm³/hr to 33,000 Nm³/hr) for peak shaving or product distribution applications.

process categories

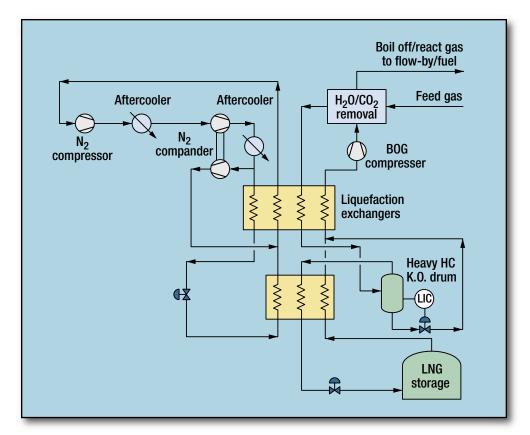
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Description: Natural gas is pretreated to remove water and carbon dioxide (CO₂). A fraction of the pretreated natural gas is used to regenerate the CO₂/water (H₂O) removal system. The remaining gas is cooled and the heavier hydrocarbons (HC) removed in a knock-out (KO) drum or multi-stage separation device. The resulting vapor product is then condensed to produce LNG. Boil-off gas (BOG) from the LNG storage and the collected heavier HCs are warmed in the exchangers and mixed with the CO₂/H₂O-laden regeneration gas. The resulting gas stream is then returned to the feed gas supply or a low-pressure fuel system.

Cooling is provided by a nitrogen (N_2) recycle refrigeration system, which utilizes an N_2 recycle compressor, an N_2 compander and a cold box which houses the liquefaction heat exchangers. N_2 is compressed in the N_2 recycle compressor and cooled in an aftercooler. A compander incorporates a compression stage and an expansion stage on a single shaft. N_2 dropping from high to low pressure across the expander wheel provides refrigeration and generates rotational force which is absorbed by the compressor wheel providing a portion of the total nitrogen compression required. A portion of the N_2 stream is expanded in the compander, providing part of the refrigeration requirement. The remaining N_2 is expanded with an expansion valve and provides the rest of the refrigeration required for liquefaction.

There are many variations in the specific configuration of the N_2 refrigeration cycle (pressures, number of expanders, expander arrangements, etc.). The configuration is driven by the need to develop the most cost-effective solution for the plant size, final refrigeration temperature required and project-specific economic evaluation criteria.

Economics: N₂ recycle plants in this size-range are inherently lower capital cost than competing mixed refrigerant technologies, while providing comparable energy efficiency.



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Installations: Two units in operation and others in development.

Reference: Schneller, G. J., J. H. Petrik and J. G.Steimer, "Addition of a nitrogen cycle LNG liquefaction system at the Holtsville LNG peakshaving facility," American Gas Association Operations Conference, Orlando, Florida, April 2003.

Licensor: Air Products and Chemicals, Inc.



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Gas Processes 2006

AP-X LNG process equipment and technology

Application: Natural gas liquefaction.

Products: Liquefied natural gas (LNG) at required heating value and quality specifications, with integrated LPG product recovery as necessary.

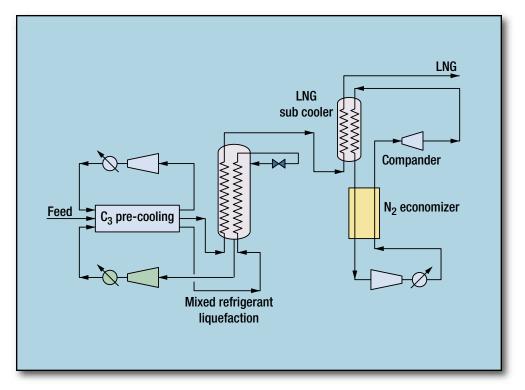
Description: The AP-X process is a hybrid of the propane pre-cooled mixed refrigerant cycle for pre-cooling and liquefying natural gas and a nitrogen gas compressor/expander cycle for sub-cooling LNG. The process achieves high efficiency and low production cost by using both cycles to their best advantage.

Propane is used to provide cooling to a temperature of about – 30°C. The feed is then cooled and liquefied by mixed refrigerant, exiting the main cryogenic heat exchanger (MCHE) at a temperature of about –120°C. Final LNG sub-cooling is done using a simple, efficient nitrogen expander loop instead of mixed refrigerant. Other embodiments include a dual MR version where a mixed refrigerant loop replaces propane for pre-cooling.

The power split between pre-cooling, liquefaction and sub-cooling refrigeration duties is flexible, and can be manipulated by changing the temperature range of the three refrigerant loops. This feature allows considerable flexibility in matching compressor driver sets to large-frame industrial turbines, electric motors or combinations of both.

Economics: The AP-X process meets industry demand for the economies of scale that can result from larger single-train capacities. Train capacities up to 10 million tpy are feasible using existing compressor and driver frame sizes, without duplicate/parallel compression equipment, and using a single main cryogenic heat exchanger. The unit cost of LNG production is reduced significantly due to the economies of scale that are achieved with the AP-X process.

Installations: Six trains currently under construction, each with capacity



of approximately 7.8 million tpy of LNG.

Reference: US Patent 6,308,521, "Hybrid cycle for the production of liquefied natural gas."

Licensor: Air Products and Chemicals, Inc.



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Gas Processes **2006**

CoP LNG Process

(formerly Phillips optimized cascade LNG process)

Application: Large base-load natural gas liquefaction facilities with optional capability for high ethane, propane or mixed LPG recovery.

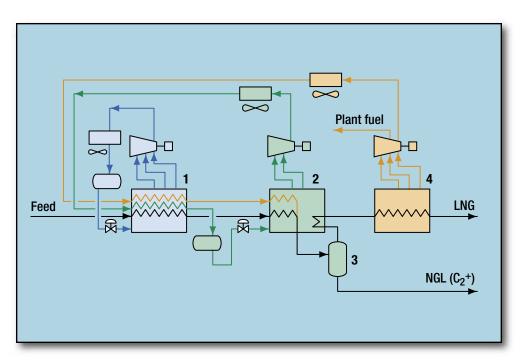
Feedstock: Naturally occurring hydrocarbon gas pretreated to remove contaminants such as moisture, hydrogen sulfide (H_2S), carbon dioxide (CO_2), mercaptans and mercury.

Description: The process uses three predominantly pure component refrigerants: propane, ethylene and methane. The first refrigerant is a multiple-stage closed-loop propane system (1). The second is a closed-loop ethylene or ethane system (2) consisting of two or more stages. A combination of brazed aluminum and core-in-kettle exchangers are used for heat exchange. Feed is routed successively through each stage of propane and ethylene. Air or cooling water removes process heat and condenses propane, while propane removes heat and condenses ethylene.

Heavier products are typically removed (3) after one or more stages of ethylene refrigeration. Fractionation design is highly dependant on feed composition and desired product recovery. Efficient designs with high ethane and propane recovery rates are available. The resulting methane-rich feed is routed to methane refrigeration.

Methane refrigeration (4) is a multiple-stage open- or closed-loop system. A recycled methane stream is used to help balance refrigeration loads and improve efficiency. Propane and ethylene are used to remove process heat. With the open-loop configuration, fuel gas is drawn off to prevent inerts from building in the refrigerant. For feeds with high nitrogen or helium, an inerts rejection system is integrated into the design.

Economics: The CoP LNG process is well-established, reliable, efficient and low-cost. Overall facility EPC costs utilizing the technology have been at or less than \$200 metric tpy of capacity. The two-in-one design allows the plant to operate with very high availability and reliability. Tur-



bine/compressors can be shut down for maintenance or replacement, while the plant continues to operate. Thermal efficiency of the process is high with designs that exceed 93%, including utilities, feed pretreatment and the remaining facility. Large train sizes of over 7.5 million metric tpy are available in multiple turbine/driver configurations with even larger train sizes in development.

Installations: ConocoPhillips brought its first installation online in Kenai, Alaska, in 1969. In more than 36 years of continuous operation, Kenai has never missed a product shipment, recording plant availability in excess of 95% and refrigeration gas turbine reliability in excess of 99%. The company began licensing the CoP LNG process technology in 1993. Since then, six trains using the technology have been successfully brought online in Trinidad and Idku, Egypt, and additional plants are under construction in Darwin, Australia, and Equatorial Guinea. Other projects are invarious stages of commercial development. ConocoPhillips Continued ▼

CoP LNG Process, continued

and Bechtel have entered into a global LNG collaboration providing design, construction, commissioning and startup for the process. The collaboration has established new benchmarks for competitive capital and operating costs, and optimal project schedules.

Licensor: ConocoPhillips Co.; CoP LNG services are also provided by Phillips LNG Technology Services Co. and Bechtel Corp. via a collaborative relationship with ConocoPhillips Co.



CRYOMAX MRE (multiple reflux ethane recovery)

process categories

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Application: A cryogenic process for gas fractionation to recover C_2 + hydrocarbons from natural gas. With this process, more than 95% of the ethane can be extracted from natural gas. High efficiencies are obtained through a multiple reflux concept associated with a turbo-expander. Multi-stream plate-fin heat exchangers increase efficient heat integration of the process.

Description: The high-pressure, dry feed gas at 25°C, 70 bars is cooled to -40°C in E1 and enters V1 where the liquid and gas are separated. The cold high-pressure gas is divided in two streams—the main cut (85%) is sent to the expander and to the demethanizer C1 that operates at 30 bars. The small segment (15%) is liquefied and sent as second reflux to C1.

The liquid pressure is reduced to 50 bars, and the liquid is partially vaporized in E1. Liquid and vapor are separated in V2. The vapor is lique-fied in E2, used as third reflux, and liquid is sent to C1.

The demethanizer overhead is reheated and compressed to sales gas pipeline specifications. A portion of the stream (10%) is recycled, cooled, liquefied and sent as first reflux. Approximately 99% ethane recovery can be reached when CO_2 content of feed gas is low.

Economics: Ethane production cost is 20% less than for a conventional process.

Installations: Locations include France, US, Venezuela, Mexico and Qatar.

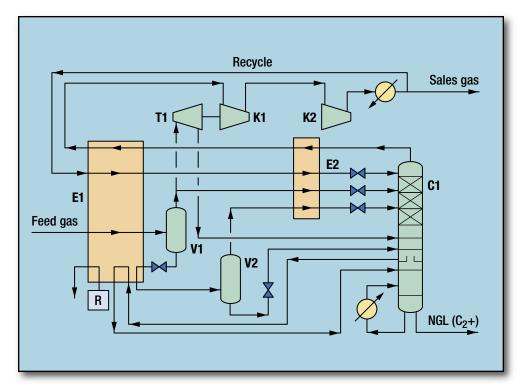
Reference: US patents 4,689,063; 5,566,554 and 6,578,379B2.

Licensor: Technip.

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CRYOMAX DCP (dual-column propane recovery)

process categories

process index

Application: A cryogenic process for gas fractionation to recover C_{3+} hydrocarbons from natural gas. With this process, more than 98% propane is extracted from natural gas. High efficiencies are achieved with a dual-column system associated with a turbo-expander. Multi-stream plate-fin exchangers increase efficient heat integration.

Description: The high-pressure dry feed gas at 25°C, 70 bars is cooled to -30°C in E1 and enters V1 where liquid and gas are separated. The cold high-pressure gas is expanded to 30 bars in expander T1, and the resulting stream feeds the purifier C1.

Liquid from V1 is sent to the purifier bottom. The liquid from the purifier is pumped to 33 bars and is reheated to 20°C to feed the deethanizer. The deethanizer C2 produces a vapor distillate that is ethane-rich. This stream is liquefied in E1 and sent to C1 as reflux. The treated gas at 30 bars is reheated and compressed to sales-gas pressure. Approximately 99.5% propane recovery can be reached when propane value is high.

Economics: Propane production cost is approximately 20% less than that for a conventional process.

Installations: Locations include Russia, Qatar, Libya and UAE.

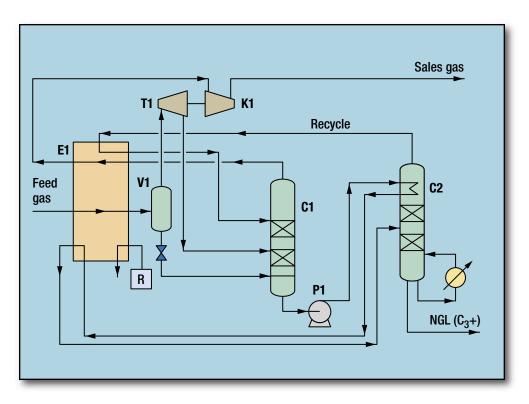
References: US Patents 4,690,702 and 5,114,450.

Licensor: Technip.

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High-Pressure Absorber—HPA

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Application: Ethane, propane and heavier hydrocarbons recovery from natural gas feed streams using a cryogenic turboexpander process. High propane recovery (>99%) is achievable. Residue compression is minimized by using a high-pressure absorber (HPA).

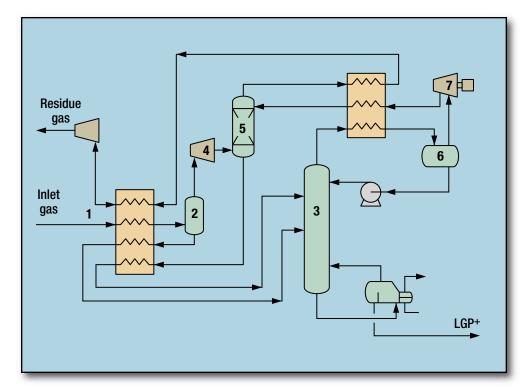
process categories

Description: Raw feed gas is treated to remove impurities such as water that would prevent cryogenic processing. Clean, dry and treated feed gas (1) is cooled against cold process streams and sent to the warm separator (2) for phase separation. Liquid from the separator is preheated against warmer streams and sent to the deethanizer (3) as bottom feed. Vapor leaving the warm separator is sent to a turboexpander (4) for isentropic expansion.

The two-phase stream exiting the expander is sent as bottom feed to a high-pressure absorber (5). Liquid exiting the absorber bottom is preheated against warm process streams and sent to the deethanizer as top feed. The deethanizer produces C_3 + liquid at the bottom and a C_2 top stream. The tower is generally provided with an external heat source for bottom reboiling.

Vapor from the tower top is partially condensed and sent to a reflux accumulator (6). Liquid is pumped as reflux, while vapor leaving the accumulator is compressed (7), cooled, partially condensed and sent to the absorber as top feed. The HPA process can also be used to recover ethane and heavier components. Ninety percent ethane recovery is achievable.

Operating conditions: This is very efficient when feed is available at high pressure. The absorber column is run at a high-pressure to minimize residue compression, while the deethanizer is run at a lower pressure to keep the tower from critical conditions. Due to this decoupling, the scheme is easily able to process a range of feed gas pressures while minimizing residue compression and maintaining stable deethanizer operation. Tower pressure decoupling in the ethane recovery mode, and



running the absorber at a higher pressure than the demethanizer, has similar savings in residue compression as with propane recovery.

Licensor: Randall Gas Technologies, ABB Lummus Global Inc., US Patent 6,712,880.



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Gas Processes 2006

Liquefin

Application: Natural gas liquefaction (LNG) process.

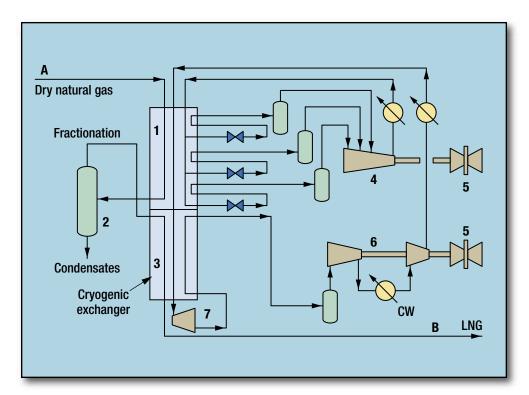
Description: Liquefin process—Dry natural gas (A) enters the liquefaction train's pre-cooling section (1) where it is cooled between -50° C and -80° C (-60° F and -110° F). The heat is exchanged with a mixed refrigerant in a bank of brazed aluminum plate-fin heat exchangers (PF-HEs). The cooled feed stream is then sent outside the liquefaction train to fractionator (2) for condensate removal. The gas returns to the cryogenic exchanger and enters the cryogenic section (3) where it is lique-fied by heat exchange in compact, energy-efficient PFHEs with a second mixed refrigerant and leaves the cryogenic exchanger as LNG (B).

Pre-cooling refrigerant system (4)—Using mixed refrigerant reduces the feed-gas temperature to a much lower level than can be achieved with propane refrigerant. This allows the pre-cooling power requirement to be balanced with that of the cryogenic section so that two identical drivers (5) operating at optimum efficiency can be used, thus lowering investment, maintenance and operating costs.

Cryogenic refrigeration system (6)—The mixed refrigerant gas entering the pre-cooling section is completely condensed by the time it leaves the cryogenic section without using separation equipment. After leaving the cryogenic section, the refrigerant is expanded (7) and re-enters the cryogenic section where the process gas and cryogenic refrigerant are condensed.

Using two mixed-refrigerant systems and modular PFHEs in a large single train has lower investment and operating costs than systems involving single-component refrigerants or multiple cooling trains feeding a common liquefaction exchanger. Because the pre-cooling and liquefaction sections comprise several parallel modules, single trains of any size—e.g., 8 million tpy—can be built. Proven extensively, the PFHEs are available from several vendors, which has a very positive effect on price and delivery time.

Economics: Detailed studies by international petroleum and E&C com-



panies comparing conventional 4.5 MMtpy to 8 MMtpy propane plus mixed refrigerant liquefaction trains with Liquefin LNG installations have shown a 15–20% specific investment cost advantage for the Liquefin train.

References: Fischer, B., F. Hughes, P-Y. Martin and J. Pigourier, "Optimizing LNG-GTL Synergies: Cost and CO₂ Emission Reduction," 5th Doha Conference on Natural Gas, March 2005, Doha.

Fischer, B. and M. Khakoo, "Platefin Heat Exchangers—An Ideal Platform for LNG Process Innovation," Gastech 2002.

Licensor: Axens.



LNG Dual Expander Cycle

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Application: LNG production for either offshore or onshore.

Description: Pretreated and dehydrated natural gas (1) is cooled in cold box (2) and then expanded to low pressure via an expansion valve or liquid expander (3) and sent to storage as LNG. Refrigeration for liquefaction is obtained by continuous expansion of gases through two independent cycles, one using methane (4) [mostly the same gas being liquefied] and the second with nitrogen (5). The methane cycle works in the warmer end; while nitrogen provides refrigeration on the cold end.

process categories

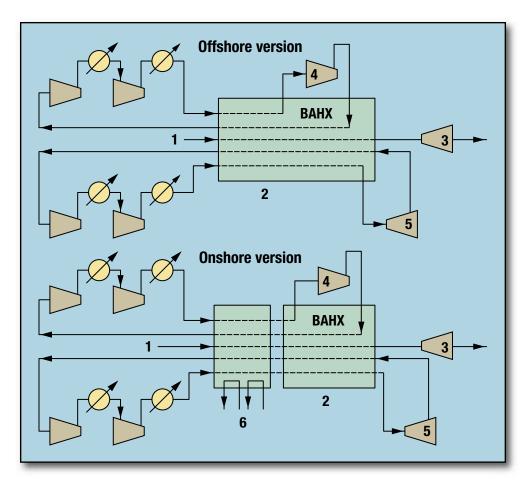
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When superimposed, these two cycles act like a binary system. This process is a unique candidate for offshore opportunities due to the refrigerants always being in a gas phase. A propane pre-cooling step can be added at the process's front end (6), to achieve a high-efficiency process for onshore base load production.

Operating conditions: Feed gas should be above 800 psig. For associated gases, LPG and condensate recovery is integrated with the same process. LNG is produced at –260°F.

Efficiency: Depending on gas composition, energy consumption varies between 11–16 kW/ton LNG/day.

Licensor: Randall Gas Technologies, ABB Lummus Global Inc., US Patent 6,412,302.





LNG end flash MLP (maxi LNG production)

HYDROCARBON

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Application: A process to increase capacity of LNG plants and minimize fuel gas production.

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Description: LNG from the main cryogenic heat exchanger at -140° C, 40 bar is expanded in T1 turbine to produce electric power. It is mixed with liquefied fuel gas recycle before entering the LNG flash drum V1 at 1.2 bars. The LNG is pumped to the storage tank through P1.

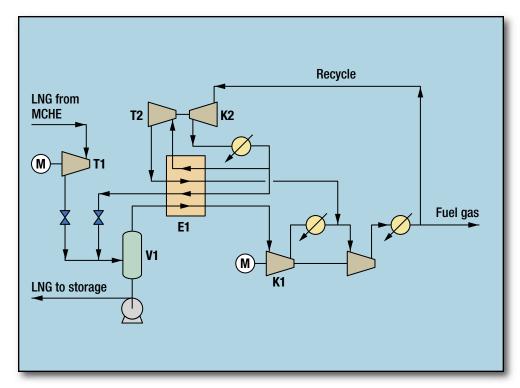
Cold flash gas is reheated to -30° C and compressed to 30 bar, thus producing fuel gas for gas turbines in K1. Part of the fuel gas is further compressed to 40 bars in K2. A portion of this stream is cooled to -80° C in E1, expanded to 8 bars at 130°C in T2. It is then reheated to 30°C and sent to the fuel gas compressor as a side stream. The second stream portion is liquefied and subcooled in E1 down to -155° C.

Economics: Additional LNG production investment of about \$60/tpy for additional LNG.

Installations: None with turbo-expander T2/K2.

Reference: LNG 13 Conference, Seoul, Paper PS2-1, US Patent 6,898,949.

Licensor: Technip.





LNG plants

HYDROCARBON

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Application: Liquefaction of natural gas for plant capacities ranging from small peak shaving applications, up to mid-size plants (4,000 tpd, 1.4 million tpa) using a mixed refrigerant cycle.

process categories

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Products: Liquefied natural gas (LNG) at atmospheric pressure. Natural gas liquids (NGL) on larger facilities.

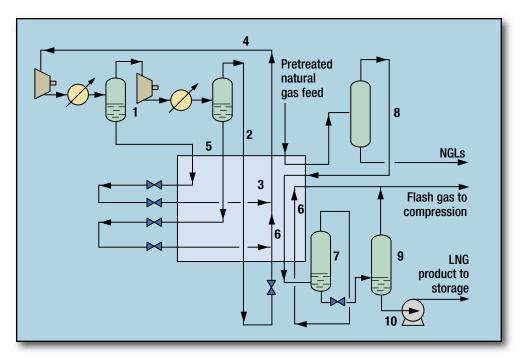
Description: Pretreated natural gas is cooled and condensed by a mixed-refrigerant cycle. The refrigerant consists of a blend of nitrogen and hydrocarbons from methane through pentane.

The refrigerant is compressed by a two-stage machine (1) (normally a gas turbine-driven centrifugal type depending upon plant capacity). The high-pressure mixed refrigerant (2) is cooled in the main exchanger (3), which normally consists of multiple, brazed aluminum plate-fin heat exchangers, against returning low-pressure mixed refrigerant (4). The subcooled refrigerant is then let down in pressure and evaporated to provide cooling. Liquids from refrigerant compression are cooled separately (5) in the main exchanger, let down in pressure and evaporated to provide increased process efficiency.

The natural gas is cooled (6) in the main exchanger prior to entering a hydrocarbon knockout pot (7) to remove components which would otherwise freeze in the downstream process. On large plants, the knockout pot may be replaced by a demethanizer column. NGLs recovered at this stage may be processed and used to provide refrigerant makeup. The natural gas leaving the knockout pot re-enters (8) the main exchanger and is condensed and subcooled against low-pressure refrigerant.

The subcooled LNG then enters a two-stage flash system (9) where it is let down in pressure before being pumped (10) to storage at nearatmospheric pressure. The LNG flash gas is fed to a flash gas compressor system to be used as fuel.

Economics: The mixed refrigerant cycle is often the most cost-effective process for LNG production, combining reasonable initial cost with low power requirements. The use of plate-fin heat exchangers allows the



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plant to be designed with high efficiency. For a 1.4 million tpy facility, a total installed cost of \$300 per tpy is feasible.

For small (peak-shaving) installations, expander cycles using nitrogen or methane may be cost-effective. Expander cycles can also be the technology of choice for offshore applications. For high efficiency on base-load installations, the cascade cycle, which uses multiple levels of pure refrigerants, can be the optimum choice.

Installations: Fifteen total, in partnership (six mixed refrigerant, nine expander plants).

Reference: Finn, A. J., G. L. Johnson and T. R. Tomlinson, "Developments in natural gas liquefaction," *Hydrocarbon Processing*, April 1999, pp. 47–59. European Patent 0090108.

Licensor: Costain Oil, Gas & Process Ltd.



LNG vaporization

HYDROCARBON

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Application: To efficiently vaporize liquefied natural gas (LNG) using heat-integrated ambient-air technology that does not require seawater or fired-heating of the LNG. Primary application includes LNG import terminals.

process categories

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Product: Sales Gas from the vaporized LNG.

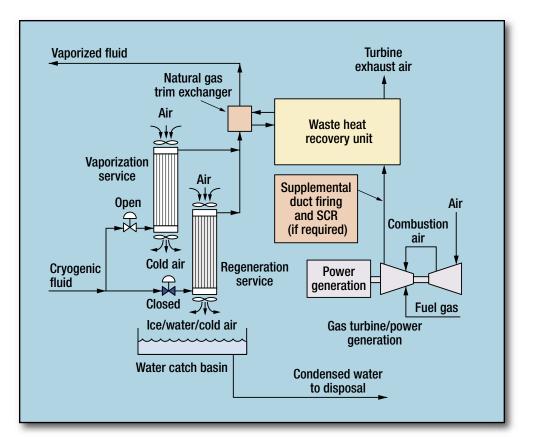
Description: In many climates, ambient-air temperature varies dramatically season to season, day to night, which makes vaporizing LNG using ambient air a problem. The integration of waste heat from power generation or other heat source with ambient-air vaporization enables using the ambient-vaporization technology in winter conditions while maintaining the desired gas outlet temperature. In addition, by maintaining a minimum proper approach temperature between the vaporized natural gas and ambient air, the required vaporization surface area is greatly reduced. **Result:** The technology is applicable to offshore as well as onshore installations.

The specialized waste-heat recovery system has a thermal efficiency similar to a submerged combustion vaporizer but uses the exhaust gas from a combustion turbine typically associated with an offshore LNG vaporization terminal. Significant quantities of additional waste heat are available by duct-firing the turbine exhaust gas to make up shortfalls in the natural gas outlet temperature. No external stand-alone fired heaters are required.

Installations: No commercial installations have been completed. Several units have been designed and await project approval.

References: US Patent Application, "Air Vaporizer," Rosetta, et al., "A fresh approach to LNG vaporization as ambient air vaporization technology is integrated with waste heat recovery," *LNG Journal*, October 2005.

Licensor: Black & Veatch Corp.





LNG-Pro

HYDROCARBON

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Application: To produce liquefied natural gas for transportation or storage. The process is adequate for base-load facilities, as well as for peak shaving units. The design is highly modularized, making it appropriate for remote sites or offshore applications. It is also a viable option to monetize stranded gas reserves.

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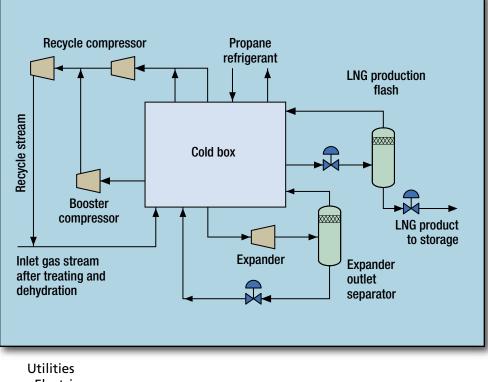
Description: This process uses a hybrid technical approach for the liquefaction of natural gas. Specifically, it is a propane pre-cooled turboexpander cycle. After being treated to remove contaminants and water that will affect the cryogenic process conditions, the feed gas is liquefied in a cold box. A side stream of the inlet gas is expanded to low pressure to generate refrigeration. The expanded gas is then sent to the cold box to supply refrigeration, and is boosted to a medium-pressure level. It is then recycled to the front end of the plant. The liquefied gas stream is expanded in a flash vessel or series of flash vessels, depending on product specifications. The liquid product is LNG, which is sent to storage. The flashed gas is sent back to provide refrigeration, and is then recycled to the front end of the unit via recycle compression. This recycle stream becomes a supplementary refrigeration stream.

This process scheme achieves energy consumption comparable with the world-class base load facilities. Energy usage is within 0.19 to 0.25 hp/lb of LNG product depending on gas sources and compositions.

Operating conditions: Ample range of pressures, temperatures and compositions. Depending on the inlet gas pressure, an inlet gas compressor could be required, but its influence is minor on energy consumption.

Performance index

	Relative hp/lb LNG
Cascade refrigeration	1.41–1.64
Mixed refrigerants	1.15–1.4
Turboexpander cycle	1
High-efficiency cycles	0.87–1.15



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Electric power	
Recycle compr.	77%
Refrig. compr.	13%
Others	10%
Cooling duty	
Recycle compr.	60%
Booster aftercooler	11%
Refrig. condenser	29%
Fuel gas usage	
Power generation	~6%

Reference: US Patent 5,755,114.

Licensors: Randall Gas Technologies, ABB Lummus Global Inc.

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LPG recovery

HYDROCARBON

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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.

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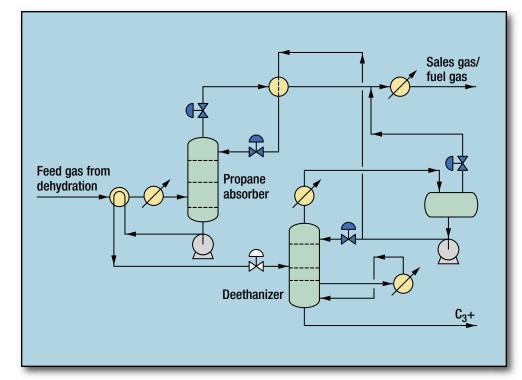
Description: Low-pressure hydrocarbon gas is compressed and dried before being chilled by cross-exchange and propane refrigerant. The chilled feed stream is then contacted with a recycled liquid ethane stream in the propane absorber. The absorber bottoms is pumped to the deethanizer. The tower overhead 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 horsepower.

Installation: First unit in operation for Pertamina. Other units in various stages of evaluation, engineering and licensing.

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

Licensor: Black & Veatch Corp.





MCR process equipment and technology

Application: Natural gas liquefaction.

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Products: Liquefied natural gas (LNG) with optional LPG production.

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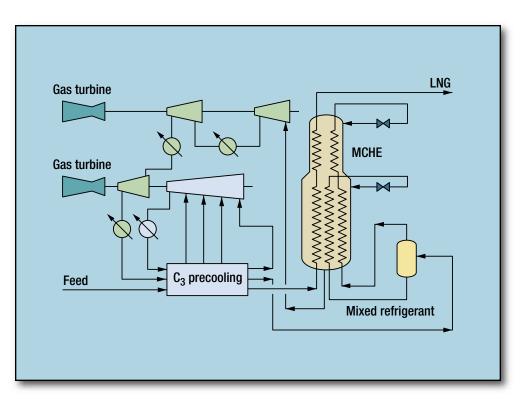
Description: The MCR process is composed of a pre-cooling step followed by liquefaction using a mixed component refrigerant refrigeration system. The most common application of the MCR process is the propane pre-cooled mixed refrigerant (C_3 -MR) cycle. A multi-stage propane refrigeration system provides pre-cooling for the mixed refrigerant and feed natural gas. Feed gas is then liquefied and sub-cooled in the MCR main cryogenic heat exchanger (MCHE) against the mixed refrigerant.

Propane and mixed refrigerant refrigeration systems are specially designed for optimum process efficiency while using proven refrigerant compressors. Large capacity trains over 5 million tpy can be designed using the Air Products Split MR compressor/driver arrangement. In this arrangement, the available power of each gas turbine driver and its helper motor/turbine is fully utilized for LNG production with a minimum number of refrigerant compressor casings. Pre-cooling can also be accomplished using a separate mixed refrigerant or ammonia absorption refrigeration system where warranted by site-specific conditions.

The process is extremely flexible with regard to feed gas characteristics, ambient conditions, product slate, turn-down operation and other production requirements. The system can be designed with steam turbine, industrial gas turbine and/or electric motor drivers.

Economics: The MCR process is highly efficient and cost-effective. Installations using the MCR process and main cryogenic heat exchanger with the Split MR compressor/driver arrangement are currently in operation with capacities of up to 5 million tpy per train.

Installations: Air Products' MCR processes are the most widely used LNG cycles in the world. Over 60 LNG trains using the MCR process are in



company index

operation or under construction worldwide.

Reference: Spilsbury, C., et al., "Optimising the LNG liquefaction process," *LNG Journal*, January/February 2005.

Licensor: Air Products and Chemicals, Inc.



Natural gas liquids (NGL) recovery

HYDROCARBON

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Application: High recovery process for NGL (ethane and heavier) using a turbo-expander scheme. The process can be operated in an ethane rejection mode and can be easily modified to a high propane (and heavier) recovery process.

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Products: Sales or residue gas meeting or exceeding pipeline or liquefied natural gas (LNG) plant feed specification, NGL suitable for export to pipeline or fractionation.

Description: Natural gas from pipeline or gas wells is conditioned (1) to remove acid gas if required, carbon-dioxide (CO₂) primarily, and dehydrated before feeding the cryogenic plant. Feedgas is cooled in a combination of brazed aluminum heat exchangers for an optimal refrigeration recovery. The cooled gas, after separation of liquids in the cold separator (2), is expanded to low pressure in turbo expander (3) to extract work from the high pressure feedgas, which is used to drive the booster compressor (6). The expander feeds the NGL fractionator (4), a packed column with side-reboiling to maximize product recovery and reduce overall horsepower requirement.

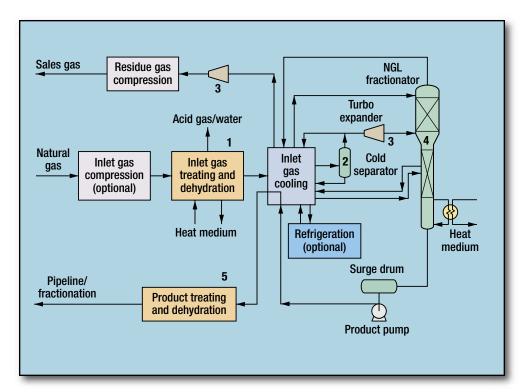
The recovered liquids are treated to remove CO_2 and sulfur species if present before fractionation or routing to pipeline. Product treating is more typical for ethane plus recovery and less applicable for a propane plus recovery process.

Utilities: *Heat medium* (closed loop hot oil): used for reboiling and amine/glycol/molesieve regeneration. It can be eliminated for certain applications.

Propane refrigeration (optional): typical for a rich feed gas.

Installations: More than twenty plants worldwide, capacity ranging from the low 100 MMSCFD to as much as 800 MMSCFD.

Supplier: CB&I Howe-Baker.





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Gas Processes 2006

NGL from LNG

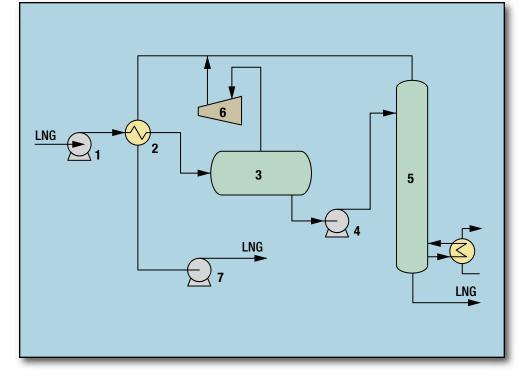
Application: To separate natural gas liquids (NGL) from liquefied natural gas (LNG) for Btu control of LNG and to enhance product value. Primary application is for LNG import terminals.

Product: NGL stream containing ethane and heavier hydrocarbons. Can be used to produce light (ethane plus), medium (propane plus) or heavy (butane plus) product stream as desired for a specific project.

Description: LNG is fed from storage to the process unit. Liquid feed pressure is increased with the feed pump (1) to proper pressure. Feed is warmed in the main exchanger (2) against cold gas. The warmed feed stream is flashed (3) to separate the liquid from the vapor. The liquid is pumped (4) to a demethanizer (5) where the NGL is separated. The vapor from this demethanizer joins the flash vapor that has been compressed (6). This stream is recondensed (2) to become LNG product, which is pumped to sales pressure and sent to LNG vaporizers. Internal operating parameter adjustments in the process unit allow the NGL stream recovery to fit a given application. Varying these parameters allows production of light or heavy NGL streams. A wide range of LNG feedstocks can be fed to a process unit and have the NGL successfully removed. Ethane recoveries of 90% are possible, as well as near-complete ethane rejection back into the LNG product.

Installations: No commercial installations have been completed. Several units have been designed and await project approval.

References: US Patent 6,564,579, "Method for Vaporizing and Recovery of Natural Gas Liquids from Liquefied Natural Gas." McCartney, "Gas Conditioning for Imported LNG," Gas Processors Association Annual Convention, San Antonio, 2003.





Licensor: Black & Veatch Corp.

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Gas Processes 2006

NGL recovery

Application: Deep recovery of NGL from natural gas with propane recovery as high as 99%. For ethane extraction, ethane recovery can be over 95%, with a propane recovery of essentially 100%.

Products: Sales gas and stable NGL.

Description: Dry feed gas (1) at a pressure of typically 70 bar is cooled and partially condensed in the main gas-gas exchanger. The resultant two-phase stream is separated (2) with the vapor being work-expanded in a turbo-expander (3). The two-phase expander exhaust stream is mixed with liquid from the separator and passed to a high-pressure wash column (4).

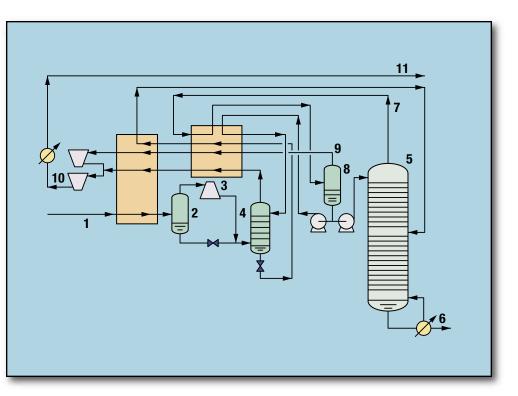
Liquid from the wash column base is reheated and fed to the de-ethanizer (5). The bottoms (6) from the de-ethanizer form the NGL product. The de-ethanizer overheads (7) are cooled and condensed and passed to a separator (8). Liquid from this separator is used to reflux both the de-ethanizer and the high-pressure wash column.

The vapor from the separator (9) is lean in NGL components. It is reheated before being passed to the sales gas compressor (10). Vapor from the wash column is reheated, blended and compressed to give the sales gas product (11).

Operating conditions: Very high propane recovery can be achieved by optimizing thermal integration with multi-stream heat exchangers and optimizing turbo-expander conditions including dual expanders for dense phase processing. Increased energy integration enables NGL recovery to be increased to very high levels with similar power consumption as conventional technology.

Installations: Twelve NGL recovery plants, with capacities up to 11 million Sm³/d.

References: Finn, A. J., T. R. Tomlinson and G. L. Johnson, "Design, equipment changes make possible high C₃ recovery," *Oil & Gas Journal*, Jan. 3, 2000, p. 37.



US Patent 6,581,410 (propane-plus) US Patent 6,363,744 (ethane-plus)

Contributor: Costain Oil, Gas & Process Ltd.

NGL-MAX

HYDROCARBON

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Application: Ethane/ethylene and heavier hydrocarbons recovery, from natural gas or refinery off gas feed streams, using a cryogenic turboex-pander process. High ethane recovery (99%) is achievable with essentially complete C_3 + recovery. Lower ethane recoveries are possible with the same process while maintaining C_3 + recovery in the 99% range.

process categories

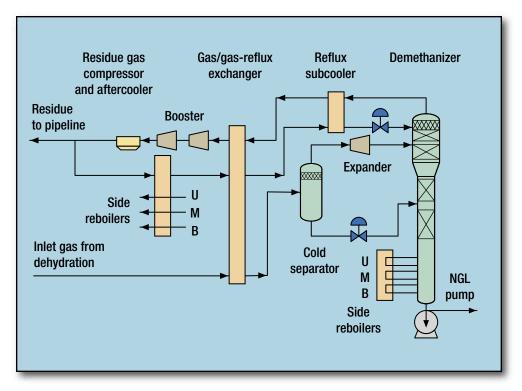
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Description: Raw feed gas that is to be processed cryogenically is treated to remove impurities such as water that would prevent cryogenic processing. Acid gas removal may be needed, if concentration is large enough to produce freezing in the plant's cryogenic section.

Clean, dry and treated feed gas (1) is cooled against cold residue gas and against cold demethanizer streams. Feed is then sent to the cold separator (2) for phase separation. Liquid (3) from the separator is sent to the demethanizer tower (4) as bottom feed. Vapor leaving the separator is split into two. The larger stream is sent to the expander (5) for isentropic expansion and sent as feed to the demethanizer. The smaller stream (6) from the cold separator is cooled, partially condensed and sent to a reflux separator (7). Liquid (8) from the separator is sent to the demethanizer as feed. Vapor stream (9) leaving the vessel is condensed and sent as second feed to the demethanizer.

The demethanizer produces at the top, a methane and lighter stream, and at the bottom a C_{2+} stream containing the desired components to be recovered. Cold residue gas (10) is warmed up in exchangers and boosted in pressure by a compressor (11). The warm and intermediate pressure residue gas is boosted to pipeline pressure by residue compressors (12) and sent for further processing. A part of the high-pressure residue gas (13) is cooled, condensed and sent to the demethanizer as top feed. This top feed is very low in C_{2+} thereby enabling very high C_{2+} recovery levels.

Operating conditions: Due to the presence of two reflux streams, the scheme is able to process feed gases with a wide range of liquid content in the feed gas. The scheme requires the demethanizer tower to run



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at a somewhat higher pressure than a single tower system. This higher pressure will make the process more CO_2 tolerant, and hence simplify or eliminate inlet gas treating.

Licensor: Randall Gas Technologies, ABB Lummus Global Inc., US Patent Pending.



NGL-Pro

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Application: To recover ethane and higher components from natural gas streams. This process is especially adequate with lean and semi-lean gas streams.

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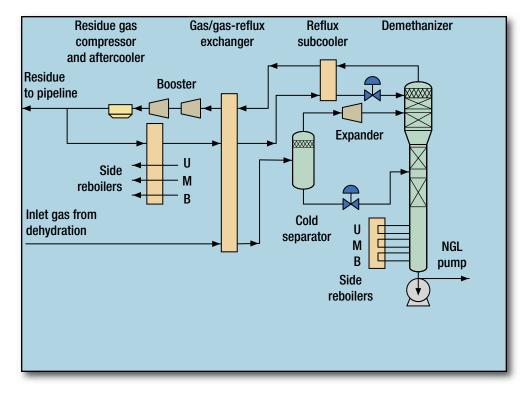
Description: The inlet gas is treated and conditioned to remove contaminants and water that cannot be processed cryogenically. The gas is partially condensed to knock out heavy hydrocarbons, and is sent to a cold separator. Removed liquids are sent to the demethanizer column, while the gas is sent to a turboexpander. The stream from the expander is sent to the demethanizer column. To increase the recovery level, a recycle/reflux stream is taken from the residue gas and is precooled, extracting refrigeration from the demethanizer column. The reflux is finally subcooled and sent to the top of the demethanizer.

This process is also adapted for the rejection of ethane and production of LPG and heavier streams. Recoveries for ethane product are 95+%. Energy consumption is between 50 and 70 hp/million scfd depending on gas conditions.

Operating conditions: Ample range of pressures and temperatures. Hydrocarbon liquid content less than 3.5 gal/thousand scf.

Reference: U.S. Patent 5,890,377.

Licensors: Randall Gas Technologies, ABB Lummus Global Inc.





Nitrogen recycle LNG liquefier

HYDROCARBON

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Application: Liquefaction of natural gas for mid-range capacities of 5 million to 30 million scfd (~5,500 Nm³/hr to 33,000 Nm³/hr) for peak shaving or product distribution applications.

process categories

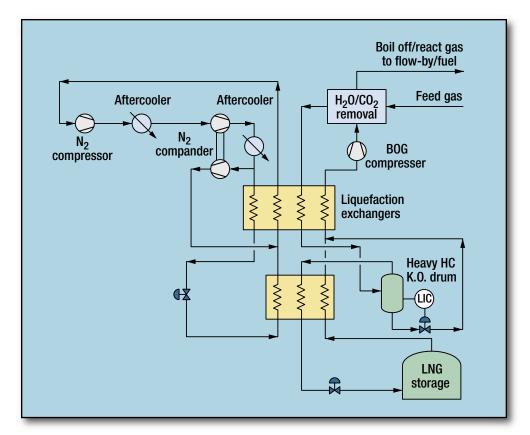
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Description: Natural gas is pretreated to remove water and carbon dioxide (CO₂). A fraction of the pretreated natural gas is used to regenerate the CO₂/water (H₂O) removal system. The remaining gas is cooled and the heavier hydrocarbons (HC) removed in a knock-out (KO) drum or multi-stage separation device. The resulting vapor product is then condensed to produce LNG. Boil-off gas (BOG) from the LNG storage and the collected heavier HCs are warmed in the exchangers and mixed with the CO₂/H₂O-laden regeneration gas. The resulting gas stream is then returned to the feed gas supply or a low-pressure fuel system.

Cooling is provided by a nitrogen (N_2) recycle refrigeration system, which utilizes an N_2 recycle compressor, an N_2 compander and a cold box which houses the liquefaction heat exchangers. N_2 is compressed in the N_2 recycle compressor and cooled in an aftercooler. A compander incorporates a compression stage and an expansion stage on a single shaft. N_2 dropping from high to low pressure across the expander wheel provides refrigeration and generates rotational force which is absorbed by the compressor wheel providing a portion of the total nitrogen compression required. A portion of the N_2 stream is expanded in the compander, providing part of the refrigeration requirement. The remaining N_2 is expanded with an expansion valve and provides the rest of the refrigeration required for liquefaction.

There are many variations in the specific configuration of the N_2 refrigeration cycle (pressures, number of expanders, expander arrangements, etc.). The configuration is driven by the need to develop the most cost-effective solution for the plant size, final refrigeration temperature required and project-specific economic evaluation criteria.

Economics: N₂ recycle plants in this size-range are inherently lower capital cost than competing mixed refrigerant technologies, while providing comparable energy efficiency.



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Installations: Two units in operation and others in development.

Reference: Schneller, G. J., J. H. Petrik and J. G.Steimer, "Addition of a nitrogen cycle LNG liquefaction system at the Holtsville LNG peakshaving facility," American Gas Association Operations Conference, Orlando, Florida, April 2003.

Licensor: Air Products and Chemicals, Inc.



Nitrogen removal (reject)

HYDROCARBON

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Application: Cryogenic removal of nitrogen from natural gas to increase calorific value and/or to reduce gas volume for compression.

process categories

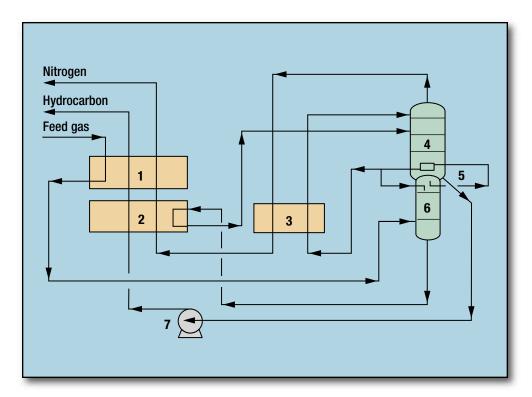
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Description: Natural gas is pretreated to remove constituents that can freeze in the subsequent cryogenic process or affect product quality. After cooling (1) against hydrocarbon product and waste nitrogen, the feed is flashed into the lower (high-pressure) distillation column (6) of the linked pair. Vapor rising through the column is rectified to yield almost pure nitrogen. It condenses against boiling hydrocarbon in the condenser/reboiler (5) located in the upper (low-pressure) column (4). If helium is present in the feed gas, a helium-rich purge stream can be withdrawn from the condenser/reboiler for further enrichment.

Liquid nitrogen is taken off the top of the lower column and subcooled (3) by low-pressure nitrogen. Part of the liquid nitrogen provides reflux to the upper column. Methane-rich liquid from the base of the lower column is drawn off, subcooled (2) and fed to the upper column. A waste-nitrogen stream, typically containing less than 0.5% methane, is drawn from the top of the upper column. A hydrocarbon stream is withdrawn from the base and pumped to product pressure by the hydrocarbon pump (7). Waste nitrogen and hydrocarbon product are heated to ambient temperature against the natural gas feed to provide refrigeration to the process.

For low-nitrogen content feeds, alternative process flowsheets using a heat-pumped single-column design, or a prefractionation column upstream of one or two further columns, give improved process performance and reduced operating cost.

Operating conditions: The double-column process is sufficiently flexible to handle natural gas with nitrogen concentrations varying from 5 mol% to 80 mol%, and can be a good choice for variable content streams associated with enhanced oil recovery (EOR). Feed gas above 27 bar can be processed without any compression. For feed gas containing heavy hydrocarbons or a low-nitrogen content, a three-column process is more



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efficient. The third column also improves plant tolerance to CO_2 , which may simplify gas pretreatment requirements.

Economics: The double-column arrangement can offer several benefits compared with alternative processes, especially for a feed gas nitrogen content above 20%. No power-consuming, heat-pump cycles are required, and machinery needs are reduced. In addition, all hydrocarbon product can leave the plant at high pressure, which reduces recompression requirements.

Installations: Ten plants on six sites with capacities from 80,000 Sm^3/h to 700,000 Sm^3/h .

Reference: Healy, M. J., A. J. Finn and L. Halford, "UK nitrogen removal plant starts up," *Oil & Gas Journal,* February 1, 1999, p. 36.

Nitrogen removal (reject), continued

Millward, R. J. and B. R. Dreaves, "A boost from N_2 rejection," *Hydrocarbon Engineering*, July 2004, pp. 60–64.

Licensor: Costain Oil, Gas & Process Ltd.



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Gas Processes 2006

PRICO (LNG)

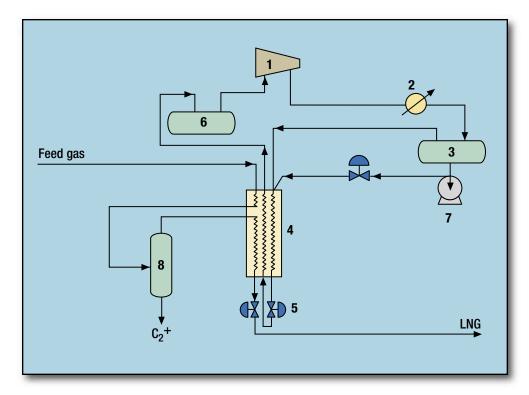
Application: Convert natural gas to liquefied natural gas (LNG) for transportation and/or storage using the PRICO mixed-refrigerant process. Applications range from large base-load LNG units to peak-shaving units and liquid fuels.

Product: LNG is produced at process pressure to be stored at –260°F and atmospheric pressure. Additional products, such as ethane, liquefied petroleum gas (LPG) and gasoline may be recovered in liquid form, when present in the feed gas.

Description: The process is a very simple, efficient, reliable and costeffective mixed-refrigerant cycle. A single mixed-refrigerant, composed of nitrogen and light hydrocarbons from methane through pentane, is circulated in a closed-refrigeration loop. Proportions of individual refrigerant components are adjusted to match the processed gas. This loop contains a compressor (1), a partial condenser (2), an accumulator (3), a refrigerant heat exchanger (4), an expansion valve (5) and a refrigerant suction drum (6). Accumulator liquids are directed to the refrigerant heat exchanger with a low-head centrifugal pump (7). A single-case centrifugal or axial-flow compressor can be used with or without intercooling. If intercooling is used, an interstage separator/pump is added.

The refrigerant heat exchanger (4) is composed of multiple plate-fin brazed aluminum cores arranged in parallel to provide desired production capacity and allow expansion easily.

Natural gas feed is pretreated for removal of carbon dioxide (CO_2) to less than 50 ppmv and dried to less than 1 ppmv water by conventional methods. Natural gas liquids (NGL) from the natural gas feed are separated in (8). The NGLs may then be separated by subsequent fractionation into desired products. Nitrogen in the natural gas feed is dealt with according to the LNG product specification requirements by adjusting the liquefaction conditions. The process matches well with gas turbine, steam turbine or electric motor-driven compression systems.



Installations: 12 units in operation and 4 additional units under development. Capacities range from 4 MMscfd to 180 MMscfd for baseload, peak shaving and clean fuel plants.

References: Price, B. C., "Small-scale LNG facility development," *Hydrocarbon Processing*, January 2003.

Price, B. C., "Bigger baseloads," *Hydrocarbon Engineering*, February 2003.

Licensor: Black & Veatch Corp.



Super Hy-Pro

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Application: The Super Hy-Pro process is a further development of its predecessor—the Hy-Pro process—and is designed for the high recovery of liquid hydrocarbons from natural gas, mainly LPG.

process categories

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Description: The inlet gas is treated and conditioned for processing at low temperatures. After this initial step, the gas is cooled to a point to partially condense certain hydrocarbons. Gas and liquids are separated in a cold separator. The gas is routed to the turboexpander where it is expanded into a proprietary-designed cold-absorption column of the liquids-recovery section. The liquids produced in the absorption section are routed to a recovery column. The liquids-recovery column is the main process focus, where the natural gas liquids are recovered and separated. The overhead section of the column is thermally integrated with the rest of the process, following a similar arrangement as is used in the Hy-Pro process.

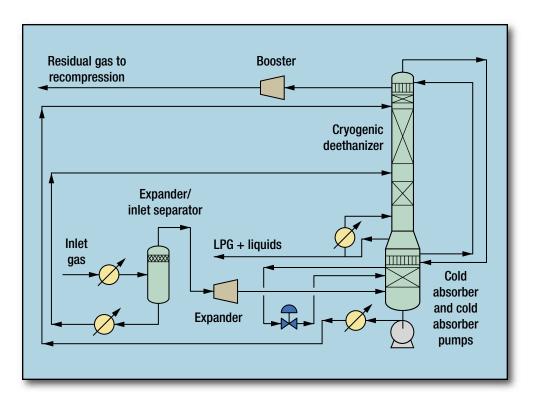
Depending on the gas richness, a refrigeration system may be required to aid product recovery. Product recoveries for propane exceed 95%.

Typical energy consumption, depending on the characteristics of the feed gas, is about 45–65 hp/million scfd, not considering utilities and treating.

Operating conditions: Ample range of pressures, temperatures and compositions.

Installations: More than 10 facilities overseas for Hy-Pro and Super Hy-Pro.

Licensors: Randall Gas Technologies, ABB Lummus Global Inc.





CRG processes—pre-reforming, derichment, methanation

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Application: Adiabatic steam reforming of hydrocarbon from natural gas through LPG to naphtha feeds. May be used for the derichment of natural gas (LNG plants), as an adiabatic pre-reformer or in the methanation of H_2 /CO-rich streams in SNG manufacture.

process categories

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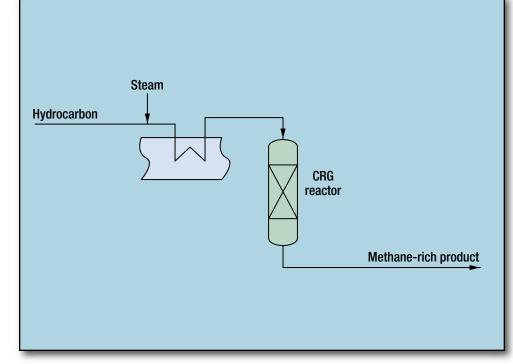
Description: Fixed bed of nickel-based catalyst converts hydrocarbon feeds in the presence of steam to a product stream containing only methane together with H₂, CO, CO₂ and unreacted steam. This stream may be exported as product, used as feed for further processing in a conventional fired reformer or as feed to additional CRG processing steps when the methane content of the product can be further enhanced. Using a CRG pre-reformer enables capital cost savings in primary reformer as a result of reduction in radiant box heat load and 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: CRG processes operate over a wide range of temperatures from 250°C to 650°C, and at pressures up to 75 bara.

Installations: CRG process technology covers 40 years of experience with over 150 plants built and operated. Ongoing development of the catalyst has led to almost 50 such units since 1990.

References: Littlewood, S., et al., "Prereforming: Based on high-activity catalyst to meet market demands," *Ammonia Plant Safety & Related Facilities,* Vol. 40, p. 3, AIChE.

Licensor: The CRG process and catalyst are licensed by Davy Process Technology. The CRG process is available through a number of process licensees worldwide, and the catalyst is manufactured and supplied under license by Johnson Matthey Catalysts.



AQUISULF

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Application: Decrease H_2S content in liquid sulfur condensed in SRUs and routed to sulfur degassing facilities. Maximum H_2S content is 10 ppm.

process categories

Description: A degassing unit is required to achieve 10 ppm H_2S in liquid sulfur. The degassing is done in a concrete pit or sulfur degassing vessel that is divided into two compartments. The first compartment (1) is equipped with a recirculation and cooling pump (3) and a spraying system. The second (2) is equipped with a recirculation and transfer pump (4) also with a spraying system. A partition wall separates the two areas.

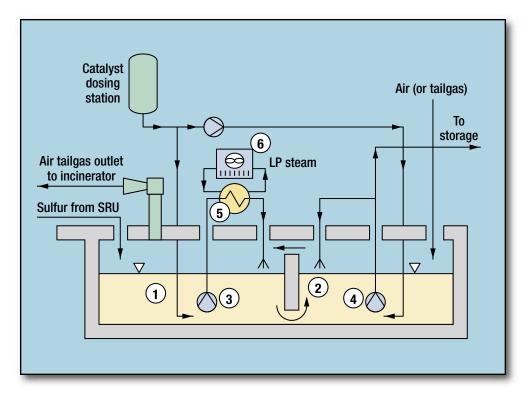
Sulfur arrives continuously into the first compartment where it is sprayed. It flows to the second compartment through an opening located at the bottom of the partition wall. The sulfur is sprayed again in the second compartment where degassing is completed. The degassed liquid sulfur is then transferred under level control to sulfur storage. To quickly mix the AQUISULF catalyst with sulfur, the catalyst is injected at the suction side of each sulfur recirculation pump.

The optimal temperature for degassing is reached by cooling the sulfur (5). The heat generates LP steam that is condensed in the air cooler (6). The pit vapor phase is swept with atmospheric air sucked in by a steam ejector. Sweeping gas flows from the second compartment to the first through a hole located at the top of the partition wall. The gas and H_2S are sent to the incinerator through a steam ejector.

Economics: AQUISULF, including the sulfur pit and sulfur degassing vessel, respectively, accounts for approximately 20% of the Claus unit cost.

Installations: More than 80 AQUISULF units are in operation or under design worldwide.

Reference: Nougayrede, J. and R. Voirin, "Liquid catalyst efficiently removes H₂S from liquid sulfur," *Oil & Gas Journal*, July 1989.



Licensor: Lurgi AG.

process index

CAP—compact alkanolamine plant

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Application: Selective removal of hydrogen sulphide (H_2S) in the presence of carbon dioxide (CO_2) , based on the novel co-current ProPure gas-liquid contactor and a regenerative solvent.

process categories

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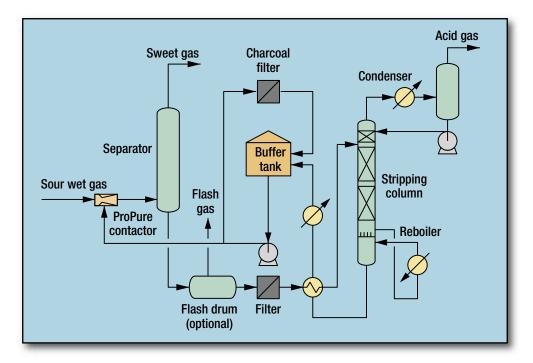
Description: The key technology of the CAP is the ProPure co-current contactor, which is a gas flow-driven "one-shot" contactor. The co-current contactor replaces the counter-current tower in a conventional amine plant. The small liquid droplets generated promote a high gas-liquid mass transfer rate at low to intermediate permanent pressure drops.

CAP's selectivity is achieved by the short retention time combined with the high gas-solvent exposure area throughout the contactor. Compared to counter-current contactors, the gas residence time is considerably shorter, typically 50–100 times shorter. Therefore, CO₂ co-absorption is significantly reduced, allowing higher solvent H₂S-loading capacity. Tertiary amines, such as MDEA, yield selective H₂S-removal as the solvent proton reaction with H₂S is instantaneous whereas the reaction with CO₂ undergoes several (slow) intermediate reactions. The higher the ratio between the CO₂ and H₂S concentrations, the more competitive CAP becomes.

Due to operating at high gas velocities, its size is much smaller compared to conventional equipment. The selective nature results in significantly lower circulation rates, which reduces the amine regeneration system's overall size.

Economics: For a case with inlet concentrations of 2% CO₂ and 20 ppmv H₂S and an H₂S-outlet specification of 3 ppmv, a 50% reduction in circulation rate resulting in weight reduction of 35% is estimated compared to conventional technology. This is mainly due to the reduced amine circulation rate. The limited footprint requirement makes CAP feasible for retrofit installations on existing offshore fields.

In order to maintain similar attractive features at higher H_2S inlet concentrations, or to further reduce the circulation rate at lower H_2S concentrations, CAP will be configured with two or more contactor stages (the above example would result in a circulation rate reduction of over 80%).



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Installations: Extensive tests have been carried out at the Statoil Mongstad refinery and at ProPure's test facility (2001–2003). During 2004– 2005, CAP technology has been qualified at Gaz de France's gas processing and distribution plant at Chemery, France, with sour hydrocarbon gas at pressure 80–100 bar. The qualification has been supported by a JIP of Total, Statoil, ConocoPhillips and Gaz de France.

Reference: Connock, L., "Finding the best solution," *Sulphur*, No. 283, November/December 2002.

Nilsen, F. P., H. Lidal and H. Linga, "Selective H₂S removal in 50 ms," GPA Annual Conference, Amsterdam, The Netherlands, September 2001.

Nilsen, F. P., H. Lidal and I. Nilsen, "Novel contacting technology selectively removes H₂S," *Oil & Gas Journal*, May 2002.

Licensor: ProPure AS.



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Gas Processes 2006

Claus, modified

Application: Recover sulfur from acid-gas streams that contain hydrogen sulfide (H_2S) and ammonia (NH_3) .

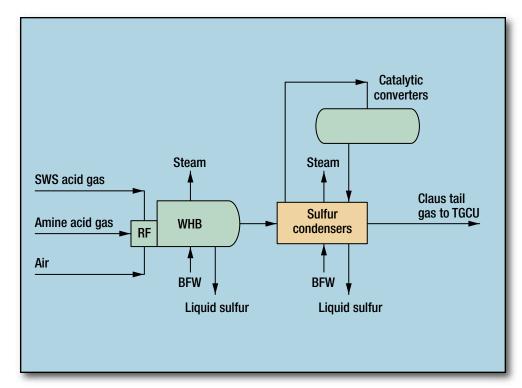
Product: Bright yellow sulfur with 99.9 % purity and less than 10 ppmw of dissolved H_2S after degassing. Front-end Claus tail gas is either processed in a tail gas cleanup (TGCU) unit for further sulfur recovery, or routed to the Claus incinerator where residual H_2S is oxidized to SO_2 .

Description: Acid gases from sweetening units and sour-water strippers are sub-stoichiometrically burnt with ambient air (or air plus oxygen) in a refractory-lined furnace to convert 1/3 of H₂S to SO₂. Subsequently, elemental sulfur is produced in accordance with the Claus reaction between 2/3 of the H₂S and produced SO₂. Ammonia and hydrocarbons contained in the feed gas are also destroyed. High-pressure steam is generated in a waste-heat boiler (WHB), which cools the acid gas from the high-flame temperature to the lower catalytic reactor (converter) temperature. Further sulfur conversion is achieved in two or three stages of catalytic reaction in converters. Each converter is normally preceded by a reheater and followed by a sulfur condenser. Several methods are available for reheating process gas.

Operating conditions: The temperature inside the combustion chamber depends upon the type and quantities of species accompanying the H_2S and O_2 . Generally, the operating temperature ranges between 925°C–1,200°C, but can be increased to 1,450°C if NH_3 is present in the feed gas. Total pressure drop of the process gas depends upon the numbers of converter stages. Typically, pressure drop can vary between 0.3 bar and 0.5 bar.

Sulfur recovery efficiency depends on the feedstream composition and the number of catalytic stages; typically, it ranges between 94.5% and 97.5 %.

Economics: Capital cost is approximately \$10 million/100-tpd sulfur re-



covery unit designed to achieve 95% recovery efficiency from typical amine off gas. Operating costs can be considered negligible if credit for steam generation is taken into account.

Installations: Since the 1970s, more than 60 modified Claus units have been built worldwide by SIIRTEC NIGI.

Licensor: BP through SIIRTEC NIGI.



Claus, oxygen-enriched

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Application: Debottleneck existing sulfur recovery units (SRU) or reduce size, capital and operating costs for new facilities by using oxygen, either to enrich or to replace combustion air.

process categories

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Product: Bright yellow, high-purity sulfur. Claus tail gas is either processed in a tail gas cleanup unit (TGCU), or routed to the Claus incinerator where residual hydrogen sulfide (H_2S) is oxidized to SO_2 .

Description: In an air-based Claus plant, nitrogen from the combustion air usually comprises more than half of the molar flow through the plant. By replacing air with oxygen, plant capacity can be increased significantly. The level of air enrichment with oxygen and, hence, the level of uprating, depend upon the feed-gas composition.

Process variations:

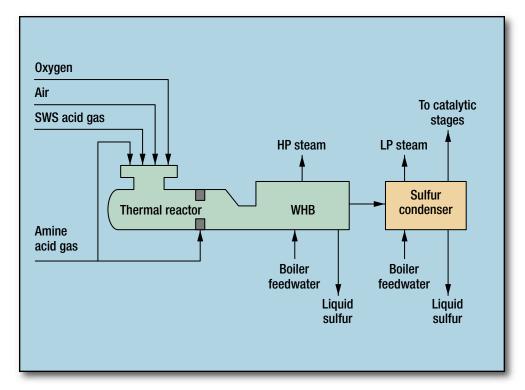
• Up to about 30% oxygen , only minor modifications to the plant would be expected.

• Above 30% oxygen concentration, a proprietary oxygen-compatible burner would be required using the SURE burner. Some limited modifications could be expected.

• For capacity increases in excess of about 100%, the SURE double combustion process could be used to achieve the desired expansion.

Operating conditions: The process uses a higher combustion temperature. The operating temperature is kept below 1,650°C—the normal refractory limit. Sulfur recovery efficiency for an oxygen-based Claus process is slightly better than that of air-based Claus and typically ranges between 95% and 98%, depending on process variables.

Economics: The cost of revamp is generally between 10% and 30% and only includes the cost for additional new plant capacity. The cost of a new oxygen-based Claus facility can save up to 35% of the installed cost for an air-based alternative.



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Installations: Several units have been designed and revamped by SIIRTEC NIGI in cooperation with Parsons and BOC. Two new units were constructed for IGCC project.

Licensor: SIIRTEC NIGI (up to 30% O_2), SURE Parsons/BOC through SIIRTEC NIGI.



Cold Bed Adsorption (CBA)

HYDROCARBON

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Application: Recover elemental sulfur from acid-gas streams that contain hydrogen sulfide (H_2S), or treat Claus tail gas for additional sulfur recovery. CBA beds can be retrofitted in existing units to increase the sulfur recovery.

process categories

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Product: Bright yellow, commercial grade sulfur. Tail gas leaving the CBA reactor is normally routed to the incinerator and thermally oxidized.

Description: The CBA is a dry-bed catalytic process which extends and enhances the characteristics of the Claus reaction in two ways:

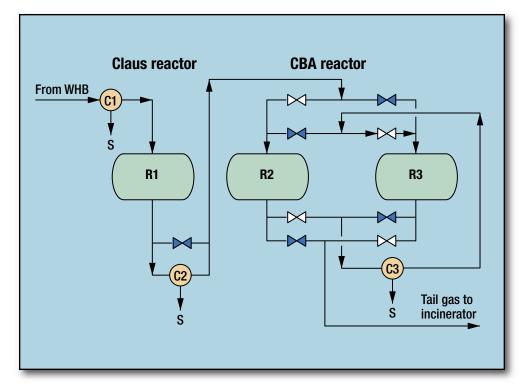
• Operating the CBA reactors near the sulfur dew point extends the Claus reaction equilibrium and can achieve higher sulfur conversion.

• Using the catalyst as an in-situ capture point for the produced sulfur drives the reaction to completion.

A common flowsheet involves two CBA reactors, operating cyclically, downstream of a Claus converter. Gas leaving the sulfur condenser is fed directly to a CBA reactor on adsorption duty. The formed sulfur is adsorbed on the catalyst bed. The bed on regeneration duty is heated by diverting some hot gas from the Claus reactor to drive off and recover the sulfur. This regeneration gas stream is re-combined with the main process gas for treatment in the adsorption bed. Effluent gas from the plant may be sent to a thermal oxidizer. Other flowsheet configurations may also be used, where required, to meet specific sulfur recovery or retrofit objectives.

Operating conditions: The temperature in the CBA reactor can vary from 120°C to 150°C during the adsorption cycle and 300°C to 350°C during regeneration. The total pressure drop of the CBA section is around 0.1–0.15 bar. Sulfur recovery can be over 99%.

Materials of construction: Mainly carbon steel. CBA reactors can be either aluminized or refractory-lined carbon steel. Cyclic valves should be constructed of SS 316.



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Installations: Many CBA plants have been built with capacities of 1,300 to 2,000 tpd. The most recent CBA plant built by SIIRTEC NIGI is for Hindustan Petroleum Co. Ltd., at Visakhapatnam, India. This plant uses two units with 65-tpd capacity for each unit.

Licensor: BP through SIIRTEC NIGI.



COPE

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Application: The COPE Oxygen Enrichment Process allows existing Claus sulfur recovery/tail gas cleanup units to increase capacity and recovery, can provide redundant sulfur processing capacity, and can improve combustion performance of units processing lean acid gas.

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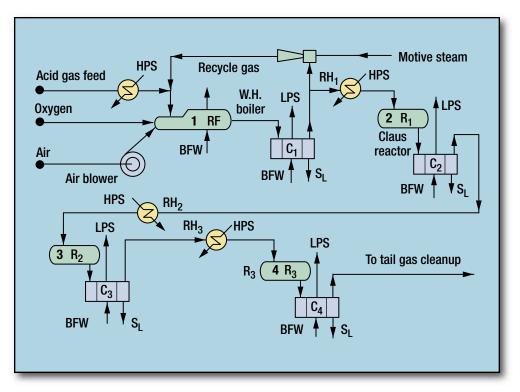
Description: The sulfur processing capacity of typical Claus sulfur recovery units can be increased to more than 200% of the base capacity through partial to complete replacement of combustion air with pure oxygen (O_2). SRU capacity is typically limited by hydraulic pressure drop. As O_2 replaces combustion 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 O₂ 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 O₂ enrichment to the maximum reaction furnace refractory temperature limit of 2,700°F–2,800°F. Higher O₂ 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% O₂.

Flow through the remainder of the SRU (2, 3, and 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. Overall SRU sulfur recovery is typically increased by 0.5% to 1%. A single proprietary COPE burner handles acid gas, recycle gas, air and O_2 .

Operating conditions: Combustion pressure is from 6 psig to 12 psig; combustion temperature is up to 2,800°F. Oxygen concentration is from 21% to 100%.

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.



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Operating costs are a function of O_2 cost, reduced incinerator fuel, and reduced operating and maintenance labor costs.

Installations: Twenty-five COPE trains at 15 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.

Licensor: Goar, Allison & Associates, Inc., and Air Products and Chemicals, Inc.



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CrystaSulf

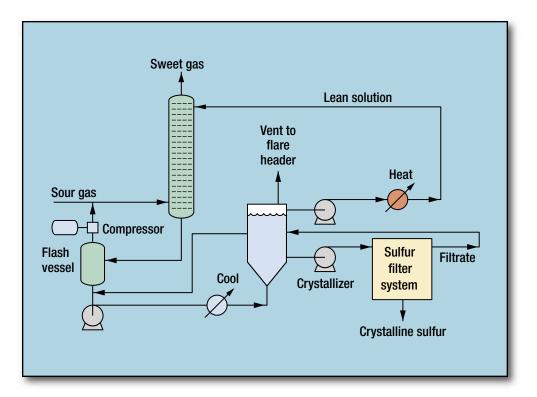
Application: Removes hydrogen sulfide (H_2S) from gas streams such as natural gas, refinery fuel gas, the hydrogen recycle stream in refinery HDS, high-carbon dioxide (CO_2) streams in EOR plants and geothermal vent gas. Also removes H_2S , sulfur dioxide (SO_2) and elemental sulfur vapor from Claus tail gas in natural gas processing plants and petroleum refineries. It can treat any high- or low-pressure gas stream. CrystaSulf is the most economical choice for H_2S removal from gas streams containing between 0.2 and 25 long tons per day (ltpd) of sulfur.

Description: Gas phase H_2S is converted to elemental sulfur in a single process step using a proprietary nonaqueous sorbent. The sulfur formed remains dissolved in the solution; thus, no solids are present in the circulating scrubbing liquor. Sulfur is removed from the system by cooling in a crystallizer/filter system. No surfactants, wetting agents or antifoams are needed.

Scrubbing solution circulation rates are low (e.g., 20–50 gpm/ltpd sulfur) and product sulfur purity is high (98+% sulfur). It can be blended with Claus sulfur or used in agriculture. Chemical makeup costs are approximately \$250/lt sulfur. Capital and operating costs are less than other options, and the process requires no solution blowdown. For Claus tail gas treating, the tail gas is fed directly to the CrystaSulf absorber, thus eliminating the reducing gas generator, waste heat boiler, hydrogenation reactor and water quench. None of the gas needs to be recycled back to the Claus unit.

Operating conditions: Atmospheric to 2,000+ psi; 120°F to 180°F. CO_2 , COS and CS_2 in the inlet gas do not react and do not affect the system. Inlet gas hydrocarbons do not cause foaming or sulfur settling problems for CrystaSulf.

Installations: Eighteen months of pilot plant testing was conducted on a 300-psig CO_2 stream. Three licenses sold. Startup of first commercial unit occurred in July 2005, at the GasPort terminal in Emden, Germany.



References: Technical papers and publications are available at www. crystatech.com.

Licensor: CrystaTech is the exclusive licensor of CrystaSulf. The Hanover Co. and Gas Technology Institute (GTI) are investors in CrystaTech and provide engineering and research support to CrystaTech.



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D'GAASS

Application: The D'GAASS Sulfur Degassing Process removes dissolved H_2S and H_2S_x from produced liquid sulfur. 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.

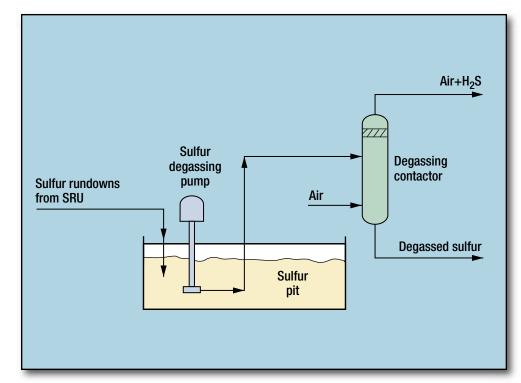
Operation at elevated pressure and a controlled temperature accelerates the oxidation of H_2S and polysulfides (H_2S_x) to sulfur. The degassed sulfur can be sent to storage or directly to loading without additional pumping. Operation at elevated pressure allows the overhead vapor stream to be routed to the traditional incinerator location, or to the SRU main burner or TGTU line burner—thus eliminating the degassing unit as an SO₂ emission source.

Economics: D'GAASS achieves 10 ppmw combined H_2S/H_2S_x in product sulfur without using catalyst. 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, catalysts, etc., are required.

Installations: Nineteen units in operation. Twenty-four additional trains in engineering and construction phase with total capacity over 23,500 long ton per day (LTPD).

Reference: US Patent 5,632,967.

Nasato, E. and T. A. Allison, "Sulfur degasification—The D'GAASS process," 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.

Licensor: Goar, Allison & Associates, Inc.



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ELIMINATOR

Application: ELIMINATOR technology removes H_2S and light mercaptan species from a variety of process gas or liquid streams in a safe, efficient and easy-to-operate manner.

Description: A number of different treatment methodologies may be used to apply liquid ELIMINATOR to a sour gas or liquid stream:

• Line injection—Liquid ELIMINATOR product is either sprayed into a gas stream, or directly injected into a liquid stream, and the spent ELIMI-NATOR is then separated in either a vertical knockout pot or a horizontal separation vessel

• Sparge tower—Sour gas is bubbled up through a static solution of liquid ELIMINATOR

• Packed tower—Sour gas is contacted with circulating liquid ELIMI-NATOR in a counter-current, packed-bed scrubber tower

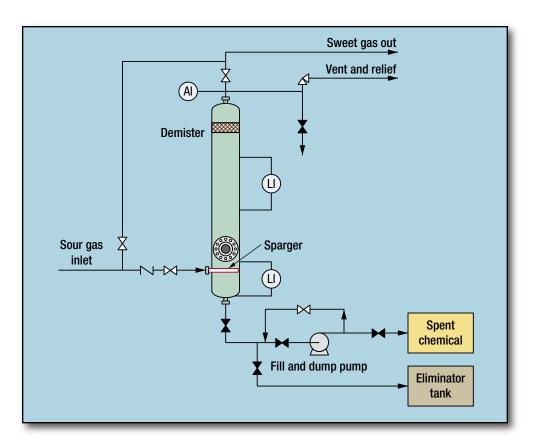
• Venturi scrubber—Sour gas is pulled into a venturi scrubber by the motive force of a circulating ELIMINATOR stream (used mostly for low-pressure systems).

In all the above, liquid ELIMINATOR product removes H_2S and light hydrocarbons through conversion into a safe, easy-to-remove and dispose of amine resin compound. Following contact with the ELIMINATOR product, further treatment is required.

ELIMINATOR may be used in water-saturated streams or dry streams, and works in almost any operating condition; other gas components, such as carbon monoxide, do not affect media cost and/or performance to an appreciable level.

A custom-designed ELIMINATOR unit matching design and operating conditions are available to remove H_2S and light mercaptans. Bed pressure drop requirements are only a few inches of water; the ELIMI-NATOR system is capable of providing excellent removal performance (< 0.1 ppm of sulfur) at any stream pressure (or vacuum), inlet H_2S level, and for system temperatures up to 300°F.

Changing and/or filling ELIMINATOR solution is made by a bulk delivery system; spent ELIMINATOR solution acts as a pipeline corrosion



inhibitor and can be safely disposed of in almost any sewer.

Products: A full line of ELIMINATOR products treat both low- and highpressure gas systems containing varying amounts of carbon monoxide. Products can successfully treat dry gas streams without the need for additional dehydration.

Water-based liquid treatment products are designed to remove H_2S and light mercaptans from virtually any liquid stream, and are very effective at removing the aforementioned contaminates from tank head spaces.

Economics. Operating costs are generally very low, and are typically very reliable. In addition, there is minimal operating and utility requirements; Continued ▼

Eliminator, continued

vessel design is generally quite simple, allowing for local equipment fabrication, thereby lowering capital costs.

Installations: Over 15 applications globally.

Licensor: Gas Technology Products, LLC.



EUROCLAUS process

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Applications: The EUROCLAUS process recovers elemental sulfur from hydrogen sulfide (H_2S) containing gases, which originate from gas treating plants such as alkanolamine units or physical solvent plants. Yields up to 99.7% overall sulfur recovery without any further tail gas cleanup are possible.

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Description: The EUROCLAUS process has a thermal stage followed by three catalytic reaction stages. Sulfur is removed between stages by condensers. Two reactors are filled with standard Claus catalyst while the last reactor is filled with selective oxidation catalyst.

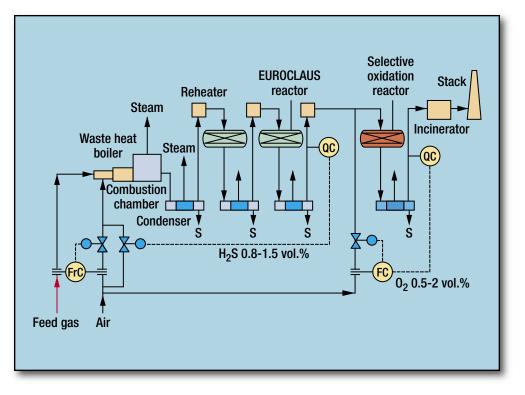
In the thermal stage, acid gas is burned with a substoichiometric amount of controlled combustion air such that the tail gas leaving the second reactor contains typically 0.8 vol.% to 1.0 vol.% of H_2S and 100–200 ppmv sulfur dioxide (SO₂). The low SO₂ content, produced with a hydrogenation catalyst, converts SO₂ to H_2S in the reactor bottom.

The last reactor oxidizes H_2S to sulfur at more than 85% efficiency. However, because this catalyst neither oxidizes H_2S to SO_2 nor reverses the reaction, total sulfur recovery up to 99.3% efficiency can be obtained. If more than 99.3% sulfur recovery is required, one additional Claus reactor stage may be installed upstream of the selective oxidation reactor.

Utilities: Basis: 100 tpd sulfur recovery unit; 93 vol% H_2S feed gas and catalytic incineration.

Útility	Consumption	Production
Steam, LP, tph	_	3.3
Steam, MP, tph	—	10.2
Electricity, kW	220	—
Fuel gas, tph	0.12	—
Boiler feed water, tph	13.5	—
Steam, LP (plant heating), tph	0.4	

Installations: Since the first commercial demonstration of the EURO-CLAUS process in 2000, more than 17 plants are in operation or under construction in the third quarter of 2005.



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Licensor: Comprimo Sulfur Solutions, a member of Jacobs Engineering Group.



FLEXSORB solvents

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Application: Remove H_2S selectively, or remove a group of acidic impurities (H_2S , CO_2 , COS, CS_2 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.

process categories

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FLEXSORB SE or SE Plus solvent is used on hydrogenated Claus plant tail gas to give H_2S , ranging down to $H_2S < 10$ ppmv; pipeline natural gas to give $H_2S < 0.25$ gr/100 scf; or FLEXICOKING low Btu fuel gas. The resulting acid gas byproduct stream is rich in H_2S .

Hybrid FLEXSORB SE solvent is used to selectively remove H_2S , as well as organic sulfur impurities commonly found in natural gas.

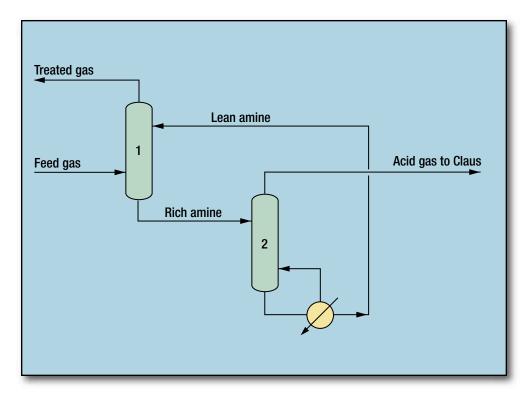
Description: A typical amine system flow scheme is used. The feed gas contacts the treating solvent in the absorber (1). The resulting rich solvent bottom stream is heated and sent to the regenerator (2). Regenerator heat is supplied by any suitable heat source. Lean solvent from the regenerator is sent 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 H_2S regenerability yielding <10 ppmv H_2S in the treated gas. Hybrid FLEXSORB SE solvent is a hybrid solution containing FLEXSORB SE amine, a physical solvent and water.

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

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, three in design FLEXSORB SE Plus—19 plants operating, eight in design Hybrid FLEXSORB SE—two plants operating, three in design Over 60 plants operating or in design.



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Reference: Fedich, R. B., et al., "Selective H₂S removal," *Hydrocarbon Engineering*, Vol. 9, No. 5, May 2004.

Fedich, R. B., et al., "Solvent changeover benefits," *Hydrocarbon Engineering*, Vol. 10, No. 5, May 2005.

Connock, Lisa, et al., "High recovery tail gas treating," *Sulphur Magazine*, No. 296, November/December 2004.

Licensor: Exxon Mobil Research and Engineering Co.



HCR—High Claus Ratio

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Application: Remove sulfur compounds present in tail gases from Claus plants and meet air pollution standards.

process categories

Description: The high Claus ratio (HCR) process consists of two sections:

• Hydrogenation and hydrolysis of sulfur compounds present in tail gases (COS, CS₂, S_x and SO₂). Tail gas is heated to about 300°C and, without hydrogen addition, is treated with Co/Mo catalyst. Gas passes through a waste-heat boiler (WHB) and is cooled to approximately 40°C in a direct contact tower.

• H_2S removal and recycle of acid gas to a Claus plant. The gas is washed in a carefully designed amine absorber, and the treated gas is incinerated. Rich amine is processed and recycled.

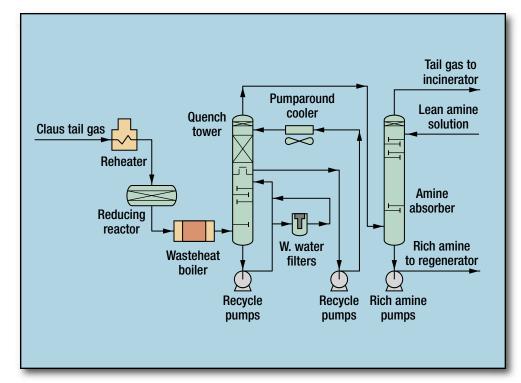
The process requires adjusting the operating criteria for the Claus unit by increasing the H_2S/SO_2 tail gas ratio. The operation is very steady and has high service factors that are achieved during upset conditions from upstream units. Hydrogen or reducing gas from external sources are not required in the hydrogenation reactor.

Operating conditions: The pressure drop of the unit is 0.20-0.30 bar and the operating pressure is almost atmospheric. Treated gas contains less than 250 ppmv of H₂S.

Economics: Process uses standard equipment and carbon steel almost everywhere. No consumption of reducing gas or caustic chemicals is required. Process analyzers are not mandatory.

Reduction in utilities and chemical costs are approximately \$1.50/t of sulfur produced. Lower operating and maintenance labor is about one-eighth man per shift.

Installations: The first commercial HCR plant was started up in November 1988 at Agip Plas's facility (an affiliate of Agip Petroli S.p.A.) in Robassomero, Italy. Since then, more than 10 HCR plants are under con-



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struction with capacities ranging from 1.5 tpd up to 270 tpd.

Licensor: SIIRTEC NIGI.

process index



Merox

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

process categories

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

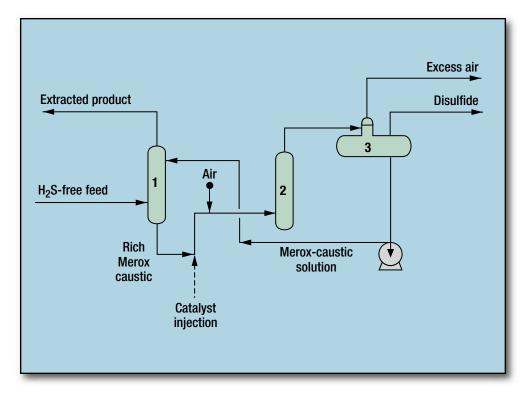
Description: Merox units are designed in several flow configurations, depending on feedstock type and processing objectives. All are characterized by low capital and operating costs, ease of operation and minimal operator attention.

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 and condensate 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. A new additive, Merox Plus reagent, can be used to greatly extend catalyst life.

Heavy gasoline, condensate and kerosine/jet fuel may 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.

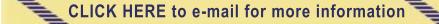
Installations: Capacity installed and under construction exceeds 13 million bpsd. More than 1,600 units have been commissioned to date, with capacities between 40 bpsd and 140,000 bpsd. UOP has licensed gas Merox extraction units with capacities as high as 2.9 billion scfd for mercaptan control.



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Licensor: UOP LLC.

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NATCO Shell-Paques technology

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Application: Direct treat selective removal of hydrogen sulfide (H_2S) from low-, medium- and high-pressure produced hydrocarbon natural gas streams. The Shell-Paques process is also applicable for amine regenerator acid gas, debottlenecking existing sulfur recovery units, processing Claus tail gas and for replacing or converting alternative aqueous processes, which are prone to plugging. The process is ideally suited to environmentally sensitive areas where venting, incineration or reinjection of H_2S gas are not desirable options.

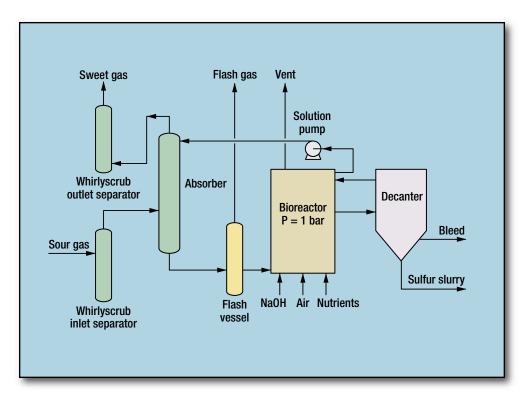
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Description: A gas stream containing H_2S contacts an aqueous soda solution containing thiobacillus bacteria in an absorber. The soda absorbs the H_2S and is transferred to an aerated atmospheric bio-reactor tank allowing sweet gas to be produced. As a controlled air stream is passed through the bio-reactor tank, the bacteria biologically oxidize the sulfides, excrete elemental sulfur and regenerate the soda solution. The elemental sulfur is decanted and filtered or centrifuged from the process. The sulfur can be used for agricultural purposes or is safe for landfill disposal.

Economics: The Shell-Paques technology is economically favorable for sulfur removal ranges between 200 lbs per day to 25 tons per day. The sulfur produced is hydrophilic. Shell-Paques systems operate reliably, with no sulfur plugging or fouling of equipment, and with significantly lower chemical cost vs. alternate aqueous iron technologies. The process requires less equipment to maintain and operate vs. conventional amine/Claus technology.

Operating conditions: The Shell-Paques technology operates most efficiently for inlet gas ranges from 60°F to 100°F and between 2 psi and 1,300 psi. Higher inlet gas temperatures require additional cooling equipment. The partial pressure of H_2S should be less than 75 psia while the partial pressure of CO_2 should be less than 100 psia.



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Installations: The biological treatment technology has been extensively confirmed by more than 34 worldwide low-pressure biogas applications. There are five Shell-Paques high-pressure applications worldwide.

Licensor: NATCO Group Inc.

OxyClaus

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Application: Increase capacity up to 200% in existing Claus sulfur recovery units, or for a more economical design of grassroots Claus sulfur recovery units.

process categories

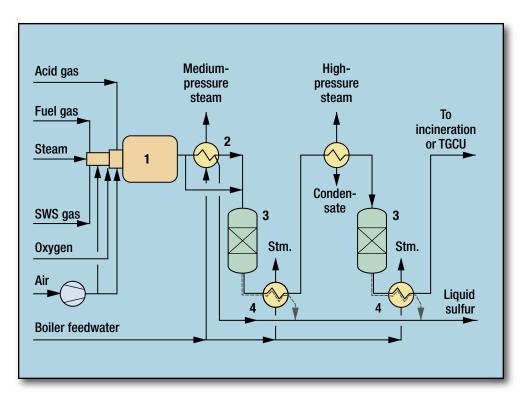
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Description: The modified Claus reaction is carried out with direct oxygen combustion. By using a proprietary thermal reactor burner (1), levels of 80–90% net oxygen can be utilized. Combustion temperature moderation is achieved without the need for any type of gas recycle. Oxygen is combusted with the acid gas in the center of an extremely hot flame core, while air is introduced around the outside of this flame, combusting the balance of the acid gas. Considerable cracking of H₂S to hydrogen and sulfur occurs in the hot flame core as thermodynamic equilibrium is approached. Carbon dioxide is also reduced to carbon monoxide. These endothermic reactions provide proven temperature moderation consistent with conventional refractory/insulating brick materials. The level of produced hydrogen then decreases in the waste-heat boiler as the hot gas is cooled, since equilibrium of the H₂S-cracking reaction is favored by high temperatures. Heat generated by the exothermic reverse reaction is removed in the waste-heat boiler (2). Downstream recovery of elemental sulfur is accomplished by the conventional modified Claus process using a series of catalytic reactors (3) and sulfur condensers (4). No specialized equipment or changes to conventional design practices are required.

Ammonia-containing sour water stripper offgas can also be processed. The ammonia is combusted with air in a separate central burner muffle at near-oxidizing conditions.

Units may be operated in a base-load mode with air only. Peak shaving, as well as operation at full design capacity, is accomplished with air and oxygen.

Economics: For a reference 200-tpd sulfur recovery unit (Claus and tail gas unit) requiring 99.9% overall sulfur recovery, capital cost savings of \$1.6 million to \$2.5 million are achievable with oxygen enrichment as



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compared to an air-only design.

Based on typical pipeline oxygen costs of \$35 per ton, even if oxygen enrichment were used 100% of the time, it would take over eight years for oxygen costs to equal the incremental capital savings.

Installations: More than 35 Claus sulfur recovery units with OxyClaus are in operation or under design worldwide.

Reference: Stevens, D. K., L. H. Stern and W. Nehb, "OxyClaus technology for sulfur recovery," Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, 1996.

Licensors: Lurgi AG and Black & Veatch Corp. (US only)



SRU

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Application: To recover liquid sulfur from hydrogen sulfide (H_2S) -containing gases such as acid gas from gas-sweetening units, acid gas from sour-water strippers or offgas from sulfur degassing facilities.

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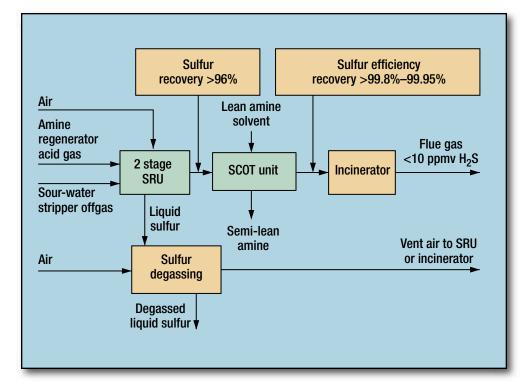
Description: The main reactions are well-known Claus reactions. Ammonia (NH_3), present in the sourwater stripper offgas, is processed in the main burner directly with other feed gas streams. Practical complete NH_3 destruction is ensured by choosing the proper high-intensity burner and preheating feed gas.

The Claus unit is designed to suppress SO_3 formation at the reaction furnace and subsequent line burners. The sulfur complexes, even with NH₃ in the feed, can typically run for 3 to 4 years without a maintenance shutdown. The Claus tail gas is routed to a SCOT unit, where the sulfur components are recovered (see SCOT).

Liquid sulfur produced in the Claus unit is degassed in the Shell sulfur degassing facilities (see "sulfur degassing" for more details). In this process, the H_2S level in liquid sulfur is reduced to below 10 ppmw, without using catalyst, which improves safety during liquid sulfur handling. Offgas of the sulfur stripper can be routed to the Claus unit or to an incinerator.

The incinerator downstream the Claus/SCOT unit is designed such that a maximum of 10-ppmv H_2S can slip through, the remainder of the H_2S and any other sulfur component are oxidized to sulfur dioxide (SO₂). A thermal incinerator can be designed with a heat-recovery section for superheating steam produced in the Claus unit or gas preheating. A catalytic incinerator, using propriety catalyst, can be applied in case there is the need to take the fuel gas consumption into account. The fuel consumption of a catalytic incinerator is considerably lower compared to a thermal incinerator.

Installations: Units with sulfur capacities up to 4,000 tpsd for refineries and gas plants.



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References: Hoksberg, et al., "Sulfur recovery for the new millennium," *Hydrocarbon Engineering*, November 1999.

Verhulst, "Safeguarding of the sulfur recovery process," Bovar/Western Research Sulfur Seminar, Budapest, 1993.

Licensor: Shell Global Solutions International B.V.



SulFerox

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Application: Removal of hydrogen sulfide (H_2S) from a large range of gas streams giving a sulfur production of 0.1–20 tpd. Gas applications include: natural gas, amine tail gas, enhanced oil recovery CO₂ recycle, refinery gases, geothermal, syngas, offshore production gas, digester offgas and offgas from wastewater treatment plants. The full range of H_2S concentrations (from a few ppmv to almost 100%v of H_2S) can be treated to 1-ppmv H_2S . Turndown properties—both on H_2S concentration and total gas flow—are very good, and the process shows excellent flexibility. If gas flows become too large (in excess of 10 million Nm³/d), the combination of an amine unit coupled to a SulFerox unit becomes more economical. The sulfur product can be obtained as a filter cake or alternatively as molten sulfur of high quality. The sulfur cake can be land filled as a nonhazardous waste or—depending on local regulations—directly used as a fertilizer.

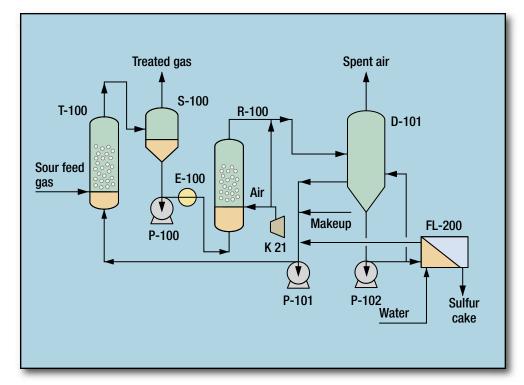
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Description: SulFerox is a redox-based process that converts H_2S in sour gas to elemental sulfur (S) in the contactor through reaction with a proprietary aqueous ferric iron chelate solution. Various contactor types are available, such as sparged towers, spray towers and pipeline contactors. The sparged tower is the most versatile contactor and will be selected whenever pressure drop allows. After contacting the sour gas and SulFerox solution in the (sparged tower) contactor, the gas/liquid mixture is separated. In the separator, the solution and treated gas is separated yielding the treated sweet gas—leaving the unit via an optional knockout vessel—and the depleted SulFerox solution.

After optional degassing, the reduced iron chelate solution is regenerated via reaction of Fe_2 + back to Fe_3 + with oxygen from an air source in the regenerator vessel. Via a thickener vessel, part of the solution is sent for filtration and sulfur recovery; the major portion of the stream is returned to the contactor.

In addition, the resulting filtrate is returned to the process for maximum solution recovery, thus, optimally using the chelate solution. De-



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pending on the feed gas conditions, the contactor and separator can be combined in one vessel as can be done with the regenerator and surge vessel. This gives a two-vessel configuration suited for amine regenerator offgas.

Operating conditions: Operating pressures vary from just over atmospheric to 500 psig. The SulFerox process itself operates at temperatures of $110^{\circ}F-140^{\circ}F$. However, the feed gas temperature can be between $75^{\circ}F-130^{\circ}F$. The feed gas must be free of hydrocarbon liquids. Gas at other conditions may need pretreatment first (cooling, dewpointing). Although the applicability of the SulFerox process is very wide, some feed gas contaminants, such as high levels of NH₃, HCN and SO₂, might affect the economics of the process.

Installations: Thirty units in operation.

SulFerox, continued

References: Smit, C. J. and E. C. Heyman, "Present status SulFerox process," Process GRI Sulfur Recovery Conference, 9th meeting, 1999. Oostwouder, S. P., "SulFerox process update," Process GRI Sulfur Recovery Conference, 8th meeting, 1997.

Licensor: Shell Global Solutions International B.V.



Sulfint HP

HYDROCARBON

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Application: Selective hydrogen sulfide (H_2S) removal from high-pressure gases with direct conversion of H_2S into elemental sulfur (S). Residual H_2S levels in the treated gas can be lower than 1 ppm vol.

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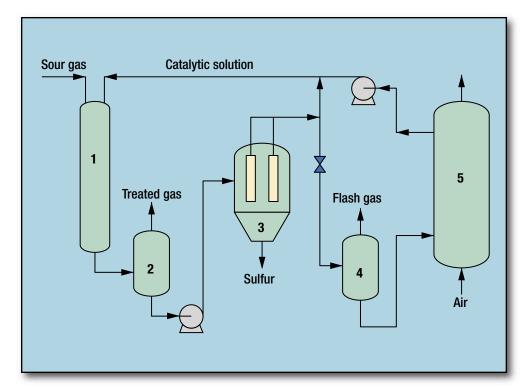
Description: The Sulfint HP uses the well-known concept of redox desulfurization. However, this process has been specifically designed to treat high-pressure gases. The feed gas is contacted with the redox catalytic solution (aqueous iron chelate-based solution) in a co-current absorber (1). The H_2S is absorbed by the catalytic solution, reacts with the catalyst and is converted into elemental S. Desulfurized gas is recovered from the top of the separator vessel (2). The sulfur-loaded solution is then pumped through a multi-cartridge, high-pressure filter (3). The filtered solution can be partly recycled to the absorber (1) and partially expanded for regeneration.

The expanded solution, after separation of the dissolved gases (4) is regenerated with air in the oxidizer vessel (5). The whole process operates at near-ambient temperature, and no thermal regeneration nor chilling is needed. High-pressure filtration mitigates foaming/plugging problems, especially after the expansion of the solution. Due to direct recycle of the filtered solution to the absorber, pumping costs are minimized. This process is highly selective; only H_2S is removed (no CO_2 co-absorption and very little hydrocarbons co-absorption).

Economics: For units treating 100–300 MMscfd of gas with a sulfur production 0.1–10 tpd, the CAPEX will be 20–50% lower than for conventional processes.

Installations: An industrial pilot plant is treating up to 1.7 MMscfd of gas under 1,160 psia and has been operated successfully for more than 6,000 hours.

Reference: Le Strat, P. Y., et al., "New redox process successful in high-pressure gas streams," *Oil & Gas Journal*, November 26, 2001, pp. 46–54.



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Licensors: Prosernat IFP Group Technologies and Le Gaz Integral.



Sulfur degassing

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Application: Remove hydrogen sulfide (H_2S) and hydrogen poly-sulfides (H_2S_x) dissolved in liquid sulfur.

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Safety: Hydrogen sulfide is a highly toxic and potentially explosive gas. A concentration of 600 ppmv is lethal and is explosive at approximately 3.5% vol. Dissolved H_2S_x is decomposed, and H_2S is released in storage, during loading and unloading and also during transportation, thus leading to potentially dangerous conditions.

Product: Liquid sulfur containing 10 ppmw of H_2S or less.

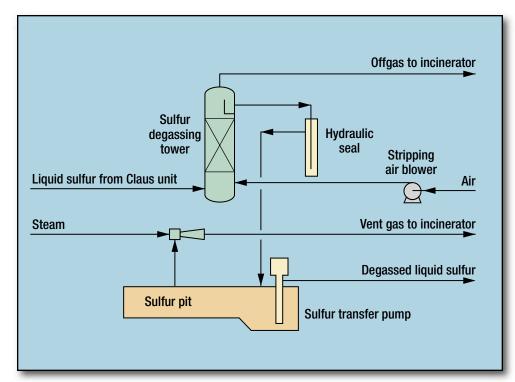
Description: Liquid sulfur flowing from the Claus plant to the sulfur pit contains typically 250–350 ppmw of $H_2S + H_2S_x$. Sulfur is degassed using an active gas-liquid contacting system to release dissolved gas. Adding chemicals is not required. Sulfur from the pit is pumped into the degassing tower where it is contacted counter-currently with hot compressed air over a fixed catalyst bed. Degassed sulfur is returned to the product section of the sulfur pit.

Operating conditions: The operating temperature in the sulfur degassing tower can vary from 125°C to 150°C depending on the temperature in the sulfur pit. The operating pressure drop is around 0.3–0.5 bar. Treated sulfur has a residual H_2S level in the range of 5–10 ppmw.

Materials of construction: Mainly carbon steel. Aluminized steel may be used for the degassing tower.

Installations: Several units are in operation, design or under construction with unit capacities up to 300 tpd.

Licensor: BP through SIIRTEC NIGI.



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Gas Processes 2006

SULFUR-RITE

Application: SULFUR-RITE technology removes hydrogen sulfide (H₂S) and light mercaptan species from a variety of process gas or liquid streams in a safe, efficient and easy-to-operate manner.

Description: Sour gas or liquid enters the treatment vessel near the top, and is distributed evenly throughout the cross-sectional area, in order to fully contact the granular, solid media bed. The sour gas or liquid then flows downward through the bed, contacting the SULFUR-RITE media, which removes H_2S and light hydrocarbons through conversion into a safe, easy-to-remove and dispose of iron pyrite compound. Following contact with the media, the sweetened gas or liquid exits the vessel near the bottom—no further treatment is required.

SULFUR-RITE media prefers high humidity to water-saturated gas streams; other gas components, such as carbon monoxide, do not affect media cost and/or performance to an appreciable level. For treating liquid hydrocarbons, such as gasoline or natural gas liquids, the stream may be dry and free from water.

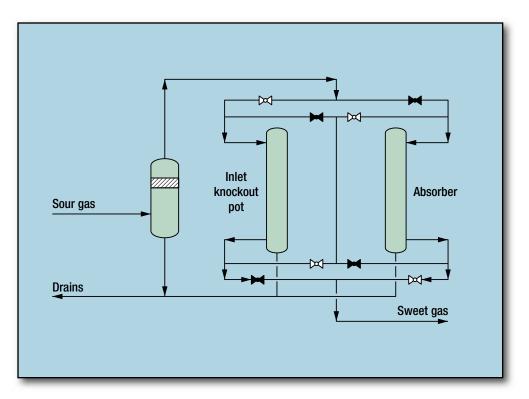
Customized units matching a particular design and/or operating conditions are available. Typically, bed pressure drop requirements are only a few inches of water; the SULFUR-RITE system is capable of providing removal performance (< 0.1 ppm of sulfur) at any stream pressure (or vacuum), inlet H₂S level, and for system temperatures up to 300°F.

Changing and/or filling SULFUR-RITE media is made easy with a bulk delivery system of 2,000-pound supersacks, which are specifically designed for smaller systems. Spent media material has many non-disposal recycle uses, such as road material making, brick manufacturing and agriculture industries.

Products: The following are SULFUR-RITE materials and their general uses:

ARI-710—Treats anaerobic gas streams where only $\mathrm{H}_2\mathrm{S}$ must be removed

ARI-720—For removal of both H₂S and light mercaptans from an-



aerobic gas streams

ARI-730LP—For removal of both H_2S and light mercaptans from air streams or streams containing significant oxygen; also provides very low pressure drop through the media bed

ARI-740HL—For removal of both H_2S and light mercaptans from liquid hydrocarbon and water streams

ARI-750XL—For removal of both H_2S and light mercaptans from anaerobic gas streams, where an extended media bed life cycle is required.

Economics: Operating costs are less than liquid scavengers, and for low-pressure treatment systems, have much greater reliability. In addition, there is minimal operating and utility requirements; vessel design is generally quite simple, allowing for local equipment fabrication, thereby lowering capital costs.

SULFUR-RITE, continued

Installations: Over 15 applications globally.

Licensor: Gas Technology Products, LLC.



SUPERCLAUS process

HYDROCARBON

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Application: The SUPERCLAUS process recovers elemental sulfur from hydrogen sulfide (H_2S) containing gases originating from gas treating plants such as alkanolamine units or physical solvent plants. Modern SUPERCLAUS plants should be able to process H_2S /ammonia (NH_3) containing gases as well, originating from sour water strippers, to yield up to 99.4% overall sulfur recovery without any further tail gas cleanup.

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Description: The SUPERCLAUS process has a thermal stage followed by three catalytic reaction stages with sulfur removed between stages by condensers. Two reactors are filled with standard Claus catalyst while the last reactor is filled with a new selective oxidation catalyst.

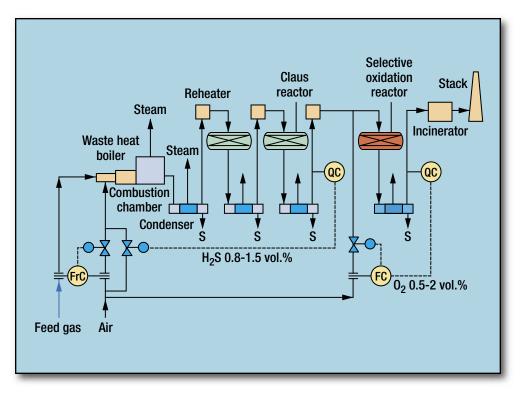
In the thermal stage, the acid gas is burned with a substoichiometric amount of controlled combustion air such that the tail gas leaving the second reactor contains typically 0.8 vol.% to 1.0 vol.% of H_2S . The catalyst in the third reactor oxidizes H_2S to sulfur at more than 85% efficiency.

However, because the new catalyst neither oxidizes H_2S to SO_2 and water nor reverses the reaction; total sulfur recovery up to 99% can be obtained. If sulfur recovery more than 99% is required, one additional Claus reactor stage will be installed upstream of the selective oxidation reactor.

Utilities: Basis: 100 tpd sulfur recovery unit; 93 vol.% H₂S feed gas and catalytic incineration.

ity	Consumption	Production
am, LP, tph	—	3.3
am, MP, tph	—	10.2
ctricity, kW	220	—
l gas, tph	0.12	—
ler feed water, tph	13.5	—
am, LP (plant heating), tph	0.4	—
am, MP, tph ctricity, kW I gas, tph ler feed water, tph	0.12 13.5	

Installations: Since the first commercial demonstration of the SUPER-CLAUS process in 1988, more than 125 plants with a capacity up to



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1,165 tpd are in operation or under construction in the third quarter of 2005.

Licensor: Comprimo Sulfur Solutions, a member of Jacobs Engineering Group.



ACORN methane wash

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Application: To produce a high-purity carbon monoxide (CO) stream, and a high-purity hydrogen stream, plus a ratio-adjusted synthesis gas stream, if required, for use as a chemical feedstock. The synthesis gas stream is typically the product of steam methane reforming (SMR).

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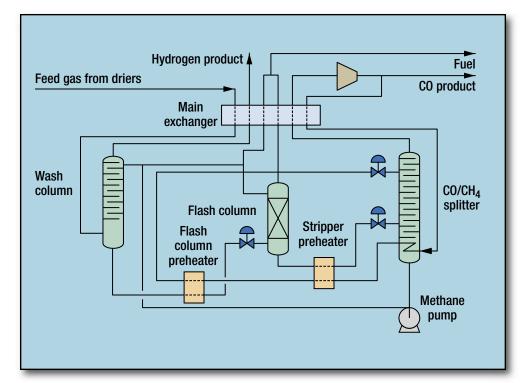
Description: Feed gas for CO recovery is pretreated to remove carbon dioxide and water, which will freeze at the cryogenic temperatures encountered in the process. The pretreated feed gas is cooled in the main exchanger and fed to the bottom of the wash column (1). The column is refluxed with liquid methane to produce a hydrogen wash-product free of CO, but saturated with methane (2–3%). The hydrogen is then rewarmed and recovered as a product. The liquid from the wash column (2) where hydrogen dissolved in the methane (CH₄) is rejected to fuel gas. To minimize CO losses, this column is also refluxed with liquid CH₄.

The hydrogen-free liquid from the flash column is heated and flashed to the CO/CH₄ splitter column (3). The CO from the overhead is rewarmed and compressed. Part of this stream is delivered as product; the remainder is cooled and recycled within the process. It is first used to reboil the splitter column and preheat the column feed streams. It is then flashed for refrigeration and the liquid is used as reflux for the splitter column. The CH₄ liquid from the bottom of the splitter is pumped to the wash column for use as reflux. The net CH₄ is vaporized in the main exchanger and leaves as the byproduct fuel gas.

Variations of this cycle have been developed to meet special requirements. In all cases, however, the hydrogen stream is produced at high pressure and the CO is available at low pressure. If CO is desired, a product compressor is usually required.

Installations: Seven.

Licensor: Air Products and Chemicals, Inc.



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ACORN partial condensation

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Application: To produce a high-purity carbon monoxide (CO) stream, and a moderate-purity hydrogen (H_2) stream, plus a ratio-adjusted synthesis gas stream for use as a chemical feedstock. The synthesis gas stream is typically the product of a partial oxidation reaction (POX).

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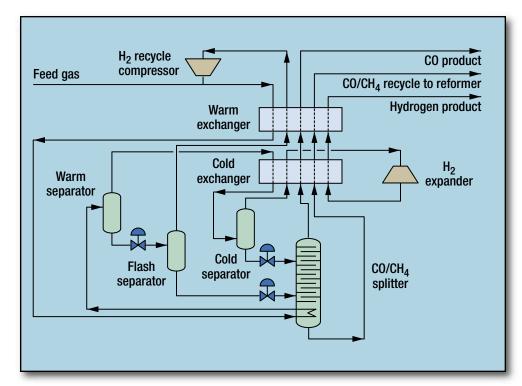
Description: Feed gas for CO recovery is pretreated to remove carbon dioxide and water, which will freeze at the cryogenic temperatures encountered in the process. The feed gas is cooled against products in the warm exchanger, and is then further cooled, providing heat for reboiling the CO/CH₄ splitter. Condensed CO and methane (CH₄) are removed from uncondensed vapor in the warm separator. Vapor from the warm separator is cooled in the cold exchanger where most of the remaining CO is condensed and separated in the cold separator. The liquid from this vessel is a high-purity CO stream used as reflux for the CO/CH₄ splitter.

Liquid from the warm separator is reduced in pressure and flashed in the flash separator to remove dissolved H_2 . The vapor from this separator is rewarmed, compressed and recycled to the feed to recover CO. The liquid from the flash separator is sent to the CO/CH₄ splitter. The CO overhead from this tower is warmed and recovered as product. The bottoms, containing CO and CH₄, is also warmed and is available as byproduct fuel gas. The H₂ from the cold separator is warmed in the cold exchanger, expanded to provide refrigeration for the cycle, warmed in the cold and warm exchangers and it leaves the process at 97–98% purity.

Variations on this basic cycle are possible depending on feed gas pressure and gas composition, and desired product purity. The H_2 product is delivered at high pressure, but the CO exits the process at low pressure. Therefore, a CO-product compressor is usually required to deliver the product to a downstream process.

Installations: Eleven.

Licensor: Air Products and Chemicals, Inc.



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Gas-to-liquids (GTL)

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Applications: To produce a zero-sulfur, pumpable syncrude from remote gas fields or from associated gas. The process can operate on a range of natural gas feedstocks including fields containing high carbon dioxide levels. The process is suited for remote or offshore locations where space and weight are of particular concern.

process categories

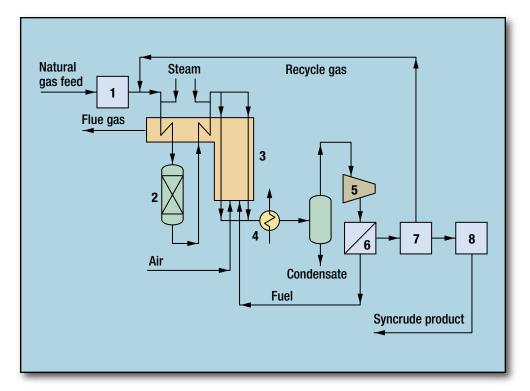
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Description: Natural gas is pre-treated to remove sulfur using conventional desulfurization technology (1). Steam and recycle gases are added and the feed is further heated before passing to the CRG pre-reformer (2). Using a nickel catalyst, the CRG pre-reformer converts heavier hydrocarbons to methane and partially reforms the feedstock. Addition of steam and further preheating are completed before the mixed gas passes to the compact reformer (3).

The Davy/BP compact reformer is a multi-tubular, counter-current reactor, which, in the presence of a nickel catalyst, produces a mixture of carbon oxides and hydrogen. Heat for this endothermic reaction is provided by external firing of excess hydrogen produced by the process with supplementary natural gas as required. Gas leaving the reformer is cooled (4) and generates sufficient steam to satisfy process heating requirements. Excess condensate is then removed.

Dry syngas is compressed in a single-stage centrifugal compressor (5) and passes to a membrane-separation package (6) where the surplus hydrogen is recovered and reused as fuel. The non-permeate product from the membrane separation is fed to the conversion section (7) where the syngas is converted into a mixed paraffin and wax product using a cobalt catalyst. The reaction system can either be a fixed bed or slurry type depending on unit size and project needs. Unconverted syngas is recycled to the compact reformer feed.

The wax products from the conversion section can be hydrocracked to produce a pumpable syncrude using conventional hydrocracking technology (8).



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Operating conditions: A wide range of reformer operating conditions are possible to optimize the process efficiency.

Installations: The compact reformer and fixed-bed FT processes have been successfully demonstrated in BP's test facility in Nikiski, Alaska. This facility has been in operation since second-quarter 2003.

Licensor: Davy Process Technology.



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Gas Processes 2006

Gas-to-liquids (GTLs)

Application: To produce ultra-clean fuels from natural gas or coal. The fuels, diesel, kerosine, naphtha and LPG contain no sulfur, aromatics or heavy metals. This process can be designed for onshore or offshore applications. Furthermore, it is self-sufficient in utilities and can be configured to export electricity.

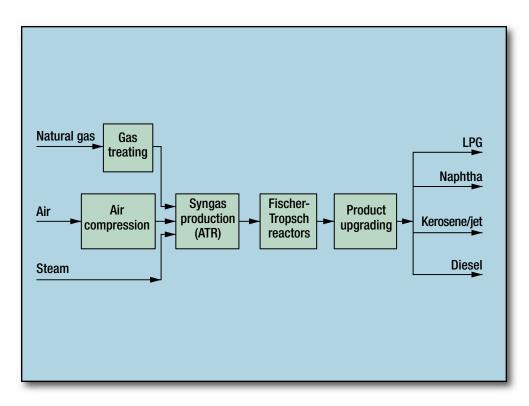
Description: The distinguishing characteristic of Syntroleum's Fischer-Tropsch (FT) process is using air to produce synthesis gas. Air, natural gas and steam are mixed and react in a proprietary auto-thermal reformer (ATR) to produce synthesis gas with an H₂:CO ratio of approximately 2:1. The synthesis gas is compressed and sent to the FT reactors. Using a proprietary cobalt catalyst, the carbon monoxide (CO) is hydrogenated into paraffinic, synthetic hydrocarbons. The catalysts yield an Anderson-Shultz-Fluory distribution with an alpha between 0.88 and 0.94, depending on the formulation.

Unreacted synthesis gas from the FT reactors is used as process fuel for turbines, heaters and other equipment. Both the ATR and the FT reactions generate byproduct heat and water, which are recovered and reused within the process.

The streams of synthetic crude are combined and refined into ultraclean diesel, kerosene, naphtha and LPG. Compared to conventional crude oil, refining FT crude is less severe, i.e., lower H_2 consumption, lower temperature and pressure, and longer catalyst life, due to the absence of sulfur, aromatics and heavy metals.

Operating conditions: Approximately 10,000 scf of gas produces one barrel of product. Plants can be economically designed for gas feedrates from 25 million scfd to 1,000 million scfd or more.

Economics: With the Syntroleum process, air is used in place of pure oxygen from an air-separation unit. Using air combined with the high-activity catalyst technology, this process can offer considerable capital and operating cost savings as compared to other competing processes.



Reference: US Patent 6,265,453.

Licensor: Syntroleum Corp.

Gas-to-liquids (GTL)

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Application: To produce transportable middle distillate products from natural gas. The process has a high carbon efficiency built around ConocoPhillips' proprietary COPox catalytic partial oxidation syngas process and ConocoPhillips' proprietary Fischer-Tropsch (FT) gas conversion process. ConocoPhillips GTL is an efficient option to monetize large and small stranded-gas reserves.

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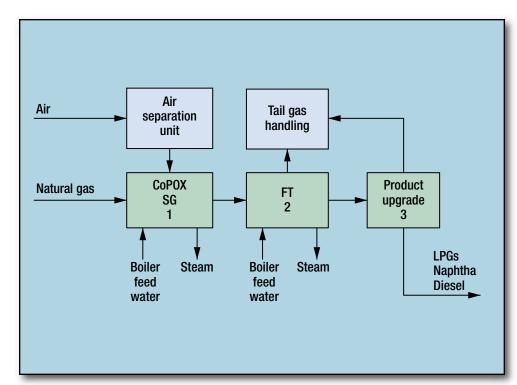
Description: The front-end process (1) is based on ConocoPhillips' unique and highly proprietary COPox catalytic partial oxidation syngas technology. The hydrocarbon feed conversion and selectivity to carbon monoxide (CO) and hydrogen (H_2) is higher than conventional equilibrium syngas production methods. The ConocoPhillips reactors have a high throughput and operate at relatively mild conditions.

The middle process (2) is based on ConocoPhillips' proprietary FT gas conversion technology. The FT process features a highly active catalyst that generates a paraffinic product spectrum with a high ASF alpha distribution and low methane selectivity. A higher alpha implies the production of a greater proportion of heavy hydrocarbons at the expense of less production of lighter hydrocarbons. Different reactor configurations can be used to minimize overall reactor volume and to tailor the desired product slate.

The FT product is finished in a back-end product upgrading unit (3) that includes hydro processing using both conventional and ConocoPhillips proprietary technology.

The efficient ConocoPhillips COPox syngas and FT conversion technologies are configured with an overall process design that delivers a high carbon efficiency while minimizing the required capex. The integrated process maximizes the use of the exothermic reaction heat and minimizes recycles.

Operating conditions: The ConocoPhillips COPox syngas process operates within a range of conditions depending on inlet gas composition. Typical operating temperature range is 600–1,000°C. The ConocoPhillips



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FT process operates within a typical temperature range of 200–250°C.

Installations: ConocoPhillips has a plant in Ponca City, Oklahoma, capable of producing 400 barrels per day (bpd).

Licensor: ConocoPhillips will be the licensor to its equity affiliates.



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Gas Processes 2006

MegaSyn

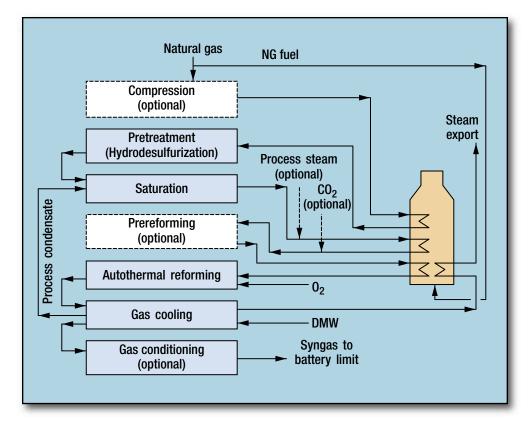
Application: Large-scale syngas production, essentially hydrogen (H_2) and carbon monoxide (CO), from natural gas or other gaseous hydrocarbons for methanol, ammonia, Fischer-Tropsch and other synthesis plants in one train.

Description: The hydrocarbon feedstock is preheated and desulfurized. The gas is then saturated with water by a circulation loop fed by process condensate. Before routing the feedgas to the autothermal reformer (prereforming is optional), this gas is preheated by a fired heater. Superheated gas is then sent to the autothermal reformer. If required, carbon dioxide (CO_2) can be fed to the prereformed gas.

In the autothermal reformer (ATR), the hydrocarbon feed is converted with oxygen to mainly CO and H₂ over a nickel-containing catalyst bed. The heart of the ATR is the mixer device, which facilitates the highly exothermic reaction between oxygen and hydrocarbon. Due to high temperatures in the ATR flame zone, reforming reactions take place here. The gas equilibrium composition is established within the catalyst bed. The temperature at the ATR outlet is 900°C to 1,050°C. Thus, high methane conversions are achieved. The reformed gas is cooled down to generate high-pressure steam, preheat feedgas, boiler feed water and circulation water loop.

Economics: Typical figures are presented for a syngas generation plant delivering syngas to Fischer-Tropsch synthesis. Consumption per 1 million scfd syngas:

Natural gas (feed + fuel):	441 million Btu
Oxygen:	0.22 million scfd (over the fence)
CO ₂ :	0.09 million scfd
Demineralized water:	0.98 tons
Cooling water:	11.5 tons
Electricity:	22.4 kWh
Export steam:	18.5 tons
Specific investment:	€224,000/million scfd syngas



Installations: World's largest natural gas-based syngas generation plant, and world's largest (single-train) autothermal reforming unit. A total of 30 autothermal units.

Licensor: Lurgi AG.



Multipurpose gasification

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Application: Production of synthesis gas, essentially H_2 and CO, from a wide range of gaseous to extra heavy liquid hydrocarbons, as well as emulsions and slurries. Recent new applications are in (chemical) waste gasification. The main advantage over comparable processes is its extreme feedstock flexibility in the quench mode. A boiler mode for highest efficiency is also available.

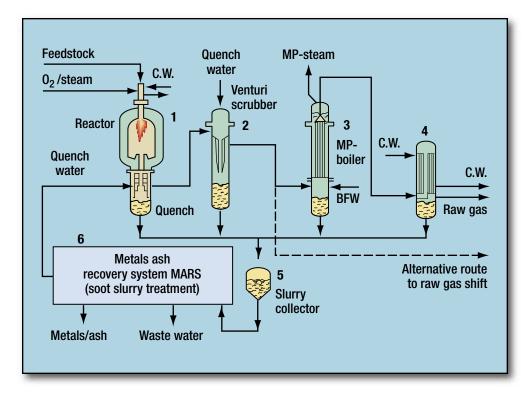
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Description: Continuous noncatalytic partial oxidation process. The quench mode is shown above: hydrocarbon feedstock, moderator (H_2O , CO_2 or N_2) and oxidant (pure or diluted O_2 , air) are fed through a special burner into the reactor (1), a refractory-lined pressure vessel. Operating conditions are automatically controlled. Hot gas leaves the reactor at the bottom, passing the quench where water is injected to lower the temperature near the saturation temperature. Quench water washes out most particulates as unconverted carbon (soot) and ash.

Further cleaning occurs in a venturi scrubber (2) from where the gas passes to a medium-pressure steam boiler (3) for heat recovery and to the final cooler (4) before further processing. In hydrogen production, the hot, wet gas from the venturi is passed directly to a raw gas shift conversion. The soot/ash slurry from the process contains virtually all metals and ashes from the feedstock. It is withdrawn via a slurry collector (5) and processed in the metals ash recovery system (MARS) (6). There, soot/ash is filtered from the slurry and incinerated under controlled conditions, yielding a saleable metal/ash product. Filtered water is returned for quenching. Excess water is stripped and sent to conventional wastewater treatment.

Operating conditions: Actual gasification temperatures of 1,200°C to 1,500°C, pressures from atmospheric to 70 bar (or higher, if economically justified). Feedstock and oxidant preheat possible in a wide range from 100°C to 600°C, depending on type of feed. Product yields and composition vary with moderator rate and type of feed. Water quench is selected for highest feedstock flexibility. At low-salt contents, the boiler mode can



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recover heat as high-pressure steam, raising overall efficiency.

Economics: Characteristic consumption and production rates per ton of heavy residue feedstock: 1 to 1.1 t O_2 (100%), export 0.5 t MP steam (quench) to 2.2 t HP steam (boiler mode), 2.2 t raw syngas (dry) equiv. to 2,600 Nm³ H₂ + CO. Cold gas efficiency is 82% to 85%. In boiler mode, thermal efficiencies including HP steam generated are about 95% based on feedstock HHV. This makes the process attractive for syngas production and for an IGCC power plant. A highly integrated and efficient power complex will be in the range of \$1,200/kW total invested cost.

Installations: A large-scale industrial plant operates in Germany, demonstrating full feedstock and product flexibility by feeding to a methanol and IGCC complex. Another plant gasifies residue asphalt, producing syngas for an ammonia plant. Continued ▼

Multipurpose gasification, continued

Reference: Liebner, W. and C. Erdmann, "MPG—Lurgi Multipurpose Gasification—Recent Applications and Experiences," World Petroleum Congress 2000, Calgary, Canada, June 2000.

Licensor: Lurgi AG.



Syngas (H₂ + CO)

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Application: Production of syngas (H_2 + CO) from hydrocarbon (HC) feedstocks by steam reforming.

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Feedstocks: Hydrocarbons ranging from natural gas to naphtha.

Description: The generic flowsheet consists of feed pre-treatment, prereforming (optional), steam-hydrocarbon $(+CO_2)$ reforming, CO_2 removal and purification by cold box or pressure swing adsorption (PSA). However, it is often tailored to satisfy specific requirements.

Feed pre-treatment normally involves removing sulfur, chlorine and other catalyst poisons after preheating the hydrocarbon feed to appropriate level.

The treated feed gas and recycle CO_2 (from the CO_2 removal section) mixed with process steam is reformed in a fired reformer (with adiabatic pre-reformer upstream, if applied) after necessary super-heating. The net reforming reactions are strongly endothermic. Heat is supplied by combusting purge gas from the purification system, supplemented by makeup fuel in multiple burners in a top-fired furnace.

Reforming severity is optimized for each specific case. Waste heat from the reformed gas is recovered through steam generation. Process condensate resulting from heat recovery and cooling of the reformed gas is separated and generally reused in the steam system after necessary treatment.

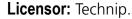
After cooling the reformed gas is sent to the CO_2 removal section, where CO_2 is removed from the reformed gas before it enters the purification system to produced desired quality of syngas. The entire steam generation is usually on natural circulation, which adds to higher reliability.

Installations: Technip has been involved in over 10 syngas plants worldwide.

Recycle H₂ Process steam Compression/ Feed Export pretreatment pumping HC feedstock steam Steam Makeup fuel Purge gas system Pre-reformer (optional) BFW Fuel system Compression Vent steam Recycle PG **Convection Reformer** Stm boiler CO_2 BFW section Dosing preparation BFŴ Steam system Optional comb. air preheater coils To steam Process system Process coils condensate Ľ Cooling Air Flue gas train stack DMW Purge to fuel system Recycle/byproduct H₂ CO₂ removal Purification section system Compression Syngas product

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Syngas-advanced SMR

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Application: Produce a CO-rich synthesis gas.

Products: Pure CO and H_2 , or mixtures of CO and H_2 (synthesis gas), are used to manufacture many chemicals, e.g., acetic acid, oxo-alcohols and isocyanates.

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Description: Advanced steam reforming in a fired-tubular reformer is the predominant process route for medium-sized synthesis gas plants. The Topsøe radiant-fired reformer and reforming catalysts enable operating at low steam-to-carbon ratios, high reformer outlet temperature and high heat flux.

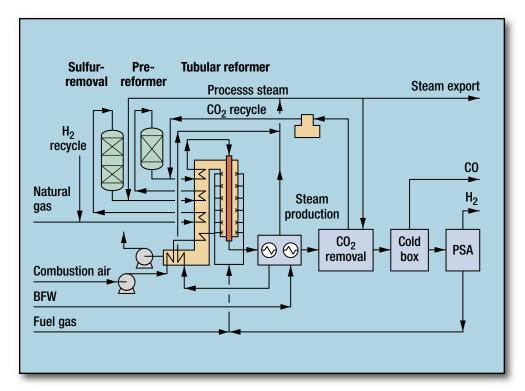
The hydrocarbon feedstock can be natural gas, LPG or naphtha. For heavy feedstocks, an adiabatic pre-reformer is advantageous upstream of the tubular reformer. Carbon dioxide (CO_2) import and/or CO_2 recycle is applied to produce CO-rich synthesis gas.

The unit typically consists of feed desulfurization, pre-reforming, tubular reforming, CO_2 recovery and recycle, and final purification. Purification of the synthesis gas by membrane, cold box and PSA is dependent on the required end-product specifications.

Operating conditions: Typically, CO-rich synthesis gas is obtained at feed ratios of $H_2O/CH_4 = 1.5$ to 2.0 with CO_2 recycle and/or CO_2 import. This results in H_2/CO ratios down to 1.8 at a reformer exit temperature of 950°C (1,740°F). Even lower H_2/CO ratios can be obtained by CO_2 reforming using the SPARG process or by applying a high-activity, noblemetal reforming catalyst.

Economics: Production of CO-rich synthesis gases at advanced steam reforming conditions offer significant savings in operating and investment costs.

References: Winter Madsen, S., et al., "Advanced reforming technologies for synthesis gas production," Symposium on Large Chemical Plants, Antwerp, September 1998.



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Vannby, R. and C. Stub Nielsen, "Operating experience in advanced steam reforming," Symposium on Large Chemical Plants, Antwerp, October 1992.

Winter Madsen, S. and J-H. Bak Hansen, "Industrial aspects of CO₂ reforming," AIChE Spring Meeting, Houston, March 1997.

Licensor: Haldor Topsøe A/S.



Syngas (autothermal)

HYDROCARBON

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Application: Production of carbon monoxide and hydrogen for petrochemical use. Typical consumers are oxo-alcohol synthesis units and methanol synthesis units.

process categories

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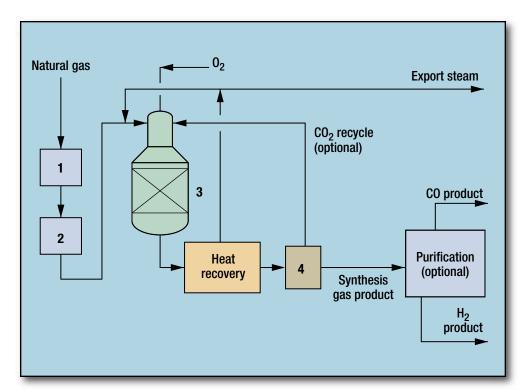
Products: Synthesis gas containing carbon monoxide and hydrogen. The synthesis gas can be used directly for chemical production or, alternatively, can be further processed to yield high-purity carbon monoxide and high-purity hydrogen.

Description: The feed is preheated (1) and then desulfurized in a conventional hydrotreating-zinc oxide system (2). Steam is added to the desulfurized feed. Carbon dioxide recycle (optional) is also added. The feed mixture is sent to the autothermal reformer (3) a refractory-lined vessel containing catalyst and a burner. The feed mixture is burned with oxygen in the burner located near the top of the reformer vessel. Partial oxidation reactions occur in a combustion zone just below the burner. The mixture then passes through a catalyst bed where reforming reactions occur. The gas exits at about 1,700°F to 1,900°F, depending on the final product specifications.

The exit gas is cooled and passed through a carbon dioxide removal unit (4). The resulting process gas consists primarily of carbon monoxide and hydrogen and is available as product synthesis gas. This synthesis gas can be used to make a variety of chemicals, including methanol and oxo alcohols. Alternatively, the gas can be further processed (typically by cryogenic separation) to yield high-purity carbon monoxide and highpurity hydrogen.

Carbon dioxide can be recycled to adjust the H_2/CO product ratio. For natural gas feedstocks, the H_2/CO product ratio ranges from about 2.7 (for no CO_2 recycle) to 1.6 (for full CO_2 recycle).

Autothermal reforming technology is similar to secondary reforming for ammonia production, except that oxygen is used as feedstock instead of air. Oxygen is required since nitrogen would dilute the H_2/CO product gas purity.



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Economics: The economics can be favorable for autothermal reforming when oxygen is available at relatively low cost. For natural gas feed-stocks, the optimum H_2/CO product ratio is about 1.6 to 2.7.

Reference: Tindall, B. M and M. A. Crews, "Alternative technologies to steam-methane reforming," *Hydrocarbon Processing*, November 1995.

Supplier: CB&I Howe Baker.



Syngas-advanced SMR

HYDROCARBON

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Application: Produce a CO-rich synthesis gas.

Products: Pure CO and H_2 , or mixtures of CO and H_2 (synthesis gas), are used to manufacture many chemicals, e.g., acetic acid, oxo-alcohols and isocyanates.

process categories

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Description: Advanced steam reforming in a fired-tubular reformer is the predominant process route for medium-sized synthesis gas plants. The Topsøe radiant-fired reformer and reforming catalysts enable operating at low steam-to-carbon ratios, high reformer outlet temperature and high heat flux.

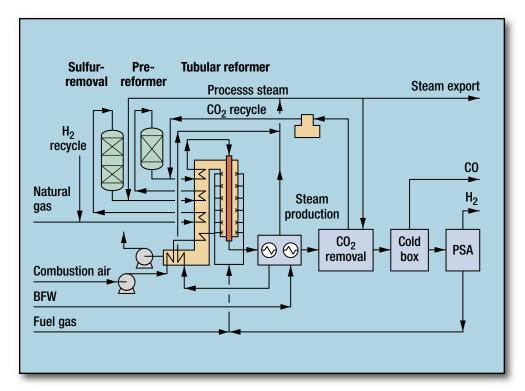
The hydrocarbon feedstock can be natural gas, LPG or naphtha. For heavy feedstocks, an adiabatic pre-reformer is advantageous upstream of the tubular reformer. Carbon dioxide (CO_2) import and/or CO_2 recycle is applied to produce CO-rich synthesis gas.

The unit typically consists of feed desulfurization, pre-reforming, tubular reforming, CO_2 recovery and recycle, and final purification. Purification of the synthesis gas by membrane, cold box and PSA is dependent on the required end-product specifications.

Operating conditions: Typically, CO-rich synthesis gas is obtained at feed ratios of $H_2O/CH_4 = 1.5$ to 2.0 with CO_2 recycle and/or CO_2 import. This results in H_2/CO ratios down to 1.8 at a reformer exit temperature of 950°C (1,740°F). Even lower H_2/CO ratios can be obtained by CO_2 reforming using the SPARG process or by applying a high-activity, noblemetal reforming catalyst.

Economics: Production of CO-rich synthesis gases at advanced steam reforming conditions offer significant savings in operating and investment costs.

References: Winter Madsen, S., et al., "Advanced reforming technologies for synthesis gas production," Symposium on Large Chemical Plants, Antwerp, September 1998.



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Vannby, R. and C. Stub Nielsen, "Operating experience in advanced steam reforming," Symposium on Large Chemical Plants, Antwerp, October 1992.

Winter Madsen, S. and J-H. Bak Hansen, "Industrial aspects of CO₂ reforming," AIChE Spring Meeting, Houston, March 1997.

Licensor: Haldor Topsøe A/S.



Syngas—autothermal reforming

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Application: Produce reformed gas for various synthesis processes and/ or hydrogen (H_2) and/or carbon monoxide (CO).

process categories

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Feed: Natural gas, refinery offgases, LPG, naphtha or mixtures thereof.

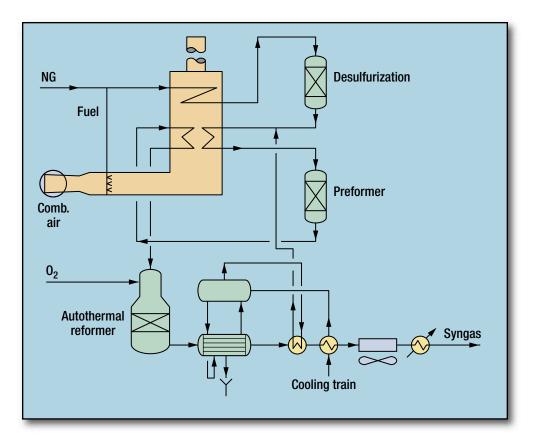
Product: Synthesis gas for the production of CO, H_2 , ammonia, methanol, Fischer-Tropsch products, synthetic fuels and oxo-chemicals.

Description: Autothermal reforming can be used as an alternative to conventional steam reforming to accommodate the production of CO-rich reformed gases. The feed is preheated and desulfurized before entering the adiabatic reactor combustion chamber. At the autothermal reformer (ATR) top, the feed mixture is burned with oxygen (O_2), air or O_2 -enriched air in a partial oxidation chamber.

The main feature of the Uhde ATR design is the unique arrangement of water-cooled O_2 nozzles in the ATR dome. This method allows for complete mixing without any internals in the combustion zone, thus ensuring a long burner life and enhanced reliable operation. The steam reforming reactions take place mainly in a bed consisting of a nickelbased catalyst.

The reformed gas leaves the ATR at about 1,000°C to 1,100°C and its sensible heat is mainly utilized to produce high-pressure steam. The gas is finally cooled before entering the required product purification sections, such as carbon dioxide (CO₂) removal, membrane or cryogenic separation, among others, as requested by the individual application. The process scheme can further include CO₂ addition or recycle to the ATR to further boost the system economics.

Installations: Uhde's ATR technology is derived from Uhde's well-proven secondary reformer design which has successfully demonstrated its reliability in many ammonia plants worldwide. The water-cooled burner nozzles arrangement has been operated successfully with O₂ over 10 years in a 12,000-Nm³/h H₂/CO production unit together with Uhde's



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proprietary combined autothermal reforming (CAR) technology.

Reference: Babik A. and J. Kurt (Uhde), "Slovakian refiner operating new hybrid hydrogen production process," *Oil & Gas Journal,* March 21, 1994, OGJ SPECIAL.

Licensor: Uhde GmbH.



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Gas Processes 2006

Syngas—steam reforming

Application: Produce synthesis gas for various demands and for hydrogen (H_2) and/or carbon monoxide (CO) production using advanced steam reforming methods.

Feed: Natural gas, refinery offgases, LPG, naphtha or mixtures thereof.

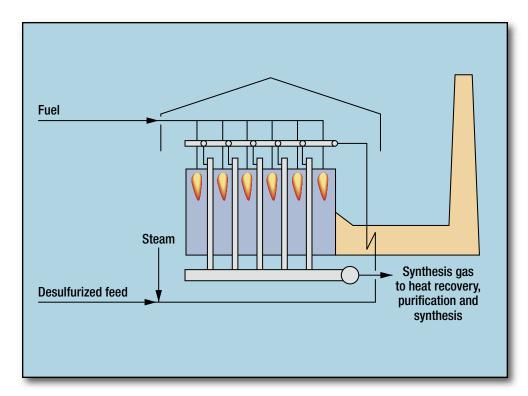
Product: Syngas for H_2 , CO, ammonia, methanol, Fischer-Tropsch synfuels, oxo-synthesis products, etc.

Description: The steam reforming process comprises high-temperature conversion of desulfurized feed with steam to produce H_2 , CO and carbon dioxide (CO₂). The design conditions of the steam reformer vary and depend on the application, with discharge temperatures ranging from 740°C to 950°C and pressures up to 50 bar.

This wide range of operating conditions necessitates a versatile reformer design. The Uhde steam reformer features a well-proven topfired design with a unique proprietary "cold" outlet manifold system to enhance reliability and vertical tubes made of centrifugally cast alloy steel containing a nickel-based catalyst. A further speciality of Uhde's syngas plant design is an optional bi-sectional steam system for the environmentally friendly full recovery of process condensate and production of high-pressure export steam with a proven process gas cooler design.

The Uhde steam reformer concept also includes a fully pre-fabricated and modularized shop-tested convection bank to further enhance the plant quality standard and minimize construction risks. The final process stages are completed according to individual product requirements and may include CO shift, pressure swing adsorption, CO₂ removal (e.g., MDEA), membrane or cryogenic separation, as required for the desired products.

Other typical process options are feed evaporation, CO_2 recycle, adiabatic feed pre-reforming and/or HT/LT shift to process, e.g., heavier feeds and/or optimize feed/fuel consumption and steam production. Uhde's design allows combining maximized process heat recovery and



optimized energy efficiency with operational safety and reliability.

The Uhde reformer design is particularly advantageous for the construction and reliable operation of large-scale reformers and has proven its suitability over the past decades. Uhde offers either standard or tailormade designs and applies either customer or own design standards.

Installations: The first Uhde reformer with a "cold" outlet manifold went onstream in 1966. In 1977 and 1984, two large Uhde steam reformers with 540 reformer tubes each were commissioned, and these units are still in operation. More than 60 Uhde reformers have been built worldwide and the largest reformer based on Uhde technology consists of 960 tubes.

Uhde has recently commissioned a large ammonia/urea complex based on natural gas in Qatar and two world-scale H_2 plants for Shell Continued \blacksquare

Syngas—steam reforming, continued

Canada Ltd., Canada, and SINCOR C.A., Venezuela, and is presently executing eight reformer projects worldwide: Four reformers in large-scale ammonia/urea complexes in Egypt and Saudi Arabia, and the other four in large-scale H_2 plants.

Reference: Beyer, F, J. Brightling, P. Farnell and C. Foster, "Steam Reforming—50 years of development and the challenges for the next 50 years," AICHLE Ammonia Safety Symposium 2005, Toronto, Canada, September 2005.

Licensor: Uhde GmbH.



ADIP

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Application: The regenerative-amine process removes hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from natural gas, refinery gases and synthesis gas. Hydrogen sulfide can be reduced to low sulfur levels. The process can also be applied to remove H_2S , CO_2 and carbonyl sulfide from liquefied petroleum gas or natural gas liquids (NGL) to low levels. Bulk CO_2 removal from synthesis gas with flash regeneration is another application.

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The process sequence—ADIP/Claus/SCOT—can be used advantageously with an integrated ADIP system that handles selective H_2S removal upstream and the SCOT process treating the Claus offgas.

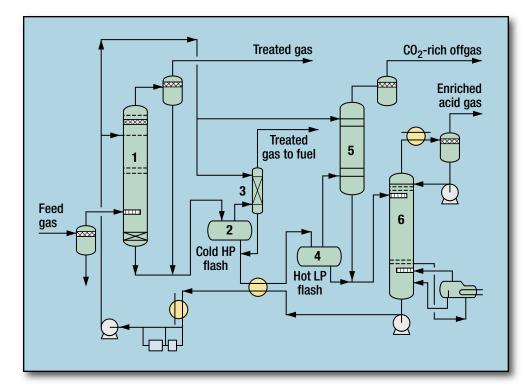
Description: The ADIP process uses aqueous solutions of the secondary amine, di-isopropanolamine or the tertiary amine, methyl di-ethananol-amine. Amine concentrations up to 50%wt can be applied.

The process has low observed corrosion rates and a controllable foaming tendency of the solvent due to an optimized design. Its lineup can be very diverse, depending on the application. High integration of separate process units is possible.

The simplest system resembles those of other amine processes. The ADIP liquid treating consists of an extractor followed by mixer/settlers for COS removal. Common regeneration for separate amine absorbers is often applied. Solvent composition will be optimized for customer requirements.

For a typical design, the co-absorbed hydrocarbons from the absorber (1) are flashed (2) from the solvent and used as fuel gas after treatment (3). The solvent is flashed again (4) to release CO_2 from the enrichment absorber (5), thereby improving the acid-gas composition from the regenerator (6) to the Claus unit.

Operating conditions: A very wide range of treating pressures and contaminant concentrations can be accommodated. Sulfur specifications of 100 mbara H_2S in gas and 10 ppmw in liquid hydrocarbon streams can be met. In liquid hydrocarbon, COS can be removed down to 5 ppmw. Improved Claus feed gas quality can be met by improving the H_2S/CO_2



company index

ratio in the acid gas. Bulk CO_2 removal from a high percentage to several percentage points is easily attained.

Installations: More than 400 ADIP units are in operation or under construction. Applications include: natural gas, liquefied natural gas, refinery gases and liquefied petroleum gases and synthesis gases.

References: "ADIP as the preferred solvent for amine treatment in refinery applications," Laurance Reid Conference, March 1999.

"Process applications of the ADIP and Sulfinol process," Gas Processing Symposium, Dubai, United Arab Emirates, April 1999.

Licensor: Shell Global Solutions International B.V.



ADIP-X

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Application: This regenerative-amine process is highly suitable for bulk and deep carbon dioxide (CO_2) removal from gas streams. It also removes hydrogen sulfide (H_2S) , some COS and mercaptans from natural gas, refinery gas and synthesis gas. H_2S can be reduced to low-sulfur levels. This process achieves a higher loading capacity and reduced equipment size compared to general aqueous amine solvents.

process categories

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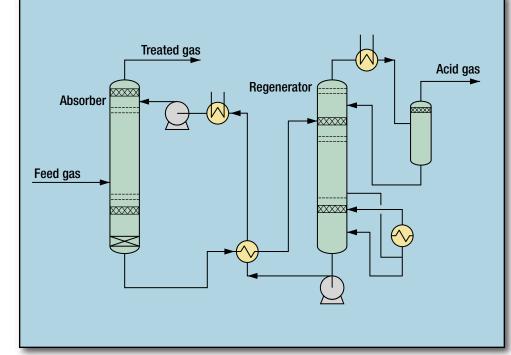
Description: The ADIP-X process uses aqueous solutions of the tertiary amine, methyl diethananolamine and an additive. Amine concentrations up to 50%wt can be applied. The process has low observed corrosion rates and a controllable foaming tendency of the solvent due to an optimized design. Its lineup can be very diverse, depending on the application. High integration of separate process units is possible. The simplest system resembles those of other amine processes. Common regeneration for separate amine absorbers is often applied and may consist of one or more flash/steam strip regeneration steps. Solvent composition will be optimized for customer requirements.

Operating conditions: A very wide range of treating pressures and contaminant concentrations can be accommodated. CO_2 specifications below 50 ppmv in gas streams can be met. H_2S specifications down to 100 mbar are also achievable. Bulk CO_2 removal from a high percentage to several percentage points is easily attained.

Installations: ADIP-X is applied in one natural gas application.

References: "CO₂ removal from natural gas; accelerated process selection," Gas Processing Association, New Orleans, March 2004.

"Accelerated amines technology for carbon dioxide removal at Brunei LNG," *LNG Journal*, September/October 2004.



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Licensor: Shell Global Solutions International B.V.



AdvAmine (formerly Advanced Amines)

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Applications: AdvAmine is a complete portfolio of amine (DEA, MDEA and formulated MDEA) based processes to sweeten natural gases. AdvAmine processes cover all types of acid gas removal applications, for any type of feed gas composition and product specifications as low as hydrogen sulfide (H_2S) <1 ppm and carbon dioxide (CO_2) <50 ppm.

process categories

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Description: The AdvAmine portfolio is based on the extensive industrial and operational experience of TOTAL which developed these technologies [initially SNEA-(P), ELF Group]. It includes the following processes:

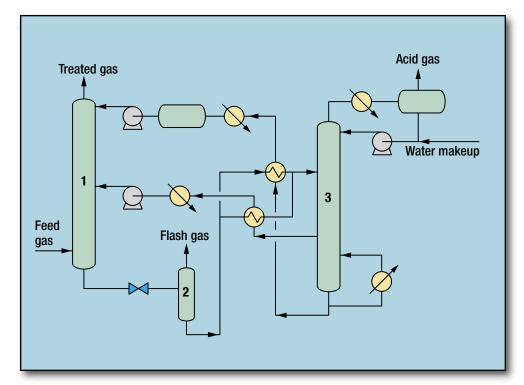
• **Hi**Load**DEA**: A process based on using high-concentration (4 mol DEA/I) and high-loading (mol acid gas/mol DEA) DEA, for high-performance complete deacidification

• **MDEA**max: A process based on using pure MDEA aqueous solution for selective H₂S removal or H₂S enrichment applications

• energized**MDEA**: For all complete deacidification applications, with a range of patented additives (called "energizers"). energized-**MDEA** offers specific advantages like partial/total flash regeneration of the solvent for CO₂ removal applications.

For all these processes, various flow schemes are available, from the conventional absorber/thermal regenerator process up to more sophisticated flow schemes. For instance, the Double Split Flow scheme, shown on the figure, maximizes acid gas removal and minimizes energy requirement, by using a flow of semi-lean amine, withdrawn from an intermediate level of the thermal regenerator (3) and sent back at an intermediate level of the absorber (1). Energy requirement can also be minimized with *energized*/**MDEA** by partial flash regeneration of the solvent. With **Hi**Load**DEA** and *energized*/**MDEA**, a proprietary absorber design is also available which allows high COS hydrolysis levels (up to 95% COS removal).

Installations: More than 120 units, among which about a third are oper-



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ated by TOTAL, with unit capacities between 0.3 Nm³/d and 25.2 Nm³/d.

References: Bonis, M. and et al., "A critical look at amines: A practical review of corrosion experience over four decades," 83rd Annual GPA Convention, New Orleans, Louisiana, March 14–17, 2004.

Khaja, A. and et al., "Successful revamp of MDEA unit at Qatar Petroleum increases capacity," 84th Annual GPA Convention, San Antonio, Texas, March 13–16, 2005.

Licensor: Prosernat – IFP Group Technologies.



aMDEA process

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Application: Removal of carbon dioxide (CO_2) , hydrogen sulfide (H_2S) , COS and RSH from synthesis gas, natural gas or other gases.

process categories

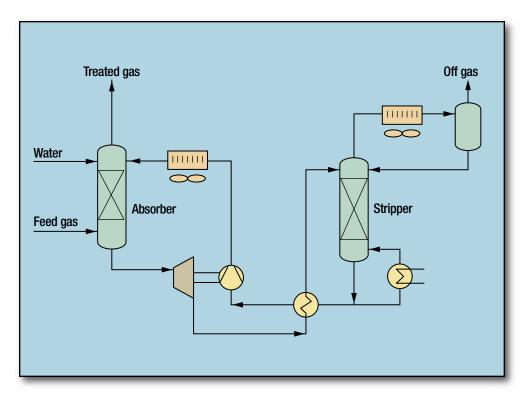
Products: Treated gas to meet pipeline, liquefied natural gas (LNG) plant, ammonia plant or petrochemical plant specifications. Acid offgas with very low inert gas content. Production of food-grade CO₂ is possible.

Description: Acid components, found in the feed gas, are removed by absorption with an aqueous solution of MDEA and an activator system. The rich solution leaving the absorber is regenerated by flashing and/ or stripping through one or more regenerating steps. Different process configurations can be combined with various solvent types and concentrations to meet requirements for individual applications. It is possible to customize gas treatment to the customers' economic priorities.

Operating conditions: Reference plants cover a range from 3,000 Nm³/ hr to 810,000 Nm³/hr feed gas capacity, absorber temperatures from 30°C to 90°C, absorber pressures from atmospheric range up to 120 bar and feed gas compositions from 0.5 to 25 vol.% CO₂ and 0 to 15 vol.% H₂S. Treatment at higher pressures with more CO₂/H₂S in the feed gas is achievable.

Economics: The process is highly energy efficient due to the elevated acid-gas loadings achievable with the solvent; this enables using low circulation rates and reduced energy consumption, as well as reducing required equipment size. Energy consumption for CO₂ removal from ammonia synthesis gas: 1 kWh/kmol CO₂ electrical power and 32 MJ/kmol CO₂ thermal energy. Thermal energy consumption for natural gas treatments: 15–20 MJ/kmol CO₂ and H₂S removed (flash regeneration).

Additional advantages: Very low hydrocarbon co-absorption, no degradation products, no corrosion (mainly carbon steel equipment can be used), low foaming tendency, no reclaimer operation is necessary, and the solvent is nontoxic and biodegradable.



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Installations: More than 200 plants in operation and over 30 units are under design or construction, mostly treating synthesis gas, natural gas and hydrogen streams.

Licensor: BASF AG.

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Gas Processes 2006

Amine Guard FS

Application: Remove CO_2 and H_2S from natural gas; CO_2 from ammonia syngas, etc., with a solution containing one of the UCARSOL family of formulated solvents offered by Dow. When desired, H_2S can be removed selectively to provide a superior Claus plant feed and reduce regeneration requirements.

Product: Purified gas to meet pipeline, LNG plant, GTL plant, ammonia plant or petrochemical plant specifications as appropriate.

Description: The typical flow scheme is that the treating solution scrubs acid gases from the feed in an absorber column (1) in the diagram. The rich solution is regenerated by reducing its pressure and stripping with steam in the stripper tower (2). Waste heat is commonly used to provide the steam.

Regeneration energy is minimized by choosing the optimum UCAR-SOL solvent for the situation, using high-solvent concentrations and proper selection of flow scheme.

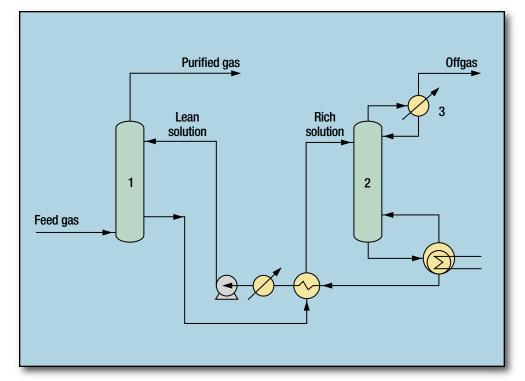
Operating conditions: Absorption pressure is atmosphere to 1,200 psi, as available. Feed temperature is 85°F to 150°F. Acid gas content may be 5–35%.

Economics: For a 25 million-scfd natural gas unit having a feed gas containing $10\% CO_2$ and $1\% H_2S$, typical costs are as follows:

	Pipeline
Investment, \$million	14.0
Operating costs, \$million/y	6.0

Installations: Over 500 units worldwide, mostly treating natural gas, ammonia syngas and hydrogen streams.

Licensor: UOP LLC.





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Gas Processes 2006

Ammonia Claus technology—ACT

Application: Sulfur recovery from hydrogen sulfide (H₂S) contained in ammonia (NH₃) bearing feeds, typically acid gases from sour water strippers (SWSs).

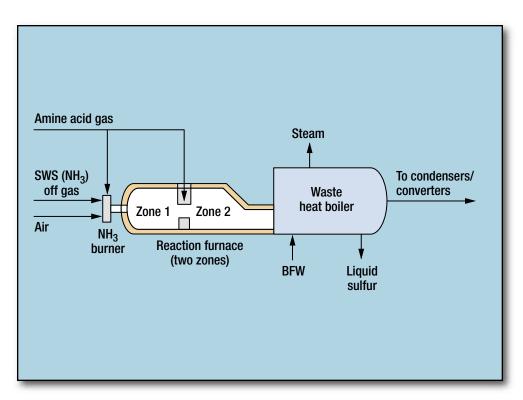
Product: Bright yellow high-purity sulfur and NH_3 decomposition in elemental species like nitrogen and water (H_2O).

Description: Conventional straight-through Claus plant configuration applying a single-zone reactor furnace that can operate when NH_3 volume concentration in the feed gas is lower than a few tenths of a percent. At higher NH_3 concentrations, especially from an SWS gas stream, which is mainly NH_3 , H_2S and H_2O , it becomes necessary to destroy NH_3 in order to avoid severe operational problems that may occur in the sulfur recovery units (SRUs).

In fact, NH₃ in the presence of H_2S forms ammonium (poly) sulfide, which solidifies at temperatures below 150°C and tends to plug sulfur condensers, sulfur run-down lines and seal pots. In addition to plugging problems, NH₃ in sulfur recovery gas feeds increases plant size, related cost and decreases sulfur recovery.

To fully destroy NH₃, the straight-through type plant can still be applied but with different burn configurations conceived to attain the operating conditions needed for NH₃ decomposition. In ACT, a dual-stage burn strategy is used by applying a "two-zone furnace" design in which an NH₃-bearing stream is burned with part of the amine acid gas (NH₃ "free" stream) in Zone 1 at high temperature, followed by reinjecting the remaining amine acid gas into Zone 2 of the reaction furnace. In addition, a high-intensity properly designed burner, having excellent mixing characteristics, is used to easily reach the required high temperature levels.

Operating conditions: The operating temperature in the ACT "two-zone furnace" configuration can vary between 1,350°C and 1,650°C and the ACT pressure drop is around 0.3 bar. By adopting ACT, an NH₃-bearing



feed can be treated up to a level of NH_3 concentration in the furnace effluent gas that is not harmful for regular SRU operation.

Economics: ACT uses standard equipment and carbon steel almost everywhere.

Commercial plants: Several ACT plants have been built with NH₃ concentration in the feed stream ranging from 0.5% to 30%. The most recent plant, under construction, is at Gorlice, Poland, for Lurgi Bipronaft (Lurgi Group Co.) with 14% vol. of NH₃ in the feed gas.

Licensor: SIIRTEC NIGI.



Benfield

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Application: Removal of CO_2 and H_2S from natural gas, syngas, etc. Removal of CO_2 from ammonia syngas, ethylene oxide recycle gas, etc.

process categories

Product: Purified gas to meet pipeline or LNG plant, ammonia plant or petrochemical plant specifications as appropriate.

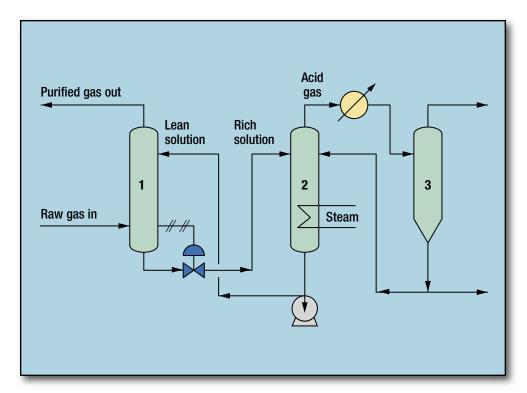
Description: Acid gases are scrubbed from the feed in an absorber column (1) using potassium carbonate solution with Benfield additives to improve performance and avoid corrosion. The rich scrubbing solution is regenerated by reducing its pressure and stripping with steam in the stripper tower (2). Waste heat is commonly used to provide the steam. In the LoHeat version, the hot, lean solution is flashed by sending the steam through ejectors to reduce the energy requirements. In the HiPure version, acid gases are reduced to very low levels by polishing using an integrated DEA absorption loop.

Operating conditions: Absorption pressure is 150 psi to 1,800 psi, as available. Feed temperature is about 150°F to 250°F. If the feed is available at a higher temperature, that heat will be used to supply regeneration heat. Acid gas content may be 5–35%. Heavy hydrocarbons are easily handled. If no H_2S is present, oxygen contents of several percent are handled without difficulty or solvent degradation.

Economics: The extensive use of carbon steel, the elimination of a rich/ lean solution heat exchanger, the heat recovered by LoHeat and the low cost of the solution chemical make the process attractive for a wide range of applications. For a 500 million-scfd natural gas unit having a feed gas containing 6% CO_2 and 1% H_2S , typical costs are as follows:

	Pipeline	LNG feed
Investment, \$million	14.0	20.0
Operating costs, \$million/y	5.0	6.0

Installations: Of the more than 700 units worldwide, more than 65 treat natural gas, over 200 treat ammonia syngas and about 110 are in hydro-



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gen plants. The remainder are in SNG, partial oxidation, coal gasification and petrochemical applications.

Licensor: UOP LLC.

process index



Calcor process (carbon monoxide)

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Application: To produce carbon monoxide (CO) from natural gas or liquefied petroleum gas (LPG) through carbon dioxide (CO_2) reforming.

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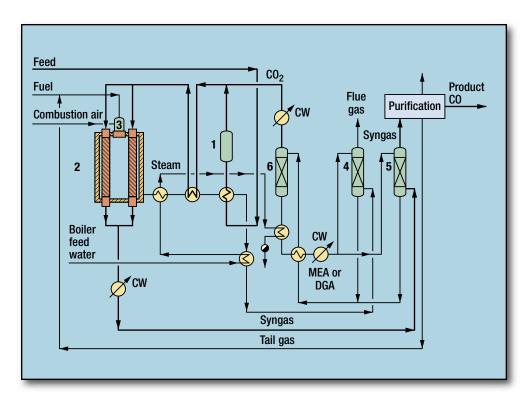
Description: Calcor is a CO_2 reforming process combined with a CO_2 recovery unit and a CO purification step. The Calcor Standard process is designed to operate under low pressure and uses catalytic reforming operating at high temperatures. To protect the catalyst, the feed has to be desulfurized.

After pre-heating and mixing with hydrogen (H₂), the feed is sent to sulfur removal (1) in which sulfur compounds are hydrogenated and adsorbed in a ZnO-layer. The desulfurized feed is then mixed with CO₂ and pre-heated again by utilizing flue gas heat in an appropriate amount, prior to entering the reformer (2). While passing the reformer tubes, which are filled with catalysts of different activities and shapes, the mixture of CO₂ and feed is converted into synthesis gas. The synthesis gas consists of CO together with H₂, CO₂, water and trace methane (CH₄), typically below 5 ppm. The heat for this endothermic reaction is provided by a high-velocity burner (3), which burns fuel and tail gas from the CO purification unit.

After leaving the reformer, the synthesis gas is cooled to ambient temperature prior to undergoing CO_2 removal and recovery. In this step, the CO_2 from the reformer flue gas, as well as the CO_2 from the synthesis gas, are absorbed in packed towers (4/5) by a caustic solution, e.g., monoethanolamine (MEA).

The CO_2 is separated from the scrubbing liquid in a stripper (6) and recycled to the reforming process. The synthesis gas, now typically consisting of 70 vol% CO and 30 vol% H₂ and still carrying traces of CO₂ and CH₄, enters the CO purification step. Depending upon the CO purity required, a low-temperature process or semi-permeable membrane process may be applied.

Economics: With CO_2 recovery from the reformer flue gas, as well as from the synthesis gas, the Calcor Standard process generates almost one



company index

CO molecule out of every C-atom imported into the process as feed and fuel. Thus, a 97–99% carbon yield almost reaches the theoretical maximum. Producing one metric ton of CO requires either 816 Nm³ natural gas (calculated as 100% CH_4), or 531 kg LPG as the main utility.

Installations: Eight plants are built worldwide that range in capacity up to 850 Nm³/h of pure CO.

Reference: Teuner, S., P. Neumann and F. von Linde, "The Calcor Standard and Calcor Economy processes," *OIL GAS European Magazine*, Vol. 27, No. 3, September 2001.

Licensor: Caloric Anlagenbau GmbH.



CO₂ recovery

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Application: Recover high-purity, including food-grade, CO₂ from oxygen-containing gases such as boiler flue gases, gas turbine exhausts and waste gases using Kerr-McGee/ABB Lummus Global absorption/stripping technology.

process categories

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Description: CO_2 -containing feed gases are first cooled and scrubbed (1), if necessary, to reduce SO_2 levels. The gases are boosted slightly in pressure before entering the recovery system.

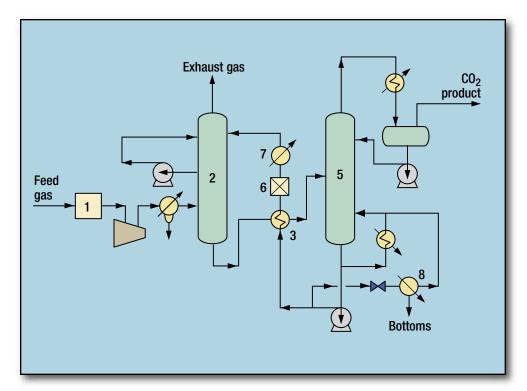
The system is based on absorption/stripping using a monoethanolamine (MEA) solution. Feed gases are sent to an amine absorber (2) where they are scrubbed with MEA to recover CO_2 . The scrubbed gases are vented to the atmosphere after water washing in the absorber's top to minimize MEA losses. Rich solution from the MEA absorber is preheated in an exchanger (3), flashed and sent to a stripper (5) where CO_2 is recovered overhead. Condensate from the stripper overhead is returned to the system.

Lean MEA from the stripper (5) is cooled (3, 7), filtered (6) and returned to the absorber. Periodically, a batch reclaiming operation (8) is conducted to purge MEA degradation products and to recover MEA by decomposing heat-stable salts.

CO₂ recovered from the stripper overhead may be compressed and used as a vapor product, or dried and liquefied using a standard ammonia refrigeration system to produce a liquid product.

Operating conditions: Operating units have exhibited availability factors in excess of 98%. Absorption and stripping operations take place at slightly above atmospheric pressure. Moderate levels of SO_2 and NO_x in the feed are acceptable. SO_2 prescrubbing is required only with SO_2 levels higher than 25 ppmv.

Economics: Typical capital investment for a 200-tpd CO₂ plant is \$9 million. Liquefaction facilities would add roughly \$4 million to the capital investment. Utility consumptions used in a design are determined from



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utility costs and availability. Typical utility and chemical requirements per ton of CO₂ recovered are as follows (for the recovery section only):

Steam, LP, t	1.9 to 2.7
Water, cooling, gal:	23,000
Power, kWh:	100
Chemicals, \$	1.00

Installations: Four units are operating on coal-fired boiler flue gases. Two plants produce gaseous chemical-grade CO_2 and two produce food-grade liquid. Capacities range from 150 tpd to 800 tpd. Maximum train capacity for high CO_2 content feeds is approximately 2,700 tpd.

Licensors: Randall Gas Technologies, ABB Lummus Global Inc.



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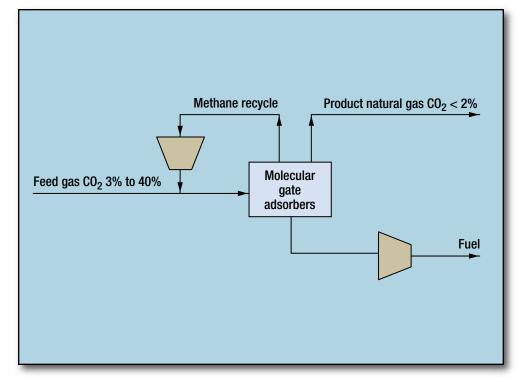
Gas Processes 2006

CO₂ removal—Molecular Gate

Application: Simultaneously removes carbon dioxide (CO_2) and water from contaminated natural gas. Feedstocks include coalbed methane and natural gas. Water-saturated feeds and CO_2 levels of 3% to 40% can be treated. Product is pipeline-quality natural gas with characteristic CO_2 levels of less than 2%. The process uses a specialty adsorbent for CO_2 removal in a patented, proprietary, pressure swing adsorption (PSA) system.

Description: Water-saturated feed, at pressure levels between 100 psig and 800 psig, is routed through a series of adsorber vessels. One or more vessels are removing the water and CO₂ while pipeline-quality natural gas flows through the adsorbent bed at essentially feed pressure. Typically, between three and eight adsorber vessels are used. When the adsorbent is saturated with water and CO_2 , the spent vessel is removed and replaced with a regenerated one. It is depressurized and produces a low-pressure, methane-rich stream for compression/ recycle to the feed and a low-pressure fuel stream containing CO_2 to be rejected. To maximize adsorbent capacity, impurities are removed through a single-stage vacuum blower. If the feed contains C_3 + components in large quantities, an NGL recovery section can be added to produce a mixed NGL product containing these components at high recovery rates. The system is flexible for a wide range of CO₂ concentrations and has turndown capability to 20%. Modular construction facilitates installation.

Economics: The technology can be cost-effectively applied to a wide range of flowrates. A small, 2-MMscfd unit's typical total installed cost is \$0.30/Mft³ of feed processed. This cost decreases to less than \$0.15/Mft³ for a 10-MMscfd design. Modular construction allows low-cost installation and equipment relocation flexibility.



Reference: Mitariten, M. J., "The Molecular Gate adsorption process operating experience at Tidelands Oil Production facility," The Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, July 2004.

Licensor: Engelhard Corp.



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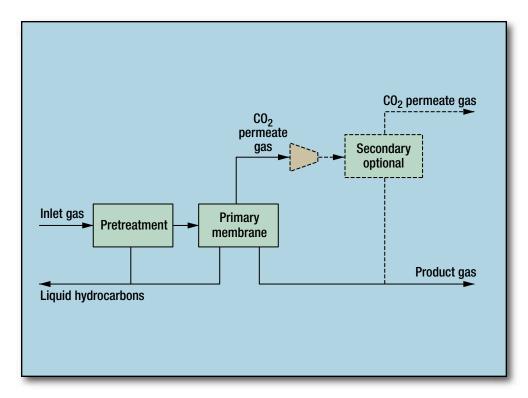
NATCO Cynara membrane technology

Application: Carbon dioxide (CO_2) removal from hydrocarbon gas streams. Membrane technology is used to process associated gas from enhanced oil recovery (EOR) to recover hydrocarbon gas, NGL condensate and high-purity CO_2 for reinjection. The process is also used off-shore and onshore for CO_2 removal from produced natural gas with medium to high levels of CO_2 , as well as from low CO_2 gas streams to meet pipeline gas specifications. The durable hollow fiber design can handle liquid hydrocarbons from rich gas that condense during the separation process.

Description: The Cynara membrane element contains thousands of asymmetric, hollow membrane fibers which selectively separate CO_2 from hydrocarbons. The CO_2 dissolves into the polymeric fiber and exits on the lower pressure side of the membrane, while the hydrocarbon gas stream sustains minimal pressure drop. Vertically oriented membrane cases allow liquid hydrocarbons to be transported along with product gas. Multiple configurations can be adapted to meet various process objectives. Cynara membrane systems are designed with pretreatment appropriate for the application.

Economics: Cynara membrane technology is economically favorable for processing gas streams containing between 10% and 90% CO_2 , though it has been successfully applied in lower CO_2 applications. Compact systems process from 5 to 700 million standard cubic feet per day (scfd) of gas, are skid packaged to reduce installation cost, and are reliable and easy to operate. Liquids recovery, lower operating cost and environmental factors favor Cynara membrane systems over solvents and other membrane technologies.

Operating conditions: Operating temperature and pressure can be optimized for membrane performance and facility efficiency, with inlet operating pressure ranging between 300 psia and 1,100 psia. Partial pressure of the CO_2 should be less than 500 psia.



Installations: Over 30 installations worldwide, including the first commercial CO_2 membrane facility (550 million scfd, operated for more than 20 years with >98.6% availability) and the largest offshore CO_2 membrane facility (700 million scfd).

Licensor: NATCO Group Inc.



Dew Point Control-Sorbead Adsorbents

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Application: The Sorbead Quick Cycle Dew Pointing process applies Sorbead adsorbent beads packed into an adsorber column. It selectively removes water (H_2O) and hydrocarbons from natural gas. When the adsorbent is saturated, stripping with hot regeneration gas regenerates it. Condensing the stream when leaving the regenerating adsorber separates H_2O and heavy hydrocarbons as a liquid product.

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Description: In a typical natural gas plant, two, three or four adsorbers are applied to allow for online regeneration. As the process relies on selective adsorption of heavy hydrocarbons and H_2O , the attainable dewpoint specification is virtually independent of the natural gas pressure. This is a major advantage over low-temperature separation technology when natural gas is available at a relatively low pressure (<100 Bar, <1,500 psi) or when only limited pressure drops over the treating unit is allowed.

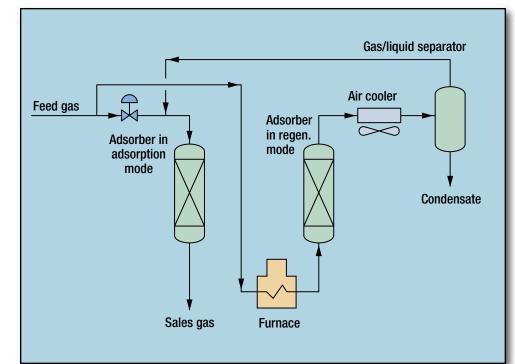
The process is very flexible with respect to feed gas and turndown ratio; this only influences the cycle time, which is an operational variable. The excellent turndown capabilities and short startup time make the process ideal for peak shaving and underground storage facilities. The process can be designed to selectively remove aromatics and other contaminants for membrane protection applications.

Installations: Engelhard was involved with over 200 Sorbead-based dewpointing units and provides design and operation support.

References: Schulz, T., J. Rajani and D. Brands, "Solving storage problems," *Hydrocarbon Engineering,* June 2001, p. 55.

Shulz, T. and A. Laukart, "Natural gas treatment—The adsorption process in comparison with glycol dehydration," The Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, 1995.

Licensor: Engelhard Corp.



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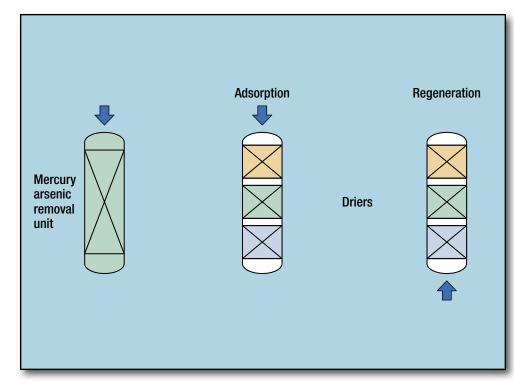
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Gas contaminants removal—Multibed

Application: Remove mercury (Hg), arsenic, water, CO_2 , other oxygenates, tertiary butyl catechol (TBC), NH₃ and sulfur species from natural gas, industrial gases and petrochemical streams using Axens Multibed technology.

Description: This technology uses combinations of special aluminas and zeolite molecular sieve adsorbents that are installed as beds in the same or separate vessels. (The configuration will depend on the specific application.) The aluminas function as catalysts or adsorbents for chemical or physical removal of contaminants such as HCl, Hg, AsH₃, TBC and water. The molecular sieves remove contaminants by physical adsorption.

In multibed processing, Hg can be removed either upstream or downstream of the gas dehydration step. The treated gas can contain less than $0.01\mu g/Nm^3$ Hg and less than 1 ppmv of other contaminants. Most adsorbents are thermally regenerated with nitrogen or light-hydrocarbon streams.



Operating parameters: Operating conditions are:

Inlet temperature, °F	40–140
Inlet pressure, psig	40–1,400
Regeneration gas temperature, °F	350-600
Phase	liquid or vapor

Installations: Currently, over 60 installations worldwide are treating natural and industrial gases and other hydrocarbon streams from refining, gas and petrochemical sectors.

References: Savary, L. and P. Travers, "Axens Multibed System—An Improved Technology for Natural Gas Purification," 11th GPA-GCC Technical Conference, May 2003, Muscat, Oman.

Savary, L., "From Purification to Liquefaction: Gas Processing Technologies," 12th GPA-GCC Technical Conference, May 2004, Kuwait.

Licensor: Axens.



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Gas Processes 2006

IRON SPONGE

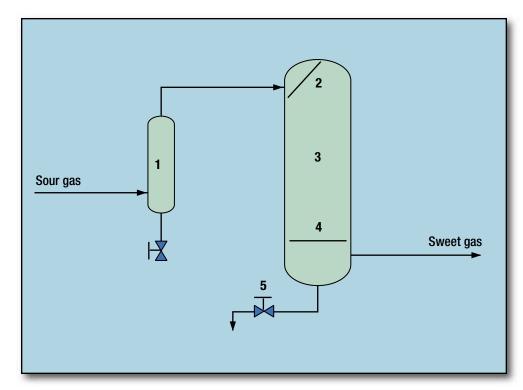
Application: To remove hydrogen sulfide (H_2S) and mercaptans from natural gas streams at low- or high-pressure conditions at or near the well head.

Process description: Iron sponge (iron oxidized onto wood shavings) uses a simple packed tower (3) on a flow-through support (4). After liquid separation (1), the deflected (2) sour gas flows down to contact with the reactive iron oxide, simply and effectively converting H_2S into a solid. The iron sulfide stays in the packed tower, effectively removing it from the gas stream. Iron sponge also removes mercaptans, the malodorous sulfur compounds found in some gas, producing a deodorized, sweet gas.

For iron sponge to effectively perform, it must be maintained within a range of water levels. This requirement is usually satisfied if the gas is saturated with water vapor, as is frequently the case. If it is not the case, a simple water spray will correct it. An excess of water is tolerated very well by iron sponge as long as the excess is drained off (5), so as not to flood the bed. Because the reaction of iron oxide with H_2S produces a small quantity of water, monitoring the drip water volume is an effective method of confirming the presence of sufficient moisture. Since the iron oxide is impregnated onto the wood, it will not wash off or migrate with the gas.

Operating conditions: The process should be located as close to the source of gas as possible to eliminate as many corrosion problems as possible caused by the H₂S. The process should be used after a gas/liquid separator and before the dehydration process. The maximum temperature should not exceed 120°F, and the minimum of 50°F, or whatever is necessary to avoid hydrate formation for the system pressure and composition of the gas.

The gas purification is not pressure sensitive, and is not affected by other gas constituents. Carbon dioxide levels are not a problem for treatment, but liquid hydrocarbons should be removed before the IRON SPONGE process.



Since the process is so simple, minimum operator time is required. It runs unattended for days at a time.

Manufactured and supplied by: Connelly-GPM, Inc.

KVT SULFOX HK process

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Application: The SULFOX HK process is a wet catalytic oxidation process where highly concentrated waste gases containing sulfuric compounds, such as hydrogen sulfide (H_2S) and carbon disulfide (CS_2), are treated and sulfuric acid (H_2SO_4) is recovered. In the case of low raw gas concentrations, additional combustion of liquid sulfur to increase the amount of recovered acid and to save fuel is possible.

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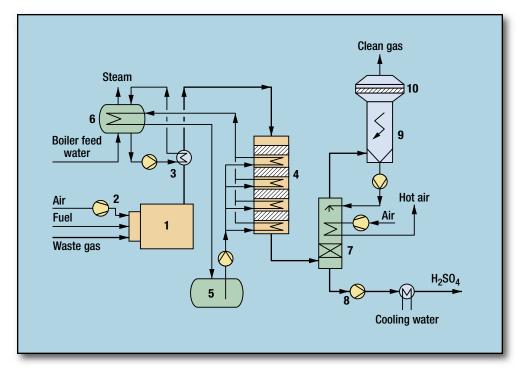
Description: Waste gas is combusted in the combustion chamber (1) at temperatures of 900°C–1,000°C. Depending on the amount and concentration of the waste gas, combustion and dilution air is added by the combustion air blower (2). The evaporator (3) cools the gas to about 400°C, which is also the reactor inlet temperature. In the reactor (4), there are three or four V₂O₅-catalyst beds, where SO₂ to sulfur trioxide (SO₃) oxidation and further formation of gaseous H₂SO₄ takes place. Usually a liquid salt system (5) is used to remove surplus energy resulting from the exothermic oxidation process. The gas is cooled close to the condensation temperature before entering the concentration column. Liquid salt is recooled in the steam drum (6) by producing steam of variable conditions.

Gas enters the concentration column (7) from the bottom. Passing over the ceramic saddle packing in the lower part and the tube side of the a glass tube heat exchanger in the upper section, the gaseous acid is condensed and concentrated to about 96%. Ambient air is used for cooling on the tube side of the glass tube heat exchanger. The concentrated acid collected in the bottom is cooled in the acid cooler (8) to about 50°C and then discharged to the customer's storage facility.

The acid aerosol formed during the condensation process is removed in the wet electrostatic precipitator (9) and, with the activated carbon filter (10), the SO_2 emissions are reduced to a minimum.

Economics: A standard plant for a European location with typical size and a capacity of 25,000 Nm³/h (raw gas including combustion and dilution air) is approximately \$10 million for delivery, erection and startup.

Electric power consumption is about 300 kWh. The amount of pro-



duced steam and recovered acid depends on the raw gas concentration. Overall conversion rate for sulfuric compounds is >99.5%.

Installation: Currently, there is one installed SULFOX HK plant for the petroleum industry, which is in the startup phase.

References: "Global sulfur update," *Hydrocarbon Engineering,* April 2003, p. 37.

Kanzler, W., "SULFOX—Wet oxidation process," Sulphur 2002, Vienna, Austria, October 2002.

Kanzler, W. and G. Amlacher, "SULFOX, an economical and proved process technology for off-gas cleaning in viscose industry," 3rd Viscose Congress, Bad Ischl, Austria, June 2002.

Licensor: Kanzler Verfahrenstechnik GmbH.



KVT SULFOX NK process

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Application: In the SULFOX NK process, sulfuric compounds such as hydrogen sulfide (H_2S) and carbon disulfide (CS_2) are converted catalytically to sulfur trioxide (SO_3), which, in presence of water vapor, forms sulfuric acid (H_2SO_4). The SULFOX NK process is designed for handling raw gas concentrations up to 20 g/Nm³ H₂S and CS₂ (in total).

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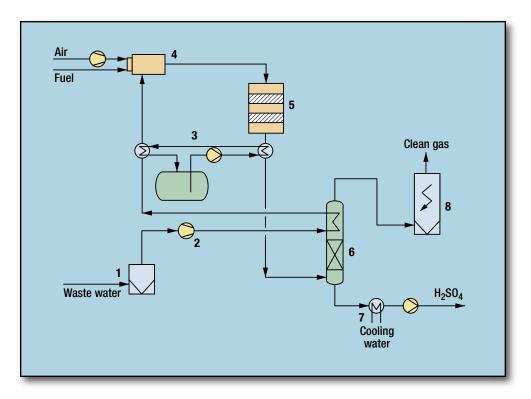
Description: Following the pre-filter (1), where solid or liquid particles are separated, the main fan (2) transports the gas through the plant. The raw gas is preheated to the catalyst operating temperature in the glass tube heat exchanger and in the internal heat transfer system (3), which uses liquid salt as heat in the transfer medium. The burner in the combustion chamber (4) supplies the necessary energy for startup and non-autothermal operations. Passing over the platinum- and the vanadium-catalyst beds in the reactor (5), the sulfuric compounds are oxidized and gaseous H_2SO_4 is formed.

After the reactor, the gas is cooled close to its condensation point using the liquid salt system. In the glass tube heat exchanger, part of the concentration column (6), the H_2SO_4 is condensed and concentrated to 94 wt%–96 wt%.

The acid collected in the bottom of the column passes the acid cooler (7) before it is pumped to the storage facility. The wet electrostatic precipitator (8) removes the acid aerosol formed during the condensation process. Additional reduction of SO_2 emissions can be achieved with an activated carbon bed that is situated on top of the electrostatic precipitator.

Economics: A standard plant with a capacity of 40,000 Nm³/h is approximately \$7 million including construction and startup. Electric power consumption is in the range of 200 kWh and the amount of recovered acid depends on the raw gas concentration.

Installation: There are currently five installed SULFOX NK plants with capacities ranging from 9,000 Nm³/h to 45,000 Nm³/h.



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References: "Global sulfur update," *Hydrocarbon Engineering*, April 2003, p. 37.

Kanzler, W., "SULFOX—Wet oxidation process," Sulfur 2002, Vienna, Austria, October 2002.

Kanzler, W. and G. Amlacher, "SULFOX, an economical and proved process technology for off-gas cleaning in viscose industry," 3rd Viscose Congress, Bad Ischl, Austria, June 2002.

Licensor: Kanzler Verfahrenstechnik GmbH.



LRS 10—CO₂ removal

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Application: Remove CO_2 from natural gas, SNG or ammonia syngas. The purification process is applicable in facilities for LNG plants and petrochemical applications.

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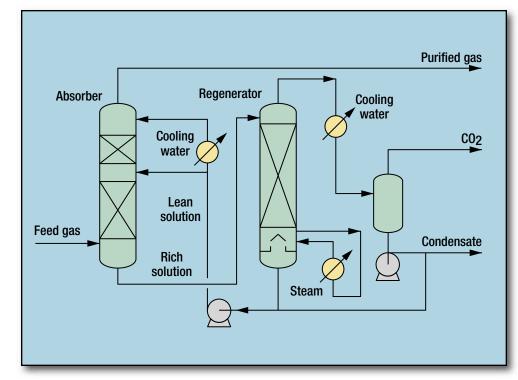
Description: Rich-CO₂ feed gas is passed to the absorber column containing potassium carbonate solutions and LRS10 additives. The used solution goes through the regeneration system and purified gas exits the top of the absorber. The rich solution is regenerated either in a reboiler facility or directly with steam. The recovered potassium carbonate/LRS10 solution is pumped back to the absorber for further reaction. Feed gas containing about 20% CO₂ has been treated successfully, typically to CO₂ levels of 1% in the processed gas, depending on process arrangement. Process configuration changes can lower CO₂ slippage levels from 500 ppm to 1,000 ppm in some designs.

Economics: A plant utilizing typically 3% LRS10 in a potassium carbonate system has been shown to offer improved performance over CO_2 removal systems such as Benfield (DEA promoted potassium carbonate) by up to 10%. Opex savings are realized through:

- Increasing gas throughput of typically 10%
- Lower regeneration energy by about 10%
- Reduce CO₂ slippage in the outlet gas by up to 50%
- Improve column operations by moving away from column constraints.

Installations: Thirty plants worldwide, mainly retrofits, in the ammonia, hydrogen, natural gas and chemicals industries.

Licensor. Advantica Ltd.



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MEDAL membrane—Simplified Biogas System

Application: Selectively removes carbon dioxide (CO_2) , water vapor, oxygen (O_2) , hydrogen sulfide (H_2S) and volatile organic chlorides (VOCs) from raw biogas (landfill gas) to upgrade the Btu value.

Product: Purified high Btu gas, predominantly methane, meeting customer or pipeline specifications.

Description: MEDAL natural gas membrane modules are made up of millions of hollow-fiber membrane filaments. The hollow-fibers are assembled in a patented counter-current-flow permeator. Modules are combined in pressure vessels to provide maximum system performance and to minimize space requirements.

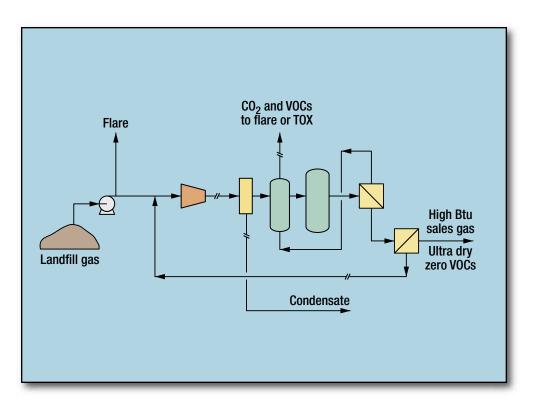
The feed stream from the landfill (from which CO_2 needs to be removed) passes through the membrane module's feed chamber at high pressure. CO_2 , water vapor and H_2S pass through the membrane from the high pressure chamber to the low pressure chamber called the permeate. Methane and nitrogen (N₂) are enriched in the high pressure residual gas.

Prior to the membrane, a proprietary pre-treatment system is utilized for drying the raw landfill gas and removes VOCs, including siloxane.

Typically, a two stage design is used to limit the hydrocarbon losses to less than 10%. Typical feed rates vary from less than 1 MMscfd to as high as 10 MMscfd with sales gas CO_2 content at about 1%. Typical feed pressure is 200 psig.

MEDAL natural gas membrane units are simple to operate and have no moving parts thereby requiring minimum maintenance. Additionally, the membrane units are modular enabling easy expansion and making them the ideal choice for remote locations.

Economics: Typical processing cost for CO_2 removal using the MEDAL Simplified Biogaz System is about \$0.35 per MMBtu sales gas.



Installations: Pilot plants at 3 landfills, 2 full scale systems in 2006.

Licensor: Air Liquide S.A. (MEDAL, L.P.)

Morphysorb (acid gas removal from natural gas)

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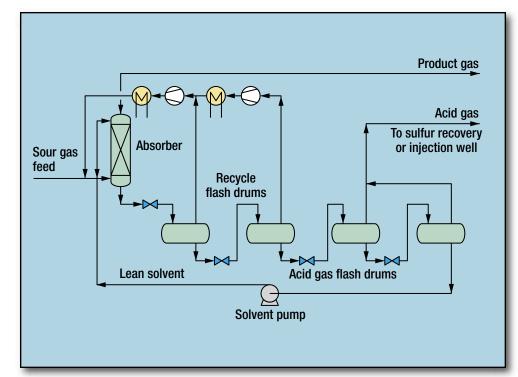
Application: Hydrogen sulfide (H_2S), carbon dioxide (CO_2), COS and RSH removal from natural gas or syngas by physical absorption. Bulk-acid gas removal with simple flash regeneration. Removes impurities to pipeline specification with additional thermal regeneration step. Highly selective H_2S removal, even at high CO₂ partial-pressures. Simultaneous dehydration and BTEX removal.

Description: For bulk acid gas removal, the Morphysorb process simply requires solvent flash regeneration as the acid gas compounds are physically dissolved. Applications vary from product gas specifications of several percent for the acidic components down to about 2% for CO_2 alone. Additional thermal regeneration is required for H_2S removal down to pipeline specification (4 ppmv H_2S , 2% CO_2) or removal of CO_2 to liquefied natural gas (LNG) specification (50 ppmv CO_2 , 4 ppmv H_2S).

The process flow diagram shows a bulk-acid gas removal unit as an example. The feed gas enters the absorber bottom, flows upward through a packed bed, where it is treated with the regenerated solvent, and leaves the absorber at the top.

The enriched solvent exits the absorber bottom and is flashed consecutively into the recycle flash drums. The offgas from these drums is recycled to the absorber feed by a two-stage compressor minimizing methane losses. The solvent is further flashed into the acid gas flash drums for regeneration. The acid gas is produced at two pressure levels for high-pressure downhole reinjection or for further processing in a sulfur recovery unit. The regenerated Morphysorb solvent is pumped back to the absorber.

Due to the solvent's specific nature (low co-absorption of C_1 to C_3 hydrocarbons, high acid gas capacity, non-corrosive, low-vapor pressure and non-toxic), the process exhibits the following features: low recycle gas flow and higher hydrocarbon product yield, low solvent circulation rate, extensive carbon steel usage as construction material and low sol-



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vent losses in the product and acid gas.

Operating conditions: Typical feed conditions range from 400 psi to 1,300 psi with a 5% to 70% acid gas content (CO_2 and H_2S). Depending on the process application, product specifications vary from a few ppmv to several percent for bulk removal.

Installations: Two plants: A 300 million-scfd feed gas capacity commercial plant, removing 1,000 tpd of acid gas for downhole reinjection. A pilot plant installation with a 1 million-scfd feed gas capacity.

References: Palla, N., A. Jamal, D. Leppin, O. von Morstein, J. Menzel and M. Hooper, "Kwoen gas plant -1: Morphysorb process proves feasible in first commercial plant," *Oil & Gas Journal*, July 5, 2004, pp. 54–59.

Morphysorb (acid gas removal from natural gas), *continued*

"Kwoen gas plant—Conclusion: Duke Energy installs first Morphysorb unit at Kwoen gas plant," *Oil & Gas Journal*, July 12, 2004, pp. 52–57.

Von Morstein, O., J. Menzel, N. Palla and D. Leppin, "An ace at removal," *Hydrocarbon Engineering*, February 2004, pp. 51–55.

Licensor: Uhde GmbH



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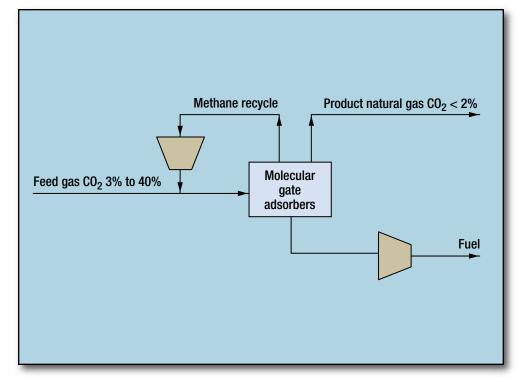
Gas Processes 2006

CO₂ removal—Molecular Gate

Application: Simultaneously removes carbon dioxide (CO_2) and water from contaminated natural gas. Feedstocks include coalbed methane and natural gas. Water-saturated feeds and CO_2 levels of 3% to 40% can be treated. Product is pipeline-quality natural gas with characteristic CO_2 levels of less than 2%. The process uses a specialty adsorbent for CO_2 removal in a patented, proprietary, pressure swing adsorption (PSA) system.

Description: Water-saturated feed, at pressure levels between 100 psig and 800 psig, is routed through a series of adsorber vessels. One or more vessels are removing the water and CO₂ while pipeline-quality natural gas flows through the adsorbent bed at essentially feed pressure. Typically, between three and eight adsorber vessels are used. When the adsorbent is saturated with water and CO_2 , the spent vessel is removed and replaced with a regenerated one. It is depressurized and produces a low-pressure, methane-rich stream for compression/ recycle to the feed and a low-pressure fuel stream containing CO_2 to be rejected. To maximize adsorbent capacity, impurities are removed through a single-stage vacuum blower. If the feed contains C_3 + components in large quantities, an NGL recovery section can be added to produce a mixed NGL product containing these components at high recovery rates. The system is flexible for a wide range of CO₂ concentrations and has turndown capability to 20%. Modular construction facilitates installation.

Economics: The technology can be cost-effectively applied to a wide range of flowrates. A small, 2-MMscfd unit's typical total installed cost is \$0.30/Mft³ of feed processed. This cost decreases to less than \$0.15/Mft³ for a 10-MMscfd design. Modular construction allows low-cost installation and equipment relocation flexibility.



Reference: Mitariten, M. J., "The Molecular Gate adsorption process operating experience at Tidelands Oil Production facility," The Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, July 2004.

Licensor: Engelhard Corp.



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Gas Processes 2006

Nitrogen rejection

Application: Reject nitrogen from natural gas to increase heating value.

Description: Natural gas feed to the nitrogen rejection unit (NRU) is partially condensed and fed to the top of the high-pressure (HP) column. A reboiler driven by condensing the feed provides stripping vapors in the column. The bottoms from the first stripping column are enriched in hydrocarbons and depleted in nitrogen. This HP residue is boiled in the warm NRU exchanger and sent to residue gas compression. Enriched in nitrogen, the overhead vapor from the column is sent to the cold end of the NRU.

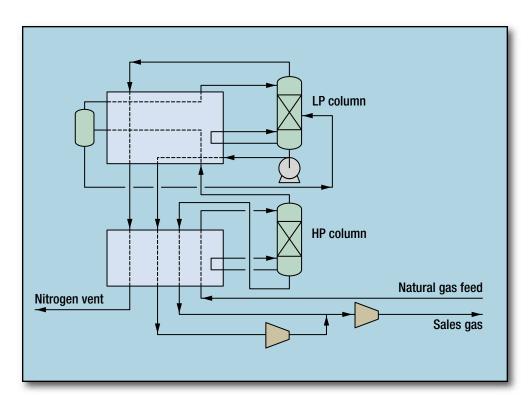
Vapor from the HP column is partially condensed against returning residue streams. The vapor and liquid are separated in a vertical separator drum. The vapor stream, enriched in nitrogen, from the drum is further condensed and is fed as reflux to the low-pressure (LP) column.

Liquid from the drum is the feed to the LP column. Vapor generated in the reboiler strips the descending liquid of nitrogen, creating the remainder of the residue product. The liquid flowing down the column scrubs the methane from the vapor, creating a high-purity nitrogen vent stream from the top of the column.

Liquid product from the LP column is pumped to LP residue pressure. This stream is boiled against the condensing HP vapor from the overhead of the first stripping column. The nitrogen vent stream and LP residue stream are warmed in both exchangers in the NRU along with the HP residue gas stream. The residue streams are sent to recompression for export to pipeline systems. Nitrogen is vented to the atmosphere or recompressed for reinjection.

Operating conditions: The dual-column NRU process has good CO_2 tolerance and feed flexibility, handling feeds from 5 mol% to 80 mol% nitrogen and pressures as low as 250 psig (17 barg).

Economics: The dual-column NRU has high hydrocarbon recovery (>99.9%). This process is particularly well-suited for streams with less



than 20% nitrogen in the feed, and is easily adapted to recover helium (HeRU) as well. The hydrocarbons are recovered at two pressure levels, reducing recompression requirements. The amount of hydrocarbons recovered from the second column is greatly reduced, requiring a smaller cryogenic pump.

Installations: Eight NRU and HeRU installations, with three using the dual-column process with capacities from 30 million scfd to 70 million scfd.

Reference: Janzen, K. H. and S. R. Trautmann, "Innovative NRU design at Pioneer Natural Resources' Fain gas plant," 2000 GPA Convention.

Licensor: Air Products and Chemicals, Inc.



OmniSulf

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Application: Natural gas from reservoirs now being explored is of increasingly poorer quality. By contrast, demands on gas quality are rising. This is particularly true when the gas is used as feedstock for liquefied natural gas (LNG) production. Polishing the gas from trace contaminants such as COS, mercury and, specifically, mercaptans is becoming evermore important; aside from classic hydrogen sulfide (H₂S), carbon dioxide (CO₂) and water removal task.

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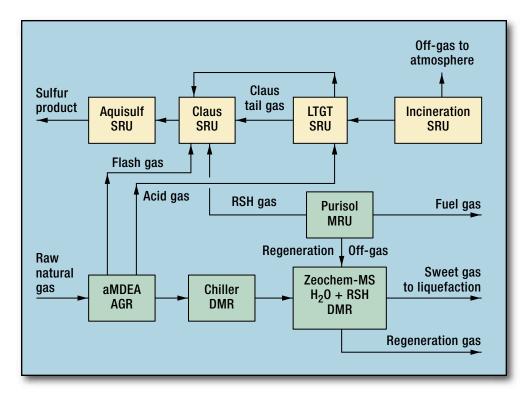
Description: The OmniSulf concept encompasses the following proprietary key processes: Acidic components are eliminated using BASF's aMDEA process (AGR). The cleaned gas is routed to a DMR unit that removes moisture and mercaptans with Zeochem's special 13X zeolite technology. Where necessary, the sweet gas can be routed further to a mercury removal unit operated with impregnated activated carbon. The DMR is thermally regenerated at regular intervals. Mercaptans are recovered from the regeneration gas using Purisol technology. The gas can then be fed to the fuel gas system.

All gas streams containing sulfur are routed to a sulfur recovery unit (SRU). Elemental sulfur is produced in the Claus process (equipped with Lurgi Multi-Purpose Burner). A Lurgi tail gas treating (LTGT) and acid gas enrichment system is combined with the Claus unit to boost sulfur recovery. The sulfur product is then treated further by applying an AQUISULF degassing process (AQU) which removes H_2S concentrations below 10 ppm. Vent gases are incinerated (INC) before being released to the atmosphere.

As the sulfur market is saturated, acid gas re-injection is increasingly selected as a viable alternative. The OmniSulf concept can be tailored to gas re-injection.

Installations: Three contracts for the OmniSulf process have been signed for plants in the Middle East.

Reference: Tork, T. and M. M. Weiss, "Natural Gas Sweetening," *Hydrocarbon Engineering*, May 2003.



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Licensor: Lurgi AG.

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PURASPEC

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Application: PURASPEC processes remove low levels of sulfur and mercury compounds from hydrocarbon gases and liquids to meet pipeline, chemical grade or environmental specifications.

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Description: PURASPEC uses absorbent fixed beds to irreversibly react with impurities to be removed. There are no feedstock losses; only the impurity binds within the absorbent. The process is flexible to accommodate changes in throughput. There is no operator intervention required to run the process, and change-out can be done by contract labor.

During operation, there are no vents, flares or noise sources. Used absorbent can be reprocessed and disposed in an environmentally friendly manner. A typical lead-lag configuration is shown. However, single vessels are operated and have been used to phase expenditure. Axial and radial flow reactor designs are available. Radial flow reactors have been used in duties where a very low-pressure drop is required.

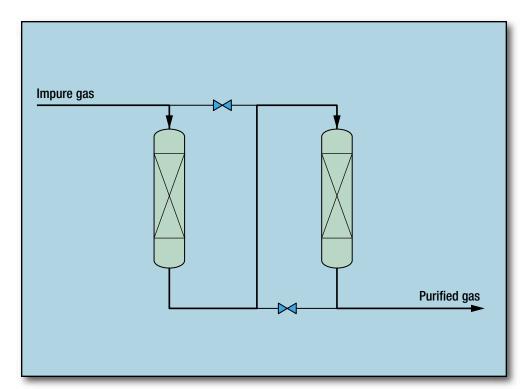
Hydrogen sulfide (H_2S) removal from natural and associated gas can achieve impurity levels as low as ppbv at the bed exit. In liquid duties (propane and liquefied petroleum gas), H_2S is removed to meet copper strip 1A quality.

Mercury can be removed from natural gas to levels below 10 ng/ Nm^3 (liquefied natural gas quality). In liquid duties (propane, butane, naphthas), mercury can be reduced to <1 ppbw.

Operating conditions: PURASPEC operates effectively over wide temperature and pressure ranges from 20°F to 400°F and atmospheric to 2,000 psi. No heat input is required.

Installations: There are over 100 operating units worldwide treating natural gas rates up to 2 billion scfd and NGLs up to 5,000 tpd for major oil and gas companies.

References: Spicer, G. W. and C. Woodward, "H₂S control keeps gas from big offshore field on spec," *Oil & Gas Journal*, May 27, 1991, p. 76. Carnell, P. J., H. K. W. Joslin and P. R. Woodham, "Fixed bed pro-



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cesses provide flexibility for COS, H₂S removal," *Oil & Gas Journal,* June 5, 1995, p. 52.

Rhodes, E. F., P. J. Openshaw and P. J. H. Carnell, "Fixed-bed technology purifies rich gas with H₂S, Hg," *Oil & Gas Journal*, May 31, 1999, p. 58.

Licensor: Johnson Matthey Catalysts.



Purisol

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Application: Removal of acid gases from natural gas, fuel gas and syngas by physical absorption in NMP (N-methyl-pyrrolidone). Typical cases: 1. High CO_2 contents to low residual level, 2. Bulk acid gas removal to moderate purity by simple flash regeneration, 3. Selective H₂S removal. Ideally suited for (3) in an IGCC based on POX of coal or oil, as NMP, is the most selective solvent on the market. 4. Selective removal of mercaptans from gas streams, e.g., from spent regeneration gas coming from a molecular sieve mercaptan removal unit from natural gas. It is a cheap, stable, noncorrosive and easily available solvent with a broad range of further industrial applications.

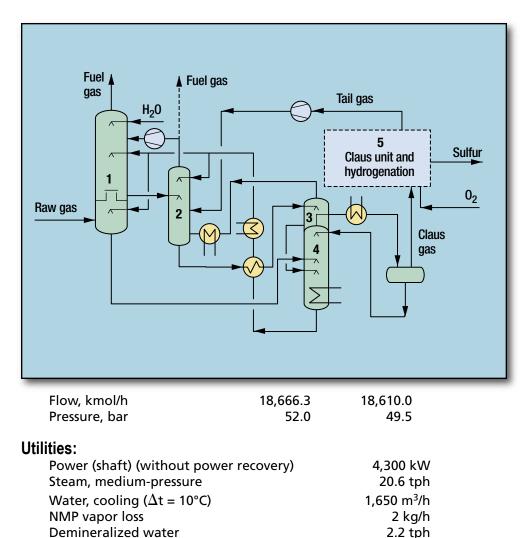
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Description: Raw gas from a POX of heavy residue is cooled; HCN and organic sulfur compounds are removed in prewash (1). H_2S is removed in the main absorber (1) by hot-regenerated, lean solvent cooled slightly below ambient temperature. NMP traces are backwashed on top of (1) with H_2O . Laden solvent from (1) is flashed at medium pressure in a reabsorber (2). H_2S traces in the flash gas are reabsorbed by a small quantity of lean NMP. The sulfur-free gas from (2) is compressed back to the produced fuel gas (1). Flashed solvent from (2) is heated by hot lean solvent and flashed again (3). Hot-flashed gas is cooled and sent back to the reabsorber (2). Solvent from (3) is finally hot-regenerated in (4). The resulting cooled acid gas, very rich in H_2S , is processed in an Oxy-Claus unit, the tail gas is hydrogenated, formation water is removed by quenching, recompressed to the reabsorber (2) for desulfurization and finally ends up in fuel gas.

This closed cycle is offgas free and leads to increasing overall efficiency of the IGCC plant.

Material balance for a 500-MW IGCC power plant in mol%

	Raw gas	Fuel gas
H ₂	43.12	43.36
N ₂ + Ar	1.49	2.31
$CO + CH_4$	45.9	45.95
CO ₂	8.27	8.38
$H_2S + COS$	1.20	< 50 ppm



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Installations: Seven units in operation or under construction.

Licensor: Lurgi AG.

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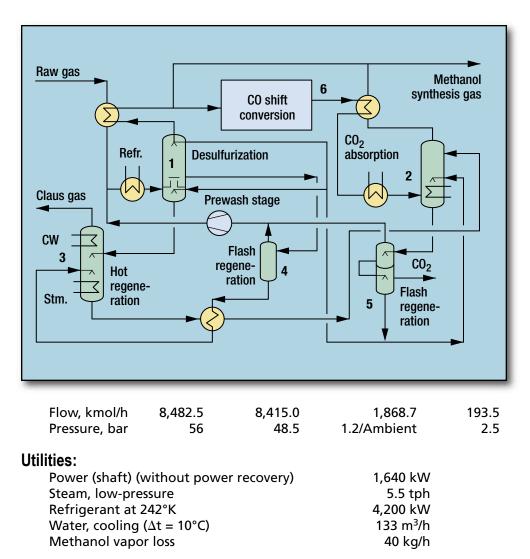
Rectisol

Application: Acid gas removal using an organic solvent at low temperatures. In general, methanol is used for H_2S , COS and bulk CO₂ removal, whereby trace contaminants such as HCN, NH₃, BTX, mercaptans and carbonyls are also removed. Processing a raw gas coming from coal gasification, oil residue gasification or tar gasification is possible to produce a clean gas with less than 0.1 ppm sulfur and CO₂ content down to the ppm range.

Description: Rectisol unit for the selective desulfurization and CO₂ removal in the production of methanol, ammonia and Fischer-Tropsch synthesis gas. Raw gas is cooled and trace contaminants are removed in the prewash (1). Prewashed gas is desulfurized (1) by using CO_2 -laden solvent down to 0.1 pp. H₂S-laden solvent is regenerated first by flashing to medium pressure (4) to recover H₂ and CO, and, second, by stripping with methanol vapors (3). The H₂S-enriched gases are sent to a Claus unit. A CO shift conversion can be located upstream of the Rectisol wash (raw gas shift) or between the desulfurization step and the CO₂ absorption as depicted in the sketch (clean gas shift conversion). The absorber (2), in the lower section, the gas CO_2 content is reduced to about 5% using flash-regenerated methanol (5). Remaining CO_2 is removed using hot regenerated (3), cold methanol in the upper section. The flashed CO_2 is free of sulfur and can be discharged to atmosphere, sequestered or used elsewhere. The refrigeration balance of the system is maintained by a conventional refrigeration unit. Methanol is injected in the raw gas cooling to prevent icing. The condensed methanol/water mixture is separated in a methanol/water column (not shown).

Material balance for a 2,000-tpd methanol plant in mol%

	Raw gas	Syngas	CO ₂	Claus gas
H ₂	43.80	67.69	0.59	1.38
N ₂ + Ar	0.25	0.25	< 0.01	0.03
$CO + CH_4$	52.57	29.03	0.26	8.96
CO ₂	2.30	3.03	99.15	42.28
$H_2S + COS$	1.08	< 0.1 ppm	traces	47.35



Installations: More than 100 units in operation or under construction.

Licensor: Lurgi AG.

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SELEXOL

Application: A process that can:

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• Selectively remove H_2S and COS in integrated gasification combined cycle (IGCC), with high CO₂ rejection to product gas (+85%) and high-sulfur (25% to 80%) feed to the Claus unit

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• Selectively remove H_2S/COS plus bulk removal of CO_2 in gasification for high-purity H_2 generation for refinery or fertilizer applications

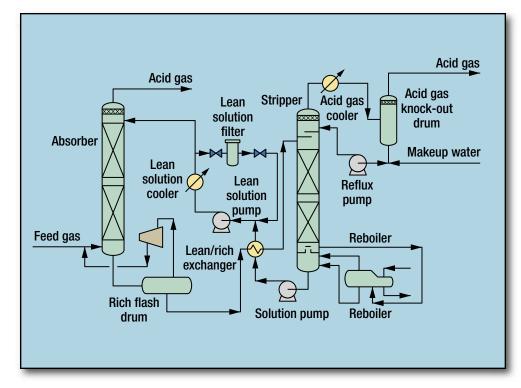
 \bullet Remove mercaptan, COS and $\rm H_2S$ from molecular sieve regeneration gas in CNG and GTL front-end treating.

Description: This process uses Dow's SELEXOL solvent—a physical solvent made of a dimethyl ether of polyethylene glycol, which is chemically inert and not subject to degradation. The process also removes COS, mercaptans, ammonia, HCN and metal carbonyls. A variety of flow schemes permits process optimization and energy reduction. Carbon steel can be used for the construction materials of equipment and piping due to the process's non-aqueous nature and inert chemical characteristics.

Acid gas partial pressure is the key driving force. Typical feed conditions range between 300 psia and 2,000 psia, with acid gas composition ($CO_2 + H_2S$) from 5% to more than 60% by volume. The product specifications achievable depend on the application and can range from ppmv up to percent levels of acid gas.

Installations: More than 60 SELEXOL units have been put into commercial service. The SELEXOL process is used in many applications, ranging from natural gas to synthetic gas, and has been the dominant acid-gas removal system for gasification project awards.

Licensor: UOP LLC.



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Separex Membrane Systems

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Applications: CO_2 and water vapor removal from natural gas or associated gas to meet pipeline specifications for onshore or offshore locations. Hydrogen and helium purification and upgrading low GHV gas for fuel. Debottlenecking existing solvent scrubbing systems or providing bulk CO_2 removal upstream of new installations. Hydrocarbon recovery from enhanced oil recovery floods for CO_2 reinjection and landfill gas purification.

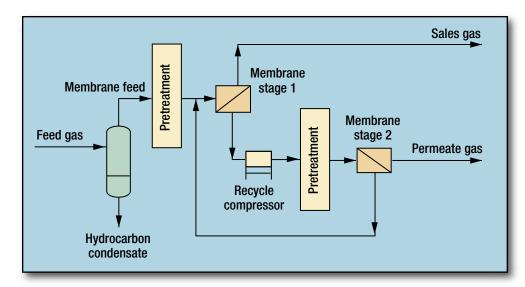
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Products: Purified gas meeting pipeline specifications, high-quality fuel gas for turbine, reformer or power generation; or high-purity CO_2 gas for reinjection.

Description: Separex Membrane Systems are simple, dry systems requiring minimal moving parts. Feed gas, after liquids separation, is conditioned at the pretreatment before being processed in a one- or two-stage membrane system. As the CO_2 -rich feed gas mixture passes over the polymeric membrane at high pressure, it separates into two streams. Carbon dioxide, hydrogen sulfide and water vapor permeate readily through the membrane, collecting on the low-pressure permeate side. The high-pressure residual retains most of the methane, ethane, other hydrocarbons and nitrogen. In a two-stage system, the first stage low-pressure permeate is compressed for further treatment at the second-stage membranes to recover hydrocarbons.

Hydrocarbon recovery can be as high as 99% for a two-stage design, and 95% for a single stage without compression, depending upon feed composition, pressure levels, system configuration and product requirements. Feedrates vary from 1 million scfd to 1,000 million scfd, with CO_2 levels from 3% to 75% and feed pressures from 400 psig to 1,600 psig.

Designed for operational simplicity, Separex Membrane Systems are an excellent choice for offshore and remote locations. They require minimal rotating equipment, no chemical reagent replacement and minimal maintenance. The prefabricated units are skid mounted to minimize installation costs and plot space.



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MemGuard Pretreatment Systems are utilized when feed streams are heavy or if dewpoint control is required.

Economics: For natural gas upgrading to pipeline specification, the processing costs are lower than, or comparable to, an amine unit. However, the Separex Membrane System eliminates the need for the glycol dehydration unit found in typical treating plants. The economics of smaller installations or remote operations favor membrane systems over traditional treatment options. CO₂ removal costs range between \$0.05 and \$0.15 per 1,000 scf of feed gas, depending on removal requirements, feed pressure, system configuration and product specifications.

Installations: Separex Membrane Systems have been successfully used in gas field operations since 1981. Over 60 units have been built or are under construction. The largest operating unit processes over 400 million scfd of natural gas.

Licensor: UOP LLC.

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Shell HCN/COS hydrolysis technology

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Application: The catalytic conversion of HCN and COS is a cost-effective technology to abate the harmful effects these components have in gas streams. This hydrolysis technology has three main fields of application:

1. Syngas treatment upstream of an amine unit for coal or oil gasification processes

2. Other syngas treatments where HCN and/or COS presence is not acceptable to downstream processing units such as gas-to-liquid processes, e.g., the Shell middle distillate synthesis process

3. FCC dry gas treatment to avoid problems in downstream treating units.

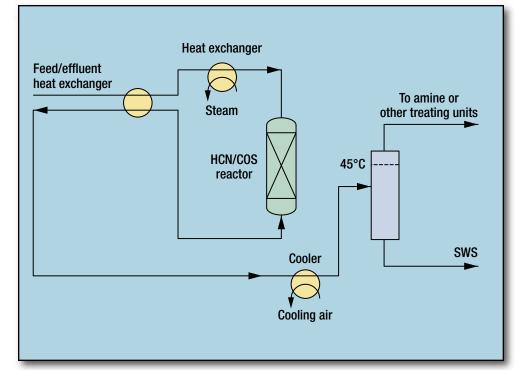
Description: In the gasification process, for example, syngas is produced, which is mainly comprised of hydrogen and carbon monoxide. However, contaminants such COS and HCN are also formed. A deep removal of both these contaminants is not possible using "conventional" amine treating solvents. However, catalytic HCN/COS hydrolysis technology is a cost-effective alternative to avoid the harmful effects of these compounds downstream of the process.

Syngas is water scrubbed for soot removal. Consequently, the water saturated gas is heated to a desired temperature before the syngas enters an HCN/COS hydrolysis reactor. In this reactor, catalytic hydrolysis of HCN and COS takes place producing CO, H₂S, CO₂ and ammonia.

After the HCN/COS reactor, the syngas is first cooled and then fed into an ammonia scrubber to remove the water-soluble components. The condensed water is sent to water treatment and the syngas is routed to downstream processing units.

Installations: At present, one unit is in operation and one unit is mechanically complete. License agreements have been signed to supply the technology to two other companies.

Licensor: Shell Global Solutions International B.V.



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Shell sulfur degassing process

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Application: To remove dissolved hydrogen sulfide (H_2S) and H_2S_x from liquid sulfur coming from Claus units. Liquid sulfur from Claus units contains approximately 300 ppmw dissolved H_2S and H_2S_x . To meet environmental and safety restrictions, the liquid sulfur should be degassed such that less than 10 ppmw H_2S remains.

process categories

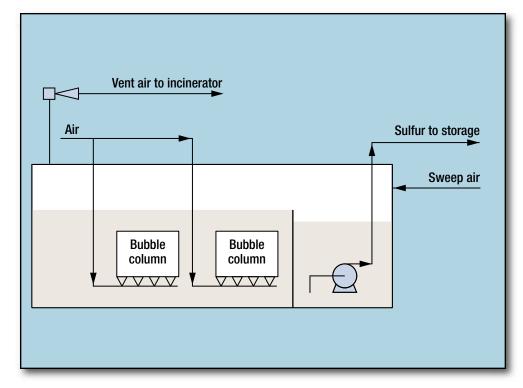
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Description: Sulfur from the Claus unit is run down into either a concrete sulfur pit or a steel vessel. It is then circulated over a stripping (bubble) column by bubbling air through the sulfur. By agitating the sulfur in this way, H_2S is released. Sweep air is passed over the top of the sulfur to remove released H_2S . The vent gasses are usually sent to an incinerator via an ejector. The degassed sulfur is then pumped into storage. The advantage to this process is that there are no moving parts and no catalyst is required; consequently, the process is easy to operate.

Economics: The Shell sulfur degassing process has been developed to decrease residence time and, consequently, capital expenditure. Operational costs are kept low as no catalyst is required.

Installations: There are currently more than 150 Shell sulfur degassing units in operation with capacities varying from 3,000 tpd to 4,000 tpd of sulfur.

Licensor: Shell Global Solutions International B.V. and Jacobs Nederland B.V.



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Selexsorb

Application: Purify ethylene feed stream to polyethylene production processes. Treated ethylene gas contains less than 0.2 ppmv CO_2 and H_2O and less than 1.0 ppmv oxygenates.

Description: Upstream of Selexsorb towers, the feed ethylene stream is prepurified via acetylene converter (1), tower (2) of reduced copper catalyst and bed (3) of CuO. Water and oxygenates are removed by combination bed (4) of Selexsorb CD Selective Adsorbent (H_2O and oxygenate removal) and Selexsorb CD selective adsorbent (oxygenate adsorption). Final treating step involves adsorption of CO₂ with bed (5) of Selexsorb COS selective adsorbent. Selexsorbs are thermally regenerated with nitrogen or light hydrocarbon streams. The selective adsorbents will purify: comonomer, fresh diluent, recycle diluent and reaction controlling gas (hydrogen, nitrogen) to polyethylene processes. In ethylene treating service (CO₂ adsorption), Selexsorb COS has proven its value in protecting Ziegler-Natta type catalysts in polyethylene plants worldwide.

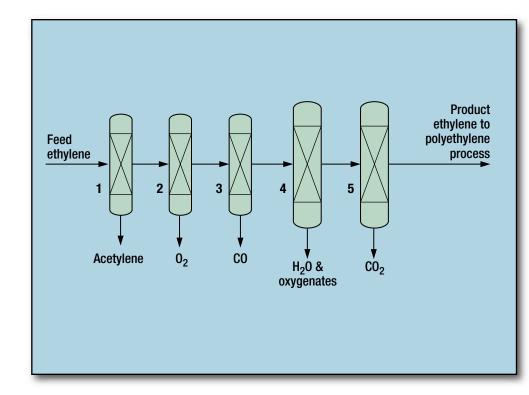
Operating conditions: (typical)

Inlet ethylene temperature, °F	40 to 120
Inlet pressure, psig	50 to 1,500
Inlet contaminant, ppmv	
CO ₂	0.5 to 50
H ₂ O	0.5 to saturated
Oxygenates	2.0 to 50
Regeneration gas temperature, °F	450 to 600
Regeneration gas pressure, psig	10 to 200

Installations: More than 300 installations worldwide for the treatment of ethylene and propylene feed streams to polymer plants.

Reference: Cherry, C. E., "Selective adsorbents for treating propylene feed streams," *Hydrocarbon Engineering*, June 2005.

Contributor: Engelhard Corp.





Sour water stripper (SWS)

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Application: Remove dissolved hydrogen sulfide (H_2S) and ammonia (NH_3) from sour water (H_2O) before conveying it to waste H_2O treatment. Sour H_2O comes from many sources such as catalytic cracking units, hydrocrackers, flare seal drums, etc. Normally, refinery SWS are designed for feed concentration ranging from 500 ppmw to 15,000 ppmw each of NH_3 and H_2S . The molar ratio of NH_3 to H_2S generally ranges between 0.75 and 2, and averages about 1.2. pH is commonly from 7 to 9.3. The process can also be designed to take account of mercaptans, phenols and some aromatics. There are several SWS types, all of which operate by passing sour H_2O through a multi-stage stripping tower.

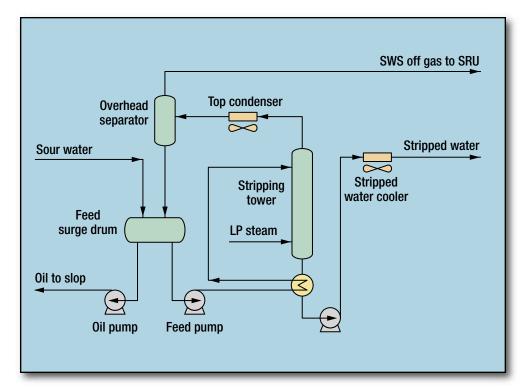
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Description: SWS contains a fractionating tower, which removes H_2S and NH_3 from sour H_2O along with some mercaptans, aromatics and phenols. The tower is normally refluxed to reduce H_2O in the overhead offgas and reduce downstream processing units (i.e., sulfur plants) size and cost. Steam is the most commonly used stripping medium, but flue gas, fuel gas and natural gas can also be used.

Typically, the sour H_2O feed stream is preheated by heat exchange with hot stripped H_2O prior to tower entry. Stripping steam is introduced into the tower bottom. H_2S and NH_3 are stripped out by counter-current contact with the steam. Typically, H_2S and NH_3 are stripped to ppm level.

Operating conditions: Operating pressure is generally set at a level to provide enough pressure to deliver offgas to its destination. A tower top pressure of 1.3–1.7 barg is typically enough when the offgas is sent to a sulfur recovery plant.

Overhead separator operating temperature should be set in the range of 82°C–90°C. A lower temperature can lead to plugging problems due to the formation of ammonium hydrosulfide, while a higher temperature results in more H₂O vapor in the offgas affecting downstream equipment size. Fluids handled in SWS facilities are corrosive. Proper construction material selection is an important aspect in SWS design.



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Commercial plants: More than 25 SWS plants have been built globally with capacities ranging from 1.5 m³/h up to 120 m³/h.Recently an SWS plant was designed for AGIP GAS BV LIBYAN BRANCH consisting of two units whose capacity is 25 m³/h sour H₂O each.

Licensor: SIIRTEC NIGI.

process index



SPREX (sulfur pre-extraction process)

Application: Pre-extraction of hydrogen sulfide (H_2S) from sour natural gas streams containing high amounts of H_2S (typically more than 10 vol%) yielding a treated gas stream with a reduced H_2S content and a liquid H_2S stream suitable for reinjection.

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Description: The natural gas feed stream enters the contactor column (1) where it is contacted with the cold liquid reflux from the low-temperature separator (LTS) (4). The cold gas stream from the top of the contactor is sub-cooled in the gas/gas heat exchanger (2) followed by the final cooler (3) and then goes to the LTS (4). The final cooler (3) can use, for instance, some external refrigerant (like propane in the SPREX 30). The liquid from the bottom of the LTS (4) is pumped (5) back as a reflux to the top of the contactor (1). The cold gas from the top of the LTS (4) goes to the gas/gas heat exchanger (2). This gas has a reduced content of H₂S, depending on the process operating conditions, typically a few vol%. It is then suitable for final purification by an amine process such as AdvAmine (8) and the resulting acid gas stream can be compressed (9) and reinjected.

The bottom of the contactor (1) is equipped with a reboiler (6) to minimize hydrocarbon content in the produced liquid stream from the bottom. This liquid stream, consisting mainly of H_2S with some carbon dioxide (CO₂), water and hydrocarbons, is recovered under a pressure similar to the natural gas feed pressure and can therefore easily be reinjected through a pump (7).

SPREX exists in two versions:

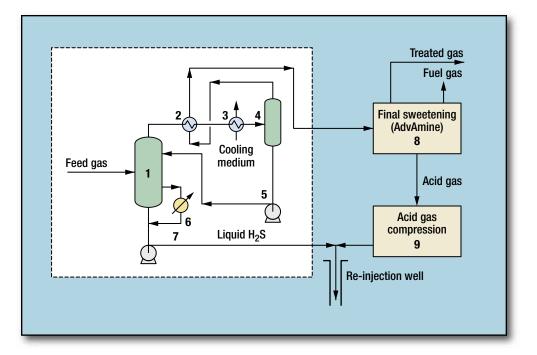
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• SPREX 30: The temperature in the LTS is about -30° C (-22° F). The operating conditions of the contactor are such that no hydrates are formed in the process and therefore no gas dehydration is required upstream of the SPREX unit.

• SPREX 60: The temperature in the LTS can be reduced down to below -60° C (-76° F) and operating conditions remain above H₂S and CO₂ freezing points. Upstream gas dehydration is then required but higher acid gas removal rates can be achieved with lower residual H₂S levels in the treated gas.



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Economics: It has been found that, for a sour gas with 35 vol% H_2S and 7 vol% CO_2 , combining SPREX 30 with final amine sweetening (8) and acid gas compression (9), would allow CAPEX reduction of 17% and reduced energy consumption of 35% when compared to a conventional amine + acid gas compression scheme.

Installation: One industrial demonstration plant (70,000 Sm³/d capacity) at Total's Lacq field, France.

Reference: Lallemand, F. and et al., "Highly sour gas processing: H_2S bulk removal with the Sprex process," IPTC Conference, Doha, Qatar, November 21–23, 2005.

Licensor: Sprex is developed jointly by Total, IFP and Prosernat and is licensed through Prosernat.



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Gas Processes 2006

SulfaTreat Direct Oxidation (DO)

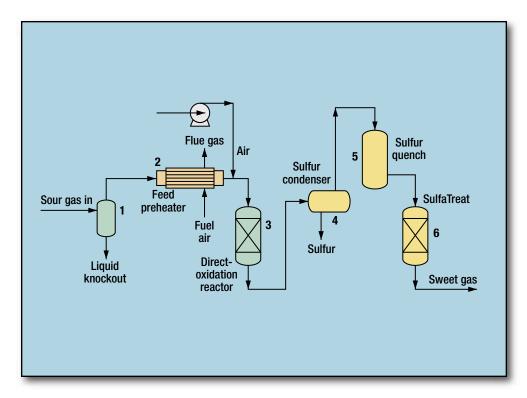
Application: SulfaTreat DO is a process and a catalyst that remove sulfur compounds, primarily hydrogen sulfide (H_2S), from sour-gas streams. The process has the same capacity as liquid redox but none of the associated operational problems.

Description: Sour gas passes through a gas/liquid separator (1) to eliminate free liquids and particles. It is then heated (2) to approximately $350^{\circ}F(177^{\circ}C)$ and moves (3) through a small bed of the patented Direct Oxidation catalyst to remove 90% of the H₂S component of the gas stream by oxidizing it to elemental sulfur (still in the gaseous form) and water. The gas stream then passes through a standard sulfur condenser (4). Optional polishing steps (5 and 6) can be applied to sales gas.

Economics: SulfaTreat Direct Oxidation will remove up to 30,000 ppm per stage (and up to 25 tons per day) of H_2S . The patented, dry catalyst eliminates the use of liquid chemicals, delivering the industry-recognized simplicity of the dry SulfaTreat scavenger. Typical catalyst life is two to three years, and a properly designed system can adapt to variable flow rates without loss in treating efficiencies.

Installations: This process is currently being qualified for treatment of natural gas and carbon dioxide.

Licensor: SulfaTreat, a business unit of M-I L.L.C.





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Gas Processes 2006

SulfaTreat—Gas or air H₂S removal

Application: Various SulfaTreat processes treat contaminated gas and air with a granular media that selectively removes hydrogen sulfide (H_2S) and some light mercaptans.

Description: Gas or vapor flows through the media, reacting with H_2S forming a stable and environmentally compliant byproduct at any point in its life cycle. Product consumption is not adversely affected by other gas components. The media prefers high humidity levels to fully water-saturate gas. Computer-assisted design matches operating conditions with desired results, such as maximum outlet allowed pressure drops (needs only a few inches W.C.) and long bed life. It works in any gas pressure or vacuum, inlet H_2S concentration and at temperatures up to 300°F. System sizes range from removing a few pounds up to over a ton H_2S daily, and to as low as 0.1-ppm maximum outlet, depending on system design.

Products:

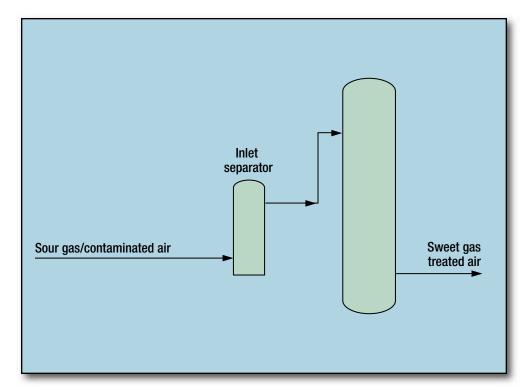
SulfaTreat: Media removes H₂S in fully water-saturated gas.

SulfaTreat–HP: Media removes H_2S and light mercaptans in undersaturated gas and is faster than SulfaTreat in fully water-saturated gas.

SulfaTreat–410HP: Media performs like SulfaTreat-HP but with a low-pressure drop required. It is faster-reacting and has twice the H_2S loading capacity in gas or air streams containing oxygen.

SulfaTreat–XLP: A concentrated high-capacity product lasting 2 to 4 times longer in the same vessel, it extends the operating period and reduces operating costs.

Economics: Operating costs are less than liquid reactants and have greater reliability. Operator attention is minimal. Vessels are simple and non-proprietary in design, thus lowering installation cost. Products can be used alone or may be combined with other processes that remove contaminants other than H_2S .



Installations: Over 2,000 applications globally.

Licensor: SulfaTreat, a business unit of M-I L.L.C.

SulfaTreat–HC

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Application: SulfaTreat–HC is a granular material that removes aggressive sulfur compounds, primarily hydrogen sulfide (H₂S), in a variety of clear liquid streams. The treatment of propane/propylene, butane, LNG, NGL, gasoline and other light-liquid hydrocarbon streams reduces corrosion so the stream can pass copper-strip testing and meet H₂S limits. Dry or water-saturated liquid hydrocarbon can be treated, as well as water or brines for removal of dissolved H₂S prior to disposal.

process categories

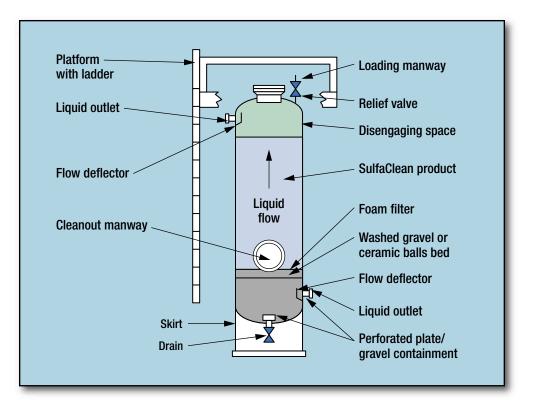
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Description: Liquids flow upward through the SulfaTreat–HC media. Flow rates and system designs depend on fluid type and contaminants quantity. Systems range from single vessels or multiple parallel flow to lead/lag style applications. A properly designed system can adapt to variable flow rates without loss in treating efficiencies.

Economics: The SulfaTreat–HC media removes up to 7.5 wt% H_2S . Its costs are often one-fourth the cost of zinc oxide products. It is competitive with caustic systems when accounting for regulatory, personal safety and disposal issues. The vessels are simple and inexpensive. Converted mole sieve, zinc oxide or iron sponge units can usually be used without modification.

Installations: This system has numerous placements worldwide. This process is currently being qualified for treatment of diverse streams such as MTBE and isooctane.

Licensor: SulfaTreat, a business unit of M-I L.L.C.



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Sulfinol

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Application: Removal of hydrogen sulfide (H_2S), COS, RSH, other organic sulfur compounds and bulk or deep removal of carbon dioxide (CO₂) from natural, synthetic and refinery gases. Total sulfur compounds in the treated gas can be reduced to ultra-low ppm levels, as required for refinery fuel and pipeline-quality gases.

process categories

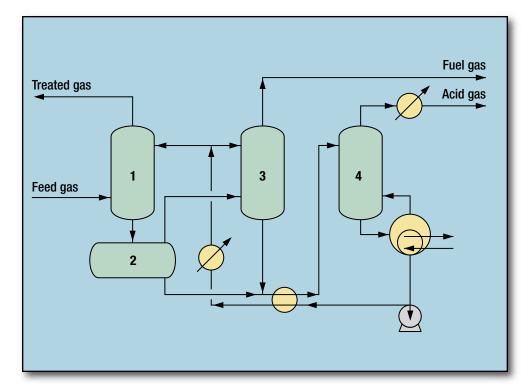
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An improved application is to selectively remove H_2S , COS, RSH and other organic sulfur compounds for pipeline specification, while co-absorbing only part of the CO₂. Deep CO₂ removal for LNG plants is another application, as well as bulk CO₂ removal with flash regeneration of the solvent. The process sequence—Sulfinol/Claus/SCOT—can be used advantageously with an integrated Sulfinol system that handles selective H_2S removal upstream and the SCOT process that treats the Claus offgas.

Description: The mixed solvent consists of a chemical-reacting alkanolamine, water and physical solvent Sulfolane (tetra-hydrothiophene dioxide). The actual chemical formulation is customized for each application. Unlike aqueous amine processes, Sulfinol removes COS, RSH and other organic sulfur compounds to stringent total sulfur specifications. The process achieves 4-ppm H₂S pipeline specification at low steam consumption. Observed corrosion rates are low and very little foaming is experienced; both are controlled through the application of optimized design.

The system lineup resembles that of other amine processes. In most applications, co-absorbed hydrocarbons from the absorber (1) are flashed (2) from the solvent and used as fuel gas after treatment in a fuelgas absorber (3). Loaded solvent is regenerated (4).

Operating conditions: Very wide ranges of treating pressures and contaminant concentrations can be accommodated. Refinery fuel gas and gas pipeline specifications, such as 40-ppmv total sulfur and 100-ppmv H_2S , are readily met. Removal of organic sulfur compounds is usually done for the circulation set by H_2S and CO_2 removal. In LNG plants, a



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50-ppmv CO₂ specification is easily attained.

Installations: Over 200 units have been licensed worldwide, covering natural gas treating, synthesis gas and refinery gases.

References: "Gas pretreatment and their impact on liquefaction processes," GPAI, March 1999, Nashville, Tennessee.

"Process application of the ADIP and Sulfinol Process," Gas Processing Symposium, Dubai, United Arab Emirates, April 1999.

"Best practice for deep treating sour natural gases (to LNG and GTL)," Gastech, March 2005.

Licensor: Shell Global Solutions International B.V.



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Gas Processes 2006

Sultimate

Application: Improve sulfur recovery yield by properly treating the effluent of two, three or four Claus unit converters by recycling the required remaining sulfur components and minimizing release to the incinerator. The recycle is based on regenerating a selective amine used to clean up incinerator feed.

Description: The Sultimate unit is a Claus tail gas treatment in four steps to limit the breakthrough of sulfur species sent to the incinerator. In Step One (1), the Claus unit tail gas is heated to the minimum temperature necessary to maximize conversion of the present sulfur species into hydrogen sulfide (H_2S) in presence of a reducing gas. This conversion occurs in a reactor filled with catalyst.

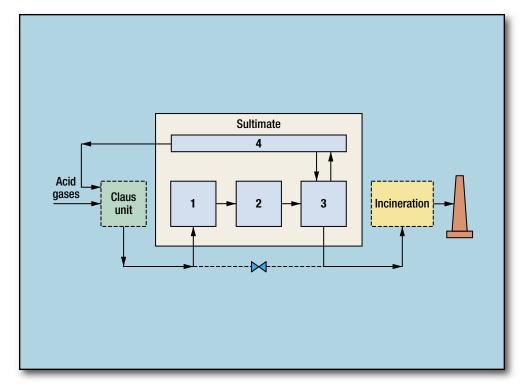
The second step (2) removes 20-40% of the gas's humidity (more or less depending on the Claus feed). The produced water has to be treated to remove dissolved H₂S. Step Three (3) uses selective amine solution **MDEA**max to pick up 90% to 98% of the H₂S remaining in the process gas thus releasing a small amount of H₂S at the inlet of the incinerator as required. The rich amine solution is routed to regeneration.

The fourth step (4) regenerates the **MDEA**max solution. The released gas, from the regeneration of the rich amine solution, is an acid gas (more or less rich, depending on the required performance and the Claus feed quality) which is re-routed at the Claus inlet.

Operating conditions: A process unit can easily and significantly upgrade the performance of any Claus unit, due to:

• An efficient reduction of all undesirable sulfur species released by the existing or new Claus unit

 \bullet Selective removal of re-formed ${\rm H_2S}$ to re-route back to the Claus unit.





Licensor: Prosernat IFP Group Technologies.

ThioSolv SWAATS process (<u>Sour Water</u> <u>Ammonia to Ammonium Thios</u>ulfate)

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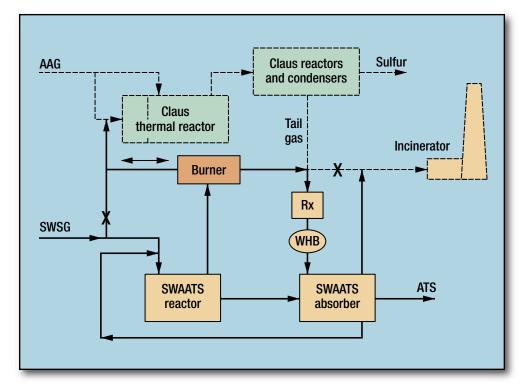
Application: Converts ammonia (NH₃) in sour water stripper gas (SWSG) to low-toxicity ammonium thiosulfate (ATS) solution. Also treats Claus tail gas to achieve low SO_x emissions. The high chemical selectivity of the process also enables it to economically remove hydrogen sulfide (H₂S) or sulfur dioxide (SO₂) from hydrocarbons, syngas and carbon dioxide (CO₂) as an alternative to amine treating or absorptive desulfurization.

Description: Ammonia and a stoichiometric amount of H_2S are selectively absorbed from the SWSG. The reject H_2S , Claus tail gas and supplemental amine acid gas are selectively oxidized to convert all sulfur species to SO_2 , which is then scrubbed out in a low pressure-drop system to yield a vent gas with low SO_x concentration.

 $6NH_3 + 4SO_2 + 2H_2S + H_2O \rightarrow 3(NH_4)_2S_2O_3 \text{ (ATS)}$

SWAATS consumes the NH_3 from in the SWSG; no purchased NH_3 is required. The process prevents or reverses equipment plugging by converting any elemental sulfur in Claus tail gas to soluble thiosulfate.

Economics: For each ton of sulfur in SWSG diverted to SWAATS, about 3 tons of capacity for amine acid gas sulfur is freed up in Claus. The value of the process increases as higher hydrodesulfurization (HDS) severity increases denitrogenation of ultra-low-sulfur diesel pool streams to over 90% and hydrotreating of FCC feed yields large amounts of ammonia. Avoids CAPEX to expand SRU capacity or OPEX for oxygen enrichment. Greatly improves capacity, operability and catalyst life in Claus by removing the ammonia from its feed. OPEX <\$60/ton of sulfur captured from as ATS. CAPEX to convert SWSG and scrub tail gas is less than for SCOT alone. Consumes no external chemicals, reducing gas or fuel. Exports 4.5 ton of MP steam per ton of sulfur recovered. Operational simplicity reduces overall cost of operation and maintenance for the combined SRU. Licensor removes ATS produced.



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Installations: SWAATS process was developed from the Coastal ATS process that has been successfully desulfurizing acid gas and Claus tail gas in a Coastal plant since 1980. SWAATS incorporates improvements to cut both CAPEX and OPEX. First licensed unit is under construction and is scheduled for startup first-quarter 2006. Second unit is currently in the design phase.

References: US Patent 6,534,030.

Berry, R., "Treating hydrogen sulfide: When Claus is not enough," *Chemical Engineering*, Oct. 6, 1980, p. 92.

Licensor: ThioSolv, LLC.



Twister supersonic gas conditioning

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Application: Twister is a gas conditioning technology. Applications include natural gas dehydration, hydrocarbon dewpointing, natural gas liquids (NGL)/liquefied petroleum gas (LPG) extraction, heating value reduction and bulk hydrogen sulfide (H₂S) removal.

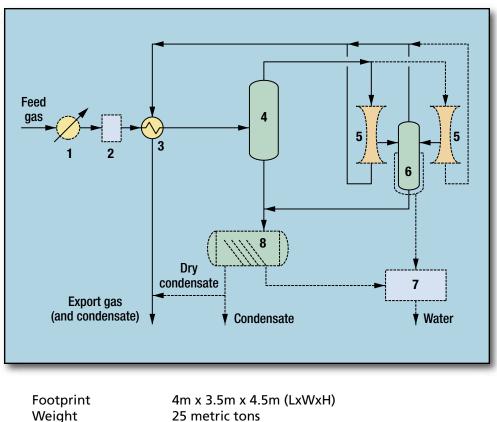
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Condensation and separation at supersonic velocity is the key to unique benefits. An extremely short residence time prevents hydrate problems, eliminating chemicals and associated regeneration systems. The simplicity and reliability of a static device, with no rotating parts and operating without chemicals, ensures a simple facility with a high availability, suitable for unmanned operation.

Description: Feed gas is cooled using a combination of air/seawater coolers (1) and gas/gas cross-exchange (3). In case of deep NGL extraction, upstream dehydration will be required (2). Inlet cooling is operating just outside the hydrate regime. Condensed liquids are removed in an inlet separator (4). The gas is directed through Twister tubes (5). The tubes (5) expand the gas isentropically to supersonic velocity, cooling the gas to cryogenic temperatures and condensing water and NGLs, which are then separated using an in-line cyclone separator.

The separate product streams are recompressed using a diffuser, reducing the velocity. The gaseous liquid stream contains slip gas, which is removed in either a two- or three-phase liquid degassing vessel (6) and recombined with the dry gas stream. Dry export gas is directed through the exchanger (3) to cool the feed stream. In case the operating conditions of the degassing vessel (6) are within the hydrate regime, Twister BV proprietary Hydrate Separator (improved design of conventional LTX technology) is used to melt the hydrates. Depending on the application, water and condensate from the separators (4,6) is treated, processed, re-injected and/or disposed (7,8).

Economics: Typical capital investment for a 100 million scfd package is \$2 million.



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Power 21 Pressure drop 25

4m x 3.5m x 4.5m (LxWxH)
25 metric tons
2 kW, excluding power for tracing and LTX heating (75 kW)
25%-35%

Installations: Two 300-million scfd trains including 12 Twister tubes on Sarawak Shell Berhad/Petronas B11 platform offshore Malaysia. One 35-million scfd train for Shell SPDC Utorogu field onshore Nigeria.

Licensor: Twister BV.

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Hydrogen

Hydrogen and liquid hydrocarbon recovery–cryogenics Hydrogen–PRISM membrane

NGL and LNG

Air Products Nitrogen Recycle LNG Liquefier AP-X LNG process equipment and technology

MCR process equipment and technology Nitrogen recycle LNG liquefier

Synthesis gas

ACORN partial condensation ACORN methane wash

Treating

Nitrogen rejection

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Technology Solutions, a division of ConocoPhillips, is a premier provider of technology solutions for the vehicles of today and the oilfields and energy systems of tomorrow. Backed by modern research facilities and a strong tradition of innovation, we develop, commercialize and license technologies that help oil and gas producers, refiners and manufacturers reach their business and operational. From enhanced production methods, to gasoline sulfur removal processes to valuable catalysts that enhance fuel cell operation, Technology Solutions prepares producers, refiners and consumers alike for a cleaner, more beneficial future.

Strengths of Our Business

• Focused efforts on developing and commercializing technologies that enable refiners to economically produce clean fuels and upgrade hydrocarbons into higher value products

• Strategic alignment with both Upstream and Downstream energy segments to effectively capitalize on extensive R&D, commercial and operational expertise

- Strong relationship-building and problem-solving abilities
- Customer inter-facing and advocacy

Industries Served

Technology Solutions supports both Upstream and Downstream energy segments, including:

- Carbon and petroleum coke
- Gasification
- Sulfur chemistry
- Hydrocarbon processing and upgrading
- Upstream technologies
- Enhanced recovery

Corporate Overview

Headquartered in Houston, ConocoPhillips (NYSE:COP) is an integrated petroleum company with interests around the world. It is the third-largest integrated energy company in the U.S., based on market capitalization, oil and gas proved reserves and production; and the second-largest refiner. Worldwide, of non government-controlled companies, ConocoPhillips has the eighth-largest total of proved reserves and is the fifth-largest refiner.

For More Information:

Email: TechnologySolutions@conocophillips.com Web: www.COPtechnologysolutions.com

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Synthesis Gas

Gas-to-Liquids (GTL)