#### 2012 Gas Processes Handbook

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*Hydrocarbon Processing's* Gas Processes 2012 handbook showcases recent advances in licensed technologies for gas processing, particularly in the area of liquefied natural gas (LNG). The LNG industry is poised to expand worldwide as new natural gas discoveries and production technologies compliment increasing demand for gas as a low-emissions fuel.

With the discovery of new reserves come new challenges, such as how to treat gas produced from shale rock—a topic of particular interest for the growing shale gas industry in the US. The Gas Processes 2012 handbook addresses this technology topic and updates many others.

The handbook includes new technologies for shale gas treating, synthesis gas production and treating, LNG and NGL production, hydrogen generation, and others. Additional technology topics covered include drying, gas treating, liquid treating, effluent cleanup and sulfur removal.

To maintain as complete a listing as possible, the Gas Processes 2012 handbook is available on CD-ROM and at our website for paid subscribers. Additional copies may be ordered from our website.

Photo: Lurgi's synthesis gas complex in Malaysia. Photo courtesy of Air Liquide Global E&C Solutions.

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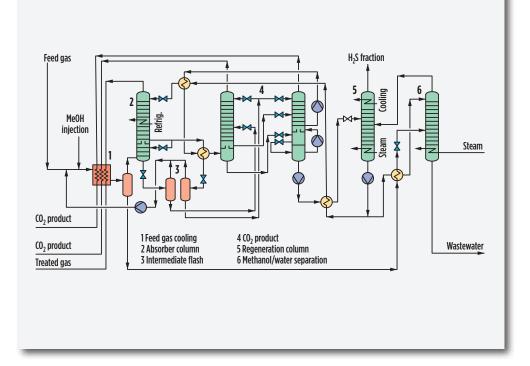
# **Acid Gas Treating by Rectisol**

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

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

The Rectisol wash unit operates at temperatures below 0°C. To lower the feed gas temperatures, it is cooled against cold-product streams before entering the absorber tower. At the absorber tower, CO<sub>2</sub> and  $H_2S/COS$  are removed. The CO<sub>2</sub> content of the purified gas is adjusted to a specific requirement, which can be from 5 vppm up to 5 mol%. Sulfur components like  $H_2S$  and COS can be removed below 0.1 vppm. The Rectisol process does not need a COS hydrolysis for total COS removal. By an intermediate flash, co-absorbed products such as hydrogen ( $H_2$ ) and carbon monoxide (CO) are recovered, thus increasing the product recovery rate.

To reduce the required energy demand for the  $CO_2$  compressor, the  $CO_2$  product is recovered in two different pressure steps (medium pressure and lower pressure). The  $CO_2$  product is essentially free of sulfur (H<sub>2</sub>S and COS) and water. The  $CO_2$  products can be used for enhanced oil recovery (EOR) and/or sequestration, or as pure  $CO_2$  for other processes. The benefit of the RWU is that no additional downstream COS hydrolysis and/or sulfur treatment is required. Since the  $CO_2$  product is water-free, the compressor material can be designed from carbon steel instead of stainless steel. Depending on the allowable  $CO_2$  level in the treated gas, nearly 99% of the  $CO_2$  from the feed gas can be concentrated in the two  $CO_2$  product streams.



In the regeneration column, the loaded methanol is fully regenerated. In the  $H_2S$  fraction, the sulfur components are concentrated in a sulfur-enriched stream, suitable for downstream sulfur recovery units. Even for low-sulfur-containing feed gas streams, the Rectisol wash can economically produce a high-sulfur-enriched  $H_2S$  fraction. After cooling, the methanol is used in the absorber tower to wash out CO<sub>2</sub> and  $H_2S/$ COS. The water contained in the feed gas is withdrawn from the process in the methanol/water separation. The amount of water purged from the process is driven by water concentration in the feed gas (water saturation at battery limit).

# Acid Gas Treating by Rectisol, cont.

#### **Economics:**

From different gasification types (GE-Texaco, Shell, Conoco Phillips, ECUST, etc.)
Adjusted in CO <sub>2</sub> content (5 vppm to 5 mol%) H <sub>2</sub> S + COS < 0.1 vppm (without additional downstream treatment)
Up to 99%
For EOR and/or sequestration Substantially free of H <sub>2</sub> S and COS without COS hydrolysis Water-free without additional drying
Suitable for downstream sulfur recovery unit; also for low-sulfur-containing feed gases.

**Installations:** Nearly 65 Rectisol wash units have been engineered by Linde worldwide. Most of the plants are located in China, and the remainder are located in the US, Africa and Europe.

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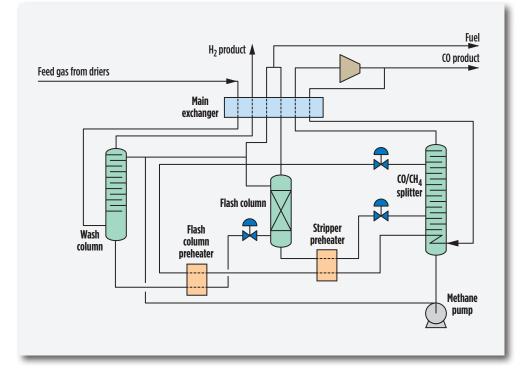
## **ACORN methane wash**

**Application:** To produce a high-purity carbon monoxide (CO) stream, and a high-purity hydrogen ( $H_2$ ) 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).

**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  $H_2$  wash product free of CO, but saturated with methane (2–3%). The  $H_2$  is then rewarmed and recovered as a product. The liquid from the wash column is preheated, reduced in pressure and separated in the flash column (2) where  $H_2$  dissolved in the methane (CH<sub>4</sub>) is rejected to fuel gas. To minimize CO losses, this column is also refluxed with liquid CH<sub>4</sub>.

The  $H_2$ -free liquid from the flash column is heated and flashed to the CO/CH<sub>4</sub> 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 CH<sub>4</sub> liquid from the bottom of the splitter is pumped to the wash column for use as reflux. The net CH<sub>4</sub> 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  $H_2$  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:** There are 10 installations worldwide.

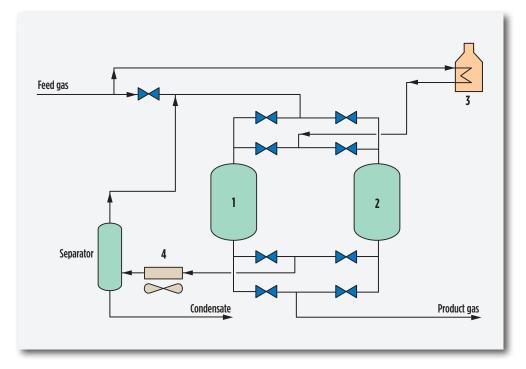
Licensor: Air Products and Chemicals Inc. CONTACT

# ADAPT (gas dehydration and hydrocarbon dewpointing)

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

**Description:** Undesirable components in high-pressure natural gases are simultaneously removed within a solid adsorbent bed (1). Tailored adsorbents selectively remove gas-phase components, thus meeting required product gas specifications. 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 preheated (3) feed or product gas regenerates the saturated bed, which depends on the application requirements. Regeneration temperature depends on the application, but typically it is 275°C. The 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:

- Low pressure drop
- Large individual train capacity
- Flexibility to handle variable conditions and compositions
- 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 are up to 40°C. Plants can be skid-mounted or modular-enabling phased-asset development. Typical feed gas flows are from 15 MMscfd to over 1,500 MMscfd.

**Economics:** Equipment costs vary with scale and application, but typically range from \$5 million for a 100-MMscfd plant to \$30 million for a 1,500-MMscfd plant.

**Installations:** 11 plants in operation or under construction in the UK, the Netherlands, Russia, Egypt, Pakistan and Australia. Total throughput for current ADAPT plants is approximately 17,000 MMscfd of natural gas.

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# ADAPT (gas dehydration and hydrocarbon dewpointing), cont.

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

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# AdvaCap

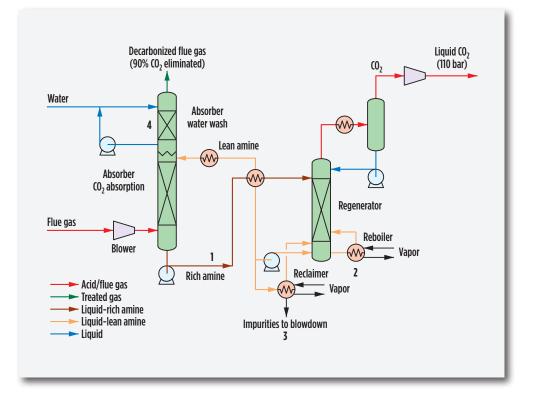
**Applications:** AdvaCap is a portfolio of amine-based processes to capture  $CO_2$  from low-pressure gases containing  $O_2$ , such as flue gases. The first commercially available process of this kind is the HiCapt process developed by IFP.

**Description:** HiCapt is based on extensive research, laboratory pilot tests and industrial pilot tests completed over many years by IFP experts. It also benefits from Prosernat's experience of amine-based gas sweetening processes. The flue gas is treated in an absorption column in which the raw gas is contacted counter-current with fresh solvent to remove 90% of the  $CO_2$  from the raw gas, and the rich solvent is regenerated thermally in a stripping column. Specific design features allow for the minimization of:

Solvent flow (1) Reboiling duty (2) Solvent degradation (3) Emissions (CO<sub>2</sub> and byproducts) in treated gas (4).

**Installation:** HiCapt is based on laboratory tests as well as pilot tests carried out at an industrial demonstration plant treating 10,000  $\text{Nm}^3/\text{h}$  of coal-fired power plant flue gas to capture 2 t/h of CO<sub>2</sub>.

**References:** Dugas, R., P. Alix, E. Lemaire, P. Broutin and G. Rochelle, "Absorber Model for CO<sub>2</sub> Capture by Monoethanolamine Application to CASTOR Pilot Results," GHGT9, Washington, D.C., November 2008.



Alix, P. and L. Raynal, "Pressure Drop and Mass Transfer of a High Capacity Random Packing: Application to CO<sub>2</sub> Post-combustion Capture," GHGT9, Washington D.C., November 2008.

**Licensor:** AdvaCap technologies are developed jointly by IFP and Prosernat, and they are licensed by Prosernat. <u>CONTACT</u>

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# **AdvAmine**

**Applications:** AdvAmine is a complete portfolio of amine-based processes (DEA, MDEA and formulated MDEA) 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.

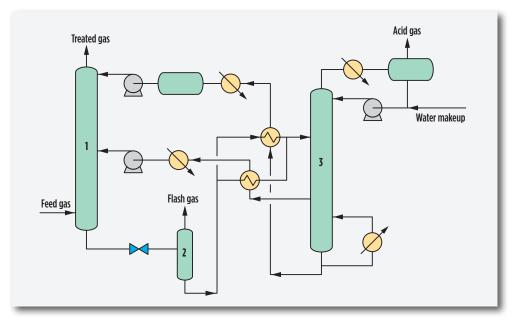
**Description:** The AdvAmine portfolio is based on the extensive industrial and operational experience of Total, which developed these technologies for more than 50 years. It includes the following processes:

• HiLoadDEA: 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

• MDEAmax: A process based on using pure MDEA aqueous solution for selective  $H_2S$  removal or  $H_2S$  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 CO<sub>2</sub> 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 in the figure maximizes acid gas removal and minimizes energy requirement. A flow of semi-lean amine is 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 HiLoad-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 140 units, of which one third are operated by Total, with unit capacities between 0.3 Nm<sup>3</sup>/d and 35.2 Nm<sup>3</sup>/d.

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

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

Bonis, M. et. al., "Corrosion control on amine plants: new compact unit design for high acid gas loading," SOGAT, Abu Dhabi, April 2008.

Licensor: Prosernat IFP Group Technologies CONTACT

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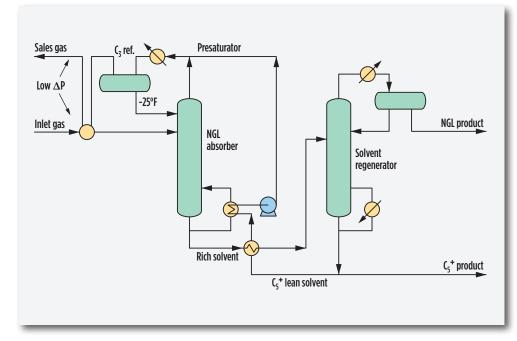
# **AET NGL Recovery**

**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 or refinery gas streams.

**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 light 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. Excess solvent forms a specification  $C_5^+$  product.

**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: Ethane recovery can exceed 96%, and  $C_3$ + recovery is typically 98+%. NGL component flexibility: Online switching, from 96+%  $C_2$  and 99+%  $C_3$  to < 2%  $C_2$  and 98+%  $C_3$ , with simple controls. Incidental  $C_2$  recovery of approximately 30% is also an economic option. Upgrading simple refrigeration plants: Add-on unit enhances propane recoveries, from typical 30%–55% to 98+%, by processing cold separator gases.



**Installations:** Four units in operation.

**References:** Oil & Gas Journal, Vol. 95, No. 39, September 29, 1997. "Upgrading Straight Refrigeration Plants for NGL Enhancement— A Follow-Up," GPA 77th Annual Convention, Dallas, Texas, March 1998. US Patent Nos. 5,561,988 and 5,687,584.

Licensor: Advanced Extraction Technologies Inc. CONTACT

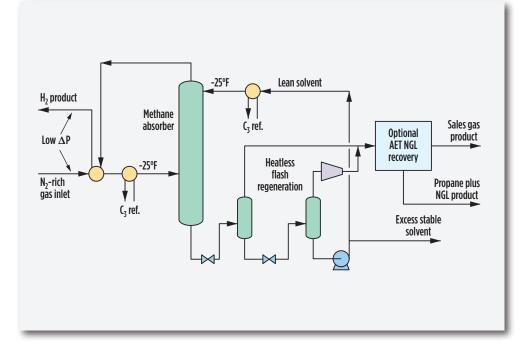
# **AET Process HRU**

**Application:** The patented AET Process Hydrogen Recovery Unit (HRU) utilizes noncryogenic absorption to recover and purify hydrogen  $(H_2)$  from fuel gas, blowdown or  $H_2$  recycle streams.

**Description:** Methane and heavier hydrocarbons are absorbed into a chilled solvent, which is made up of heavier components of the feed gas. Purified  $H_2$  exits the top of the absorber. The absorbed light hydrocarbons are released from the solvent at reduced pressure, and then routed to fuel or to additional processes. Heavier hydrocarbon components leave the system as excess liquid solvent. Solvent from the lowest-pressure flash is recycled to the absorber.

Operating conditions: Feed gases from 240 psig to 3,000 psig can be processed. The purified  $H_2$  is recovered at close to inlet pressure. The lowest process temperature is typically -25°F. Lowest pressure is the low-pressure flash, at close to atmospheric pressure. Excess solvent is available at absorber pressure. Sales gases can be made available at any pressure. Acid gases leave with the sales gas and do not have to be removed. Construction is of -50°F carbon steel.

**Economics:**  $H_2$  recovery and purity of 95% are typical design targets for recovery from waste streams. If an  $H_2$  loop is purified, economics are based on the effect of higher  $H_2$  partial pressure. If a blowdown or fuel stream contains recovered  $H_2$ , the value of the  $H_2$  vs. makeup and any effect of fuel balance are important, along with the availability of  $H_2$  makeup.



**Installations:** Five commercial AET Process NRUs (identical process). A Pilot HRU was funded and successfully demonstrated by a major international oil and gas company.

**References:** US Patents Nos. 5,462,583; 5,551,972; 6,698,237B2; 7,563,307; patents pending

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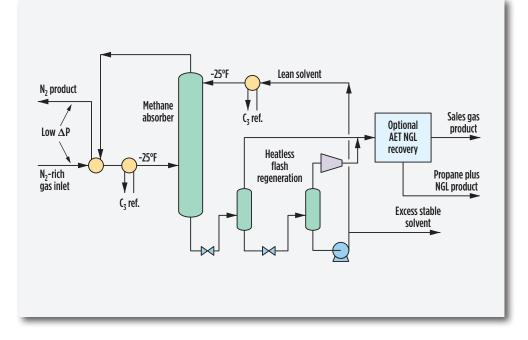
# **AET Process NRU**

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

**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 heatless flash regeneration step is returned to the top of the methane absorber as lean solvent. For most applications, there are no solvent makeup requirements, and excess solvent produced from inlet gas creates a stable liquid product.

**Operating conditions:** Wide gas operating pressure range: 240 psig to 1,200 psig feeds without inlet gas compression. Low pressure drop for  $N_2$ : 15–30 psi is typical and suitable for noncryogenic helium production and  $N_2$  reinjection. Inexpensive metallurgy: Lowest temperature, limited by  $C_3$  refrigeration, permits use of predominantly carbon steel metallurgy. Feed pretreatment:  $CO_2$  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: Methane recovery typically exceeds 98%. Low-nitrogen-content sales gas: Sales gas product at < 2 mol% N<sub>2</sub>. Wide feedstock flexibility: For constant inlet gas flow, inlet composition can vary between 15 mol% and 50 mol% N<sub>2</sub> without impacting sales gas. Construction schedule: typically eight months.



**Installations:** Five commercial units in operation.

**References:** "Noncryogenic N<sub>2</sub>-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; 6,698,237B2; 7,442,847; 7,337,631.

Licensor: Advanced Extraction Technologies Inc. CONTACT

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# AMINEX

**Application:** The AMINEX treating system extracts H<sub>2</sub>S and COS from propane with an amine solution using FIBER FILM Contactor technology.

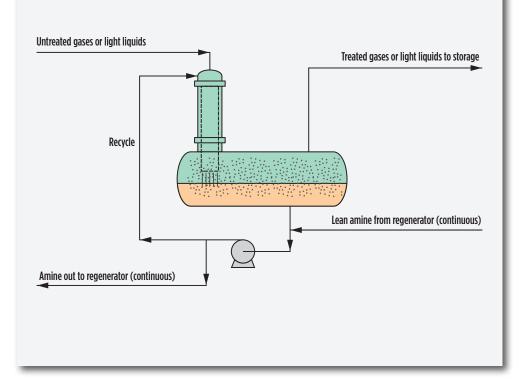
**Description:** In an AMINEX system, the amine phase flows along the fibers of the FIBER FILM Contactor as it preferentially wets the fibers. The propane phase flows through the amine-wetted fibers as the  $H_2S$  and COS are extracted into the amine phase. The two phases disengage in the separator vessel with the rich amine flowing to the amine regeneration unit and the treated propane flowing to storage.

**Economics:** FIBER FILM Contactor technology requires smaller-processing vessels, thus saving valuable plant space and reducing capital expenditures.

Installations: 29 licensed units worldwide.

Reference: Hydrocarbon Processing, April 1984.

Licensor: Merichem Co. CONTACT



# Ammonia Claus technology (ACT)

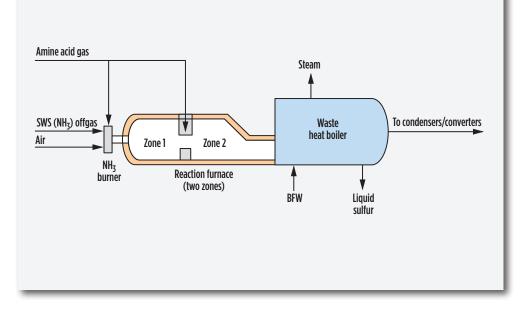
**Application:** Sulfur recovery from hydrogen sulfide  $(H_2S)$  contained in ammonia  $(NH_3)$ -bearing feeds, typically acid gases from sour water strippers (SWSs).

**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 percentages. 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  $NH_3$  to avoid severe operational problems that may occur in the sulfur recovery units (SRUs).

In fact,  $NH_3$  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,  $NH_3$  in sulfur recovery gas feeds increases plant size and related costs, and decreases sulfur recovery.

To fully destroy NH<sub>3</sub>, the straight-through type of plant can still be applied but with different burn configurations conceived to attain the operating conditions needed for NH<sub>3</sub> decomposition. In ACT, a dual-stage burn strategy is used by applying a "two-zone furnace" design in which an NH<sub>3</sub>-bearing stream is burned with part of the amine acid gas (NH<sub>3</sub> "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.

By adopting ACT, an  $NH_3$ -bearing feed can be treated so that the  $NH_3$  concentration in the furnace effluent gas does not adversely affect the SRU operation.



Economics: In the economic area of a conventional Claus unit.

**Installations:** Several ACT plants have been built with  $NH_3$  concentration in the feed stream ranging from 0.5% to 30%. The most recent units were built for Eni S.p.A. and Galp Energia S.A.

**Reference:** The paper "Ammonia destruction in Claus unit" is available on request.

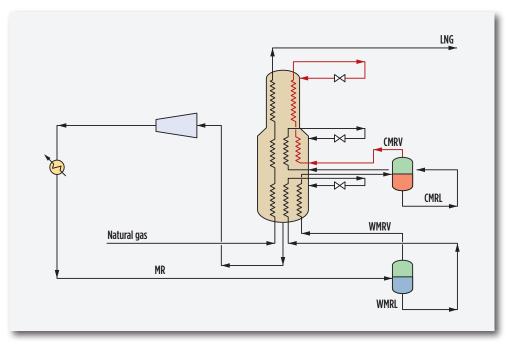
Contributor: Siirtec Nigi S.p.A. CONTACT

## **AP-SMR Single Mixed-Refrigerant LNG Process**

**Application:** To produce liquefied natural gas (LNG) from a natural gas or other methane-rich feedstock.

**Description:** The refrigeration to liquefy the natural gas is supplied by a mixture of nitrogen, methane, ethylene, propane, and mixed butanes known as mixed refrigerant (MR). This mixture is adjusted to provide the optimum cooling and liquefaction in the main cryogenic heat exchanger (MCHE). Pretreated feed gas enters the warm bundle of the MCHE, which consists of three consecutive bundles: warm, middle and cold. Natural gas is cooled by warm mixed-refrigerant liquid (WMRL) that was cooled through the warm bundle as well as expanded across the "warm" Joule-Thomson (JT) valve. The natural gas is further cooled and liquefied in the middle bundle by cold mixed-refrigerant liquid (CMRL) expanded across the "middle" JT valve that was cooled in the warm and middle bundles. The liquefied natural gas then enters the cold bundle, where it is subcooled by cold mixed-refrigerant vapor (CMRV) that was cooled in the warm, middle and cold bundles before being expanded across the "cold" JT valve. The liquefied and subcooled feed gas exits the MCHE and is let down to tank pressure before being sent to the LNG storage tank.

**Installations:** Four plants in operation and two under construction, ranging in capacity from less than 200 tpd to over 1,000 tpd.



**Reference:** Bronfenbrenner, J. C., et al., "Selecting a Suitable Process," LNG Industry, Summer 2009.

Licensor: Air Products and Chemicals Inc. CONTACT

## **AP-X LNG process equipment** and technology

Application: Natural gas liquefaction.

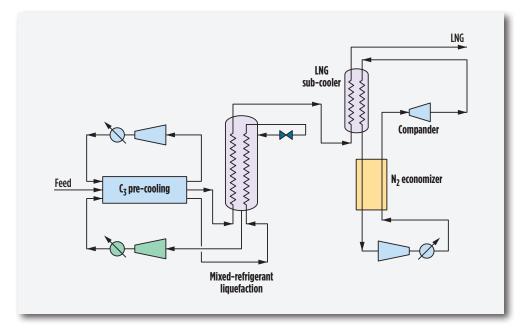
**Products:** Liquefied natural gas (LNG) at required heating value and quality specifications, with integrated LPG product recovery as necessary.

**Description:** The AP-X process is a hybrid of the propane precooled mixed-refrigerant (MR) cycle for precooling and liquefying natural gas, and a nitrogen gas compressor/expander cycle for subcooling LNG. The process achieves high efficiency and low production cost by using both cycles to their best advantages.

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

The power split between precooling, liquefaction and subcooling 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 steam turbines, industrial gas turbines and/or electric motor drivers.

**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 in operation, each with a capacity of approximately 7.8 million tpy of LNG.

**Reference:** US Patent No. 6,308,521, "Hybrid cycle for the production of liquefied natural gas."

Licensor: Air Products and Chemicals Inc. CONTACT

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# AQUISULF

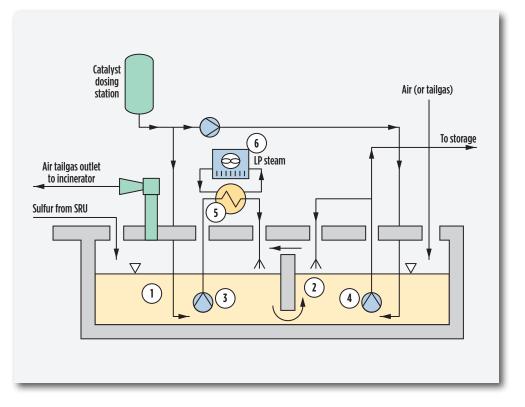
**Application:** Decrease hydrogen sulfide ( $H_2S$ ) content in liquid sulfur condensed in SRUs and routed to sulfur degassing facilities. Maximum  $H_2S$  content is 10 ppm.

**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 a Claus process gas or atmospheric air that is 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 or back to a Claus combustion chamber 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 H<sub>2</sub>S from liquid sulfur," *Oil & Gas Journal*, July 1989.

**Licensor:** Lurgi GmbH, Air Liquide Global E&C Solutions, Lurgi Technologies <u>CONTACT</u>

# **Calcor process (carbon monoxide)**

**Application:** To produce carbon monoxide (CO) from natural gas or liquefied petroleum gas (LPG) through carbon dioxide (CO<sub>2</sub>) reforming.

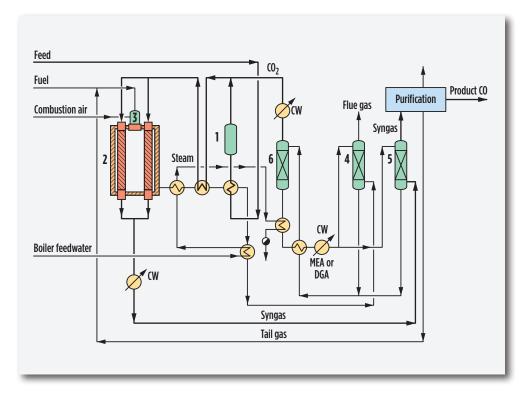
**Description:** Calcor is a  $CO_2$  reforming process combined with a  $CO_2$  recovery unit and a CO purification step. The Calcor Standard process is designed to operate under low pressure and uses catalytic reforming operating at high temperatures. To protect the catalyst, the feed must be desulfurized.

After preheating and mixing with hydrogen (H<sub>2</sub>), 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 CO<sub>2</sub> and preheated 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 CO<sub>2</sub> and feed is converted into synthesis gas (syngas). The syngas consists of CO with H<sub>2</sub>, CO<sub>2</sub>, water and trace methane (CH<sub>4</sub>), 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 syngas is cooled to ambient temperature prior to undergoing  $CO_2$  removal and recovery. In this step, the  $CO_2$ from the reformer flue gas, along with the  $CO_2$  from the syngas, are absorbed in packed towers (4, 5) by a caustic solution, e.g. monoethanolamine (MEA).

The CO<sub>2</sub> is separated from the scrubbing liquid in a stripper (6) and recycled to the reforming process. The syngas, now typically consisting of 70 vol% CO and 30 vol% H<sub>2</sub> and still carrying traces of CO<sub>2</sub> and CH<sub>4</sub>, enters the CO purification step. Depending on the CO purity required, a low-temperature process or a semi-permeable membrane process may be applied.

**Economics:** With  $CO_2$  recovery from the reformer flue gas, as well as from the syngas, the Calcor Standard process generates almost one CO mole-



cule 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  $\text{Nm}^3$  of natural gas (calculated as 100% CH<sub>4</sub>) or 531 kg of LPG as the main utility.

**Installations:** 10 plants have been built worldwide with capacities of up to 850 Nm<sup>3</sup>/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 CONTACT

# Caloric HM process (hydrogen)

**Application:** To produce hydrogen  $(H_2)$  from methanol (MeOH) using steam reforming.

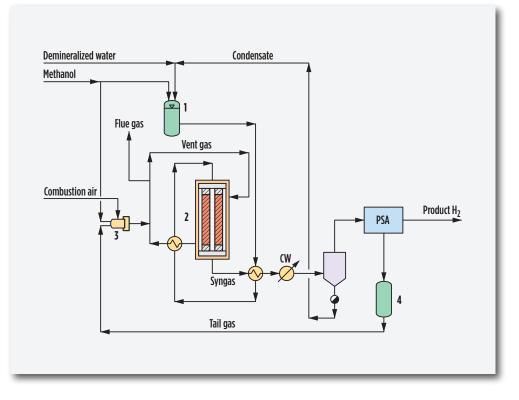
**Description:** The HM process uses MeOH reforming combined with a pressure swing absorption (PSA) purification step to produce high-purity  $H_2$ . MeOH and demineralized water ( $H_2O$ ) are mixed in a tank (1). This is vaporized and superheated in heat exchangers by hot synthesis gas leaving the 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/ $H_2O$  vapor mixture is converted into synthesis gas consisting of  $H_2$ , CO, CO<sub>2</sub>, methane (CH<sub>4</sub>) and  $H_2O$  vapor. In the cooler, the synthesis gas is cooled to ambient temperatures, while, simultaneously,  $H_2O$  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 the discharge of thermal oil.

**Economics:** To produce 1,000  $\text{Nm}^3/\text{h}$  of H<sub>2</sub>, the following utilities are required:

- 630 kg/h MeOH
- 360 kg/h demineralized  $H_2O$
- 55 kW electric power
- 13 m<sup>3</sup>/h cooling  $H_2O$



**Installations:** 20 plants have been built worldwide, with capacities of up to 1,500 Nm<sup>3</sup>/h of pure  $H_2$ .

**Reference:** Neumann, P. and F. von Linde, "Opportunities for an economical H<sub>2</sub> supply," *Inform,* Vol. 14, No. 5, May 2003.

Licensor: Caloric Anlagenbau GmbH CONTACT

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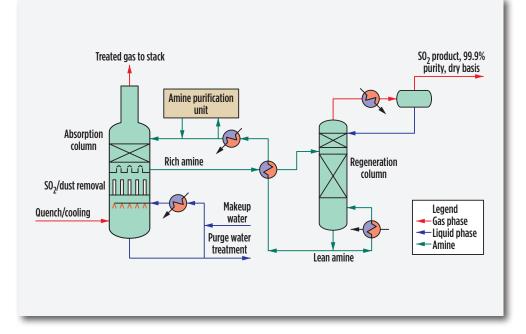
## **Cansolv SO<sub>2</sub> Scrubbing for flue gas treating**

**Application:** This regenerative process, which uses an amine-based absorbent that is resistant to oxidative environments, is suited for high-efficiency removal of  $SO_2$  from flue gases. The process is highly selective to  $SO_2$  and, as such, all carbon dioxide is slipped. The process produces a high-quality, water-saturated  $SO_2$  byproduct that can be converted to sulfur in a conventional SRU or used to produce sulfuric acid.

**Description:** This patented technology uses an aqueous amine solution to achieve highly efficient, selective absorption of  $SO_2$  from flue gas. The formulation consists of a concentration of 25 wt% amine, with the balance consisting of up to 10 wt% amine-bound sulfate as activator and water making up the difference.

Flue-gas is first quenched and saturated in a water prescrubber. Next, the gas contacts the lean amine solution in a counter-current absorption column.  $SO_2$  is absorbed, and the treated gas exits the absorber to the atmosphere.  $SO_2$ -rich amine from the absorption column is first pumped through a lean/rich amine heat exchanger for energy recovery, and then pumped to the regeneration column. Steam stripping regenerates the lean amine solution, and the  $SO_2$  is recovered as a pure, water-saturated product. Lean amine is pumped from the stripper reboiler to the absorption column through the lean/rich amine heat exchanger and the lean amine cooler. Byproduct  $SO_2$  is directed to byproduct management systems to be converted to liquid  $SO_2$ , sulfuric acid or elemental sulfur.

Flue-gas may contain dust and strong acid compounds which may be wholly or partially captured in the absorber. Additionally, a small fraction of the absorbed sulfur dioxide will react in-situ to form a thermally stable strong acid. Consequently, a slipstream of lean amine is filtered for suspended solids and subsequently treated using ion exchange for strong acid level control.



**Operating conditions:** The absorber operates at atmospheric pressure and a temperature between 30°C and 65°C. Inlet  $SO_2$  concentrations can vary considerably with commercially proven values of up to 15 mol%. Emissions as low as 10 ppmv can be achieved. The regeneration column operates at slightly positive pressure (up to 0.8 barg).

**Advantages:** Within Cansolv, regeneration steam (low-pressure) is generally considered as the largest consumable. Low-pressure steam consumption can be significantly reduced with internal heat recovery lineups, such as mechanical vapor recompression systems and external waste heat recovery systems. In addition to reducing emissions, this process can debottleneck an existing SRU by reducing dependence on thermal oxidation of  $H_2S$ , thereby achieving higher sulfur recovery effi-

# Cansolv SO<sub>2</sub> Scrubbing for flue gas treating, cont.

ciency or decoupling sulfuric acid plant emissions from an upstream feed source. In lineups for treating contaminated sour natural gas, the process helps achieve high sulfur recovery efficiency while enabling simplification of the lineup and reducing capital and operating costs.

**Installations:** 15 units have been constructed worldwide, with an additional nine in different phases of design or construction.

Licensor: Cansolv Technologies Inc. CONTACT

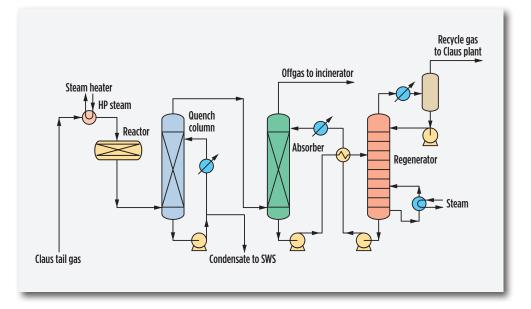
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## Claus Tail Gas Treating (LT-SCOT Process)

**Application:** The Shell Claus Offgas Treating (SCOT) process has been developed to remove sulfur compounds from Claus tail gas to comply with stringent air emissions regulations. The conventional SCOT process is able to easily meet less than 250 ppmv total sulfur in the SCOT offgas, which corresponds to an overall sulfur recovery efficiency of 99.9% on intake. The LT-SCOT has the same recovery capabilities, but it reduces the total installed cost by 15% compared to the conventional SCOT unit. For revamp situations, LT-SCOT will save utility costs when compared to conventional SCOT.

**Description:** The LT-SCOT process essentially consists of a reduction section and an ADIP absorption section of special design. In the reduction section, all the sulfur compounds (other than  $H_2S$ ) present in the Claus tail gas (i.e.,  $SO_2$ , COS,  $CS_2$  and elemental sulfur) are completely converted into  $H_2S$  over a cobalt/molybdenum catalyst at 220°C in the presence of  $H_2$  or a mixture of  $H_2$  and CO. The Claus tail gas feed to the SCOT process is heated to 220°C with a heat exchanger, with optionally added  $H_2$  or a mix of  $H_2/CO$ . If reducing gas,  $H_2$  or CO, is unavailable, an inline burner can be applied, operating sub-stoichiometrically to produce reducing gas.

The heated gases then flow through a catalyst bed where sulfur compounds, including CS<sub>2</sub> and COS, are reduced to H<sub>2</sub>S. The gas from the reactor is cooled by direct contact cooling with water to 40°C. Water vapor in the process gas is condensed, and the condensate is sent to a sour water stripper. The cooled gas, which normally contains up to 3 vol% H<sub>2</sub>S and up to 20 vol% CO<sub>2</sub> or more, is counter-currently washed with an alkanolamine solvent in an absorption column designed to absorb almost all H<sub>2</sub>S but relatively little CO<sub>2</sub>.



The treated gas from the absorption column contains only traces of  $H_2S$  and is oxidized in a standard Claus incinerator. The concentrated  $H_2S$  is recovered from the rich solvent in a conventional stripper and is recycled to the Claus unit. The LT-SCOT units are designed for minimum pressure drop so they can be easily added to existing Claus units. If insufficient pressure is available, a gas booster can be installed, preferably between the cooling tower and the absorption tower.

**Utilities:** Typical utility consumption of an LT-SCOT unit for a 100-t/d sulfur intake to the Claus plant. Basis: 71 vol%  $H_2S$  content and 11 vol%  $NH_3$  content in Claus feed gas.

4 barg steam consumption	t/h	3.0 (for add-on SCOT)
40 barg steam	t/h	0.4
Electricity	kW	70 (for integrated SCOT)
Electricity	kW	95 (for add-on SCOT)

# Claus Tail Gas Treating (LT-SCOT Process), cont.

**Installations:** For LT-SCOT, 24 units have been designed, of which eight are in operation. Newly designed units will all feature the LT-SCOT process, as it differs from regular SCOT units only in the catalyst operation temperature.

**Licensor:** Jacobs Comprimo Sulfur Solutions, a member of Jacobs Engineering Group, authorized licensor on behalf of Shell Global Solutions B.V. <u>CONTACT</u>

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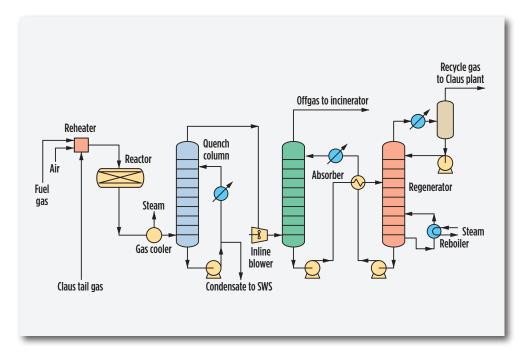
#### Claus Tail Gas Treating (SCOT Process)

**Application:** The Shell Claus Offgas Treating (SCOT) process has been developed to remove sulfur compounds from Claus tail gas to comply with stringent air emissions regulations. The standard SCOT process is able to easily meet less than 250 ppmv total sulfur in the SCOT offgas, which corresponds to an overall sulfur recovery efficiency of 99.9% on intake.

**Description:** The SCOT process essentially consists of a reduction section and an ADIP absorption section of special design. In the reduction section, all the sulfur compounds (other than  $H_2S$ ) present in the non-incinerated Claus tail gas (i.e.,  $SO_2$ , COS,  $CS_2$  and elemental sulfur) are completely converted into  $H_2S$  over a cobalt/molybdenum catalyst at 300°C in the presence of  $H_2$  or a mixture of  $H_2$  and CO. The Claus tail gas feed to the SCOT process is heated to 300°C with an inline burner or heat exchanger, with optionally added  $H_2$  or a mix of  $H_2/CO$ . If reducing gas,  $H_2$  or CO, is unavailable, an inline burner is operated sub-stoichiometrically to produce reducing gas.

The heated gases then flow through a catalyst bed, where sulfur compounds, including  $CS_2$  and COS, are reduced to  $H_2S$ . Process steam is generated by cooling the gas to about 165°C in a heat recovery boiler and, subsequently, by direct contact cooling with water to 40°C. Water vapor in the process gas is condensed, and the condensate is sent to a sour water stripper.

The cooled gas, which normally contains up to 3 vol%  $H_2S$  and up to 20 vol%  $CO_2$  or more, is counter-currently washed with an alkanolamine solvent in an absorption column designed to absorb almost all  $H_2S$  but relatively little  $CO_2$ . The treated gas from the absorption column contains only traces of  $H_2S$  and is burned in a standard Claus incinerator. The concentrated  $H_2S$  is recovered from the rich solvent in a conventional stripper and is recycled to the Claus unit.



The SCOT units are designed for minimum pressure drop so that they can be easily added to existing Claus units. If insufficient pressure is available, a gas booster can be installed, preferably between the cooling tower and the absorption tower.

**Utilities:** Typical additional utility consumption of a SCOT unit for a sulfur intake of 100 t/d to the Claus plant. Basis: 71 vol%  $H_2S$  content and 11 vol%  $NH_3$  content in Claus feed gas.

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# Claus Tail Gas Treating (SCOT Process), cont.

**Installations:** More than 200 SCOT units for the treatment of tail gas from Claus plants, ranging in capacity from 3 t/d to 4,000 t/d of sulfur production, are in operation throughout the world, demonstrating the reliability and flexibility of the process.

**Licensor:** Jacobs Comprimo Sulfur Solutions, a member of Jacobs Engineering Group, authorized licensor on behalf of Shell Global Solutions B.V. <u>CONTACT</u>

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#### Claus, oxygen-enriched

**Application:** Debottleneck existing sulfur recovery units (SRUs) or reduce size, capital and operating costs for new facilities by using oxygen  $(O_2)$  to enrich the combustion air.

**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  $O_2$ , plant capacity can be increased significantly. The level of air enrichment with  $O_2$  and, hence, the level of uprating, depend upon the feed gas composition:

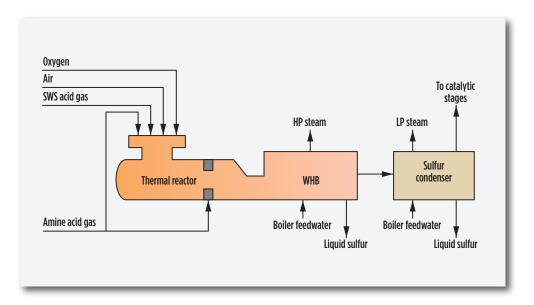
- Up to about 30%  ${\rm O_2},$  only minor modifications to the plant (mainly to the burner) would be expected

- Above 30% (but less than 45% in a refinery application)  $O_2$  concentration, a proprietary  $O_2$ -compatible burner would be required; some limited modifications could be expected

- Above 45%  $\mbox{O}_2\mbox{concentration, special technology must be implemented.}$ 

Sulfur recovery efficiency for an  $O_2$ -based Claus process is slightly better than that of air-based Claus.

**Economics:** For a refinery application, the cost of both a revamp and a new unit is related to capacity increase, and it is generally between 10% and 30% (excluding the cost of  $O_2$ ) of the installed cost of an equivalent air-based Claus unit with the same capacity.



**Installations:** Several units have been designed and revamped by Siirtec Nigi in cooperation with WorleyParsons and BOC. Several units were constructed for Eni S.p.A., and one has been designed for Galp Energia S.A.

**Reference:** "A hot and tricky process environment," *Sulphur,* July–August 2007.

Licensor: Siirtec Nigi S.p.A. (up to 35% O<sub>2</sub>). CONTACT

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### Clauspol

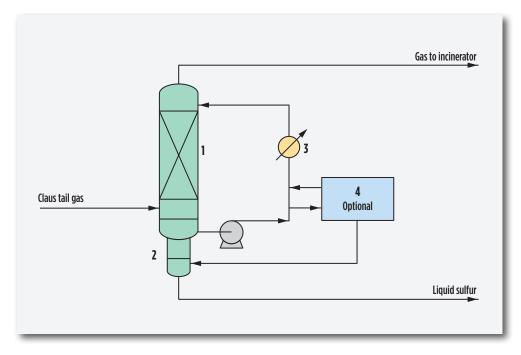
**Application:** Claus tail gas treatment with total sulfur recovery up to 99.9+%. Liquid-phase conversion of  $H_2S$  and  $SO_2$  into liquid elemental sulfur.

**Description:** Claus tail gas is contacted counter-currently with an organic solvent in a low-pressure, drop-packed column (1). Hydrogen sulfide (H<sub>2</sub>S) and SO<sub>2</sub> are absorbed in the solvent and react to form liquid elemental sulfur 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 sulfur in the solvent, pure liquid sulfur 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 sulfur recovery of 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 to 99.9+%.

**Economics:** For a Clauspol unit treating a typical Claus tail gas, in the 99.7–99.9% recovery range, the CAPEX is typically 60–80%; OPEX is less than 25% of that for a conventional hydrogenation/amine plant. Unlike 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 2001.

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

Licensor: Prosernat IFP Group Technologies CONTACT

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# **CO<sub>2</sub> recovery**

**Application:** Recover high-purity (including food-grade) CO<sub>2</sub> from oxygen-containing gases such as boiler flue gases, gas turbine exhausts and waste gases, using Lummus absorption/stripping technology.

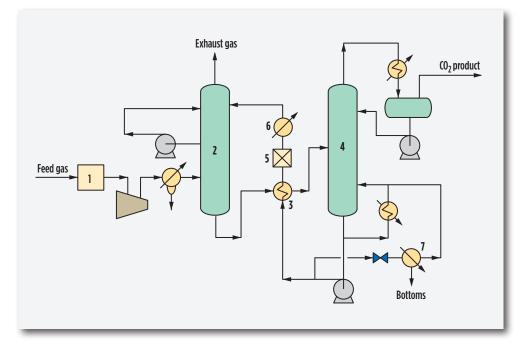
**Description:**  $CO_2$ -containing feed gases are first cooled and scrubbed (1), if necessary, to reduce  $SO_2$  levels. The gases' pressures are boosted slightly before entering the recovery system.

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 (4), where  $CO_2$  is recovered overhead. Condensate from the stripper overhead is returned to the system.

Lean MEA from the stripper (4) is cooled (3, 6), filtered (5) and returned to the absorber. Periodically, a batch-reclaiming operation (7) is conducted to purge MEA degradation products and to recover MEA by decomposing heat-stable salts.

CO<sub>2</sub> 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 slightly above atmospheric pressure. Moderate levels of SO<sub>2</sub> and NO<sub>x</sub> in the feed are acceptable. SO<sub>2</sub> prescrubbing is required only with SO<sub>2</sub> levels higher than 25 ppmv.



**Installations:** Four units are operating on coal-fired boiler flue gases. Two plants produce gaseous, chemical-grade CO<sub>2</sub>, and two produce food-grade liquid. Capacities range from 150 tpd to 800 tpd.

Licensors: Randall Gas Technologies CONTACT

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# **CO<sub>2</sub> removal (Molecular Gate)**

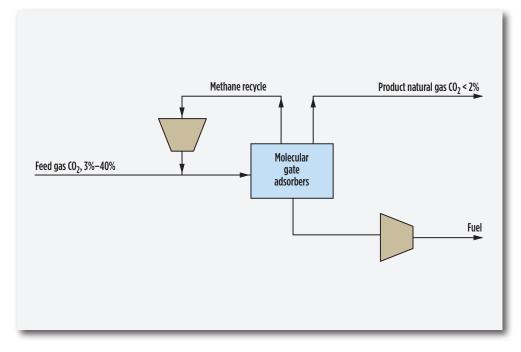
**Application:** Simultaneously removes carbon dioxide ( $CO_2$ ) and water from contaminated natural gas for pipeline, CNG or LNG feed. Feedstocks include landfill gas, digester gas, coalbed methane and natural gas. Water-saturated feeds and  $CO_2$  levels of 3%–40% can be treated. Product is pipeline-quality natural gas with characteristic  $CO_2$  levels of 50 ppm to 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 600 psig, is routed through a series of adsorber vessels. One or more vessels remove the water and  $CO_2$ , 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  $CO_2$  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 \$0.50/thousand feet (Mft<sup>3</sup>) of feed processed. This cost decreases to less than \$0.30/Mft<sup>3</sup> for a 10-MMscfd design. Modular construction allows for low-cost installation and equipment relocation flexibility.

**Installations:** 40 units are in operation.

**Reference:** "Molecular Gate Technology for Smaller-Scale LNG Facilities," GPA Annual Convention, March 2010, Austin, Texas.

Licensor: Guild Associates Inc. CONTACT

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# **Cold Bed Adsorption (CBA)**

**Application:** Recover elemental sulfur from acid gas streams that contain hydrogen sulfide  $(H_2S)$ , or treat Claus tail gas for additional sulfur recovery.

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

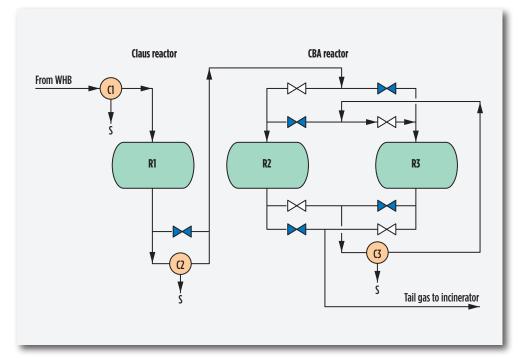
• Operating the CBA reactors near the sulfur dewpoint extends the Claus reaction equilibrium and can achieve higher sulfur conversion

• 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 recombined 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.

The temperature in the CBA reactor can vary from 120°C–150°C during the adsorption cycle and from 300°C–350°C during regeneration. Sulfur recovery can be over 99%. CBA reactors can be either aluminized or refractory-lined carbon steel.

**Economics:** Capital cost is about 85% of the cost of a combined Claus and wet tail gas treating (TGT) unit. Compared to a combined Claus and TGT unit, the operating costs are much lower since the following



consumptions are not required: heating medium for a Claus process gas reheating, cooling water and amine solution for TGT. Additionally, electricity consumption is much lower.

**Installations:** Many CBA plants have been built with capacities of 1,300 tpd to 2,000 mtpd. One of the CBA plants built by Siirtec Nigi was for Hindustan Petroleum Co. Ltd. at Visakhapatnam, India. This plant uses two units with a capacity of 65 mtpd each.

Licensor: BP through Siirtec Nigi S.p.A. CONTACT

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#### **ConocoPhillips Optimized Cascade LNG Process**

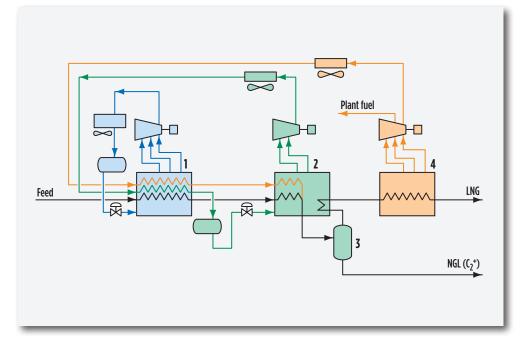
**Application:** Large baseload natural gas liquefaction facilities with optional capability for high ethane, propane or mixed LPG recovery.

**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 dependent 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 optimized cascade process is well-established, reliable, efficient and low-cost. The two-in-one design allows the plant to operate with very high availability and reliability. Turbine/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 over 40 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

### ConocoPhillips Optimized Cascade LNG Process, cont.

company began licensing the process in 1993. Since then, eight trains using the technology have been successfully brought online in Trinidad; Idku, Egypt; Darwin, Australia and Equatorial Guinea. There are 10 trains in EPC and several additional trains in various stages of commercial development. ConocoPhillips 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.; LNG services are also provided by Phillips LNG Technology Services Co. and Bechtel Corp. via a collaborative relationship with ConocoPhillips Co. <u>CONTACT</u>

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# COPE

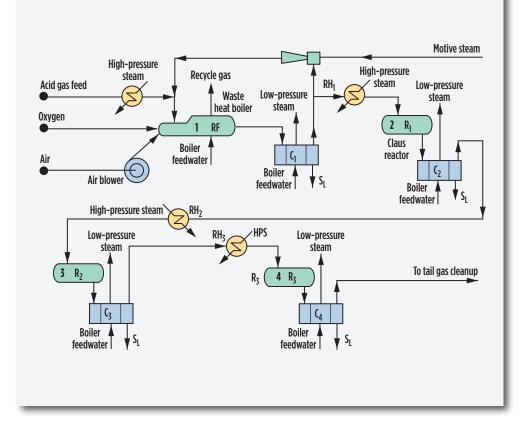
**Application:** The COPE Oxygen Enrichment Process allows existing Claus sulfur recovery/tail gas cleanup units to increase capacity and recovery, can provide redundant sulfur processing capacity and can improve combustion performance of units processing lean acid gas.

**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 O<sub>2</sub> enrichment level increases, the combustion temperature (1) increases. COPE Phase I, which does not use a recycle stream, can often achieve 50% capacity increase through O<sub>2</sub> enrichment to the maximum reaction furnace refractory temperature limit of 2,700°F–2,800°F. Higher O<sub>2</sub> enrichment levels are possible with COPE Phase II, which uses an internal process recycle stream to moderate the combustion temperature, allowing enrichment up to 100% O<sub>2</sub>.

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. Operating costs are a function of O<sub>2</sub> cost, reduced incinerator fuel, and reduced operating and maintenance labor costs.

**Installations:** 36 COPE trains at 22 locations.

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# COPE, cont.

Reference: US Patents Nos. 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.

Nasato, E. and S. Fenderson, "COPE with your sulfur," *Hydrocarbon Engineering*, August 2004.

Licensor: Goar, Allison & Associates LLC CONTACT

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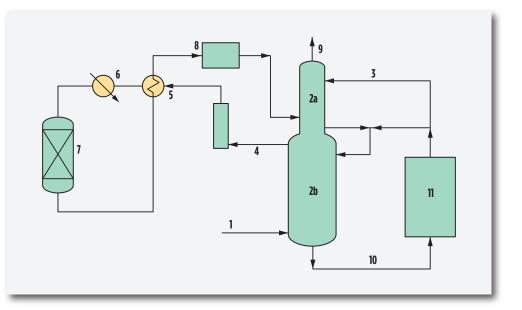
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EX COMPA

# COSWEET

**Application:** Carbonyl sulfide (COS) removal from sour natural gas streams associated with amine-based sweetening processes that allow for the simultaneous removal of COS,  $H_2S$  and/or CO<sub>2</sub>. COSWEET allows for complete removal of COS, either combined with selective  $H_2S$  removal (e.g., with the AdvAmine selective MDEAmax process) or in combination with complete CO<sub>2</sub> +  $H_2S$  removal in the amine unit (e.g., with AdvAmine HiLoadDEA or energizedMDEA). COSWEET can be easily implemented at existing gas sweetening facilities for COS removal.

**Description:** The natural stream to be treated (1) is sent to the bottom section of the amine absorber (2b). In this bottom section, most of the  $H_2S$  is removed by the amine solvent flowing from the upper section. The rich amine solvent (10) recovered from the bottom section (2) flows to the thermal regeneration section, producing a regenerated solvent stream (3) that is recycled to the absorber top section (2a). The gas stream (4) leaving the bottom section of the absorber is heated in the feed/effluent heat exchanger (5) and steam superheater (6) before going to the COSWEET reactor (7). In this reactor, COS is decomposed into CO<sub>2</sub> and  $H_2S$  on an IFP Group proprietary catalyst. After the reactor, the outlet gas stream is cooled through the heat exchanger (5) and the subcooler (8) before being admitted to the amine absorber upper section (2a). In this upper section, the gas is contacted with the regenerated solvent to achieve the required treated gas specifications in the outlet stream (9).



**Economics:** COSWEET can achieve a 99+% COS conversion. Cost evaluations have shown that CAPEX savings of 17% and OPEX savings of 10% can be achieved with the combination of COSWEET and MDEAmax, compared with an amine process allowing identical complete COS removal (down to 1-ppmv COS specification).

Reference: Published patent FR2950265 A1; WO 2011/033191 A1.

Licensor: Prosernat IFP Group Technologies CONTACT

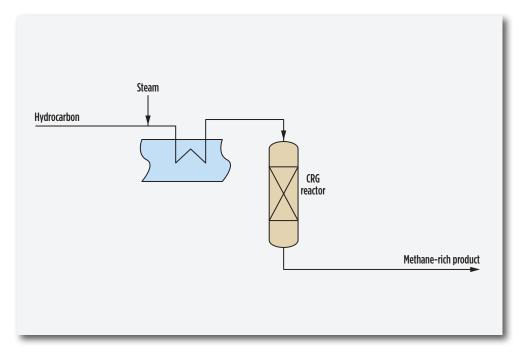
# CRG processes (pre-reforming, derichment)

**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), or as an adiabatic prereformer.

**Description:** Fixed bed of nickel-based catalyst converts hydrocarbon feeds in the presence of steam to a product stream containing only methane together with  $H_2$ , CO, CO<sub>2</sub> 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 prereformer enables capital cost savings in the primary reformer as a result of reduction in radiant box heat load, and it 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–650°C, and at pressures of 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 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, AIChE.

**Licensor:** The CRG process and catalyst are licensed by Davy Process Technology Ltd. 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. <u>CONTACT</u>

#### **CRYOMAX DCP (dual-column propane recovery)**

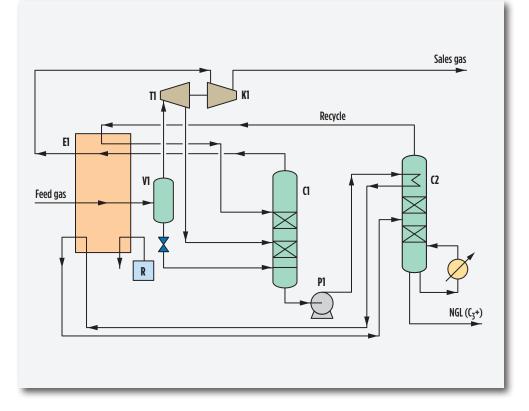
**Application:** A cryogenic process for gas fractionation to recover  $C_3$ + hydrocarbons from natural gas. With this process, more than 98% propane is extracted from natural gas. High efficiencies are achieved with a dual-column system associated with a turboexpander. Multi-stream plate-fin exchangers increase efficient heat integration.

**Description:** The high-pressure dry feed gas at 25°C, 70 bar 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 bar 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 bar 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 bar is reheated and compressed to sales gas pressure. Approximately 99.5% propane recovery can be reached when the propane value is high.

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

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



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

# **CRYOMAX Flex-e**

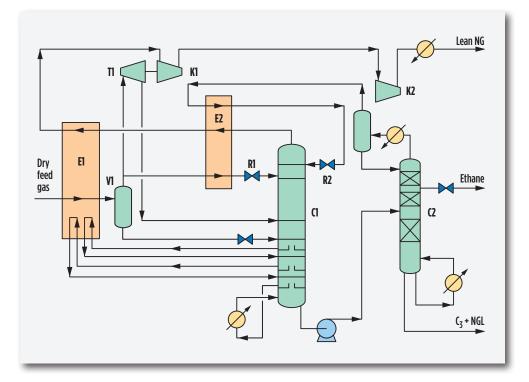
**Application:** A cryogenic process for the variable extraction of an ethane-rich stream from a natural gas. The ethane amount can be varied across a wide range, while the propane recovery rate to a separate natural gas liquid (NGL) stream remains above 99%. This provides flexibility with respect to the downstream ethane user, usually a steam cracker producing ethylene, without affecting the profitable recovery of propane in the NGL. The scheme may also be used to provide ethane refrigerantgrade makeup for methane recovery in LNG plants.

**Description:** The dry feed gas at 25°C, 70 bar is cooled to -40°C in E1 and enters V1, where liquid and gas are separated. Most of the gas is dynamically expanded to 30 bar in T1 and fed to recovery column C1. Around 15% of the gas from V1 is liquefied in E2 and fed to C1 as primary reflux R1. The liquid from V1 is reduced in pressure and sent to C1.The ethane-rich bottom product from C1 is sent to the deethanizer C2, operating at a higher pressure than C1. The cold is recovered from the lean gas, leaving C1 overhead in E2/E1 before compression in K1/K2.

The overhead product from C2 is used as secondary reflux R2 in C1. The rate of ethane recovery to the side stream at the top of C2 is controlled by adjusting the flowrate of R2 and the pressure of C1.

The quality of reflux R2 ensures that the heavy hydrocarbon content in the treated natural gas is sufficiently low for it to be produced as LNG.

**Economics:** Production costs are about 20% less than a conventional process. Project economics are improved by high propane recovery at all times.



**Installations:** None with an ethane-rich side draw.

Reference: US Patent No. 7,458,232

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# **CRYOMAX LNG**

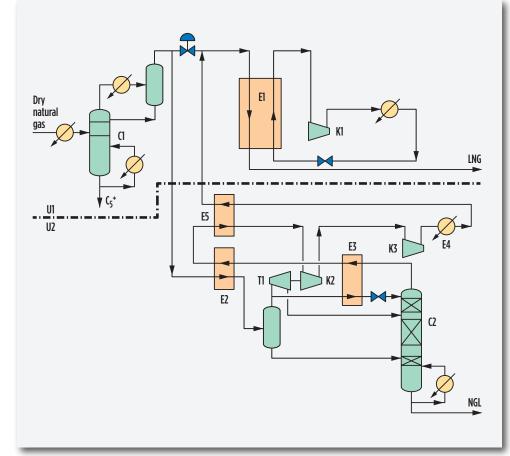
**Application:** A cryogenic process for the deep recovery of NGL from a new or an existing LNG train. Feed gas pretreatment is ensured by the steps already required for liquefaction. The process is reversible in that the LNG unit can be operated with or without the NGL recovery unit.

**Description:** Within LNG unit U1, sweet dry natural gas is made suitable for liquefaction in a refrigerated scrub column C1. Part of the overhead can be sent directly to liquefier E1 and the remainder to the NGL recovery unit U2. The recovery column C2 is fed with gas that is further chilled in exchanger E2 before expansion to low pressure in turboexpander T1 to allow fractionation. Part of the feed bypasses T1 and, after cooling in E3, is used as reflux. The cold is recovered from the lean gas in E2/E3 before compression in K2/K3 and a temperature adjustment in E4/E5. It can be fed to the liquefier E1 at the same temperature and/or pressure as the gas leaving C1. Advantages of the scheme are high ethane and/or propane recovery; a single reflux to C2 due to the absence of heavy components and operational flexibility from the decoupling of U1 and U2.

**Economics:** Capital investment per ton of ethane is approximately 70% when compared to a standalone plant located upstream of the LNG unit.

Installations: None. Two units planned in Algeria.

Reference: US Patent No. 7,237,407



# **CRYOMAX MRE (multiple reflux ethane recovery)**

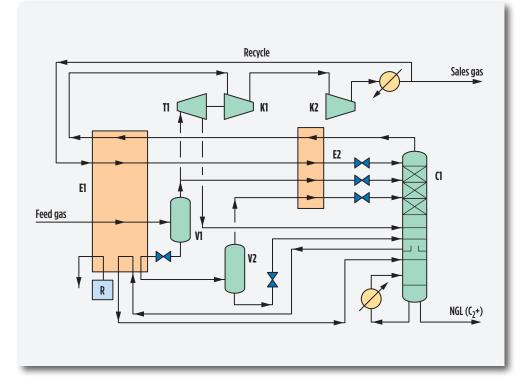
**Application:** A cryogenic process for gas fractionation to recover  $C_{2}$ + hydrocarbons from natural gas. With this process, more than 95% of the ethane can be extracted from natural gas. High efficiencies are obtained through a multiple reflux concept associated with a turboexpander. Multi-stream plate-fin heat exchangers increase efficient heat integration of the process.

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

The liquid pressure is reduced to 50 bar, and the liquid is partially vaporized in E1. Liquid and vapor are separated in V2. The vapor is liquefied in E2, used as third reflux, and the 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 the  $CO_2$  content of the 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 Patent Nos. 4,689,063; 5,566,554 and 6,578,379B2

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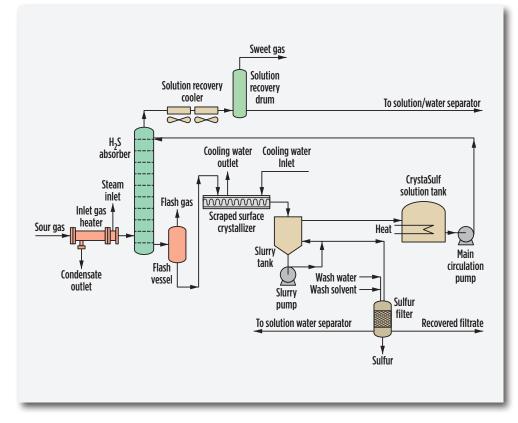
# CrystaSulf

**Application:** A non-aqueous liquid-phase Claus process that removes  $H_2S$  from any gas stream, including natural gas, refinery fuel gas, high- $CO_2$  gas streams and syngas. Gas streams containing 0.1–25.0 tpd of sulfur as  $H_2S$  often can be economically treated by this method. CrystaSulf is especially advantageous for high-pressure applications and for treating high- $CO_2$  gas streams.

**Description:** Using CrystaSulf, H<sub>2</sub>S is absorbed from gas streams by a hydrocarbon solution and reacted with SO<sub>2</sub> to form elemental sulfur. The elemental sulfur remains dissolved in solution, so there are no solids in the main circulating liquid or corrosion issues like those associated with water-based systems. The hydrocarbon liquid temperature is reduced in the scraped surface crystallizer where solid sulfur is formed. The crystallized sulfur is removed from the process by a filter system. No surfactants or antifoams are needed. Solution circulation rates are low (e.g. 20–50 gpm/tpd sulfur), and product sulfur purity is high (over 99% sulfur on a dry basis).

**Installations:** A CrystaSulf unit has been successfully deployed at one of the largest natural gas plants in Europe. Operating at 885 psig, the process removed  $H_2S$  to less than 0.2 ppmv. Another CrystaSulf unit has been installed in Australia and was scheduled for startup in the second quarter of 2012.

Licensor: URS Corp. CONTACT



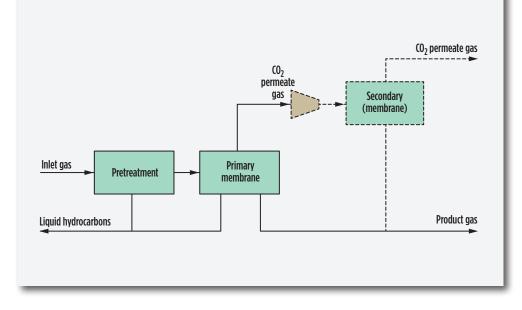
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# **CYNARA<sup>®</sup> Membrane Technology**

**Application:** Remove carbon dioxide  $(CO_2)$  from a hydrocarbon gas stream. Membrane technology is used to process conventional and unconventional gas from enhanced oil recovery (EOR) to recover hydrocarbon gas, NGL condensates and high-purity  $CO_2$  for reinjection. The process is also used offshore 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 required product gas specifications. CYNARA<sup>®</sup> membrane technology has the unique feature of handling condensing liquid hydrocarbons from rich gas while separating  $CO_2$ .

**Description:** The CYNARA<sup>®</sup> membrane element contains thousands of asymmetrical, hollow fibers that selectively separate CO<sub>2</sub> from hydrocarbons. The CO<sub>2</sub> dissolves into polymeric fiber and exists on the lower-pressure side of the membrane, while the hydrocarbon gas stream sustains minimal pressure drops and is recovered at higher pressures. 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<sup>®</sup> membrane systems are designed with pretreatment appropriate for the application.

**Economics:** CYNARA<sup>®</sup> membrane technology is economically favorable for processing gas streams containing between 10 mol% and 90 mol% CO<sub>2</sub>, although it has been successfully applied in applications with lower than 5% CO<sub>2</sub>. Compact systems process from 5 million standard cubic feet per day (MMscfd) to more than 2 billion standard cubic feet per day (Bscfd). They are skid-packaged to reduce installation cost and are reliable and easy to operate. Liquids recovery, lower operating cost and environmental factors make CYNARA<sup>®</sup> membrane systems favorable over solvents and other membrane technologies. These systems provide economic benefits through their compact size for offshore gas treatment.



**Installations:** More than 40 installations worldwide, including the first commercial  $CO_2$  membrane facility (capacity of 750 MMscfd and greater than 99% availability) and the largest offshore  $CO_2$  membrane facility (capacity of 1.2 Bscfd).

**References:** Narquest Jr., J. and M. Brantana, "High-capacity gas membrane elements reduce weight, cost," *Oil & Gas Journal,* July 24, 2006.

Callison, A. and G. Davidson, "Offshore processing plant uses membranes for CO<sub>2</sub> removal," *Oil & Gas Journal*, May 28, 2007.

Blizzard, G. and K. Hornback, "Mallet gas processing facility uses membranes to efficiently separate CO<sub>2</sub>," *Oil & Gas Journal*, April 11, 2005.

Hall, G. H. and E. S. Sanders, "Membrane technology removes CO<sub>2</sub> from liquid ethane," *Oil & Gas Journal*, July 22, 2002.

Licensor: Cameron CONTACT

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# **D'GAASS**

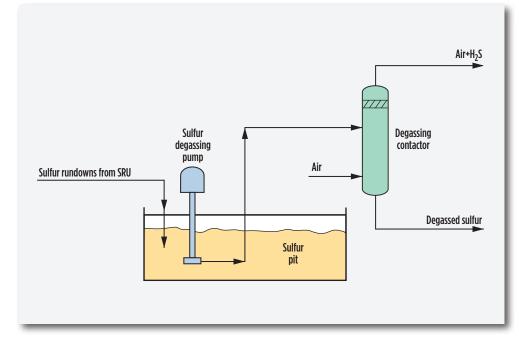
**Application:** The D'GAASS Sulfur Degassing Process accomplishes the removal of dissolved  $H_2S$  and  $H_2S_x$  from produced liquid sulfur. Undegassed sulfur can create odor problems, and it poses toxic and explosive hazards during the storage and transport of liquid sulfur.

**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 the TGTU line burner—thus eliminating the degassing unit as an SO<sub>2</sub> emission source.

**Economics:** D'GAASS achieves less than 10 ppmw of 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:** Over 50 units in operation. More than 90 licensed units in 20 countries, with a total capacity of more than 65,000 metric tons per day.



#### **References:** US Patent No. 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.

Fenderson, S. and T. A. Allison, "Degassing Developments," *Hydrocarbon Engineering*, April 2002.

Licensor: Goar, Allison & Associates LLC CONTACT

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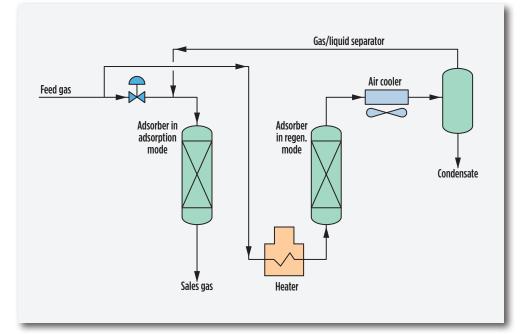
#### **Dew Point Control** (Sorbead Adsorbents)

**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.

**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 are 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 peakshaving and underground storage facilities. The process can be designed to selectively remove aromatics and other contaminants for membrane protection applications.

**Installations:** BASF has been 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.

Shulz, T. and A. Laukart, "Natural gas treatment—The adsorption process in comparison with glycol dehydration," Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, 1995.

Licensor: BASF Corp. CONTACT

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#### **Drigas**

**Application:** The Drigas process is used to dehydrate natural gas to very low dewpoints by glycol absorption, without using vacuum regeneration, solvents or stripping gas.

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

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

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

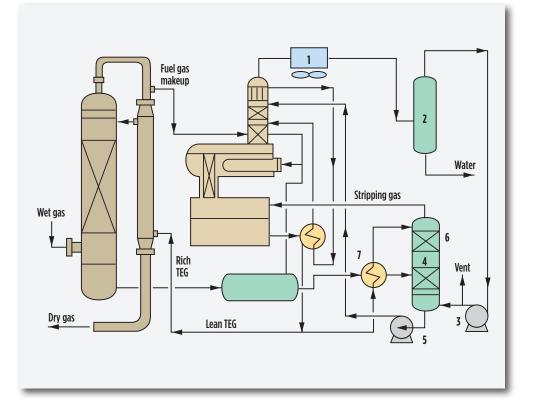
If higher concentrations are required, a second stage of absorption (6) can be incorporated into the same atmospheric column fed by a small fraction of the regenerated, lean TEG. This arrangement gives TEG purity of up to 99.99 wt%.

The main advantages of the Drigas process are:

- Very low dewpoints
- Fuel gas as a stripping agent is not required
- Low operating cost
- Low pollution.

Glycol flowrates are up to 1,000  $\text{m}^3/\text{d}$ , with TEG purity up to 99.99 wt%. Gas flowrate is up to 15 million scmd for each train, wet gas temperature is up to 60°C and pressure is up to 150 bar.

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



**Installations:** One Drigas unit with a capacity of  $200 \text{ m}^3/\text{d}$  DEG.

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

Licensor: Siirtec Nigi S.p.A. CONTACT

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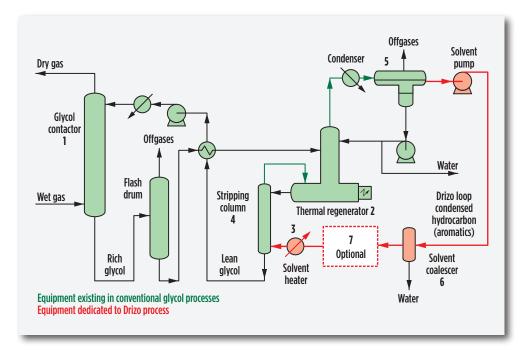
#### **Drizo gas dehydration**

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

**Description:** Water is absorbed (1) from natural gas by glycol (DEG or TEG). The glycol is then thermally regenerated in the reboiler (2). The main difference with conventional glycol processes is the Drizo Loop where liquid hydrocarbons (Drizo solvent) are vaporized (3) and used to strip the hot glycol (4), and are then recovered from the still column condenser (5) and recycled. Water, still present in the liquid hydrocarbons, is removed by a coalescer (6) and by an optional solvent dehydration package (7) (Drizo + and Drizo HP versions). The Drizo solvent is a  $C_4$ - $C_{10}$  hydrocarbon cut composed of paraffinic and aromatic (BTX) components that are usually recovered from the wet feed gas by absorption in the glycol. 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 to below 1 ppm.

**Economics:** Combining very low dewpoints with low  $CO_2$  and BTEX emissions, Drizo is an environmentally friendly process compared to the other glycol processes. Drizo is very competitive with all dehydration processes at water dewpoints below  $-30^{\circ}$ 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 molecular sieve unit.

Installations: More than 45 units.



**References:** Rigaill, C., "Solving aromatic and CO<sub>2</sub> emissions with the Drizo gas/glycol dehydration process," GPA Europe Meeting, February 2001.

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

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," GPA Annual Convention, San Antonio, Texas, March 2003.

Licensor: Prosernat IFP Group Technologies CONTACT

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# Ecoteg

**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.

**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 the outgoing streams of the regenerator.

The vent gas from 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 the 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 lean 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.

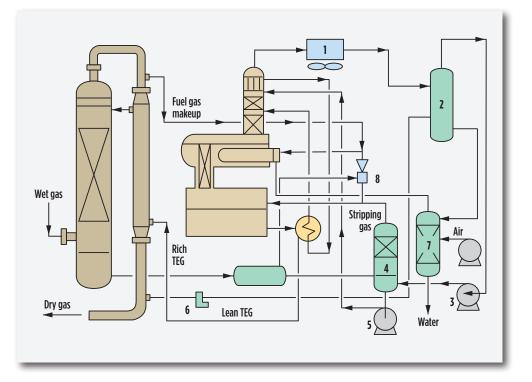
Condensed water, before disposal, is stripped through a stripping tower (7) by means of combustion air.

The main advantages of the Ecoteg process are:

• Meets more stringent regulations for disposal without additional facilities

- Low operating cost
- Low gas dewpoint.

Gas flowrates are up to 15 million scmd for each train, wet gas temperature is up to 60°C, and pressure is 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 an existing plant. Savings in stripping gas help the economics and may be a determinant when low gas dewpoints are required.

**Reference:** The paper "Ecological high-purity TEG regenerator" is available on request.

Licensor: Siirtec Nigi S.p.A. CONTACT

# **EUROCLAUS Process**

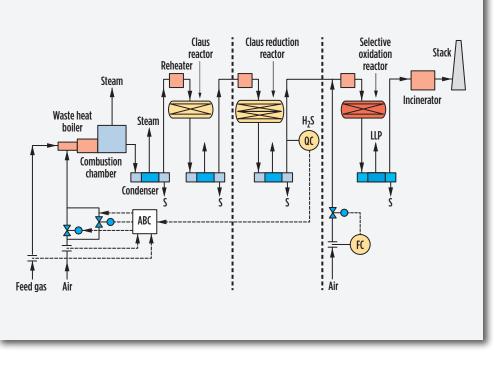
**Application:** The EUROCLAUS process recovers elemental sulfur from  $H_2S$ -containing gases originating from gas treating plants. EUROCLAUS plants are able to process  $H_2S$ /ammonia (NH<sub>3</sub>)-containing gases originating from sour water strippers. The EUROCLAUS process is an improvement from the SUPERCLAUS process. Yields from 99.3% to 99.5% overall sulfur recovery, without any further tail gas cleanup, are possible.

**Description:** The EUROCLAUS process consists of a thermal stage followed by three or four catalytic reaction stages, with sulfur removed between stages by condensers. The first two or three reactors are filled with standard Claus catalyst, while the final reactor is filled with the selective oxidation catalyst.

In the thermal stage, the acid gas is burned with a sub-stoichiometric amount of controlled combustion air; the tail gas leaving the last Claus reaction typically contains 0.8–1.0 vol% of  $H_2S$  and 100–200 ppmv SO<sub>2</sub>. This low SO<sub>2</sub> content is obtained with a hydrogenation catalyst that converts SO<sub>2</sub> to  $H_2S$  in the bottom of the last Claus reactor. The selective oxidation catalyst in the final reactor oxidizes the  $H_2S$  to sulfur at an efficiency of more than 85%. Total sulfur recovery efficiency up to 99.3% can be obtained with three reactor stages, and up to 99.5% can be achieved with four stages.

**Utilities:** Basis: 100 t/d, one Claus reactor, one Claus/reduction reactor, one selective oxidation reactor, 71 vol%  $H_2S$  and 11 vol%  $NH_3$  feed gas, thermal incineration with heat recovery, and sulfur recovery of 99.3%.

		Consumption	Production
4 barg steam	t/h	-	2.8
40 barg steam	t/h	-	12.8
Preheat/reheat 40 barg	t/h	1.7	_



Electricity	kW	310	_
Fuel gas	t/h	0.29	-
Boiler feedwater	t/h	16.5	-
Steam for plant heating	t/h	0.4	-

**Installations:** Since the first commercial demonstration of the EURO-CLAUS process in 2000, more than 40 units have started up or are under construction. Units with a total production capacity of more than 3,200 t/d have been licensed.

**Licensor:** Jacobs Comprimo Sulfur Solutions, a member of Jacobs Engineering Group <u>CONTACT</u>

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### **FLEXSORB solvents**

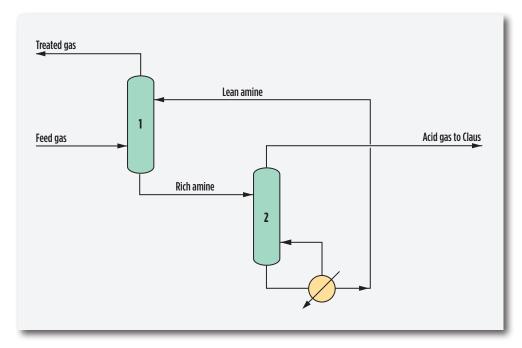
**Application:** The FLEXSORB SE technology is designed for the selective removal of  $H_2S$  in the presence of  $CO_2$  and utilizes proprietary, severely sterically hindered amines. This allows FLEXSORB SE solvent to achieve high  $H_2S$  cleanup selectively, at low solvent circulation rates.

ExxonMobil Research and Engineering Co.'s FLEXSORB SE and SE PLUS solvents are used in a variety of gas treating applications, including Acid Gas Removal (AGR), Acid Gas Enrichment (AGE) and Tail Gas Cleanup Units (TGCU). FLEXSORB technology easily fits into natural gas processing (including onshore and offshore), refining and petrochemical operations using standard gas treating equipment.

**Description:** 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). In the regenerator, acid gas is stripped from the solution with steam generated in the reboiler. Lean solvent from the regenerator is sent through rich/lean solvent exchangers and coolers before returning to the absorber.

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

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



**Reference:** Fedich, R. B. et al., "Selective H<sub>2</sub>S 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, L. et al., "High recovery tail gas treating," *Sulphur Magazine,* No. 296, November/December 2004.

Fedich, R. B. et al., "Selection cleanups," *Hydrocarbon Engineering,* No. 2, February 2008.

Licensor: ExxonMobil Research and Engineering Co. CONTACT

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#### Gas treating for natural gas/ syngas/LNG (Sulfinol Process)

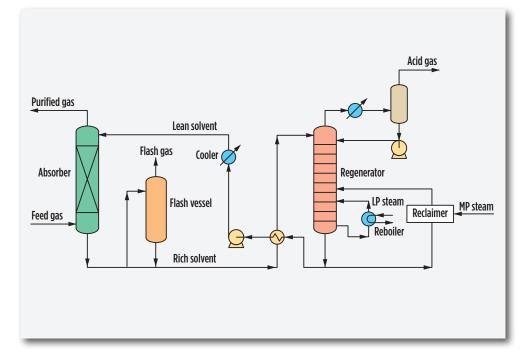
**Application:** The Sulfinol process is a regenerative process developed to reduce  $H_2S$ ,  $CO_2$ , COS and mercaptans from gases. The sulfur compounds in the product gas can be reduced to low ppm levels. This process has been developed specifically for treating large quantities of gas, such as natural gas, which are available at elevated pressures.

The Sulfinol process is unique in the class of absorption processes because it uses a mixture of solvents, which allows it to behave as both a chemical and a physical absorption process. The solvent is composed of Sulfolane, DIPA, or MDEA and water. The acid gas loading of the Sulfinol solvent is higher, and the energy required for its regeneration is lower, than those of purely chemical solvents.

At the same time, it has an advantage over purely physical solvents in that severe product specifications can be met more easily, and co-absorption of hydrocarbons is relatively low. The Sulfinol-M process is used for selective absorption of  $H_2S$ , COS and mercaptans, while co-absorbing only part of the CO<sub>2</sub>. Deep removal of CO<sub>2</sub> in LNG plants is another application. Integration of gas treating with the SCOT solvent system is an option.

**Description:** The feed gas is contacted counter-currently in an absorption column with the Sulfinol solvent. The regenerated solvent is introduced at the top of the absorber. The sulfur compounds-loaded solvent (rich solvent) is heated by heat exchange with the regenerated solvent and is fed back to the regenerator, where it is further heated and freed of the acid gases with steam.

The acid gases removed from the solvent in the regenerator are cooled with air or water, so that the major part of the water vapor they contain is condensed. The sour condensate is reintroduced into the sys-



tem as a reflux. The acid gas is passed to the sulfur recovery plant (Claus plant), in which elemental sulfur is recovered. The application of a flash vessel is optional; it depends on the heavier hydrocarbon content of the feed gas. The application of a reclaimer is also optional and depends on the amount of non-regenerative compounds in the solvent.

**Installations:** More than 210 Sulfinol units, ranging in capacity from  $10,000 \text{ Nm}^3/\text{d}$  to 32 million  $\text{Nm}^3/\text{d}$ , are in operation throughout the world, demonstrating the reliability of the process.

**Licensor:** Jacobs Comprimo Sulfur Solutions, a member of Jacobs Engineering Group, authorized licensor on behalf of Shell Global Solutions B.V. <u>CONTACT</u>

# Gas treating for refinery/natural gas (ADIP Process)

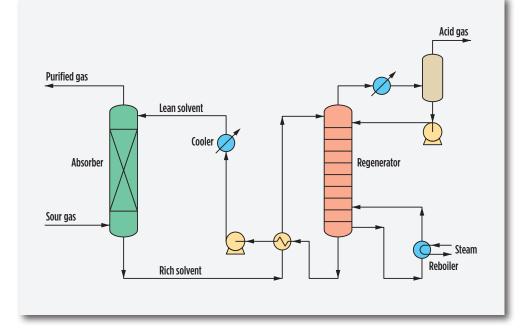
**Application:** The ADIP process is a regenerative process developed to selectively reduce  $H_2S$  in gas to very low concentrations in the presence of  $CO_2$ . The ADIP process uses an aqueous solution of diisopropanol amine (DIPA) or the aqueous solution of methyl diethanolamine (MDEA). MDEA is used for those applications in which high selectivity for  $H_2S$  is required. Depending on operating conditions, 20%–60% of the  $CO_2$  is coabsorbed if DIPA is used as the ADIP solvent, while this can be reduced to 10%–30% if MDEA is used as the solvent.

The ADIP process can also be used for enrichment of acid gas feed to a sulfur recovery plant, to achieve a higher  $H_2S$  content. Integration of gas treating with the SCOT solvent system is an option.

**Description:** The  $H_2S$ -containing gas is contacted counter-currently in an absorption column with ADIP solvent. The regenerated solvent is introduced at the top of the absorber. The  $H_2S$ -loaded solvent (rich solvent) from the absorber is heated by heat exchange with regenerated solvent and is fed back to the regenerator, where it is further heated and freed of the acid gases with steam.

The acid gases removed from the solvent in the regenerator are cooled with air or water, so that the major part of the water vapor is condensed. The sour condensate is reintroduced into the system as a reflux. The acid gas is passed to the sulfur recovery plant (Claus plant), in which elemental sulfur is recovered from the  $H_2S$ .

**Utilities:** The estimated consumption varies widely with feed composition and product specification. LP steam consumption amounts to 0.4–2.8 ton per ton of acid gas removed.



**Installations:** More than 490 ADIP units, ranging in capacity from 1,900  $Nm^3/d$  to 12.2 million  $Nm^3/d$  and 19 t/sd to 7,700 t/sd of liquid hydrocarbons, are in operation throughout the world, demonstrating the reliability of the process.

**Licensor:** Jacobs Comprimo Sulfur Solutions, a member of Jacobs Engineering Group, authorized licensor on behalf of Shell Global Solutions B.V. <u>CONTACT</u>

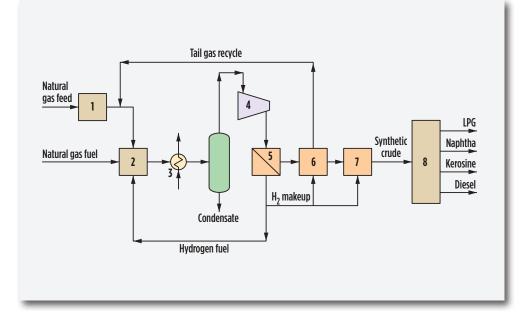
# **Gas-to-Liquids (GTL)**

**Applications:** To produce zero-sulfur synthetic fuels from natural gas. The process can operate on a range of natural gas feedstocks, including fields containing high carbon dioxide levels. The synthesis gas (syngas)generation technology can be tailored to conventional onshore locations or to remote or offshore locations where space and weight are of particular concern.

**Description:** Natural gas is pretreated to remove sulfur, using a conventional desulfurization technology (1). Steam and recycle gases are added, and the feed is further heated before being passed to the syngas-generation unit (2).

For conventional onshore locations, syngas production from natural gas occurs via the Johnson Matthey (JM)/Davy Process Technology (Davy) combined reforming process, a combination of primary steam reforming and oxygen-assisted autothermal reforming. Part of the natural gas feedstock passes directly to the autothermal reformer (ATR), and the remainder is mixed with steam and recycle gases before passing to the CRG prereformer for the conversion of heavier hydrocarbons to methane and the partial reforming of the feedstock. Addition of steam and further heating are completed before the mixed gas passes to the primary steam methane reformer (SMR), a conventional, down-fired, tubular reformer. The partially reformed gas leaving the SMR is mixed with natural gas before passing to the ATR, where they are partially combusted with oxygen and then reformed over a fixed catalyst bed to provide low-methane syngas.

For remote and offshore locations, a compact reformer is employed downstream of the CRG prereformer to produce the synthesis gas. The Davy/BP compact reformer is a multi-tubular, counter-current reactor containing nickel catalyst in the tubes. Heat for this endothermic reaction is provided by external firing of excess hydrogen ( $H_2$ ) produced by the process, with supplementary natural gas as required. Gas leaving the



syngas-generation unit is cooled (3), and it generates sufficient steam to satisfy process heating requirements. Excess condensate is removed.

Dry syngas is compressed in a single-stage centrifugal compressor (in the compact reformer flowsheet) (4) and passed to a membraneseparation package (5), where the surplus  $H_2$  is recovered and reused as fuel. The non-permeate product from the membrane separation is fed to the conversion section (6), where the syngas is converted into a mixed paraffin and wax product using a cobalt catalyst. The reaction system employs two or more stages of the Davy/BP fixed-bed FT technology. Unconverted syngas is recycled to the syngas-generation unit.

The wax products from the conversion section can be hydrocracked to produce a pumpable synthetic crude using conventional hydrocracking technology (7). The synthetic crude can be further distilled into discrete liquid fuels such as LPG, naphtha, kerosine and diesel (8).

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# Gas-to-Liquids (GTL), cont.

**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 at BP's test facility in Nikiski, Alaska. This facility operated between 2003 and 2009. The JM/Davy combined reforming technology has been successfully employed at the 3,600-mtpd EMethanex methanol plant in Egypt.

Licensor: Davy Process Technology Ltd. CONTACT

#### 2012 Gas Processes Handbook

### Gasel

Application: Synthesis gas-to-liquids processes—i.e., GTL, BTL, CTL.

**Description:** Conversion of synthesis gas (syngas) into long paraffins in a slurry bubble column reactor (SBCR) via the following FT reaction:

 $n(CO + 2H_2) \rightarrow (-CH_2-)n + nH_2O$  (with n ranging from 1 to over 90)

FT product is subsequently upgraded using hydrocracking and hydroisomerization to selectively yield middle distillates (jet and diesel) and naphtha.

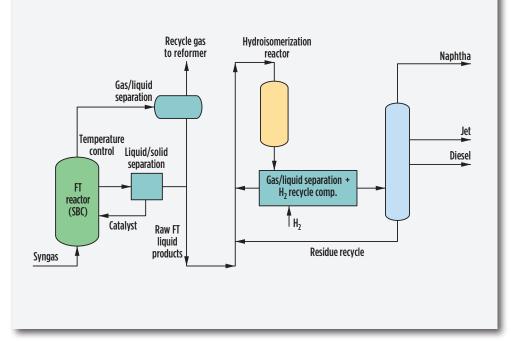
**Fischer-Tropsch synthesis:** In the SBCR, three phases coexist: syngas is brought into contact with the solid, cobalt-based FT catalyst to produce long-chain liquid hydrocarbons. These hydrocarbons are recovered by liquid/solid and gas/liquid separation systems, and the FT catalyst is recycled to the reactor.

This technology offers significant advantages, such as ideal heat removal, small catalyst particles (no diffusion limitations), the possibility of online catalyst makeup/withdrawal, and large reactor capacities (up to 15,000 bpd per train).

**F-T product upgrading:** The raw liquid product is hydrotreated (mild conditions) and isomerized using a dedicated catalyst. This catalyst has been designed to provide specific product yields and properties. The fully converted product is then separated into approximately 30% naphtha and 70% diesel.

The FT diesel is ultra-clean (no sulfur or aromatics), with a high cetane number (> 70) and good cold-flow properties (cold filter plugging point ranging from  $-20^{\circ}$ C to  $-40^{\circ}$ C). The secondary product, high-purity paraffinic naphtha, is an excellent feedstock for petrochemical production, or it can be further processed into gasoline.

Typically, a single Gasel FT train produces 15,000 bpd of naphtha and diesel from 500,000  $\rm Nm^3/h$  of  $\rm H_2$  and CO. The overall efficiency of



a GTL complex (including a natural gas reformer), expressed in terms of its carbon retention, is in the range of 70%–75%. Half of the  $CO_2$  emitted onsite is readily recoverable for  $CO_2$  capture and storage.

**References:** Fedou, S., E. Caprani, D. Douziech and S. Boucher, "Conversion of syngas to diesel," *PTQ*, Q2 2008.

Caprani, E. and S. Fedou, "Gasel, the XTL Technology Suite for the Conversion of Syngas to Diesel," CWC Conference, London, UK, May 2008.

**Licensor:** Axens; technology co-developed and co-owned by Eni S.p.A. and IFP Energies nouvelles <u>CONTACT</u>

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#### **GT-DOS<sup>™</sup> Technology**

**Application:** GT-DOS<sup>™</sup> Technology is a process used to convert hydrogen sulfide (H<sub>2</sub>S) by direct oxidation to sulfur (DOS). H<sub>2</sub>S is generally present in gas streams found in the gas processing, refining and petrochemical industries.

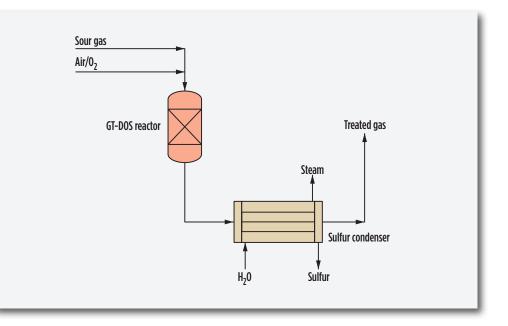
GT-DOS Technology is best employed to treat lean acid gas streams (5%  $H_2S$  concentration or less) that contain 0.1 tpd to 200 tpd of sulfur. With the capability to selectively convert  $H_2S$  to sulfur in lean acid gas streams, GT-DOS can directly treat sour gas streams without a separate acid gas treatment unit or an acid gas enrichment unit.

**Description:** Sour gas is heated to approximately 400°F (200°C) and mixed with reaction air or oxygen ( $O_2$ ) upstream of the catalytic reactor unit. In the reactor,  $H_2S$  is directly converted to sulfur by its reaction with  $O_2$ . An advanced metal oxide catalyst enables the conversion to sulfur at low or medium pressure, and it has been proven resistant to high hydrocarbon content in the inlet gas, including aromatics.

The gas stream exiting the reactor contains sulfur vapor, which is removed in the condenser where molten sulfur is produced. The sulfur produced by GT-DOS is comparable in quality to traditional Claus sulfur. Heat integration between the inlet and outlet gas streams reduces the overall utility consumption.

#### Process advantages:

- Directly treats gas streams
- Single-step process for sulfur recovery
- Single-stage conversion of up to 90% of the inlet gas  $\rm H_2S$  into sulfur
- Avoids the operating problems of liquid-based processes



- Minimal amount of equipment compared to liquid redox or biological processes
- Uses reliable, proven equipment found in the gas processing industry
- Lower operating costs compared to liquid-based processes
- Produces high-purity, saleable sulfur.

Economics: Operating costs are less than \$100/long tpd.

**Installations:** Commercialized technology is available for license. Two licensed units have been constructed.

Licensor: GTC Technology US LLC CONTACT

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# **GT-SPOC<sup>™</sup> Technology**

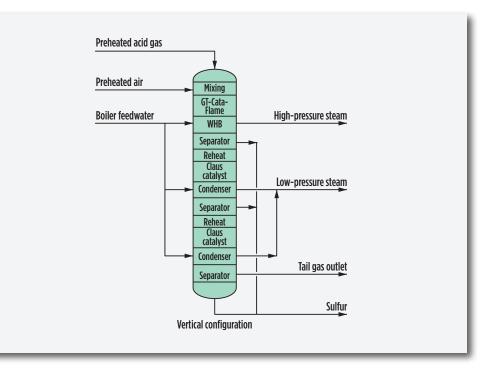
**Application:** GT-SPOC<sup>™</sup> is a sulfur partial oxidation catalytic (SPOC) technology that is an upgrade from the traditional "modified Claus" process. GT-SPOC is used for removing hydrogen sulfide ( $H_2S$ ) from typical Claus inlet gas streams, which contain 1 tpd to 1,000+ tpd of sulfur, while reducing ammonia and heavy hydrocarbons to suitable levels.

**Description:** Sour gas is mixed with air or oxygen and sent to the GT-SPOC unit. Instead of the traditional combustion furnace section common in modified Claus units, GT-SPOC uses GT-CataFlame<sup>TM</sup>, a catalytic combustion section that converts a specified amount of H<sub>2</sub>S into SO<sub>2</sub> and sulfur over a very short contact time.

The gas exits the GT-CataFlame reactor and enters a waste heat boiler, where heat is removed and steam is generated. Unreacted gases may be sent directly to the first Claus bed in a vertical vessel arrangement, as shown in the process flow diagram, or they may be directed to a conventionally arranged Claus unit. The sulfur produced by GT-SPOC is traditional Claus-quality sulfur.

#### Process advantages:

- Easier startup and shutdown
- Seamless switching between acid gas and fuel gas
- Combination of Claus stages in a single vertical vessel
- Smaller plot area requirements
- Lower CAPEX compared to traditional Claus
- Demonstrated for refinery gases containing ammonia and heavy hydrocarbons
- Reduced formation of COS and  $\ensuremath{\mathsf{CS}_2}$
- Reduced Claus catalyst requirement



- Reduction in interconnecting piping
- High-purity, saleable sulfur
- High turndown ratio
- Vertical or horizontal configuration dependent on customer's needs.

**Economics:** Operating cost is comparable to traditional "modified Claus" units, with 20%–30% lower capital costs and 30%–50% lower plot space.

**Installation:** Commercialized technology is available for license.

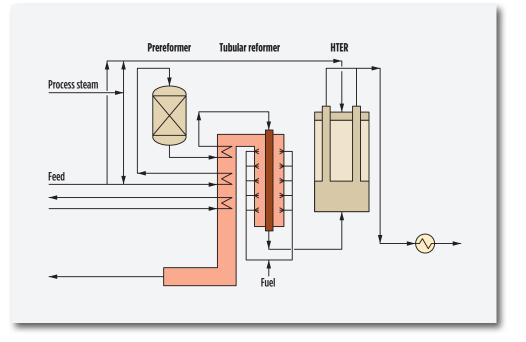
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# **Heat Exchange Reforming**

**Application:** The Haldor Topsøe Exchange Reformer (HTER) is a gasheated convection reformer operating in parallel with the tubular reformer. Process gas from the tubular reformer outlet is used as a heating medium. The main advantage of the HTER unit is the significant savings on fuel gas to the tubular reformer. The HTER can also be used in the revamp of existing plants, offering a hydrogen (H<sub>2</sub>) production capacity increase of up to 30% without requiring modifications to the existing tubular reformer.

**Description:** The HTER reformer is placed in parallel with a traditional tubular reformer. The HTER unit consists of a cylindrical, refractory-lined pressure vessel with a number of concentric, high-alloy double tubes arranged in a circular pitch. Reforming catalyst is loaded into the innermost tubes and outside of the outer tubes. Part of the feed gas is split before reaching the tubular reformer and sent to the HTER unit. The feed gas flows downward through the catalyst beds. At the bottom of the reactor, the reformed gas is mixed with hot effluent from the tubular reformer. The combined tubular reformer/HTER effluent gas then flows upward through the annuli of the double tubes and is cooled by the gas flowing downward in the catalyst bed, thus providing the necessary heat for the endothermic reforming reactions.

**Economics:** The advantages of using HTER technology are lower fuel consumption, reduced steam export and lower  $CO_2$  emissions. It also provides an economically attractive and smaller-plot-area solution for the capacity increase of existing H<sub>2</sub> plants. The combined steam methane reformer (SMR) and HTER plant can achieve feed and fuel consumption of about 3.4–3.5 Gcal/1,000 Nm<sup>3</sup> (361–372 Btu/scf) and net energy consumption of about 3.15–3.30 Gcal/1,000 Nm<sup>3</sup> (335–351 Btu/scf), depending on layout and feedstock.



**Installations:** Two licensed units in operation for expansions at existing plants, with capacity increases of up to  $30,000 \text{ Nm}^3/\text{h}$  (27 MMscfd). Six licensed units under engineering and/or construction for expansions at existing plants, with capacity increases of up to  $30,000 \text{ Nm}^3/\text{h}$  (27 MMscfd).

One licensed unit in operation for a grassroots  $H_2$  plant, with a capacity of 25,000 Nm<sup>3</sup>/h (22 MMscfd) [total plant  $H_2$  capacity is 130,000 Nm<sup>3</sup>/h (116 MMscfd)]. Six licensed units under engineering and/or construction for grassroots  $H_2$  plants, with capacities up to 30,000 Nm<sup>3</sup>/h (27 MMscfd) [total plant  $H_2$  capacities up to 200,000+ Nm<sup>3</sup>/h (180+ MMscfd)].

**References:** Andersen, N. U. and H. Olsson, "The hydrogen generation game," *Hydrocarbon Engineering*, July 2011.

## Heat Exchange Reforming, cont.

Winter-Madsen, S. and H. Olsson, "Steam reforming solutions," *Hydrocarbon Engineering*, July 2007.

Olsson, H., "Adding H<sub>2</sub> Production Capacity by Heat Exchange Reforming," XIV Refinery Technology Meet (RTM) on Energy & Environment Challenges for the Hydrocarbon Sector, Kovalam, India, September 2007.

Licensor: Haldor Topsøe A/S CONTACT

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# **High Claus Ratio (HCR)**

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

**Description:** The High Claus Ratio (HCR) process consists of two sections:

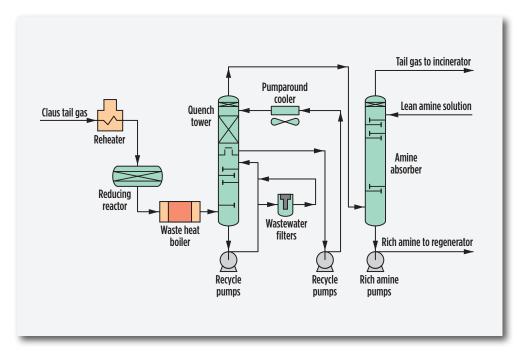
• Hydrogenation and hydrolysis of sulfur compounds present in tail gases (COS, CS<sub>2</sub>, S<sub>x</sub> and SO<sub>2</sub>). Tail gas is heated to about 230°C and, without hydrogen addition, is treated with Co/Mo catalyst. Gas passes through a waste heat boiler and is cooled to approximately 40°C in a direct contact tower.

•  $H_2S$  removal and recycle of acid gas to a Claus plant. The gas is washed in an MDEA absorber, and the treated gas is thermally oxidized. The semi-rich amine is regenerated and recycled to the absorber.

The process requires adjusting the operating condition for the Claus unit by increasing the  $H_2S/SO_2$  tail gas ratio. The operation is very steady and has high service factors. Hydrogen or reducing gas from external sources are not required. Tail gas containing less than 250 ppmv of  $H_2S_x$  can be sent to the SRU thermal oxidizer.

**Economics:** The process uses standard equipment and carbon steel almost everywhere. No consumption of fuel gas to produce the reducing gas or caustic chemicals is required. Process analyzers are not mandatory. Reduction in utilities are related to the unit cost of  $H_2$ .

**Installations:** The first commercial HCR plant was started up in November 1988 at Agip Plas's facility in Robassomero, Italy. Since then,



more than 25 HCR plants have been built with capacities ranging from 1.5 mtpd to 375 mtpd.

**Reference:** "Optimize Claus operations," *Hydrocarbon Processing,* December 2005.

The paper " $H_2S$  recovery from Claus tail gas treatment and liquid sulfur degassing" is available on request.

Licensor: Siirtec Nigi S.p.A. CONTACT

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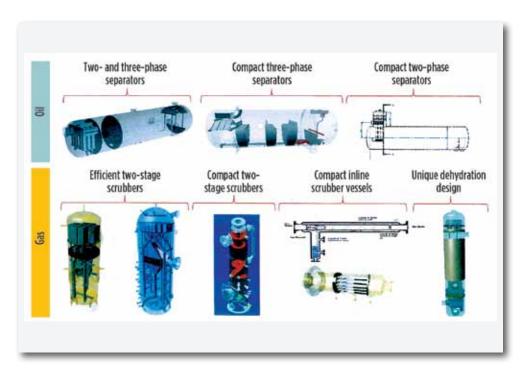
### **High-Efficiency Internals** for Gas Processing

**Application:** Removing liquid streams from a gas stream. High-Efficiency Internals are mainly used in the primary separators, where the oil and gas streams are prepared for transport from the process system. The gas is compressed for transport, and water and unwanted gases (such as  $CO_2$  and  $H_2S$ ) are captured. Compression is often carried out in multiple stages, with cooling and removal of free liquid between the stages. High-Efficiency Internals are used to separate free liquid prior to compression, protecting downstream equipment.

**Description:** High-Efficiency Internals include inlet and polishing sections for the primary separators and contactor towers. The inlet and polishing sections utilize a combination of centrifugal and gravity forces to separate free hydrocarbons from the gas. High-Efficiency Internals have been verified at operational conditions, and the efficiency can be predicted and guaranteed. This is in contrast to other vessel internals, where the operation has never been tested in real conditions. Due to the high-pressure verification of the internals, High-Efficiency Internals have always met or exceeded performance guarantees.

**Economics:** High-Efficiency Internals are typically used where compactness is of importance and where the cost of intervention to the equipment is high—i.e., the primary separators and scrubbers, as failure to meet specifications may cause compressor breakdown that will result in platform shutdowns and loss of production. High-Efficiency Internals also may save structural weight offshore and subsea.

Installations: Over 300 installations worldwide.



**References:** Torvik, R., "Njord First-Stage Separator Modification," TEK-NA seminar: Separation Technology—Oil/Gas/Water/Sand, Stavanger, Norway, September 2007.

Kvamsdal, D. et al., "Debottlenecking of the Machar Slug Catcher," Offshore Technology Conference Brasil, OTC22689, October 2011, Rio de Janeiro, Brazil.

Kvamsdal, D. et al., "High-Pressure Gas Liquid Separation, Experimental Verification of Separator Internals in Laboratory and Real Fluid Systems," Offshore Technology Conference, OTC 23306, April 2012, Houston, Texas.

Licensor: Cameron CONTACT

# **High-Pressure Absorber (HPA)**

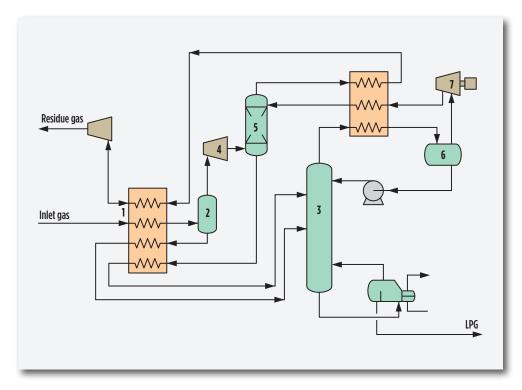
**Application:** Ethane, propane and heavier hydrocarbons recovery from natural gas feed streams using a cryogenic turboexpander process. High propane recovery (> 99%) is achievable. Residue compression is minimized by using a high-pressure absorber (HPA).

**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:** The process 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, have similar savings in residue compression as those seen with propane recovery.

Reference: US Patent No. 6,712,880

Licensor: Randall Gas Technologies CONTACT

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# Hydrogen

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

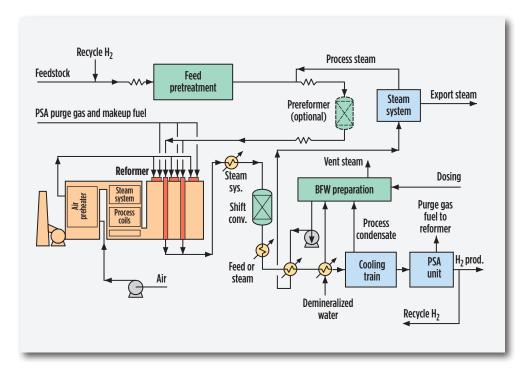
**Feedstocks:** Ranging from natural gas to heavy naphtha as well as potential refinery offgases. Many recent refinery hydrogen  $(H_2)$  plants have multiple-feedstock flexibility, either in terms of backup, or alternative or mixed feed. Automatic feedstock change-over has also successfully been applied by Technip in several modern plants with multiple-feedstock flexibility.

**Description:** The generic flowsheet consists of feed pretreatment, pre-reforming (optional), steam-HC reforming, shift conversion and  $H_2$  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 an 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 CO is further converted to  $H_2$ 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, which provides high-purity  $H_2$  product (up to < 1 ppm CO) at near-inlet pressures.



Typical specific energy consumption based on feed + fuel – export steam ranges between 3.0 Gcal/KNm<sup>3</sup> and 3.5 Gcal/KNm<sup>3</sup> of  $H_2(330 - 370 \text{ Btu/scf})$  on a lower heating valve basis, depending upon feedstock, plant capacity, optimization criteria and steam-export requirements.

Recent advances include integration of  $H_2$  recovery and generation, and recuperative reforming in a Technip Parallel Reformer (TPR), which is especially suitable for capacity retrofits.

**Installations:** Technip's H<sub>2</sub> plant technology has been applied in more than 260 plants worldwide. Most installations are for refinery application with basic features for high reliability and optimized cost.

Licensor: Technip CONTACT

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# Hydrogen

**Application:** Produce hydrogen  $(H_2)$  for refinery applications (e.g., hydrotreating and hydrocracking), along with petrochemical and other industrial uses.

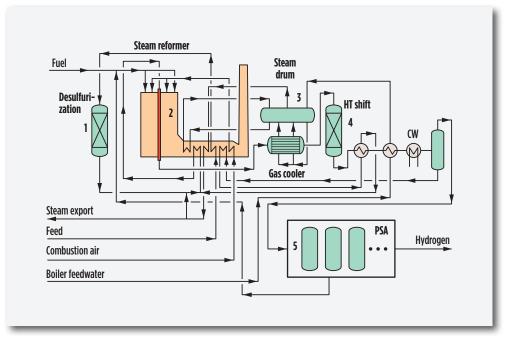
Feed: Natural gas, refinery offgases, LPG, naphtha or mixtures thereof.

**Product:** High-purity  $H_2$  (typically > 99.9%), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), high-pressure steam and/or electricity may be produced as separate, creditable byproduct.

**Description:** The feed is desulfurized (1), mixed with steam, and converted to synthesis gas in the steam reformer (2) over a nickel-containing catalyst at 20–40 bar pressure and outlet temperatures of 800°C-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 Thyssenkrupp Uhde's  $H_2$  plant design is an optional bisectional steam system for the environmentally friendly, full recovery of process condensate and the production of high-pressure export steam (3), with a proven process gas cooler design. The Uhde steam reformer concept also includes a fully prefabricated, 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 prereforming; and/or HT/LT shift to process, for example, heavier feeds and/or optimization of feed/fuel consumption and steam production. The design allows for the combination of maximized process heat recovery and optimized energy efficiency with operational safety and reliability.



The reformer design is particularly advantageous for the construction and reliable operation of large-scale reformers with  $H_2$  capacities of up to 220,000 Nm<sup>3</sup>/h (197 MMscfd) in single-train configurations. Thyssenkrupp Uhde offers standard and tailor-made designs and applies either customer or company 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 Nm<sup>3</sup> (333 MMBtu/MMscfd) or 3.09 Gcal/1,000 Nm<sup>3</sup> (329 MMbtu/MMscfd) with prereforming.

**Installations:** Recently, Uhde commissioned large-scale  $H_2$  plants for SINCOR C.A. in Venezuela (2 × 100,000 Nm<sup>3</sup>/h or 2 × 90 MMscfd), and

### Hydrogen, cont.

Shell Canada Ltd. in Canada (2 × 130,000 Nm<sup>3</sup>/h or 2 × 115 MMscfd). Uhde is presently executing four H<sub>2</sub> projects, including H<sub>2</sub> plants for Neste Oil Oyj (formerly Fortum Oil Oy) in Finland (1 × 155,000 Nm<sup>3</sup>/h or 140 MMscfd) and Shell Canada Ltd. in Canada, (1 × 150,000 Nm<sup>3</sup>/h or 135 MMscfd). More than 60 Uhde reformers have been designed and constructed worldwide.

**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.

Larsen, J., M. Michel, J. Zschommler, M. Whysall and S. Vanheertum, "Large-scale H<sub>2</sub> plants, Uhde and UOP's experience," AIChE Spring Meeting, New Orleans, Louisiana, 2003.

Licensor: Thyssenkrupp Uhde GmbH CONTACT

#### 2012 Gas Processes Handbook

# Hydrogen (steam reforming)

**Application:** Production of hydrogen  $(H_2)$  for refinery hydrotreating and hydrocracking or other refinery, petrochemical, metallurgical and food-processing uses.

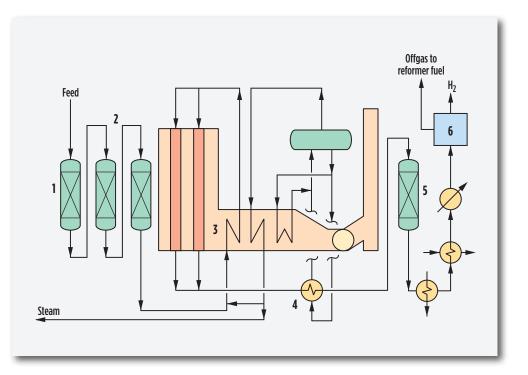
**Feedstock:** Light hydrocarbons such as natural gas, refinery fuel gas, LPG/butane, mixed pentanes and light naphtha.

**Product:** High-purity H<sub>2</sub> (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), which 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  $H_2$  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 boiler feedwater (BFW) preheater and a deaerator (DA) feedwater 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 pressure swing adsorbtion (PSA)  $H_2$  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. H<sub>2</sub> from the PSA unit is sent off plot. A small H<sub>2</sub> stream is then split off and recycled to the front of the plant for hydrotreating.

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 feedwater deaerator and pre-

# Hydrogen (steam reforming), cont.

heat 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 (MMscfd) to over 100 MMscfd capacities. Plant designs exist for capacities from 1 MMscfd to 280 MMscfd.

Supplier: CB&I CONTACT

## Hydrogen (steam reforming)

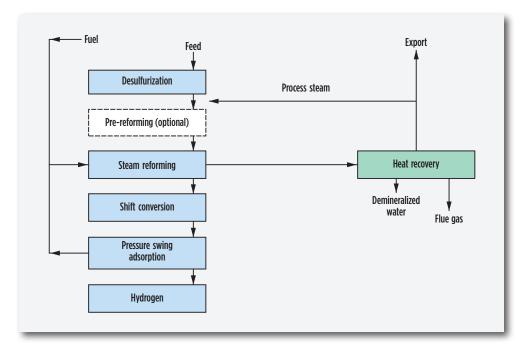
**Application:** Hydrogen ( $H_2$ ) production from natural gas, refinery gas, associated gas, naphtha, LPG or any mixture of these. Appropriate purity product (up to 99.999%) can be used in refinery upgrade processes, chemical production and metallurgy (direct reduction). Possible byproducts are export steam or electricity, depending on cost and/or efficiency optimization targets.

**Description:** The hydrocarbon feedstock is admixed with some recycle  $H_2$  and preheated to 350°C–380°C. Sulfur components are totally converted to  $H_2S$  with a CoMo catalyst and then adsorbed on zinc oxide by conversion to ZnS. The desulfurized feed is mixed with process steam at an optimized steam/carbon ratio.

The desulfurized feed is mixed with process steam at an optimized steam/carbon ratio, superheated to  $500^{\circ}\text{C}-650^{\circ}\text{C}$  and fed to the Lurgi Reformer. The feed/steam mixture passing the reformer tubes is converted at  $800^{\circ}\text{C}-900^{\circ}\text{C}$  by the presence of a nickel catalyst to a reformed gas containing H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub> and undecomposed steam. The reformed gas is cooled to approximately 330°C in a reformed gas boiler.

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

An adiabatic pre-reformer operating at an inlet temperature of  $400^{\circ}\text{C}-500^{\circ}\text{C}$  (dependent on feedstock) may be inserted upstream of the feed superheater as a process option. Feed gas is partly converted to H<sub>2</sub>, CO and CO<sub>2</sub> 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  $H_2$  yield and reducing CO content to below 3 vol%. The shift gas is cooled to 40°C, and any process condensate is separated and recycled to the process. The gas is then routed to the PSA unit, where pure  $H_2$  is separated from the shift-gas stream. Offgas is used as fuel for steam reforming.

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

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

# Hydrogen (steam reforming), cont.

**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
Water, cooling, m <sup>3</sup>	3.0
Electricity, kWh	19
Export steam, t	0.7

**Installations:** More than 125 gas reforming plants, 33 being  $H_2$  plants, with single-train capacities ranging from 1 million scfd to 200 million scfd.

**Licensor:** Lurgi GmbH, Air Liquide Global E&C Solutions, Lurgi Technologies <u>CONTACT</u>

# Hydrogen (steam reforming)

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

Feedstock: Natural gas, refinery offgas, LPG or light naphtha.

**Product:** Typical purity of 99.9%; pressure of 350 psig, with high-pressure steam or  $CO_2$  as byproducts.

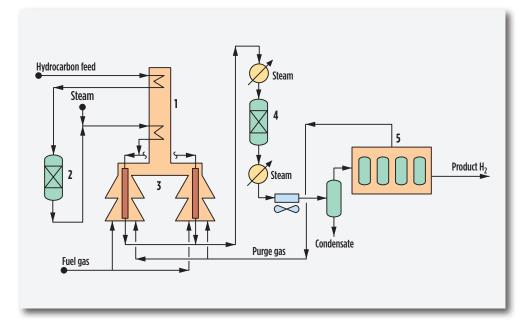
**Process description:**  $H_2$  is produced by steam reforming of hydrocarbons with purification by pressure swing adsorption (PSA). Feed is heated (1) and then purified (2) with zinc oxide to remove sulfur. The purified feed is mixed with steam and preheated further, then reformed over nickel catalyst in the tubes of the reforming furnace (3). Prereforming can be used to handle feed mixtures or minimize steam export.

Foster Wheeler's Terrace Wall reformer combines high efficiency with ease of operation and reliability. With the new Asymmetric Terrace design, radiant section design can be optimized to reduce fuel consumption. The furnace can be modularized to give unrivalled savings in costruction time and costs.

The syngas from the reformer is cooled by generating steam, then reacted with steam in the shift converter to convert CO to additional hydrogen and  $CO_2$  (4).

In the PSA section (5), impurities are removed by solid adsorbent, and the adsorbent beds are regenerated by depressurizing. Purge gas from the PSA section, containing  $CO_2$ ,  $CH_4$ , CO and some  $H_2$ , is used as fuel in the reforming furnace.

Heat recovery from reformer flue gas may be via combustion air preheat or additional steam generation. Variations include a scrubbing system to recover  $CO_2$ .



**Installations:** Over 100 plants, with recent projects ranging from 12 MMscfd to 158 MMscfd in a single train, with numerous multi-train installations.

Utility requirements (100-MMscfd plant):

Natural gas (feed plus fuel)	1,530 MMBtu/hr
Export steam (600 psig/700°F)	130,350 lb/hr
Demineralized water	254,000 lb/hr
Electricity	1,250 kw
Cooling water (18°F rise)	1,100 gal/min

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

Contributor: Foster Wheeler CONTACT

# Hydrogen (UOP Polybed<sup>™</sup> PSA)

**Application:** Production of any-purity hydrogen, typically 90% to +99.9999 mol%. Impurities efficiently removed include  $N_2$ , CO, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, Ar, O<sub>2</sub>, C<sub>2</sub>-C<sub>8</sub>+, CH<sub>3</sub>OH, NH<sub>3</sub>, H<sub>2</sub>S and organic sulfur compounds. The technology can also be used to purify CH<sub>4</sub>, CO<sub>2</sub>, He, N<sub>2</sub> and Cl; remove CO<sub>2</sub>; adjust synthesis gas stream composition ratios; and separate nitrogen from hydrocarbons.

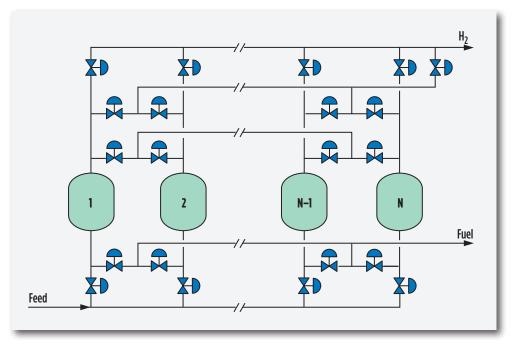
**Feed:** Steam reformer (at any point after the reformer); catalytic reformer net gas or other refinery purge streams; gasification offgases; ammonia plant purge gases (before or after the  $NH_3$  water wash); demethanizer or other ethylene plant offgases; partial oxidation gases; styrene plant offgases; methanol plant purge gases; coke-oven gas; cryogenic purification offgases or other  $H_2$  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 mol%.

**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 of over 200 million scfd.

All systems use advanced proprietary adsorbents and patented void-gas 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 pres-



ently produce streams with less than 1 ppmv impurity from feed concentrations of 40+ mol%.

Operation is automatic, with push-button startup and shutdown. After startup, the unit will produce  $H_2$  in two to four hours. Onstream factors 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  $\times$  25 ft to 60 ft  $\times$  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 a DCS. Units are designed for outdoor, unattended operation and require no utilities other than small quantities of instrument air and power for instrumentation.

# Hydrogen (UOP Polybed<sup>™</sup> PSA), cont.

**Installations:** More than 900 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, a Honeywell Company CONTACT

### Hydrogen (UOP Polysep<sup>™</sup> 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.

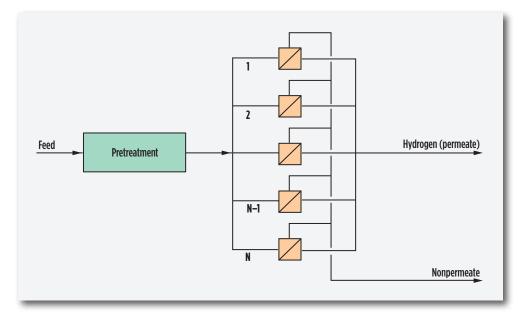
**Feed:** Refinery streams include catalytic reformer offgas, hydrotreater and hydrocracker purge gases, and fluid catalytic cracking offgas. Chemical and petrochemical feed streams are ethylene offgases, ammonia plant purge gases, methanol plant offgases, synthesis gas streams from steam reforming, 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. Polysep membranes are also used for hydrogen recovery from IGCC power-generation systems.

**Description:** The Polysep separation system is based on state-of-theart, composite, hollow-fiber polymer membrane technology. The hollow fibers are packaged in a proprietary counter-current-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 plant DCS. 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:** More than 70 units are in operation or under construction. The largest unit processes more than 350 million scfd of synthesis gas.

Licensor: UOP LLC, a Honeywell Company CONTACT

# Hydrogen recovery (cryogenic)

**Application:** Recovery of relatively pure hydrogen  $(H_2)$  from refinery and petrochemical offgas streams, such as those 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%–98% pure  $H_2$ . Valuable product streams, such as LPG, may also be recovered.

**Description:** A typical autorefrigerated cryogenic unit for recovery of  $H_2$  consists of two stages of cooling and partial condensation. Suitably pretreated feed gas is cooled and partially condensed against  $H_2$  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 condensate is separated in the second plate-fin heat exchanger (3). The methane-rich condensate is separated in the second two-phase separator (4), giving a relatively pure  $H_2$  product, which is reheated through both exchangers.

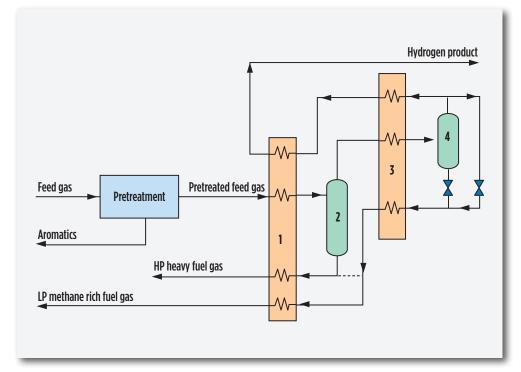
Autorefrigerated cryogenic units use refrigeration from Joule-Thomson expansion of the condensate streams and can generate  $H_2$  purities of up to 96%.

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  $\rm H_2$  product requirements, one, two or three stages of separation may be optimal.

**Operating conditions:** Typical H<sub>2</sub> recoveries are 90%–96%.

**Economics:** Cryogenic recovery of  $H_2$  is economically favored by the ability to recover other valuable products, e.g. olefins and LPG. Com-



pared with alternative technologies, cryogenic processing is the most efficient and has the lowest utilities cost. Cryogenic recovery has been used to treat gases with  $H_2$  feed concentrations as high as 80% and pressures of up to 80 barg.

#### Installations: 14

**References:** Tomlinson, T. R., "Improved operating margins with ethylene recovery," *Petroleum Technology Quarterly,* Spring 2002.

Johnson, G. L., "Olefins Recovery," *Hydrocarbon Engineering*, February 2005.

Licensor: Costain Energy & Process CONTACT

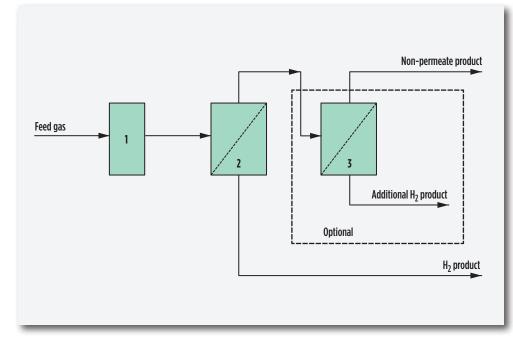
# Hydrogen (PRISM<sup>®</sup> membrane)

**Application:** A PRISM hydrogen membrane system for hydrogen recovery is a simple and efficient addition to refineries, petrochemical plants or gas processing facilities. 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 gases include those generated from steam reforming or from partial oxidation.

**Description:** System design varies by application, but typical installations consist of a pretreatment section (1), which heats the gas and removes entrained liquids, followed by a membrane separator bank (2). A second-stage membrane separator (3) may be added. Ammonia synthesis purge gas pretreatment includes a water scrubber to recover ammonia.

Each PRISM hydrogen membrane separator is constructed from thousands of hollow-tube membranes, which allow hydrogen molecules to permeate into the hollow tubes and out of the end at low pressure. The remaining hydrocarbon-rich gases flow through the vessel at high pressure for use as fuel gas or to the secondary treatment step. In a synthesis gas application, the membranes adjust the ratio of hydrogen to carbon monoxide, with the non-permeate flow becoming the final synthesis gas.

**Economics:** The passive nature of PRISM hydrogen membrane separator systems makes them reliable, easy to operate and affordable as a treatment option. The modular design facilitates scalability by adding



or removing modules as production requirements demand. The system is delivered on a fully-contained skid with all necessary assemblies and connections for easy installation. Each skid system is factory-tested to provide safe and reliable commissioning.

**Installations:** Over 500 PRISM hydrogen membrane systems are in operation worldwide. These systems include more than 85 systems in refinery applications, 225 in ammonia synthesis purge applications and 60 in synthesis gas applications.

Licensor: Air Products and Chemicals Inc. CONTACT

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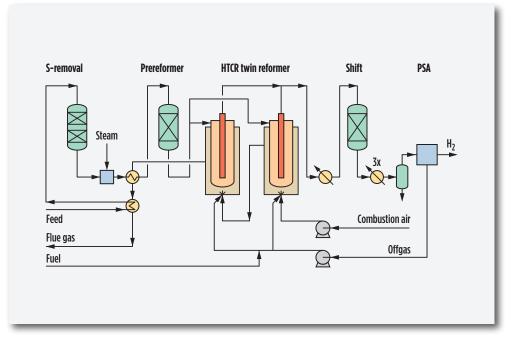
# Hydrogen, HTCR plants

**Application:** Produce hydrogen from a hydrocarbon feedstock, such as natural gas, LPG, naphtha, or refinery offgases, using the Haldor Topsøe Convective Reformer (HTCR). Plant capacities range from 5,000 Nm<sup>3</sup>/h to +50,000 Nm<sup>3</sup>/h (5 MMscfd to +45 MMscfd), and hydrogen (H<sub>2</sub>) purities from 99.5% to 99.999+% are marketed.

**Description:** The HTCR-based  $H_2$  plant can be tailored to suit customer needs with respect to feedstock flexibility. Typical plants include feedstock desulfurization, pre-reforming, HTCR reforming, shift conversion and PSA purification to obtain product-grade hydrogen. PSA offgas is 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 for the design of energy-efficient  $H_2$  plants without steam export. In the larger plants, the reforming section consists of two HTCR reformers.

**Economics:** HTCR-based H<sub>2</sub> plants provide low investment and low operating costs for H<sub>2</sub> 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. Feed and fuel consumption of about 3.3–3.4 Gcal/1,000 Nm<sup>3</sup> (350–360 Btu/scf) is achieved, depending on layout and feedstock.



**Installations:** 40 licensed units with capacities of up to  $30,000 \text{ Nm}^3/\text{h}$  (27 MMscfd).

Licensor: Haldor Topsøe A/S CONTACT

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# Hydrogen, methanol reforming

**Application:** Produce hydrogen ( $H_2$ ), typically in the capacity range of 300–600 Nm<sup>3</sup>/h, for use in oil hardening, manufacture of electronics or in the chemical industry.

**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 CO<sub>2</sub>.

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

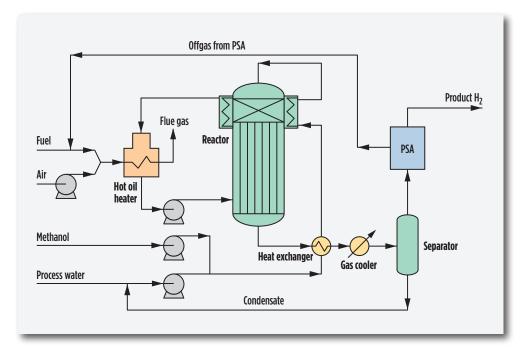
#### **Features:** Utility requirements per $Nm^3$ of $H_2$ are:

0.63
320
0.37
0.06
Cooling water, instrument air
and nitrogen

The compactness of the  $H_2$  plant allows for skid-mounted supply.

Economics: Key process features include:

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



**Installations:** 10 plants in operation worldwide.

Licensor: Haldor Topsøe A/S CONTACT

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### Hydrogen, Steam Methane Reforming (SMR)

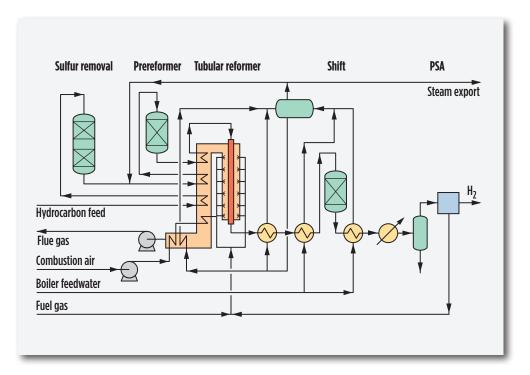
**Application:** Produce hydrogen (H<sub>2</sub>) from hydrocarbon feedstocks such as natural gas, LPG, naphtha, refinery offgases, etc., using the Haldor Topsøe radiant wall steam-methane reformer (SMR) process. Industrial experience includes capacities exceeding 200,000 Nm<sup>3</sup>/h (200 MMscfd), and H<sub>2</sub> purity ranges from 99.5% to 99.999+%.

**Description:** Haldor Topsøe SMR-based H<sub>2</sub> plants can be tailored to suit the customer's needs with respect to feedstock flexibility and steam export. In a typical H<sub>2</sub> plant, the hydrocarbon feedstock is desulfurized and, subsequently, process steam is added, and then the mixture is fed to a prereformer. 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 H<sub>2</sub>. 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  $H_2$  production costs.

**Economics:** The Advanced Steam Reforming conditions described can achieve a net energy consumption of as low as 2.96 Gcal/1,000  $\text{Nm}^3$  of H<sub>2</sub> using natural gas feed (315 Btu/scf).

**Installation:** Topsøe's reforming technology is in operation in more than 250 industrial plants worldwide.



**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.

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 CONTACT

### Hydrogen, Steam Methane Reforming

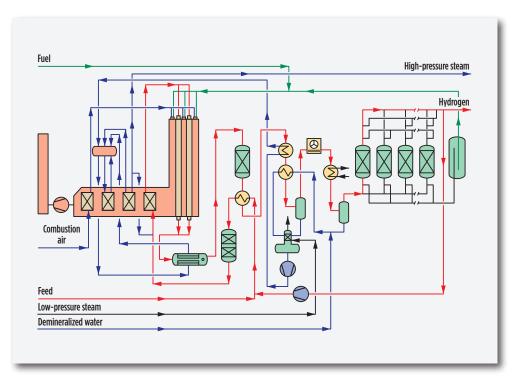
**Application:** Production of hydrogen (H<sub>2</sub>) from hydrocarbon feedstocks such as natural gas, liquefied petroleum gas (LPG), refinery offgases, naphtha, etc., using the Steam Methane Reforming (SMR) process.

**Description:** Linde has a well-proven technology for H<sub>2</sub> manufacture by catalytic steam reforming of light hydrocarbons in combination with Linde's highly efficient Pressure Swing Adsorption (PSA) process.

**Product purity:**  $H_2$  product purities up to 99.9999 mol% are possible. The basic process steps are hydrodesulfurization of feedstock, steam reforming, heat recovery from reformed and combustion flue gas to produce process and export steam, single-stage adiabatic high-temperature CO shift conversion (alternative shift concepts possible for plant optimization), and final  $H_2$  purification by PSA.

Process design and optimization for every process step and, in particular, the optimized linking of operating parameters between the two essential process steps (reforming furnace and PSA unit) are based exclusively on Linde's own process and operating know-how. Process options with prereforming for overall plant optimization (fuel savings over standalone primary reformer, reduced capital cost of reformer, higher primary reformer preheat temperatures, increased feedstock flexibility, lower involuntary steam production, and lower overall steam/carbon ratios) are possible.

**PSA:** The particular features of Linde's PSA technology are high product recovery rates, low operating costs and operational simplicity. Excellent availability and easy monitoring are ensured by advanced computer control. Extensive know-how and engineering expertise assisted by highly sophisticated computer programs guarantee the design and



construction of customized and economical plants of the highest quality. Modular skid design of the PSA plants reduces erection time and costs at the site. The fully prefabricated skids are thoroughly tested before they leave the workshop.

**Reformer furnace:** A compact firebox design with vertical, hanging catalyst tubes arranged in multiple, parallel rows. Minimized number of forced draft top-firing burners, integrated into the firebox ceiling. Compared to other designs, the burner trimming and individual adjustment to achieve a uniform heat-flow pattern throughout the reformer cross-section is substantially facilitated. Concurrent firing ensures a uniform

# Hydrogen, Steam Methane Reforming, cont.

temperature profile throughout the reformer tube length. Flame and stable combustion flow pattern is supported by the flue gas-collecting channels arranged at ground level between the hot reformed gas headers. Thermal expansion, as well as tube and catalyst weight, is compensated by the adjustable spring hanger system arranged inside the penthouse, removing mechanical stress from the hot manifold outlet headers at ground level. The radiant reformer box is insulated with multiple layers of ceramic fiber blanket insulation, is mechanically stable and is resistant to thermal stress.

**Convection section:** Depending on the  $H_2$  product capacity, the convection section—a series of serial heat exchanger coils—is arranged either vertically (with flue gas ID fan and stack at reformer burner level) or horizontally (at ground level) for ease of access and reduced structural requirements, specifically for the higher-capacity units.

#### **Economics:**

	Natural			Refinery
	gas	LPG	Naphtha	gas
Hydrogen Product				
Flowrate, Nm³/h	50,000	50,000	50,000	50,000
MM scfd	44.8	44.8	44.8	44.8
Pressure, bara	25	25	25	25
Purity, mol%	99.9	99.9	99.9	99.9
Export steam				
Flowrate, tph	31	28.9	28.6	29.2
Temperature, °C	390	390	390	390
Pressure, bara	40	40	40	40

Feed and fuel consumptio Gcal/hr GJ/hr	on 177.8 744.4	181.8 761.2	182.9 765.8	175.8 736
Energy consumption (inc Gcal/1,000 Nm³ H <sub>2</sub> GJ/1,000 Nm³ H <sub>2</sub>	luding stea 3.070 12.853	m credit) 3.210 13.440	3.222 13.490	3.072 12.862
Utilities Demineralized water, Cooling water, tph Electrical energy, kW	tph 55.6 160 850	57.5 165 920	60.6 168 945	53.2 157 780
Design flexibility Export steam ton/1,000 Nm <sup>3</sup> H <sub>2</sub> Fuel consumption GJ/1,000 Nm <sup>3</sup> H <sub>2</sub>	0.5-1.2 0.9-3.5	0.4-1.2 1.8-4.3	0.4-1.2 1.9-4.4	0.4-1.1 0.7-2.9
Investment	Typically \$1.0-1.2 MM per Nm <sup>3</sup> /h H <sub>2</sub> , depending on plant size.			

**Installations:** More than 200 new  $H_2$  plants have been built around the world for clients in the refining, chemical and fertilizer industries, with capacities ranging from under 1,000 Nm<sup>3</sup>/h to over 100,000 Nm<sup>3</sup>/h, and processing all types of feedstock. Most of these plants have been built on a lump-sum turnkey basis.

Contributor: The Linde Group CONTACT

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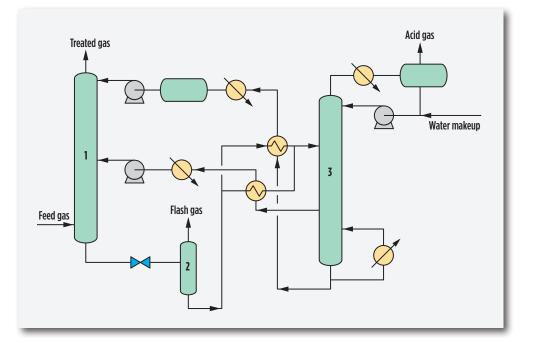
# **HySWEET**

**Application:** Natural gas sweetening (all types of  $H_2S$  and/or  $CO_2$  removal) with simultaneous removal of mercaptans, based on a hybrid solvent. HySWEET is also applicable for the removal of mercaptans and  $H_2S$  from gas streams used for the regeneration of molecular sieves contaminated with mercaptans, thus offering an optimized and integrated scheme for the complete gas sweetening chain. Specific applications of solvent substitution can be envisaged for debottlenecking or revamping operations by changing from a conventional amine solvent to HySWEET.

**Description:** HySWEET, developed by Total, is based on a mix of physical solvent, amines and water as a hybrid solvent for natural gas sweetening. The typical process configuration is similar to conventional amine processes [absorber(1), rich solvent flash drum (2), thermal regenerator (3)]; however, the configuration may be adjusted for specific applications. The physical component of the solvent has been specifically selected to combine a high absorption capacity for acid gases and mercaptans with relatively low hydrocarbon solubility, compared to other physical solvents.

Early HySWEET industrial-scale applications have been accomplished through successful solvent substitution in DEA plants; simultaneous mercaptans removal was achieved while preserving DEA as the amine component of the solvent. Other HySWEET versions are being developed to optimize all types of natural gas sweetening, including more selective removal of  $H_2S$  vs.  $CO_2$ , along with mercaptans removal (based on selective MDEA). These new versions should be delivered to the market in 2013 or 2014, with the potential for solvent substitution in units currently operated with those amines.

**Economics:** The CAPEX of a HySWEET unit designed for natural gas sweetening will be similar to that of an equivalent amine unit. The OPEX



will be about 10% less, mainly because of the reduced reboiling energy requirement vs. conventional amine solvents. HySWEET will simultaneously remove mercaptans, reducing the need for (and/or the size of) additional downstream processing units. It will also produce a lowhydrocarbon acid gas that can be directly fed to a Claus unit without specific pretreatment (e.g. acid gas enrichment), which can translate into an overall cost savings of more than 20% compared with other solutions.

**Installations:** Two industrial gas sweetening units have been operated by Total in its Lacq field in France since 2008. Another HySWEET unit is under construction at the same location.

# HySWEET, cont.

**References:** Shah, V., R. Cadours, C. Weiss and C. Benquet, "HySWEET process: An improvement in energy efficiency," ADIPEC 2010, Abu Dhabi, UAE. Cadours, R., V. Shah and C. Weiss, "HySWEET process for improved

mercaptan removal," IPTC 2009, Doha, Qatar.

Cadours, R., V. Shah, C. Weiss, F. Lallemand and D. Roquet, "Industrial operation of HySWEET, a new hybrid solvent for improved mercaptan removal," GPA European Annual Conference 2009, Venice, Italy.

**Licensor:** HySWEET technology is owned by Total, and it is licensed by Prosernat. <u>CONTACT</u>

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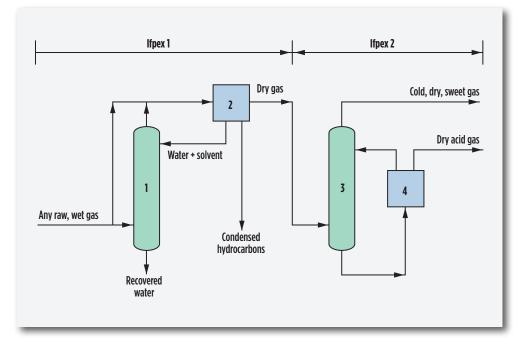
# Ifpexol

**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 dewpointing (down to -90°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 ( $CO_2$ ,  $H_2S$ ) 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 it offers reduced (about 30% lower) CAPEX. Ifpex-2 offers significant savings compared to other processes for bulk acid gas removal with acid gas reinjection.

Installations: 15 Ifpex-1 units, with capacities of 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 1998.

**Licensors:** Prosernat IFP Group Technologies and Titan SNC Lavalin **CONTACT** 

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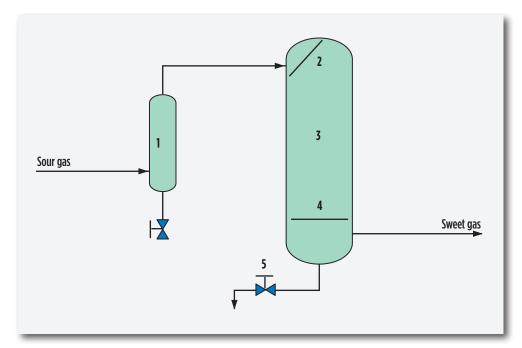
### **Iron Sponge**

**Application:** To remove hydrogen sulfide  $(H_2S)$  and mercaptans from natural gas streams at low- or high-pressure conditions at or near the wellhead.

**Process description:** Iron Sponge (iron oxidized onto wood shavings) uses a simple packed tower (3) on a flowthrough 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, thereby 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. Since 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. The iron oxide is impregnated onto the wood, so 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  $H_2S$ . 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 temperature should be



at or above 50°F, or whatever temperature 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 can run unattended for days at a time.

Licensor: Connelly-GPM Inc. CONTACT

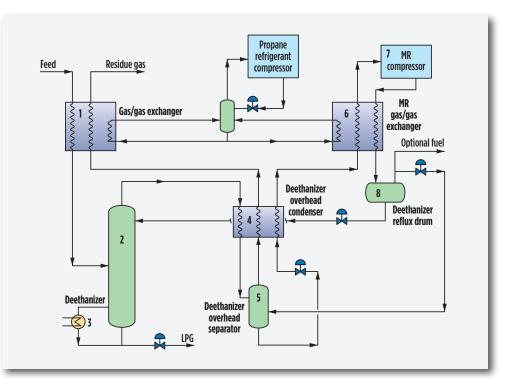
# Iso Pressure Open Refrigeration (IPOR) Process

**Application:** High LPG recovery (> 99%), without a turbo-expander, from moderate to rich feed natural gas streams with feed rates ranging from 5 MMscfd to 300+ MMscfd. This process includes the capability to recover ethane (up to 85%) or reject ethane, while maintaining high  $C_3$ + recovery. The design may be highly modularized, making it appropriate for remote sites and fast-tracked project schedules.

**Description:** In the IPOR process, dry feed gas is initially cooled and partially condensed in the gas/gas exchanger (1). The feed gas stream is then fed to the deethanizer (2) to obtain the desired product separation for the bottom LPG liquid product. Heat for the separation is provided by the deethanizer reboiler (3). The cold reflux stream is provided by the open-loop mixed refrigerant (MR).

The overhead gas stream from the deethanizer is cooled and partially condensed in the deethanizer overhead condenser (4). This gas stream flows to the deethanizer overhead separator (5), where the liquid from this separation is used as the refrigerant for the open-loop MR cycle. The vapor from this separation, the residue gas, is heated in a series of exchangers (4, 1) and then sent to pipeline compressors in the OSBL.

From the deethanizer overhead separator (5), the pressure of the MR liquid is reduced, creating a JT refrigeration effect which is then used to partially condense the overhead gas stream (4). The MR stream is then heated and vaporized as it flows through the MR gas/gas exchanger (6) before reaching the inlet to the MR compressor (7). The compressed, MR stream is cooled and partially condensed in the MR gas/gas exchanger (6). The two-phase stream flows to the deethanizer reflux drum (8), where the liquid is used to provide reflux to the deethanizer column (2), thereby completing the "open" cycle of the MR loop. Noncondensable



vapors, consisting mainly of methane, are directed back into the process via the deethanizer overhead separator (5), and they exit the process into the residue gas stream, or they may be used as fuel.

**Operating conditions:** Feed gas should be dry and below 600 psig. Operating temperatures and pressures allow for carbon steel or LTCS equipment and piping design. A heat medium and propane refrigeration stream are needed for the process. For high ethane recovery,  $CO_2$  removal may be required.

**Licensor:** Randall Gas Technologies, US and international patents pending <u>CONTACT</u>

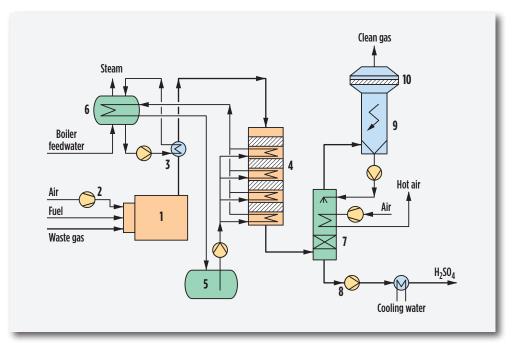
# **KVT SULFOX HK process**

**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 acid recovered and to save fuel is possible.

**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  $V_2O_5$  catalyst beds, where  $SO_2$  to sulfur trioxide (SO<sub>3</sub>), oxidation and further formation of gaseous  $H_2SO_4$  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 glass tube heat exchanger in the upper section, the gaseous acid is condensed and concentrated to 96%–98%. 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 tail gas reactor (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 Nm<sup>3</sup>/h (raw gas including combustion and dilution air) is approximately \$14 million for delivery, erection and startup.

Electric power consumption is about 300 kWh. The amount of produced steam and recovered acid depends on the raw gas concentration. Overall conversion rate for sulfuric compounds is > 99.5%.

**Installation:** There is one installed SULFOX HK plant for the petroleum industry.

**References:** Amlacher, G., "The KVT SULFOX Processes: Production of Sulfuric Acid from Waste Gases," Laurence Reid Gas Conditioning Conference, Norman, Oklahoma, March 2006.

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## KVT SULFOX HK process, cont.

"Global sulfur update," *Hydrocarbon Engineering,* April 2003. 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 offgas cleaning in the viscose industry," Third Viscose Congress, Bad Ischl, Austria, June 2002.

Licensor: MECS-SULFOX BVBA CONTACT

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# **KVT SULFOX NK process**

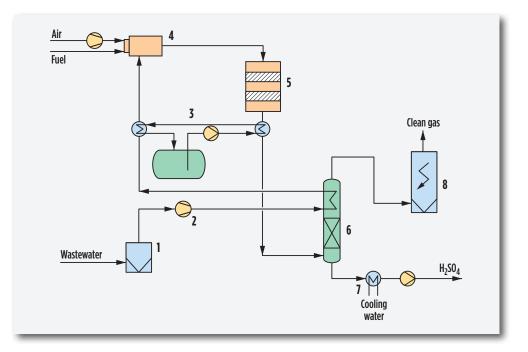
**Application:** In the SULFOX NK process, sulfuric compounds such as hydrogen sulfide ( $H_2S$ ), sulfur dioxide ( $SO_2$ ) and carbon disulfide ( $CS_2$ ) are converted catalytically to sulfur trioxide ( $SO_3$ ), which, in the presence of water vapor, forms sulfuric acid ( $H_2SO_4$ ). The SULFOX NK process is designed for handling raw gas concentrations up to 20 g/Nm<sup>3</sup> of  $H_2S$  and  $CS_2$  (in total).

**Description:** Following the prefilter (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 typically uses liquid salt as heat in the transfer medium. The burner in the preheater (4) supplies the necessary energy for startup and non-autothermal operations. Passing over the platinum- and 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 96 wt%–98 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 a tail gas reactor.

**Economics:** A standard plant with a capacity of 40,000 Nm<sup>3</sup>/h is approximately \$9 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 six installed SULFOX NK plants, with capacities ranging from 9,000 Nm<sup>3</sup>/h to 95,000 Nm<sup>3</sup>/h.

References: "Global sulfur update," Hydrocarbon Engineering, April 2003.

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 offgas cleaning in viscose industry," Third Viscose Congress, Bad Ischl, Austria, June 2002.

Amlacher, G., "The KVT SULFOX Processes: Production of Sulfuric Acid from Waste Gases," Laurence Reid Gas Conditioning Conference, Norman, Oklahoma, March 2006.

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# Liquefin

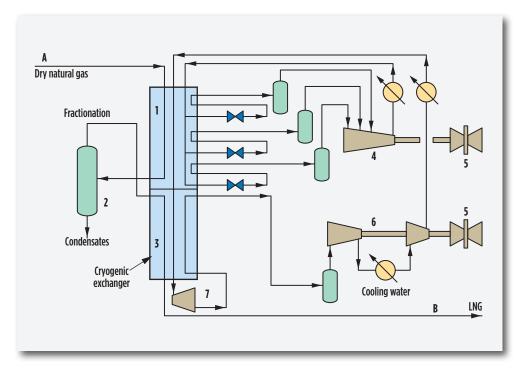
Application: Natural gas liquefaction process.

**Description:** In the Liquefin process, dry natural gas (A) enters the liquefaction train's precooling section (1), where it is cooled to between -50°C and -80°C (-60°F and -110°F). Heat is removed from the gas by mixed refrigerants (MRs) in a set of brazed aluminum plate-fin heat exchangers (PFHEs). The cooled feed stream is then sent from the liquefaction train to the fractionator (2) for condensate removal. Next, the gas returns to the cryogenic exchanger and enters the cryogenic section (3), where it is liquefied by heat exchange with a second MR in compact, energy-efficient PFHEs. By the time the gas reaches the outlet of the cryogenic exchanger, it has become LNG (B).

**Precooling refrigerant system (4):** The use of MR allows the feed gas temperature to be lowered much more than with conventional propane refrigerants. This results in an excellent balance of the power requirements of the precooling and cryogenic sections. A good power balance, in turn, means that two identical drivers (5), operating at optimum efficiency, can be used, thus lowering investment, maintenance and operating costs.

**Cryogenic refrigeration system (6):** The MR gas entering the precooling section is completely condensed by the time it leaves the cryogenic section, making the use of separation equipment unnecessary. After leaving the cryogenic section, the refrigerant is expanded (7) and recycled back to the cryogenic section, where the process gas and cryogenic refrigerant are condensed.

**Main advantages:** Using two MR systems and modular PFHEs in a large single train incurs much lower investment and operating costs when compared to systems involving single-component refrigerants or multiple cooling trains feeding a common liquefaction exchanger. Since the precooling and liquefaction sections comprise several parallel modules, single trains of any size (e.g., 8 million tpy) can be built. PFHEs have thor-



oughly demonstrated their efficiency in industrial applications and are available from a wide range of vendors. Competition between vendors has had a positive effect on both prices and delivery times.

**Economics:** Detailed studies have been published by international petroleum and E&C companies in which conventional, 4.5 MMtpy to 8.0 MMtpy, propane-plus-MR liquefaction trains are compared to the Lique-fin LNG processes. These studies show that 15%–20% investment cost savings can be achieved through the use of Liquefin technology.

**References:** Fischer, B., F. Hughes, P-Y. Martin and J. Pigourier, "Optimizing LNG-GTL Synergies: Cost and CO<sub>2</sub> Emission Reduction," Doha Conference on Natural Gas, Doha, Qatar, March 2005.

### Liquefin, cont.

Martin, P-Y., J. Pigourier and B. Fischer, "LNG process selection, no easy task," *Hydrocarbon Engineering*, May 2004.

Fischer, B. and M. Khakoo, "Plate-Fin Heat Exchangers—An Ideal Platform for LNG Process Innovation," Gastech, Doha, Qatar, October 2002.

Licensor: Axens CONTACT

# Liquid hydrocarbon treating for LPG/PP/BB (ADIP Process)

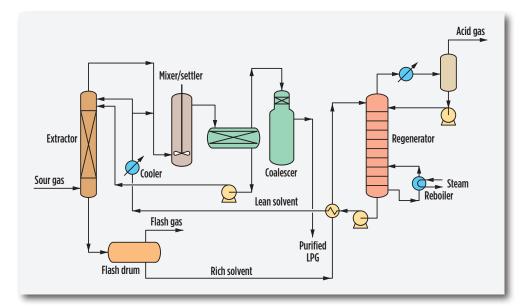
**Applications:** Besides its use as a regenerative process for the reduction of  $H_2S$  to very low levels in gases, the ADIP process is also used to selectively reduce  $H_2S$  and COS to very low levels in liquid hydrocarbons, such as propane-propylene (PP), LPG and NGLs.

The process is based on regenerative absorption with an amine solvent in contact with the acidic feed. Removal of  $CO_2$  is also possible.  $H_2S$  removal from LPG or NGLs down to 20 ppmwt or lower, and COS removal down to 5 ppmwt as sulfur, are achievable.

**Description:** In liquid hydrocarbon treating (LPG, for example), the feed stream is contacted counter-currently with lean ADIP in a packed liquid/ liquid extractor column.

If COS is present in the LPG, removal of COS is achieved by a mixer/ settler system. The lean ADIP solvent first passes through the mixer/settler system before entering the extractor. Co-current and counter-current mixer/settlers are used for COS removal.

The treated LPG then passes through a coalescer to separate entrained ADIP solution. The rich ADIP solvent is flashed to remove entrained and/or dissolved hydrocarbons before passing to the regenerator. Stripping of the rich solvent is identical to that done in gas treating.



**Installations:** More than 490 ADIP units, ranging in capacity from 1,900 Nm<sup>3</sup>/d to 12.2 million Nm<sup>3</sup>/d and 19 t/sd to 7,700 t/sd of liquid hydrocarbons, are in operation throughout the world, demonstrating the reliability of the process.

**Licensor:** Jacobs Comprimo Sulfur Solutions, a member of Jacobs Engineering Group, authorized licensor on behalf of Shell Global Solutions B.V. <u>CONTACT</u>

# LNG

**Application:** Liquefaction of natural gas for plant capacities ranging from small peakshaving applications to mid-sized plants, using a mixed-refrigerant cycle.

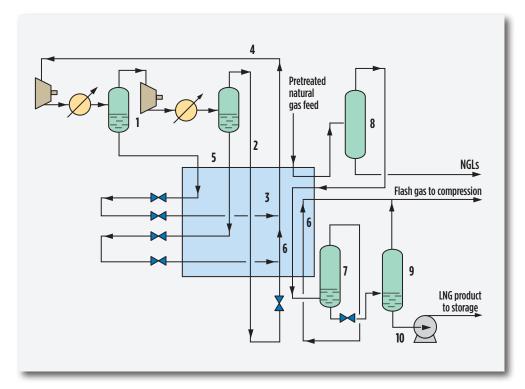
**Products:** Liquefied natural gas (LNG) at atmospheric pressure. Natural gas liquids (NGLs) on larger facilities.

**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 that 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 plant to be designed with high efficiency.

For small (peakshaving) installations, expander cycles using nitrogen or methane may be cost-effective. Expander cycles can also be the technology of choice for offshore applications.

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

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# LNG, cont.

Finn, A. J., "New FPSO design produces LNG from offshore sources," *Oil & Gas Journal,* August 26, 2002.

Finn, A. J., "Are floating LNG facilities viable options?" *Hydrocarbon Processing*, July 2009.

Licensor: Costain Energy & Process CONTACT

# **LNG Dual Expander Cycle**

Application: LNG production for offshore or onshore.

**Description:** Pretreated and dehydrated natural gas (1) is cooled in a 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 lique-faction is obtained by continuous expansion of gases through two independent cycles, one using methane (4) (essentially the same gas being liquefied) and the second using nitrogen (5). The methane cycle works on the warmer end, while nitrogen provides refrigeration on the cold end.

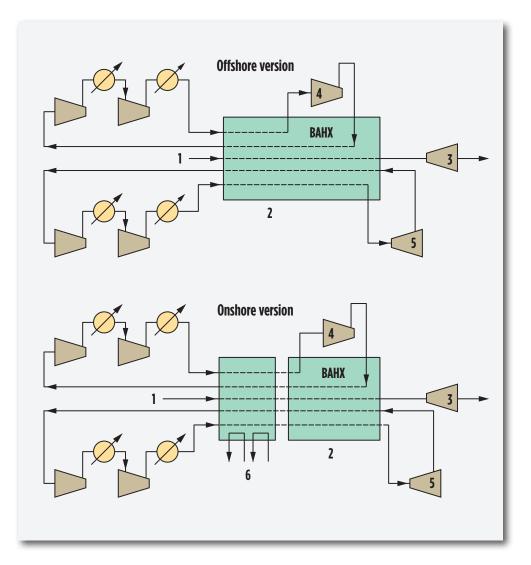
When superimposed, these two cycles act like a binary system. This process is a unique candidate for offshore opportunities due to the refrigerants always being in a gas phase. A propane precooling step can be added at the process' front end (6) to achieve a high-efficiency process for onshore baseload 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 kW/ton of LNG/day and 16 kW/ton of LNG/day.

Reference: US Patent No. 6,412,302

Licensor: Randall Gas Technologies CONTACT



# LNG end flash MLP (maxi LNG production)

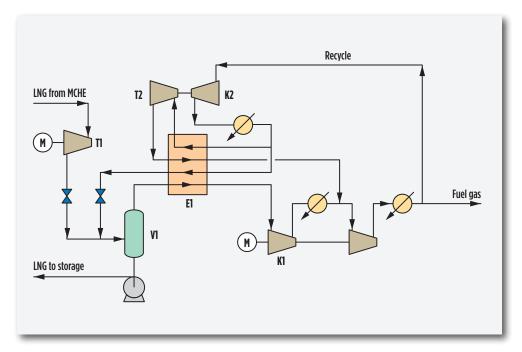
**Application:** A process to increase capacity of LNG plants and minimize fuel gas production.

**Description:** LNG from the main cryogenic heat exchanger at -140°C, 40 bar is expanded in the T1 turbine to produce electric power. It is mixed with liquefied fuel gas recycle before entering the LNG flash drum V1 at 1.2 bar. 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 bar in K2. A portion of this stream is cooled to -80°C in E1 and expanded to 8 bar 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 to -155°C in E1.

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

Installations: None with turboexpander T2/K2.



**Reference:** LNG 13 Conference, Seoul, South Korea, Paper PS2-1, US Patent No. 6,898,949

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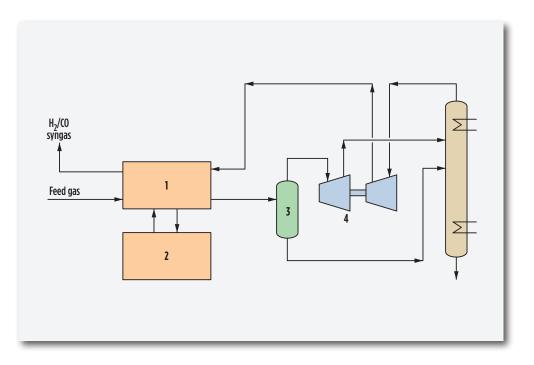
# LNG from Syngas

Application: Process gas from coal gasification and produce high-purity LNG and CO/H $_{\rm 2}$  products.

**Product:** The LNG from the process is suitable for vehicles or can be vaporized for fuel use. The  $CO/H_2$  stream can be used for methanol or other chemical production.

**Description:** The feed gas is sent to a main exchanger (1), where the temperature is reduced to below -240°F. The cooling is accomplished with a mixed-refrigeration system (2), which is a PRICO liquefaction system. The feed gas is partially condensed and separated in the cold separator (3). The gas stream is expanded in a turboexpander unit (4), and then both the liquid from separation and the cold, low-pressure gas are sent to the fractionation column (5). This column separates the LNG bottom product and the CO/H<sub>2</sub> overhead product.

The CO/H<sub>2</sub> stream is recompressed in the compressor attached to the turboexpander, where it is warmed and then exits the unit. This gas is fed to downstream processing for conversion to methanol or other products. The bottom-product LNG is sent to LNG storage, where it is stored at  $-260^{\circ}$ F. The main exchanger (4) is composed of multiple-plate, fin-brazed aluminum exchanger cores arranged in a parallel fashion to accomplish the feed gas cooling that drives the process. Pretreatment of the feed gas for CO<sub>2</sub> and water removal is necessary to prevent solids formation in the low-temperature process.



Installations: The first commercial unit in China is to be started up in 2012.

**Reference:** Hoffart, S. D., "Gas Supply Developments Using Distributed LNG Concepts," Gastech, Amsterdam, the Netherlands, March 2011.

Licensor: Black & Veatch Corp. CONTACT

### **LNG vaporization**

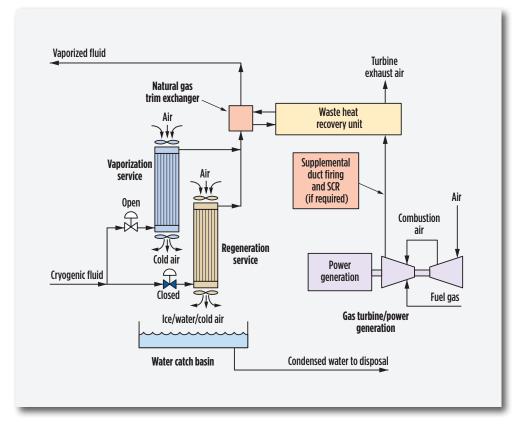
**Application:** To efficiently vaporize LNG using heat-integrated ambient air technology that does not require seawater or fired heating of the LNG. Primary application includes LNG import terminals.

Product: Sales gas from the vaporized LNG.

**Description:** In many climates, ambient air temperature varies dramatically from season to season and from day to night, which makes vaporizing LNG using ambient air a problem. The integration of waste heat from power generation, or another 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 it 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 standalone 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. "Reduce air emissions from natural gas vaporization units," *Hydro-carbon Processing*, January 2009.

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# LNG-Pro

**Application:** To produce liquefied natural gas (LNG) for transportation or storage. The process is adequate for baseload facilities, as well as for peakshaving units. The design is highly modularized, making it appropriate for remote sites or offshore applications. It is also a viable option for monetizing stranded gas reserves.

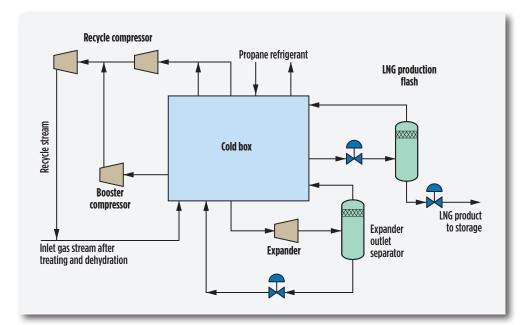
**Description:** This process uses a hybrid technical approach for the liquefaction of natural gas. Specifically, it is a propane precooled turboexpander cycle. After being treated to remove contaminants and water that will affect the cryogenic process conditions, the feed gas is liquefied in a cold box. A side stream of the inlet gas is expanded to low pressure to generate refrigeration. The expanded gas is sent to the cold box to supply refrigeration, and it 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 a 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 world-class baseload facilities. Energy usage is within 0.19 hp/lb-0.25 hp/lb of LNG product, depending on gas sources and compositions.

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

Performance index:	Relative hp/lb of LNG
Cascade refrigeration	1.41-1.64
Mixed refrigerants	1.15–1.4
Turboexpander cycle	1



High-efficiency cycles Utilities	0.87-1.15
Electric power	
Recycle compressor	77%
Refrigerant compressor	13%
Others	10%
Cooling duty	
Recycle compressor	60%
Booster aftercooler	11%
Refrigerant condenser	29%
Fuel gas usage	
Power generation	~ 6%

Reference: US Patent No. 5,755,114

Licensors: Randall Gas Technologies CONTACT

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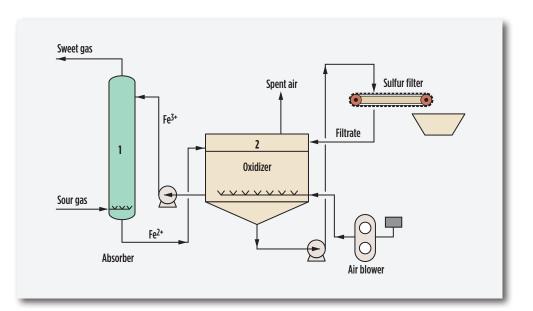
# LO-CAT

**Application:** LO-CAT removes  $H_2S$  from gas streams and produces elemental sulfur. LO-CAT units are in service treating refinery fuel gas, hydrodesulfurization offgas, sour-water-stripper gas, amine acid gas, Claus tail gas and sulfur-tank vent gas. Sulfur capacities are typically less than 25 ltpd down to several pounds per day. Key benefits of operation are high (99.9%)  $H_2S$  removal efficiency and flexible operation, with virtually 100% turndown capability of  $H_2S$  composition and total gas flow. Sulfur is recovered as a slurry, as a filter cake or as high-purity molten sulfur. The sulfur cake is increasingly being used in agriculture, but it can also be deposited in a nonhazardous landfill.

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

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

In both configurations, sulfur is concentrated in the oxidizer cone and sent to a sulfur filter, which can produce filter cake as high as 85% sulfur. If desired, the filter cake can be further washed and melted to produce pure molten sulfur.



**Operating conditions:** Operating pressures range from vacuum conditions to 1,000 psi. Operating temperatures range from  $40^{\circ}$ F-140°F. Hydrogen sulfide concentrations range from a few ppm to 100%. Sulfur loadings range from a few pounds per day to 25+ tons per day. No restrictions on type of gas to be treated; however, some contaminants, such as SO<sub>2</sub>, may increase operating costs.

**Installations:** Presently, 210 licensed units are in operation, with five units under construction.

**Reference:** Nagl, G., W. Rouleau and J. Watson, "Consider optimized iron-redox processes to remove sulfur," *Hydrocarbon Processing*, January 2003.

Licensor: Merichem Co. CONTACT

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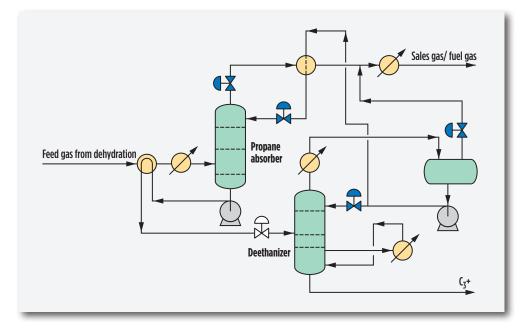
### LPG recovery

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

**Description:** Low-pressure hydrocarbon gas is compressed and dried before being chilled by cross-exchange and propane refrigerant. The chilled feed stream is then contacted with a recycled liquid ethane stream in the propane absorber. The absorber bottoms are 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 that 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:** Two units in operation. Additional units are in various stages of evaluation, engineering and licensing.



Reference: US Patent No. 6,405,561.

Currence, K. and R. Mortko, "Economic LPG Recovery from Stranded Low-Pressure Gas," GPA Convention, Grapevine, Texas, March 2008.

Licensor: Black & Veatch Corp. CONTACT

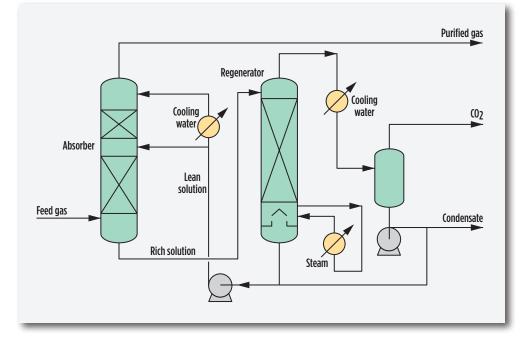
# LRS 10 (CO<sub>2</sub> removal)

**Application:** Remove  $CO_2$  from natural gas, substitute natural gas (SNG) or ammonia syngas. The purification process is applicable for retrofit of facilities at liquefied natural gas (LNG) plants, oil refineries and petrochemical applications.

**Description:** Rich-CO<sub>2</sub> feed gas is passed to the absorber column containing potassium carbonate solutions and LRS10 additives. The rich solution is routed 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, and the recovered potassium carbonate/ LRS10 solution is pumped back to the absorber for further reaction. Feed gas containing about 20% CO<sub>2</sub> has been treated successfully, typically to CO<sub>2</sub> levels of 1% in the processed gas, and, depending on the process arrangement, to 500–1,000 ppm.

**Economics:** A plant utilizing 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:

- Increased gas throughput of typically 10%
- Lower regeneration energy consumption by about 10%
- Reduced  $CO_2$  slippage in the outlet gas by up to 50%
- Improved column operations by moving away from column constraints.



**Installations:** 30 plants worldwide, mainly retrofits, in the ammonia, hydrogen, natural gas and chemical industries.

Licensor: GL Noble Denton CONTACT

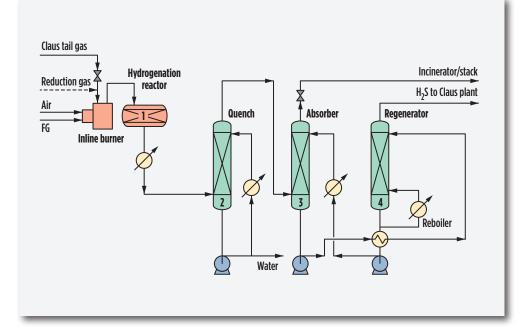
#### LTGT (Lurgi tail gas treatment) process

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

**Description:** The optimum Claus tail gas treatment converts sulfur species to hydrogen sulfide ( $H_2S$ ) and recovers it in a wet-scrubbing process. The Lurgi tail gas treatment (LTGT) process is an amine treating system with generic MDEA solvent, structured packing and plate heat exchangers when possible. This process enables the use of smaller-diameter columns, plot size, worldwide 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 absorbed by an MDEA solution in an absorber column (3). The amine solution is regenerated in a stripper column, which uses stripping steam generated in a reboiler; (4) and produces an  $H_2S$  gas stream that is recycled back to the Claus section after condensing most of its water content. 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 for selective absorption of  $H_2S$  due to chemical structure and do co-absorb  $CO_2$  to a minor extent. Primary (MEA) and secondary (DEA) amines 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 mechanism forming bicarbonates; this mechanism is slow because of slow intermediate reactions.



**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:** Twelve LTGT units have been designed or are in operation.

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

**Licensor:** Lurgi GmbH, Air Liquide Global E&C Solutions, Lurgi Technologies <u>CONTACT</u>

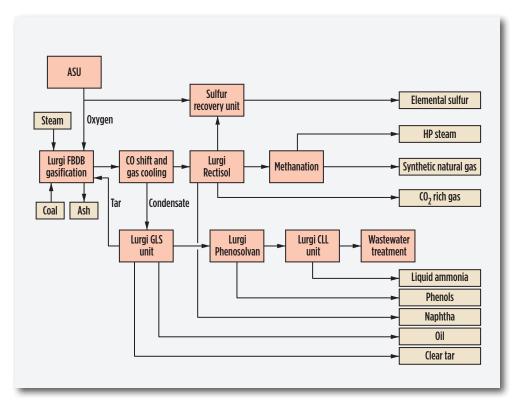
#### Lurgi Fixed Bed Dry Bottom (Lurgi FBDB) gasification process

**Application:** Lurgi FBDB coal gasification is a well-proven technology for the conversion of coal to synthesis gas, consisting mainly of  $H_2$  and CO. The strongest attribute of the Lurgi FBDB gasification process is its long track record for large-scale applications over many years of operation, along with optimum performance featuring modular design, high reliability, and gasification efficiency with low oxygen consumption.

All types of coal ranks have been commercially gasified; however, the competitive advantage of the Lurgi FBDB gasifier is the highest for low-rank, high-ash-content coal. Coal conditioning upstream of a Lurgi FBDB coal gasifier is appreciably low compared to the coal pretreatment requirements of other coal gasification principles. Air Liquide Global E&C Solutions used its experience in gasification, synthesis gas cleaning, and synthesis technologies to further improve the Lurgi FBDB coal gasification technology. The process was made more environmentally friendly and suitable for a number of applications, including synthetic natural gas (SNG), reduction gas for direct reduction iron (DRI), coal-to-liquids (CTL), chemicals and transport fuels.

**Description:** Two sizes of the Lurgi FBDB gasification reactor are commercially available in the form of the Mark 4 (Mk 4) and Mark Plus (Mk+) gasifiers. Continuous improvement, taking into account higher safety, reliability and availability by having better equipment design features, better choice of material and special manufacturing requirements, has led to the latest Mk 4 (design pressure of 40 barg) reactor. To further enhance the economic viability for high-capacity coal gasification projects (e.g., SNG plants), the new generation Mk+ gasifier is designed for doubled single-gasifier capacity and elevated pressure (design pressure of 60 barg).

The purpose of the Lurgi FBDB Mk+ gasifier is to gasify coal under pressure of approximately 50 barg, in the presence of steam and



oxygen, to produce synthesis gas. The screened coal feedstock (particle size 5 mm-50 mm) is fed into the gasifier from the top via twin coal locks, while the gasification agents, steam and  $O_2$  (ASU, 10), are fed from the bottom (1). The gasifier operates below the ash-melting temperature and, hence, the dry ash leaves the gasifier at a certain frequency, depending on the amount of ash produced via the ash lock at the bottom. Coal and ash locking are a batch process. Steam is used as a moderator to ensure that no melting/clinkering of the ash occurs. The required steam-to-oxygen ratio will be dependent on the melting properties of the ash (~ 4 kg steam/Nm<sup>3</sup>  $O_2$  for high-melting ash, and up to ~ 7 kg steam/Nm<sup>3</sup>  $O_2$  for low-melting ash).

#### Continued ▼

### Lurgi Fixed Bed Dry Bottom (Lurgi FBDB) gasification process, cont.

The produced syngas exits the gasifier at relatively low temperatures (approximately 400°C-600°C), depending on the rank and properties of the coal. The raw gas is cooled (and possibly shifted to the  $H_2$ /CO ratio required by the downstream synthesis process) in the gas cooling section (2) of the gasification island, producing dry, raw syngas. Note that part of the CO shift has already taken place inside the Lurgi FBDB reactor due to low-reaction end temperatures resulting from the countercurrent process principle and excess steam present from the agent. The raw gas will also contain  $CH_4$  and higher hydrocarbons, which makes the Lurgi FBDB process specifically suitable for SNG production. The elevated pressure of the Mk+ gasifier favors even higher  $CH_4$  yield.

Downstream gas purification units (configuration dependent on final product) purify and condition the generated synthesis gas to meet the required product specification—e.g., Lurgi Rectisol (3) to recover naphtha and remove sour gases; Lurgi Sulfur Management (4) to recover sulfur; and Lurgi Methanation (5) for SNG production, as shown in the diagram. Gas liquor condensate accumulated in the cooling section (2) is treated in the liquid chain of the process, which comprises the Lurgi GLS unit (6) for extraction of the valuable co-products (tar and oil) formed during gasification. This is followed by the recovery of phenols in the Lurgi Phenosolvan unit (7). Liquid ammonia is recovered in the downstream ammonia recovery section, the Lurgi CLL unit (8). The liquid chain then enters into the waster treatment unit (9), which takes care of the final treatment of the water to the requested purification extent. Then, the water can be completely reintroduced to the water circuit of the plant, resulting in Zero Liquid Discharge (ZLD).

**Economics:** Characteristic figures are presented for a Lurgi FBDB Mk+ gasifier per ton of typical lignite coal feedstock [on a dry-ash-free (daf) basis]. These figures are coal-specific and will vary with coal rank and ash-melting properties:

- H<sub>2</sub>-to-CO ratio: 1.5-2.5
- kg O<sub>2</sub>/kg coal, daf: 0.3–0.5
- Gas production: ~ 2,000 Nm<sup>3</sup>/ton coal, daf
- CH<sub>4</sub> in raw gas: 9–16 mol%
- Carbon conversion: > 99%
- Cold gas efficiency: > 87%
- Thermal efficiency ex-gasifier: > 94%
- Thermal rating: > 500 MW<sub>thermal</sub>

**Installations:** To date, over 100 gasifiers based on Lurgi FBDB gasification technology are in operation around the world. These installations include:

- The world's largest coal-based Fischer-Tropsch chemicals and fuels production plant, built for Sasol (Secunda, South Africa; bituminous coal)
- Coal-to-SNG plant for Dakota Gasification Co. (Beulah, North Dakota, US; lignite coal)
- Coal-to-ammonia plant for Tianji Coal Chemical Co. (Tianji, China; anthracite coal)
- Coal-to-methanol plant for Yima Coal Gasification Co. (Yima, China; sub-bituminous coal).

**References:** Blostein, B., M. Devaux, D. Gruson and F. Judas, "Coal Gasification for DRI: A New Cost-Effective Ironmaking Route," *Steel Tech,* Vol. 5, No. 1, October 2010.

Fu, G. and J. Zhu, "Lurgi FBDB Coal Gasification Technology and Latest Advances," *Sino-Global Energy,* January 2012.

Licensor: Lurgi GmbH, Air Liquide Global E&C Solutions CONTACT

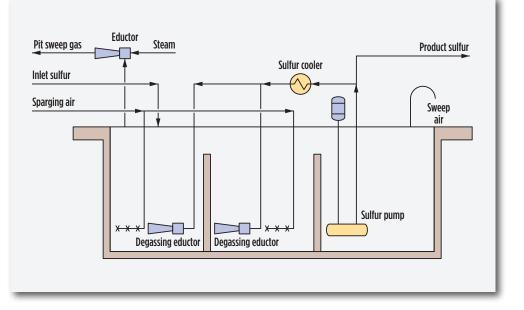
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# **MAG Degassing**

**Application:** Removal of dissolved hydrogen sulfide ( $H_2S$  and  $H_2S_X$ ) contents from liquid sulfur to less than 10-wt-ppm concentration, using the Mechanical Agitation (MAG) Degassing process. Applicable in sulfur-recovery facilities in which, typically, the sulfur product recovered contains 250–300 ppm by weight of  $H_2S$ , depending on operating conditions.

**Description:** During the degassing and storage of sulfur in the pit, the polymeric  $H_2S_X$  compounds will decompose as equilibrium is achieved at the pit operating temperature. This results in the formation of dissolved  $H_2S$  in the liquid sulfur, which will physically desorb to the gaseous phase. MAG Degassing produces a sulfur product containing less than 10-wt-ppm of dissolved  $H_2S$ .

The MAG Degassing process uses no chemical additives and is entirely contained within the sulfur pit. Sparging air from the Claus Air Blowers is used, so a separate degassing air blower is not required. In the MAG Degassing process, liquid sulfur is circulated through a set of degassing chambers and mechanically agitated by the Degassing Eductors. The dissolved  $H_2S$  evolves into the vapor phase and is swept from the pit by the Sulfur Pit Ejector. The Sulfur Pit Ejector induces a sweep air flow through the pit vapor space, which keeps  $H_2S$  concentrations safely below the lower explosive limit.



Installation: Five SRU facilities.

**Reference:** US Patent No. 5,935,498, "Method for Removing Hydrogen Sulfide from Molten Sulfur."

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#### MCR process equipment and technology

Application: Natural gas liquefaction.

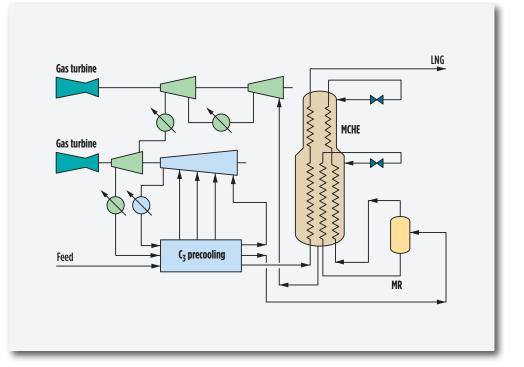
**Products:** Liquefied natural gas (LNG) with optional LPG production.

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

Propane and MR refrigeration systems are specially designed for optimum process efficiency while using proven refrigerant compressors. Largecapacity 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. Precooling can also be accomplished using a separate MR, hydrofluorocarbon (HFC) 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 turbines, industrial gas turbines 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 85 LNG trains using the MCR process are in operation or under construction worldwide.

**Reference:** Roberts, M. J. et al., "Equipment and Machinery Advances Boost the Next Generation of LNG Processes," *LNG Journal*, February 2008.

Licensor: Air Products and Chemicals Inc. CONTACT

### MEDAL membrane (hydrogen)

**Application:** Hydrogen  $(H_2)$  recovery and purification from refinery, petrochemical and ammonia plant gas streams.

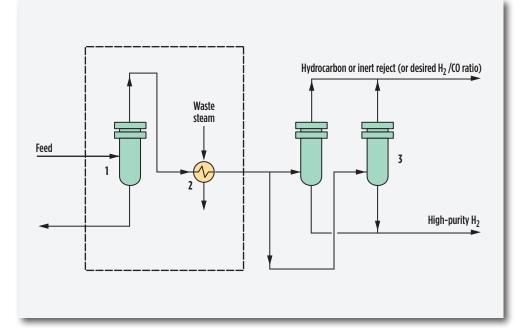
**Feed:** Refinery streams include hydroprocessing unit purge streams, catalytic reformer offgas, fuel gas streams and steam reformers (feed preparation/product purification). Petrochemical streams include olefin plant process and recycle streams, polypropylene recycle streams, meth-anol plant purge, syngas streams from steam reforming and gasification processes for  $H_2$ /carbon monoxide (CO) ratio adjustment and/or process efficiency improvement.

**Product:**  $H_2$  purity of 90% to 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 byproduct, 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.

 $H_2$  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 flowrates. 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.

**Economics:** MEDAL  $H_2$  membrane systems are characterized by low capital and operating costs, and a high return on capital.

**Installations:** Over 125 installations are in operation or under construction. MEDAL  $H_2$  membrane systems have been in operation since 1987.

**Licensor:** MEDAL, a Division of Air Liquide Advanced Technologies, US LLC CONTACT

# 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.

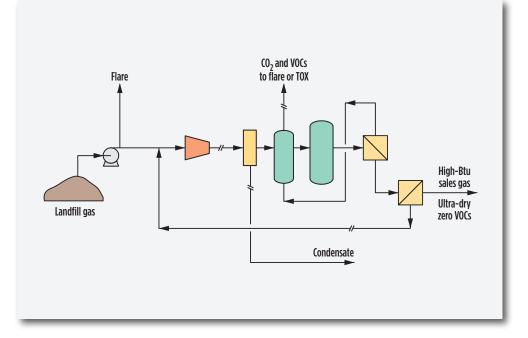
**Description:** MEDAL natural gas membrane modules are made up of millions of hollow-fiber membrane filaments. The hollow fibers are assembled in a patented counter-current-flow permeator. Modules are combined in pressure vessels to provide maximum system performance and to minimize space requirements.

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 (N<sub>2</sub>) 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 biogas system is about \$0.35 per MMBtu of sales gas.

Installations: Pilot plants at three landfills, two full-scale systems in 2006.

**Licensor:** MEDAL, a Division of Air Liquide Advanced Technologies, US LLC <u>CONTACT</u>

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**COMPANY INDEX** 

## MegaSyn

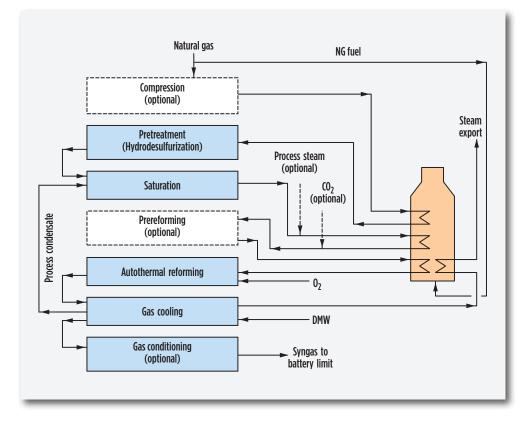
**Application:** Large-scale syngas production, essentially hydrogen  $(H_2)$  and carbon monoxide (CO), from natural gas or other gaseous hydrocarbons for methanol, ammonia, Fischer-Tropsch and other synthesis plants in one train.

**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 (pre-reforming 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 pre-reformed gas.

In the autothermal reformer (ATR), the hydrocarbon feed is converted with oxygen to mainly CO and H<sub>2</sub> 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–1,050°C. Thus, high methane conversions are achieved. The reformed gas is cooled to generate highpressure steam and preheat feed gas, boiler feedwater and the 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 <sub>2</sub>	0.09 million scfd
Demineralized water	0.98 tons
Cooling water	11.5 tons



Electricity	
Export steam	
Specific investment	

22.4 kWh 18.5 tons €277,000/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 GmbH, Air Liquide Global E&C Solutions, Lurgi Technologies <u>CONTACT</u>

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## **MERICAT II**

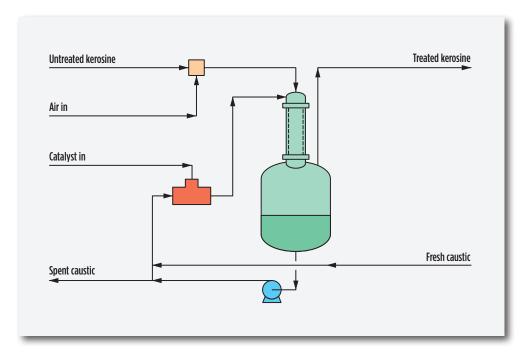
**Application:** The MERICAT II treating unit oxidizes mercaptan sulfur to disulfides to reduce product odor. The streams treated are jet fuel, kerosine, natural gasoline and selectively hydrotreated FCC gasolines.

**Description:** A MERICAT II system consists of two treaters. The FIBER FILM Contactor section removes hydrogen sulfide and naphthenic acids while converting some mercaptans to disulfides with air, oxidation catalyst and caustic solution. The partially treated hydrocarbon exits the FI-BER FILM Contactor and passes upflow through a catalyst-impregnated carbon bed saturated with caustic to convert the remaining high-boiling mercaptans to disulfides.

#### **Economics:**

- Minimal caustic and catalyst consumption
- Operating simplicity
- Minimal capital investment
- Recausticizing of the carbon bed without interruption of treating.

The FIBER FILM section keeps organic acids from entering the carbon bed. This conserves caustic and avoids fouling of the bed with sodium naphthenate soaps. Competitive downflow reactors need more frequent carbon bed caustic washes to remove these soaps as compared to MERICAT II systems. The MERICAT II onstream factor is 100%, while competitive systems requiring periodic cleaning have unpredictable onstream factors.



Installations: 45 licensed units worldwide.

Reference: Hydrocarbon Technology International, 1993.

Licensor: Merichem Co. CONTACT

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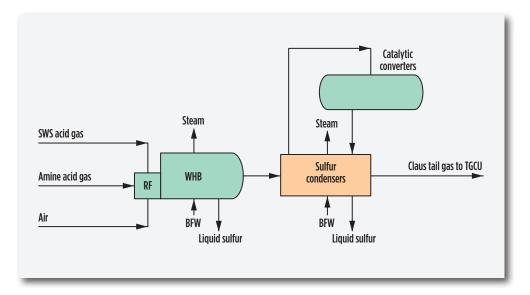
### **Modified Claus**

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

**Description:** Acid gases from sweetening units and sour water strippers (SWSs) are sub-stoichiometrically burnt with ambient air (or air plus oxygen) in a refractory-lined thermal reactor to convert one-third of the H<sub>2</sub>S to SO<sub>2</sub>. Subsequently, elemental sulfur is produced, in accordance with the Claus reaction, between two-thirds of the H<sub>2</sub>S and the produced SO<sub>2</sub>. 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.

Generally, the operating temperature ranges between 925°C and 1,200°C, but it can be increased to 1,350°C if  $NH_3$  is present in the feed gas.

With a modified Claus unit, the sulfur recovery efficiency ranges between 94.5% and 97.5%, depending on the number of catalytic converters installed and the feed composition.



**Installations:** Since the 1970s, more than 100 modified Claus units have been built worldwide by Siirtec Nigi.

**Reference:** "A hot and tricky process environment," *Sulphur,* July-August 2007.

"Sulphur from tricky feedstocks," *Sulphur,* January–Febraury 2008.

Licensor: Siirtec Nigi S.p.A. CONTACT

# Morphysorb (acid gas removal from natural gas)

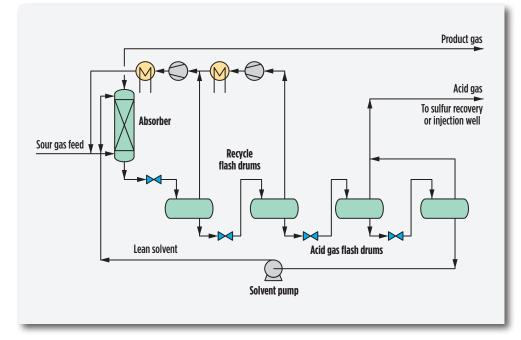
**Application:** Hydrogen sulfide  $(H_2S)$ , carbon dioxide  $(CO_2)$ , COS and RSH removal from natural gas or syngas by physical absorption. Bulk acid gas removal with simple flash regeneration. Removes impurities to pipeline specification with an additional thermal regeneration step. Highly selective  $H_2S$  removal, even at high CO<sub>2</sub> 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 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 and 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 highpressure 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, noncorrosive, low vapor pressure and nontoxic), the process exhibits the following features: low recycle gas



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flow and higher hydrocarbon product yield, low solvent circulation rate, extensive carbon steel usage as construction material and low solvent losses in the product and acid gas.

**Operating conditions:** Typical feed conditions range from 400 psi to 1,300 psi, with a 5%–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 commercial plant with 450 MMscfd of feed gas capacity (expanded in 2006), removing 1,000 tpd of acid gas for downhole reinjection; and a pilot plant installation with a feed gas capacity of 1 MMscfd.

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### Morphysorb (acid gas removal from natural gas), cont.

**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.

"Kwoen gas plant—Conclusion: Duke Energy installs first Morphysorb unit at Kwoen gas plant," *Oil & Gas Journal,* July 12, 2004.

Von Morstein, O., J. Menzel, N. Palla and D. Leppin, "An ace at removal," *Hydrocarbon Engineering,* February 2004.

Licensor: Thyssenkrupp Uhde GmbH CONTACT

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# Multibed (natural gas contaminants removal)

**Application:** Drying,  $CO_2$ , sulfur species and metallic mercury (Hg) removal from natural gas and condensate.

**Description:** The patented Multibed technology is based on the synergy of special aluminas and molecular sieves and is specifically recommended for the drying and purification of natural gas.

In the case of drying under conditions of high relative humidity, activated alumina displays a larger adsorption capacity, whereas in the case of drying at low relative humidity or higher temperature, molecular sieves would be more suitable.

Axens has accumulated extensive technical knowledge to advise on which adsorbent type or combination of adsorbent types to choose, for almost any purification problem.

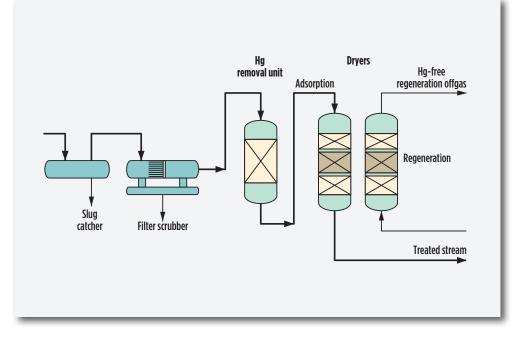
Depending on the application, fixed-bed adsorbents could be installed as beds in the same or separate vessels for flexibility. For example, in Multibed processing, elemental Hg can be removed using an adsorbent system from Axens' CMG portfolio, either upstream or downstream of the gas dehydration step. The preferred configuration is upstream to protect the entire stream behind the Hg-removal unit (MRU).

The treated gas can contain less than 0.01  $\mu$ g/Nm<sup>3</sup> Hg and less than 1 ppmv of other contaminants.

#### **Operating parameters:**

Operating conditions are: Phase Inlet temperature, °F Inlet pressure, psig Regeneration gas temperature, °F

Liquid or vapor 40-140 40-1,400 350-600



Most adsorbents are thermally regenerated with light-hydrocarbon streams, with a counter-current flow.

Installations: Over 60 installations worldwide.

**References:** Savary, L. and P. Travers, "Axens Multibed System—An Improved Technology for Natural Gas Purification," GPA-GCC Technical Conference, Muscat, Oman, May 2003.

Savary, L., "From Purification to Liquefaction: Gas Processing Technologies," GPA-GCC Technical Conference, Kuwait, May 2004.

Licensor: Axens CONTACT

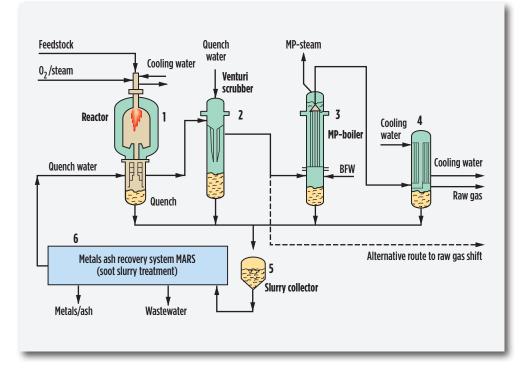
#### **Multipurpose gasification**

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

**Description:** Continuous noncatalytic partial oxidation process. The quench mode is shown in the figure: hydrocarbon feedstock, moderator  $(H_2O, CO_2 \text{ or } N_2)$  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.

For hydrogen, chemicals or Fischer-Tropsch, the wet, hot gas is further cleaned in a venturi scrubber (2) from where it is passed directly to a raw gas shift conversion. For fuel gas production, the hot gas from the venturi scrubber is passed to a medium-pressure steam boiler (3) for heat recovery and to the final cooler (4) before further processing. 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-1,500°C, pressures from atmospheric to 70 bar (or higher, if economically justified). Feedstock and oxidant preheat are possible in a wide range of



100°C-600°C, depending on the 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 recover heat as high-pressure steam, raising overall efficiency.

**Economics:** Characteristic consumption and production rates per ton of heavy residue feedstock: 1 ton to 1.1 ton of  $O_2$  (100%), export 0.5 ton MP steam (quench) to 2.2 ton HP steam (boiler mode), 2.2 ton of raw syngas (dry) equiv. to 2,600 Nm<sup>3</sup> H<sub>2</sub> + CO. Cold gas efficiency is 82%–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.

### Multipurpose gasification, cont.

**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.

**References:** Liebner, W. and C. Erdmann, "MPG–Lurgi Multipurpose Gasification–Recent Applications and Experiences," World Petroleum Congress 2000, Calgary, Alberta, Canada, June 2000.

Walter, S., U. Wolf and H. M. Schlichting, "The use of MPG Gasification for upgrading Canadian oil sands," IChemF Gasification Conference, Barcelona, Spain, 2006.

**Licensor:** Lurgi GmbH, Air Liquide Global E&C Solutions, Lurgi Technologies <u>CONTACT</u>

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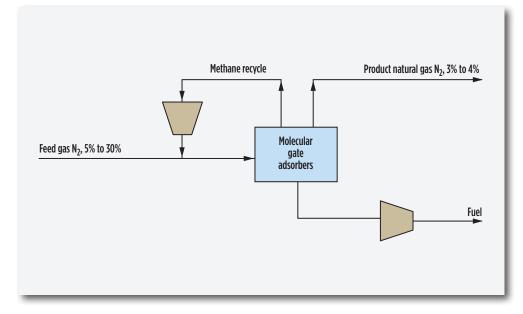
## N<sub>2</sub> rejection (Molecular Gate)

**Application:** Remove nitrogen ( $N_2$ ) from contaminated natural gas. Feedstocks include  $N_2$  contamination from 5%–30%. Product is pipelinequality natural gas with typical  $N_2$  levels of 3%–4% using the Molecular Gate process and a patented, proprietary adsorbent in a pressure swing adsorption (PSA) system.

**Description:** Natural gas at a typical pressure level of 100 psig is routed through a series of adsorber vessels. One or more vessels remove  $N_2$ , while pipeline-quality natural gas flows through the adsorbent bed at essentially feed pressure. Typically, between three and six adsorber vessels are used. When the adsorbent is saturated with  $N_2$ , 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  $N_2$  to be rejected.

To maximize adsorbent capacity,  $N_2$  is typically removed through a single-stage vacuum blower. The process is based on an adsorbent that is size selective and allows smaller  $N_2$  molecules to fit in adsorbent pores, while the larger methane molecule is unaffected. Carbon dioxide is also completely removed with the  $N_2$ , and oxygen is partially removed. The system is flexible for a wide range of  $N_2$  concentrations and has turn-down 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 total installed cost is \$0.50/ thousand ft<sup>3</sup> (Mft<sup>3</sup>) of feed processed. This is decreased to less than



\$0.35/Mft<sup>3</sup> for a 10-MMscfd design. Modular construction allows for low-cost installation and equipment relocation flexibility.

**Installations:** 40 units are in operation or fabrication.

**Reference:** "Nitrogen Removal from Natural Gas with the Molecular Gate Adsorption Process," GPA Annual Convention, March 2009, San Antonio, Texas.

Licensor: Guild Associates Inc. CONTACT

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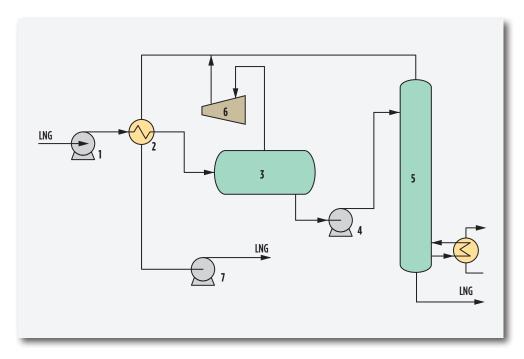
# **NGL from LNG**

**Application:** To separate NGLs from 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 streams, 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 No. 6,564,579, "Method for Vaporizing and Recovery of Natural Gas Liquids from Liquefied Natural Gas."

McCartney, D., "Gas Conditioning for Imported LNG," GPA Annual Convention, San Antonio, Texas, March 2003.

Licensor: Black & Veatch Corp. CONTACT

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### **NGL recovery**

**Application:** Deep recovery of natural gas liquids (NGLs) 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%.

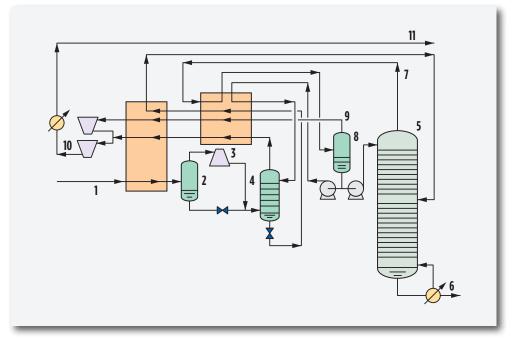
Products: Sales gas and stable NGL.

**Description:** Dry feed gas (1) at a pressure of typically 70 bar is cooled and partially condensed in the main gas/gas exchanger. The resulting two-phase stream is separated (2), with the vapor being work-expanded in a turboexpander (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 deethanizer (5). The bottoms (6) from the deethanizer form the NGL product. The deethanizer overheads (7) are cooled and condensed and passed to a separator (8). Liquid from this separator is used to reflux both the deethanizer 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 yield the sales gas product (11).

**Operating conditions:** Very high propane recovery can be achieved by optimizing thermal integration with multistream heat exchangers and optimizing turboexpander 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:** 12 NGL recovery plants, with capacities of up to 11 million  $m^3/d$ .

**References:** Finn, A. J., T. R. Tomlinson and G. L. Johnson, "Design, equipment changes make possible high  $C_3$  recovery," *Oil & Gas Journal*, January 3, 2000.

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

Contributor: Costain Energy & Process CONTACT

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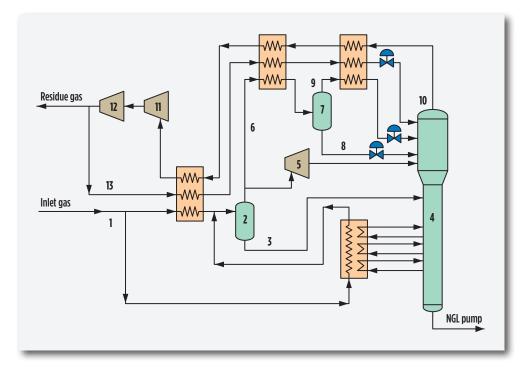
# NGL-MAX

**Application:** Ethane/ethylene and heavier hydrocarbons recovery, from natural gas or refinery offgas 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.

**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 the 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 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 crude reflux 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 an expander-driven compressor (11). The warm, intermediate-pressure residue gas is boosted to pipeline pressure by residue compressors (12). A part of the high-pressure residue gas (13) is cooled, condensed and sent to the demethanizer as reflux. This reflux is 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 allows requires the demethanizer tower to run at higher pressure, thereby minimizing residue gas compression horsepower. This higher pressure also makes the process more  $CO_2$ -tolerant and, hence, simplify or eliminate inlet gas treating.

Licensor: Randall Gas Technologies, US patent pending CONTACT

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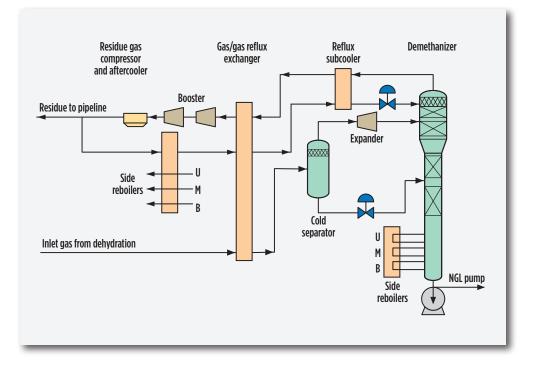
## NGL-PRO

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

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

**Operating conditions:** An ample range of pressures and temperatures. Hydrocarbon liquid content is less than 3.5 gal/thousand scf.



Reference: US Patent No. 5,890,377

Licensors: Randall Gas Technologies CONTACT

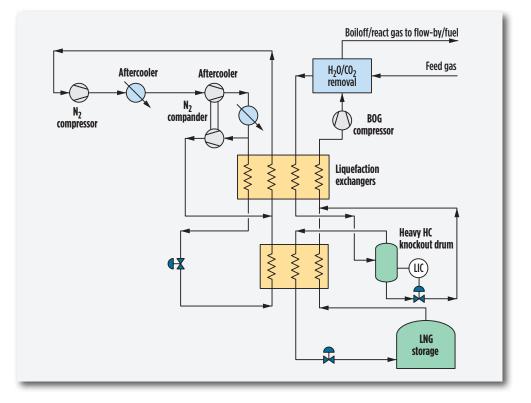
### Nitrogen recycle LNG liquefier

**Application:** Liquefaction of natural gas for peakshaving, product distribution or floating production storage and offloading (FPSO) applications.

**Description:** Natural gas is pretreated to remove water ( $H_2O$ ) and carbon dioxide ( $CO_2$ ). A fraction of the pretreated natural gas is used to regenerate the  $CO_2/H_2O$  removal system. The remaining gas is cooled, and the heavier hydrocarbons (HC) are removed in a knockout drum or multi-stage separation device. The resulting vapor product is then condensed to produce LNG. Boiloff gas (BOG) from the LNG storage and the collected heavier HCs are warmed in the exchangers and mixed with the  $CO_2/H_2O$ -laden regeneration gas. The resulting gas stream is then returned to the feed gas supply or to 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 that 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  $N_2$  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:**  $N_2$  recycle plants typically offer a lower capital solution for small-plant applications and provide an attractive liquefication process option for applications where HC refrigerants may be undesirable.

**Installations:** Three units in operation in peakshaving applications. Six  $N_2$  recycle units in operation for LNG subcooling.

**Reference:** Bronfenbrenner, J. C. and W. R. Miller, "On a smaller scale," *LNG Industry,* Winter 2008.

Licensor: Air Products and Chemicals Inc. CONTACT

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### **Nitrogen rejection**

**Application:** Reject nitrogen  $(N_2)$  from natural gas to increase heating value.

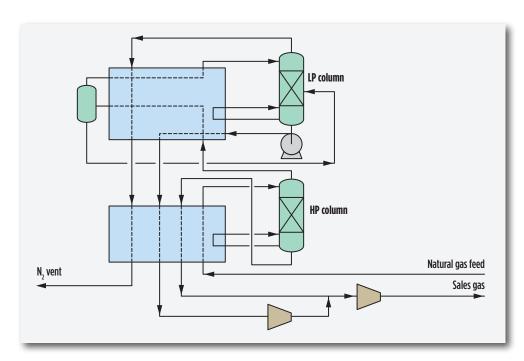
**Description:** Natural gas feed to the  $N_2$  rejection unit (NRU) is partially condensed and fed to the top of the high-pressure (HP) column. A reboiler driven by condensing the feed provides stripping vapors in the column. The bottoms from the first stripping column are enriched in hydrocarbons and depleted in  $N_2$ . This HP residue is boiled in the warm NRU exchanger and sent to residue gas compression. Enriched in  $N_2$ , 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  $N_2$ -enriched vapor stream 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  $N_2$ , creating the remainder of the residue product. The liquid flowing down the column scrubs the methane from the vapor, creating a high-purity  $N_2$  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  $N_2$  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.  $N_2$  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%  $N_2$  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%  $N_2$  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:** Nine 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," GPA Annual Convention, Atlanta, Georgia, March 2000.

Licensor: Air Products and Chemicals Inc. CONTACT

#### Nitrogen removal (reject)

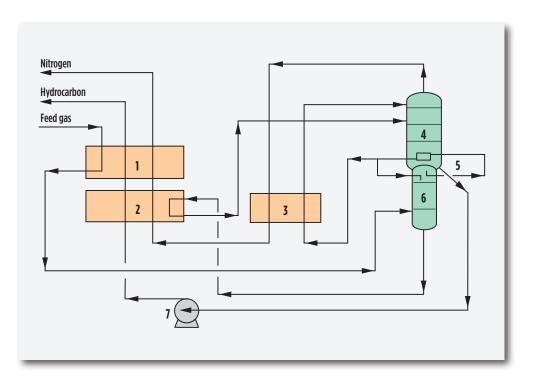
**Application:** Cryogenic removal of nitrogen from natural gas to increase calorific value and/or to reduce gas volume for compression.

**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, process flowsheets using 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 of up 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 prefreactionation process is more efficient. Cryogenic nitrogen removal is the most economical choice for natural gas upgrading.

**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.

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### Nitrogen removal (reject), cont.

**Installations:** 10 plants at six sites with capacities of 80,000 sm<sup>3</sup>/h to 700,000 sm<sup>3</sup>/h.

**References:** Millward, R. J. and B. R. Dreaves, "A boost from  $N_2$  rejection," *Hydrocarbon Engineering*, July 2004.

Finn, A. J., "Rejection strategies," Hydrocarbon Engineering, October 2007.

US Patent applications 2012/0090355 and 2012/0097520.

Licensor: Costain Energy & Process CONTACT

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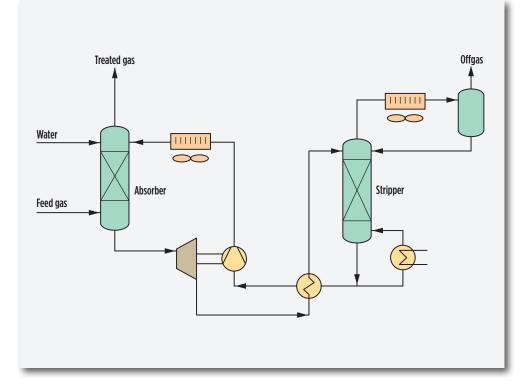
#### **OASE<sup>™</sup> Process**

**Application:** Under the OASE<sup>™</sup> brand, BASF provides customized, highperformance gas treatment technologies for traditional applications like syngas and ammonia, sales gas and LNG. BASF also has the expertise to support applications in developing markets for carbon capture/flue gas, biogas and floating LNG.

**Description:** Acid components ( $CO_2$  and  $H_2S$ ) found in the feed gas are removed by chemical absorption. The rich solution leaving the absorber is regenerated by flashing and/or stripping through one or more steps. Different process configurations can be combined with various solvent types to meet the requirements of individual applications. This flexibility also allows customization to meet the customers' economic priorities.

**Operating conditions:** Reference plants cover a feed gas capacity range of 3,000 Nm<sup>3</sup>/hr (3.0 MMscfd) to 1.6 million Nm<sup>3</sup>/hr (1,450 MMscfd), absorber temperatures from 20°C (68°F) to 90°C (194°F), absorber pressures from atmospheric range up to 120 bar (1,700 psia), and feed gas compositions from 0.1 vol% to 40 vol% of CO<sub>2</sub> and 0 vol% to 15 vol% of H<sub>2</sub>S. Treatment at higher pressures with more CO<sub>2</sub>/H<sub>2</sub>S in the feed gas is achievable.

**Economics:** The OASE<sup>™</sup> Process requires relatively low energy input, features very high plant availability and delivers high yields of high-purity gases. It is flexible enough to allow specific gas components to be separated selectively. The OASE<sup>™</sup> solvents feature high stability, requiring minimal makeup as a result. Further advantages are very low hydrocarbon co-absorption, no degradation products, low corrosion and low foaming tendency. Also, the solvents are nontoxic and biodegradable.



**Installations:** With more than 300 reference plants, BASF is one of the world leaders in the gas treating business today. Production and storage facilities in the Americas, Europe and Asia ensure very high reliability of delivery and supply of quality solvents worldwide. Furthermore, BASF's regional and local presence provides for an extensive technical, analytical and service structure that includes onsite training of the customer's personnel, process optimization, and turnaround assistance, as required.

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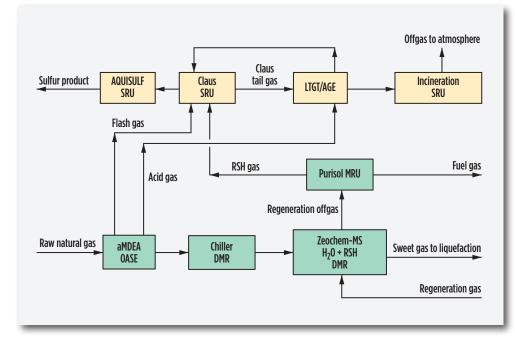
# OmniSulf

**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 of trace contaminants such as COS, mercury and, specifically, mercaptans is becoming ever more important; aside from the removal of hydrogen sulfide ( $H_2S$ ), carbon dioxide ( $CO_2$ ) and water-removal tasks.

**Description:** The OmniSulf concept encompasses the following proprietary key processes. Acidic components are eliminated using BASF's OASE process. 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 unit 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 a Lurgi Multi-Purpose Burner). A Lurgi tail gas treatment (LTGT) unit combined with an acid gas enrichment system are added to the Claus unit to boost sulfur recovery. The sulfur product is then treated further by applying an AQUISULF degassing process (AQU) that removes  $H_2S$  concentrations below 10 ppm. Offgases are incinerated (INC) before being released to the atmosphere.

As the sulfur market is saturated, acid gas reinjection is increasingly selected as a viable alternative. The OmniSulf concept can be tailored to gas reinjection.



**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.

**Licensor:** Lurgi GmbH, Air Liquide Global E&C Solutions, Lurgi Technologies <u>CONTACT</u>

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### **OxyClaus**

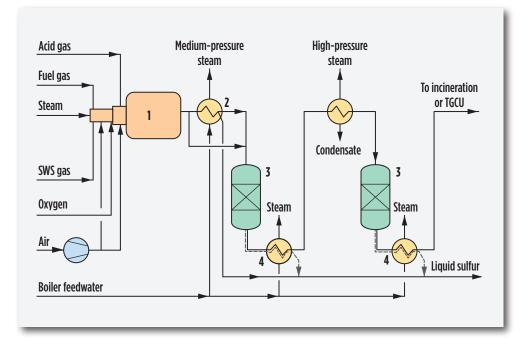
**Application:** Increase capacity up to 200% in existing Claus sulfur recovery units, or for a more economical design of grassroots Claus sulfur recovery units.

Description: The modified Claus reaction is carried out with direct oxygen  $(O_2)$  combustion. By using a proprietary thermal reactor burner (1), levels of 80%–90% net  $O_2$  can be utilized. Combustion temperature moderation is achieved without the need for any type of gas recycle.  $O_2$ 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 H<sub>2</sub>S 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  $H_2S$  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. Peakshaving, as well as operation at full design capacity, is accomplished with air and  $O_2$ .

**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  $O_2$  enrichment as compared to an air-only design.

Based on typical pipeline oxygen costs of \$35 per ton, even if  $O_2$  enrichment were used 100% of the time, it would take over eight years for  $O_2$  costs to equal the incremental capital savings.

**Installations:** More than 40 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 GmbH, Air Liquide Global E&C Solutions, Lurgi Technologies and Black & Veatch Corp. (US only) <u>CONTACT</u>

### **Oxygen enrichment for Claus units**

**Application:** Overcome bottlenecks due to limited gas throughput—typically for capacity increase—and/or decompose detrimental materials such as ammonia.

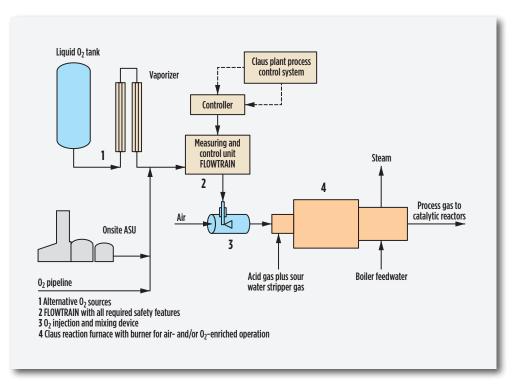
**Description:** As clean-fuels regulations become effective, refiners must recover more sulfur in their Claus plants. As a byproduct of deep desulfurization, ammonia is generated and typically must be decomposed in the Claus plant. To upgrade the sulfur recovery units (SRUs) accordingly, oxygen ( $O_2$ ) enrichment is an efficient and low-cost option.  $O_2$  enrichment can increase sulfur capacity substantially, and it is capable of decomposing ammonia from sour water stripper gas very efficiently.  $O_2$  addition can be done on three levels, depending on the required capacity increase:

**1. Up to approximately 28% O<sub>2</sub>.** Oxygen is simply added to the Claus furnace air. This can raise sulfur capacity by up to 35%.

**2.** Up to approximately 40%  $O_2$ . The burner of the Claus furnace must be replaced by an appropriate type—i.e., by a SURE<sup>m</sup> burner. Up to 60% additional sulfur capacity can be achieved with this method.

**3. Beyond 40% O<sub>2</sub>.** This option allows for 100% more capacity and beyond. Here, major modification of the Claus unit is necessary, such as implementation of a second thermal stage. O<sub>2</sub> sources can be liquid O<sub>2</sub> tanks, onsite air separation units (ASUs) or pipeline supply. O<sub>2</sub> consumption in Claus plants fluctuates widely in most cases; thus, tanks are the best choice due to ease of operation, flexibility and economy. For O<sub>2</sub> addition into the carbon steel air duct, a number of safety rules must be observed. The O<sub>2</sub> metering device FLOWTRAIN contains all of the necessary safety features, including flow control, low temperature and low-pressure alarm and switchoff, and safe standby operation. All features are connected to the Claus plants' process control system.

An efficient mixing device ensures even  $O_2$  distribution in the Claus air. A proprietary Claus burner was developed especially for application



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for air- and  $O_2$ -enriched operations. This burner provides for a short and highly turbulent flame, which ensures a good approach to equilibrium for Claus operation and for the decomposition of ammonia.

**Economics:** As  $O_2$  enrichment provides substantial additional Claus capacity, it is a low-cost alternative to building an additional Claus plant. It can save investment, work-hours and maintenance. Installed cost for  $O_2$  enrichment per Level 1 is typically below \$200,000. For Level 2, the investment cost ranges from \$200,000 to \$500,000 and depends on the size of the Claus plant. Operating costs are varied and depend on the duration of  $O_2$  usage. Typically, annual costs of  $O_2$  enrichment are esti-

#### Continued ▼

## Oxygen enrichment for Claus units, cont.

mated as 10%–40% of the operating cost for a Claus plant, providing the same additional sulfur capacity. Due to improved ammonia destruction maintenance work, corrosion levels are lower and cleaning ammonium salts from heat exchanger tubes requires less work.

**Installations:** Over 80 installations (including SURE<sup>™</sup>) in more than two dozen field trials showed applicability of low-level O<sub>2</sub> enrichment.

Contributor: The Linde Group CONTACT

### **Oxygen enrichment for FCC units**

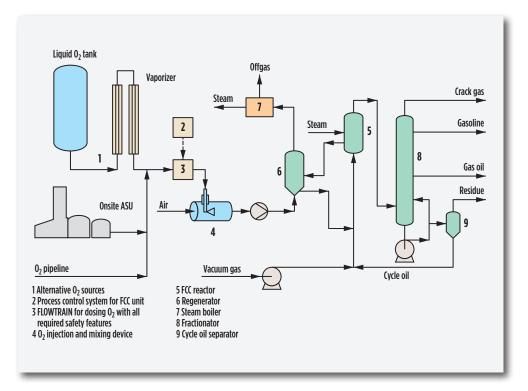
**Application:** Increase FCC throughput capacity by up to 50% and/or increase conversion in FCC units; process heavier feeds; temporarily overcome blower limitations; reduce catalyst losses.

**Description:** Clean-fuels regulations are being globally implemented. Also, transportation fuel demand continues to shift toward kerosene and diesel. Both of these scenarios contribute to the need for more flexibility in fluid catalytic cracking units (FCCUs). FCCUs must be able to treat a wider range of feeds (especially heavier feeds), with higher throughput capacity. Both goals can be achieved via oxygen ( $O_2$ ) enrichment in FCC regeneration.

In the FCC reactor, long-chain hydrocarbons are cracked into shorter chains in a fluidized-bed reactor at 480°C–550°C. This reaction produces coke as a byproduct that deposits on the catalyst. To remove the coke from the catalyst, it is burned off at 650°C–750°C in the regenerator. The regenerated catalyst is returned to the reactor.  $O_2$  enrichment, typically up to 27 vol%  $O_2$ , intensifies catalyst regeneration and can substantially raise throughput capacity and/or conversion of the FCCU.  $O_2$  sources can be liquid  $O_2$  tanks, onsite ASUs or pipeline supply.  $O_2$  consumption in FCCUs fluctuates widely in most cases, making tanks the best choice with respect to ease of operation, flexibility and economy.

For  $O_2$  addition into the carbon steel air duct, a number of safety rules must be observed. The  $O_2$ -metering device FLOWTRAIN contains all necessary safety features, including flow control, low-temperature and low-pressure alarm and switchoff, and safe standby operation. All of these features are connected to the FCC units' process control system. An efficient mixing device, OXYMIX, ensures even  $O_2$  distribution in the air feed to FCC regeneration.

**Economics:**  $O_2$  enrichment in FCC regeneration is economically favorable in many plants. For example, one refinery increased throughput by



15%. The net improvement was a 26% increase in higher-value products, such as naphtha. Likewise, lower-value products increased only 5%, as fuel gas. The net profit increased substantially. Installed cost for  $O_2$  enrichment is typically below \$250,000. Operating costs depend on the cost for  $O_2$  and the duration of  $O_2$  enrichment. Economical  $O_2$  usage can be calculated on a case-by-case basis and should include increased yields of higher-value products and optional usage of lower-value feeds.

**Installations:** Currently, more than 10 units are in operation. Test installations to quantify the effects of higher capacity and conversion levels are possible with Linde equipment.

Contributor: The Linde Group CONTACT

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### PRENFLO Gasification process (PDQ)

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

**Description:** First, the feed dust is prepared in the feed preparation unit. Approximately 80% of the dust is smaller than 0.1 mm and has a water content of approximately 1 wt%–2 wt% in the case of hard coals, and approximately 8 wt%–12 wt% for lignite.

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

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

#### Economics:

#### Main process data:

Gasification pressure: Gasification temperature: 1,40 Gas temperature at outlet of gasifier/quench: Carbon conversion:

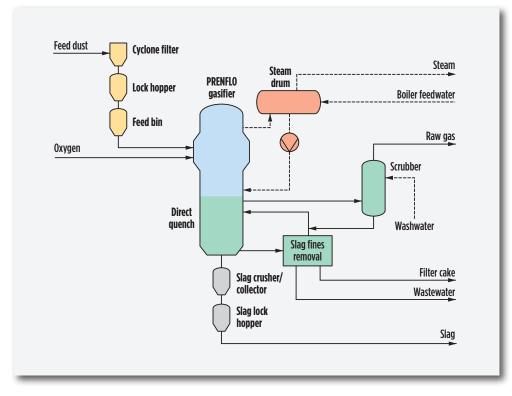
Up to 42 bar 1,400°C-1,600°C 200°C-250°C >99%

> > 85 vol% 6-8 vol% < 0.1 vol%

#### Steam/dry gas ratio: ~ 1.3

#### Typical raw gas composition:

CO +	$H_2$
$CO_2$	
$CH_4$	



**Commercial plants:** TransGas Development Systems CTL plant, West Virginia, USA, applying two PDQ gasifiers to start up in 2013. Beyond 2013, PDQ is licensed/selected for ~ 15,000 MW of new plant capacities.

**References:** Thyssenkrupp Uhde GmbH, Gasification Technologies Brochure, 2011.

Licensor: Thyssenkrupp Uhde GmbH CONTACT

# **PRENFLO Gasification process (PSG)**

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

**Description:** First, the feed dust is prepared in the feed preparation unit. Approximately 80% of the dust is smaller than 0.1 mm and has a water content of approximately 1 wt%–2 wt% in the case of hard coals, and approximately 8 wt%–12 wt% for lignite.

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

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

#### **Economics:**

Main process data

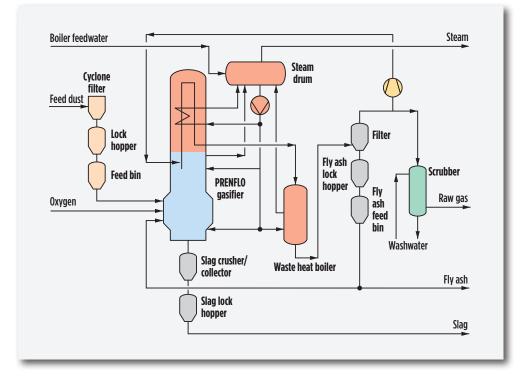
- Gasification pressure:
- Gasification temperature:
- Carbon conversion:

Typical raw gas composition:

- CO + H<sub>2</sub>
- CO<sub>2</sub>
- CH<sub>4</sub>

Up to 42 bar
1,400°C-1,600°C
> 99%
> 85 vol%

2-4 vol% < 0.1 vol%



**Commercial plants:** PRENFLO technology has been successfully commercialized in the world's largest solid feedstock-based IGCC 300-MWe net power plant in Puertollano, Spain. It has also been selected or licensed for several new plants scheduled to start up between 2014 and 2015.

**Reference:** Thyssenkrupp Uhde GmbH, Gasification Technologies Brochure, 2011.

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# PRICO<sup>®</sup> (LNG)

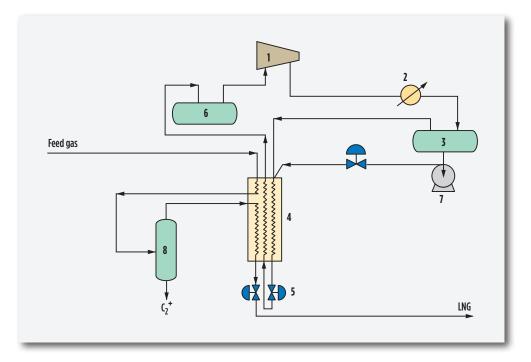
**Application:** Convert natural gas to liquefied natural gas (LNG) for transportation and/or storage using the PRICO<sup>®</sup> mixed-refrigerant (MR) process. Applications range from large baseload LNG units to peakshaving units and liquid fuels.

**Product:** LNG is produced at process pressure to be stored at -260°F and atmospheric pressure. Additional products, such as ethane, 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 cost-effective MR cycle. A single MR, 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 to 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. NGLs from the natural gas feed are separated (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 compression systems driven by gas turbines, steam turbines or electric motors.



**Installations:** 19 units in operation and nine under development. Capacities range from 4 MMscfd to 180 MMscfd for baseload, peakshaving and clean-fuel plants.

**References:** Hoffart, S. D., "Gas Supply Developments Using Distribusted LNG Concepts," Gastech, Amsterdam, March 2011.

Price, B. C., "Developing mid-scale LNG projects from a contractor's perspective," *Hydrocarbon Processing*, July 2008.

Hoffart, S. D., "Small-Scale LNG Facility Developments in China," GPA Annual Convention, Grapevine, Texas, March 2008.

Licensor: Black & Veatch Corp. CONTACT

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# **PRICO-NGL**<sup>™</sup>

**Application:** Recovery of ethylene/ethane and heavier components from various refinery offgas streams and from natural gas using the PRI-CO-NGL<sup>™</sup> mixed-refrigerant (MR) process.

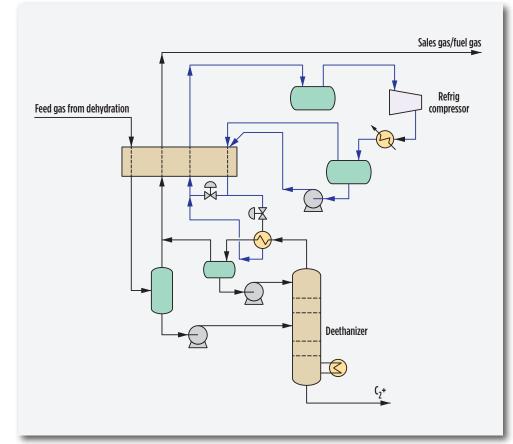
**Description:** The process is based on the well-proven and very reliable PRICO<sup>®</sup> MR cycle. A single MR composed of light hydrocarbons from methane through pentane is circulated in a closed-refrigerant loop. Proportions of individual refrigerant components are adjusted to match the processed gas and desired recovery level.

Dried hydrocarbon gas is chilled by cross-exchange and refrigerant to condense the desired components. These liquids are then fed to the deethanizer tower to remove light ends and produce a specification liquid product. The deethanizer overhead is partially condensed using a slipstream of cold refrigerant. Liquids are returned to the tower as reflux, and vapors are combined with the residue gas stream for sales or for use as fuel. The deethanizer bottoms stream contains the valuable ethylene/ ethane and heavier components that may be further processed, as required by conventional fractionation.

**Installation:** No commercial applications have been completed. The first unit is currently under design.

**Reference:** Currence, K. and R. Mortko, US Patent Application, "NGL Recovery from Natural Gas Using a Mixed Refrigerant."

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# **PURASPEC<sup>JM</sup>**

**Application:** PURASPEC<sup>JM</sup> processes remove low levels of sulfur and mercury from hydrocarbon gases and liquids to avoid corrosion of equipment and poisoning of catalysts, to meet pipeline specifications and to comply with environmental regulations.

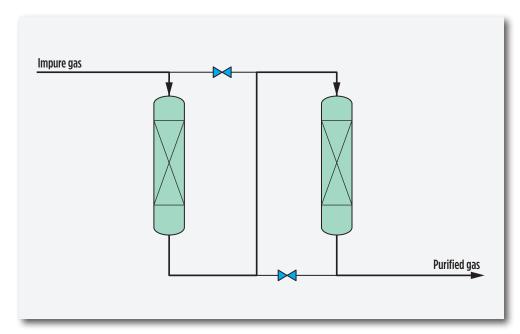
**Description:** Johnson Matthey Catalysts has more than 20 years of experience in purification solutions for the gas processing industry. The company offers PURASPEC processes, which are based on fixed beds of catalysts and chemical absorbents to remove traces of contaminants such as hydrogen sulfide ( $H_2S$ ) and mercury (Hg) from hydrocarbon gases and liquids.

There is no such thing as a standard PURASPEC process. The choice of absorbent and catalysts and the design of the reactor vessel will vary according to the type of feedstock, the level of contaminants, the pressure and temperature conditions and the pipeline or end-user purity specification.

The processes deliver a wide range of operating benefits:

- Low capital cost
- Impurity removal to very low levels
- Effective low-temperature operation
- Easy retrofit
- No feedstock losses
- High operating flexibility
- Proven reprocessing route
- Minimum operator involvement
- No releases to the environment.

PURASPEC uses absorbent fixed-bed technology to irreversibly react with the impurities to be removed. A typical lead-lag configuration is shown in the diagram. 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.



 $H_2S$  removal from natural and associated gas can achieve impurity levels as low as ppbv at the bed exit. In liquid duties (propane and LPG),  $H_2S$  is removed to meet copper strip 1A quality. Hg can be removed from natural gas to levels below 10 nanogram/Nm<sup>3</sup> (LNG quality). In liquid duties (propane, butane, naphtha), Hg can be removed down to < 1 ppbw.

**Operating conditions:** PURASPEC operates effectively over wide temperature and pressure ranges, from 20°F–400°F and from atmospheric to 2,000 psi, without any heat input required.

**Installations:** PURASPEC has been proven in over 250 installations worldwide, including offshore and onshore applications treating up to 2 billion scfd of natural gas and up to 5,000 tpd of NGLs for major oil and gas companies.

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# **PURASPEC<sup>JM</sup>,** cont.

**References:** Carnell, P. J., H. K. W. Joslin and P. R. Woodham, "Fixedbed processes provide flexibility for COS, H<sub>2</sub>S removal," *Oil & Gas Journal*, June 5, 1995.

Rhodes, E. F., P. J. Openshaw and P. J. H. Carnell, "Fixed-bed technology purifies rich gas with H<sub>2</sub>S, Hg," *Oil & Gas Journal*, May 31, 1999.

Carnell, P., V. Atma Row and R. Mansfield, "Minimising Mercury Emissions from Gas Processing and LNG Plants" *Hydrocarbon World*, 2007.

Carnell, P., V. Atma Row and R. Huang, "Reduction in mercury emissions from fossil fuels," International Conference on Mercury as a Global Pollutant, Guiyang, China, June 2009.

Atma Row, V. and M. Humphrys, "Minimising the effects of mercury on steel," GPA Europe Convention, Prague, Czech Republic, September 2011.

Licensor: Johnson Matthey Catalysts CONTACT

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## **PureMEG**

**Application:** PureMEG processes a lean, high-purity, salt-free monoethylene glycol (MEG) for reuse. The PureMEG reclamation and regeneration process is designed to deliver hydrocarbon-free and salt-free MEG for hydrate inhibition. The process reduces MEG losses by decreasing the MEG content in the disposed salt. Normally, up to 99.5% MEG recovery can be achieved.

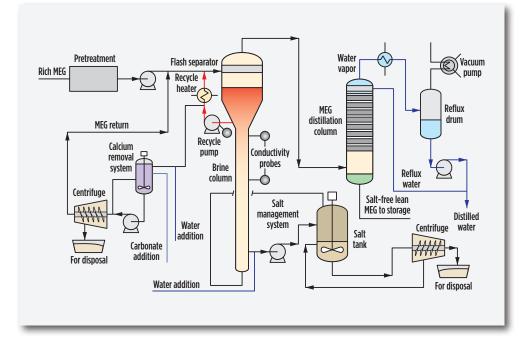
MEG is widely used by the oil and gas market in wellheads and pipelines as a hydrate suppressor to prevent hydrate formation at pipeline conditions. In offshore applications, such as deepwater gas production facilities, where the exposure to lower temperatures in subsea pipelines is common, MEG is typically used for hydrate inhibition. Hydrate inhibition is achieved by injecting MEG to decrease the hydrate formation temperature to below the operating temperature, thus preventing blockage of the pipeline by hydrates.

During the gas production process, lean glycol mixes with produced water from the formation. The production fluid—containing natural gas with associated condensate, produced water and the injected MEG—enters the production facility, where the fluids undergo phase separation. The produced fluids pass through a slug catcher and are then flashed in a three-phase production separator to separate gas, hydrocarbon liquids and the produced water and MEG mixture, which is commonly known as rich MEG. The produced gas and hydrocarbon liquids are routed onshore for sales and further processing. The rich MEG is regenerated by vacuum distillation.

**Description:** PureMEG technology has been designed to remove salts with reduced MEG losses, while also removing water to achieve the required outlet glycol purity.

The PureMEG process comprises of five sections:

1. **Pretreatment stage:** In the pretreatment stage, the rich MEG containing some dissolved gas and hydrocarbon liquids must pass



through a three-phase separator vessel. The gas is flashed, and recovered hydrocarbon liquids are sent to the production separator. The rich MEG is sent to the flash separator.

- 2. Flash separator: The rich MEG stream, comprising of produced water and MEG, is fed to the flash separator, where it is brought into contact with a hot recycle stream of MEG. The flash separator operates under vacuum. The MEG and water components of the rich MEG stream are flashed, and they exit through the top of the flash separator. They are then sent to the MEG distillation column for regeneration, while the salt components of the rich MEG stream precipitate in the flash separator.
- 3. **MEG regeneration:** The MEG regeneration section of the Pure-MEG process is a refluxed distillation column. The distillation col-

# PureMEG, cont.

umn also operates under vacuum and distills the water from the MEG water vapors coming off the top of the flash separator. Saltfree, lean MEG or PureMEG produced at the bottom of the distillation column is pumped to storage for reuse.

- 4. **Salt management:** The salt crystals that precipitate in the flash separator are separated by gravity to the bottom of the brine column, where they are transferred to the salt tank. There, the salts are concentrated before removal through a centrifuge. The salts in produced water cover a variety of species, but generally they are categorized into monovalent salts (typically, sodium and potassium) and divalent salts (typically, calcium and magnesium). The divalent salts cannot be effectively precipitated in the same manner as the monovalent salts, so a separate calcium-removal process is installed with the PureMEG process.
- 5. **Calcium removal:** Effective calcium control is accomplished as the divalent salts are collected, reacted and removed through a centrifuge, with the centrate overflow returning to the process.

PureMEG applies specialist know-how and patented design features. The key process differentiators are:

1. Reduced population of salt particles in recycle loops (patented)

- Solids content is reduced by approximately 80%–95% in the recycle circuit
- Lower particle content reduces erosion and fouling, resulting in reduced operating and maintenance costs
- 2. Removal of salt crystals
  - Salt particles that descend below the draw-off level settle at the bottom of the flash separator and enter the salt-removal system, where they are stripped of MEG

- Glycol-depleted waste salt can be disposed of directly into the sea, using either a batch or a continuous process, or they can be dried and disposed of as a cake
- Low overall MEG losses below 1 wt% in the waste salt are typically 10 times better than competing designs; PureMEG technology typically achieves full-stream reclamation.

**Economics:** PureMEG is economically favorable for offshore and onshore MEG reclamation, with fullstream or slipstream reclamation. Pure-MEG systems can be designed to reclaim and regenerate MEG and to produce lean MEG with as high as 99.5% purity. The process provides higher MEG recovery by separating reclaimed salt at atmospheric conditions, with minimal MEG losses.

**Installations:** More than 12 installations worldwide, including FPSOs, offshore platforms and onshore applications.

**Reference:** Nazzer, C. and J. Keogh, "Advanced designs of glycol reclamation plants," Offshore Technology Conference, May 2008, Houston, Texas.

Licensor: Cameron CONTACT

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# **Purisol**

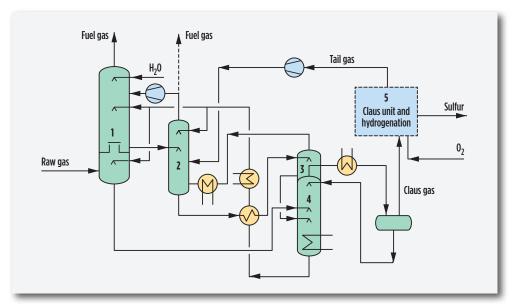
**Application:** Removal of acid gases from natural gas, fuel gas and syngas by physical absorption in NMP (N-methyl-pyrrolidone). Typical cases are:

- 1. High CO<sub>2</sub> contents to low residual level
- 2. Bulk acid gas removal to moderate purity by simple flash regeneration
- 3. Selective  $H_2S$  removal; this is ideally suited for an IGCC unit based on partial oxidation 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.

**Description:** Raw gas from a partial oxidation of heavy residue is cooled; HCN and organic sulfur compounds are removed in the 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 OxyClaus 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 <sub>2</sub>	43.12	43.36	
N <sub>2</sub> + Ar	1.49	2.31	
CO + CH <sub>4</sub>	45.9	45.95	
CO <sub>2</sub>	8.27	8.38	
$H_2S + COS$	1.20	< 50 ppm	
Flow, kmol/h	18,666.3	18,610.0	
Pressure, bar	52.0	49.5	
Utilities:			
Power (shaft) (withou	ut power recovery)	4,300 kW	

Power (shaft) (without power recovery)	4,300 kW
Steam, medium-pressure	20.6 tph
Water, cooling ( $\Delta$ t = 10°C)	1,650 m3/h
NMP vapor loss	2 kg/h
Demineralized water	2.2 tph

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## Purisol, cont.

Installations: Seven units in operation or under construction.

**Licensor:** Lurgi GmbH, Air Liquide Global E&C Solutions, Lurgi Technologies <u>CONTACT</u>

#### 2012 Gas Processes Handbook

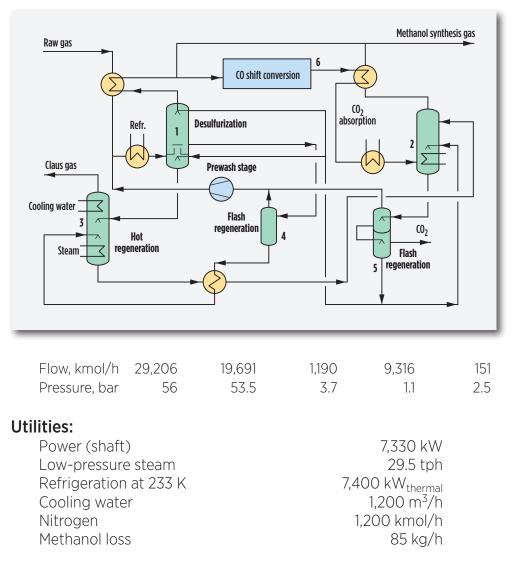
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## **Rectisol**

**Application:** Acid gas removal (AGR) using an organic solvent at low temperatures. In general, methanol is used for  $H_2S$ , COS and bulk CO<sub>2</sub> removal, whereby trace contaminants such as HCN, NH<sub>3</sub>, 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 CO<sub>2</sub> content down to the ppm range.

**Description:** Rectisol AGR for the selective removal of sulfur and CO<sub>2</sub> in the production of synthesis gas for methanol, ammonia, Fischer-Tropsch and syngas. Shifted raw gas is cooled, and trace contaminants are removed in prewash (1) followed by desulfurization (2), both using CO<sub>2</sub>-laden solvent. The final step in the upper section of the absorber is CO<sub>2</sub> removal. Coarse wash is performed with flash-regenerated methanol (5) down to 3%–5%, and further CO<sub>2</sub> removal to the required purity for the synthesis is accomplished with cold hot-regenerated methanol (7). A medium-pressure flash (4) for H<sub>2</sub>S and CO<sub>2</sub> methanol recovers co-absorbed H<sub>2</sub>/CO. H<sub>2</sub>S methanol is treated in a re-absorber for acid gas enrichment (6); i.e., low-pressure flash supported by N<sub>2</sub> stripping or vacuum flash. The CO<sub>2</sub> is free of sulfur and can be sequestered, used as product or vented to the atmosphere. The cold losses are made up by a conventional refrigeration unit. Methanol is injected into the raw gas to prevent icing, and the methanol/water condensate is separated in a methanol/water distillation column (not shown).

	Raw gas	Syngas	CO <sub>2</sub>	Vent gas	Claus gas
H <sub>2</sub>	43.42	64.38	0.17	0.01	-
N <sub>2</sub> + Ar	0.38	0.58	100 ppmv	12.64	0.97
$CO + CH_4$	22.33	32.93	1.90	0.15	_
CO <sub>2</sub>	33.43	2.20	97.87	85.70	50.82
$H_2S + COS$	0.25	< 0.1 ppmv	< 10 ppmv	< 10 ppmv	45.78



**Installations:** More than 100 units in operation or under construction.

**Licensor:** Lurgi GmbH, Air Liquide Global E&C Solutions, Lurgi Technologies <u>CONTACT</u>

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# **Resulf (Tail Gas Treating)**

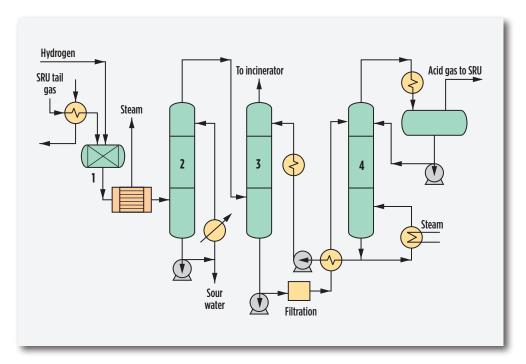
**Application:** Purification of sulfur recovery unit (SRU) tail gas for incineration. Resulf, Resulf-10 and Resulf-MM units are easily retrofitted to existing SRU complexes. They feature low unit pressure drop and can use the latest specialty solvents to lower energy consumption and maximize flexibility.

**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 and then mixed with a reducing gas containing  $H_2$ . The heated stream passes through the reactor (1), where the SO<sub>2</sub>, elemental sulfur and other sulfur-containing compounds, such as COS and CS<sub>2</sub>, are converted to  $H_2$ S. 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 methyl diethanolamine (MDEA) or formulated MDEA as a solvent. Resulf-10 units are designed using specialty amines such as formulated MDEA. Resulf-MM units use amines 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 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: Worldwide, CB&I has licensed and designed:

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

Supplier: CB&I CONTACT

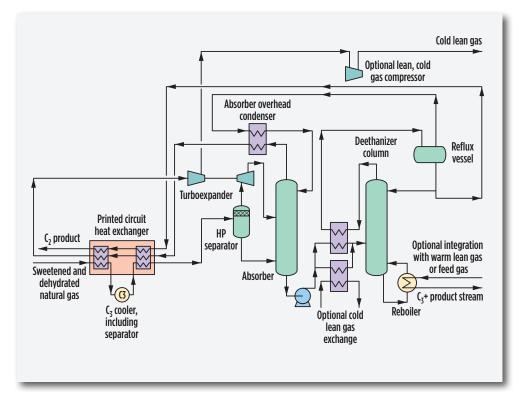
# Shell Absorber Extraction Scheme (SHAE)

**Application:** An advanced turboexpander technology scheme with efficient and advanced separation for optimum LPG extraction from natural gas. The scheme can be integrated with LNG facilities to enhance NGL recovery, and it can accept high CO<sub>2</sub> concentrations in the feed gas.

**Description:** The sweet and dehydrated natural gas feed, containing heavier hydrocarbon as well as  $CO_2$ , is precooled against the cold, lean gas from the NGL absorber and the liquid  $C_2$  stream from the deethanizer in the printed circuit heat exchanger. An optional, intermediate propane refrigerant cooling step can be added to cool the feed gas in a propane kettle, which is integrated into the propane refrigeration loop of the LNG facilities. Due to cooling of the feed gas, heavy hydrocarbon components drop out as liquid, resulting in a mixed phase exiting from the propane kettle. The condensed liquid is separated from the gas in the included separator. The gas from the separator is routed to a second pass of the printed circuit heat exchanger for further precooling against the cold, lean gas and liquid  $C_2$  product streams.

The mixed phase from the feed heat exchanger is separated in the HP separator. The separated gas is isentropically expanded in the turbo expander, and the mixed phase is fed to the NGL absorber column. Liquid from the HP separator is throttled across a valve and fed at the NGL absorber column bottom. The light gas generated due to throttling flows counter-current to the NGL liquid dropped from the expansion cooling. Due to the relatively warm operation of the NGL absorber, a considerable concentration of  $CO_2$  can be tolerated before freeze-out.

The absorber bottom liquid is pumped to the deethanizer, providing the condenser duty to the deethanizer column overhead condenser. Alternatively, the absorber bottom product can be cooled against the cold, lean gas. Depending on the fraction of heavy hydrocarbons



in the feed gas, both options can be optimized in operation to enhance recovery.

The deethanizer separates the  $C_2$  components from the  $C_3$ + NGLs. The deethanizer bottom reboiler boils off the  $C_2$  components from the  $C_3$ + NGLs to control the bottom specification. The condensed liquid in the overhead condenser is refluxed back to the deethanizer top tray to prevent  $C_3$ + components from escaping into the gas phase.

The non-condensed vapor from the deethanizer overhead accumulator is cooled and partially condensed against the absorber cold, lean gas stream, to provide reflux to the NGL absorber.

# Shell Absorber Extraction Scheme (SHAE), cont.

Lean gas leaving the feed gas printed circuit heat exchanger is recompressed in the turboexpander recompressor. Depending on the required downstream pressure, an additional compression step can be added.

**Operating conditions:** The SHAE NGL recovery scheme is preferably applied to feed gas with:

- Inlet pressure in the range of 40-90 bar
- Inlet temperature between 20°C and 50°C
- Considerable concentrations of heavier hydrocarbons with high recovery requirements
- A very low higher-heating value of LNG.

Propane recovery is greater than 99%, while ethane recovery is greater than 85%.

#### Advantages:

- Robust scheme that offers excellent performance over a wide feed gas composition range
- Integrated design with downstream LNG units
- Upstream removal does not require deep treating due to  $\mbox{CO}_2$  tolerance
- Integration, both internally in the scheme and externally with the LNG scheme, provides an energy-efficient scheme, while maintaining excellent  $C_2$  and  $C_3$ + recovery.
- Application of Shell proprietary internals reduces equipment size, enhancing the scheme economics.

**Installations:** FEED phase.

References: US Patent No. WO2007116050

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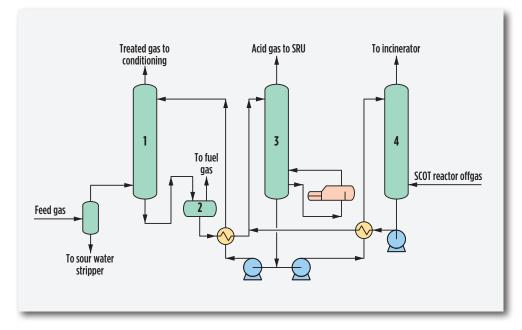
# Shell ADIP processes for gas treating (ADIP and ADIP-X)

**Application:** This regenerative-amine process is suitable for bulk and deep removal of hydrogen sulfide ( $H_2S$ ) and COS from natural gas, refinery gases, synthesis gas and other gases, with the main application area being for gases with no requirement for organic sulfur components removal. Carbon dioxide (CO<sub>2</sub>) can either be removed or slipped, when selective removal of  $H_2S$  is desired. Currently, two processes are offered: selective ADIP in the ADIP/Claus/SCOT process sequence combining upstream selective  $H_2S$  removal with the SCOT process treating for the Claus offgas, and the accelerated ADIP-X for bulk or deep removal of CO<sub>2</sub>,  $H_2S$  and COS.

**Description:** The ADIP process uses an aqueous solution of the secondary amine, diisopropanol amine (DIPA), or tertiary amine, methyl diethanolamine (MDEA). The ADIP-X process also uses a piperazine additive which is a process accelerator used in state-of-the-art processes. Amine concentrations of up to 50 wt% are typically employed, but the exact solvent formulation is tailored for individual customer requirements. The lineup of an ADIP process can be very diverse, depending on optimization requirements.

Common regeneration (as illustrated in the figure) for separate amine absorbers is often applied and may consist of one or more flash/steam stripping regeneration steps. In this case, co-absorbed hydrocarbons from the absorber (1) are flashed (2) from the solvent and can be used as fuel gas. Loaded solvent from the absorber (1) and the SCOT absorber (4) is mixed and sent to the common regenerator (3). Lean solvent from the regenerator is split and sent to both absorbers.

**Operating conditions:** Plants have been built with a wide range of contaminant concentrations, in climates ranging from desert to arctic, with



wide flexibility in the feed gas pressure and temperature as well as solvent temperature.  $H_2S$  specification down to 1 ppm can be achieved as well as  $CO_2$  specification of 50 ppm. In certain cases, for both  $H_2S$  and  $CO_2$  removal, lower specifications can be guaranteed. COS removal rates of 99% can be achieved with ADIP-X. With selective ADIP, required Claus feed gas quality can be met by improving the  $H_2S/CO_2$  ratio.

#### Advantages:

- No solvent reclaiming needed
- Very low hydrocarbon co-absorption
- Solvent chemicals can be sourced from the open market
- Higher solvent loading capacity and smaller equipment required compared to general amine processes, leading to good process economics and energy efficiency when using the ADIP-X process

# Shell ADIP processes for gas treating (ADIP and ADIP-X), cont.

• Easily integrated with other Shell technologies to enable an overall process guarantee for the entire treating complex.

**Installations:** More than 400 ADIP units in operation or under construction worldwide in natural gas/LNG plants, refineries and chemical plants. Reference plants treat feed gas compositions up to 25 mol%  $H_2S$  and up to 50 mol%  $CO_2$ .

**References:** "ADIP as the preferred solvent for amine treatment in refinery applications," Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, February 1999.

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

"CO<sub>2</sub> removal from natural gas: accelerated process selection," GPA Annual Convention, New Orleans, Louisiana, March 2004.

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

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# Shell ADIP processes for liquid treating

**Application:** This regenerative-amine process is suitable for deep removal of hydrogen sulfide ( $H_2S$ ), carbon dioxide ( $CO_2$ ) and COS from LPG or NGLs.

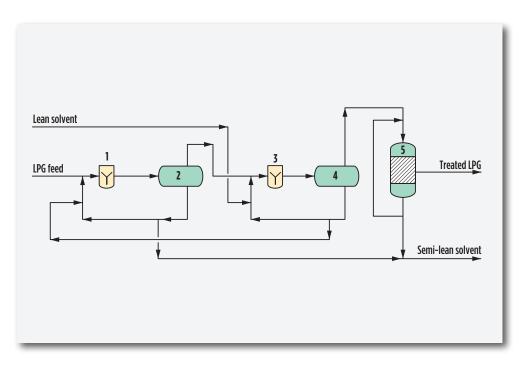
**Description:** The ADIP processes use an aqueous solution of the secondary amine, diisopropanol amine (DIPA). Amine concentrations of up to 50 wt% are typically employed, but the exact solvent formulation is tailored for individual customer requirements. The lineup of an ADIP process can be very diverse, depending on optimization requirements.

A mixer-settler lineup for COS removal from LPG is shown in the diagram. LPG feed is sent through a two-stage mixer-settler setup, (1, 2) and (3, 4), before being sent to the coalescer (5), from which treated LPG is produced.

**Operating conditions:** Plants have been built with a wide range of contaminant concentrations, in climates ranging from desert to arctic, with wide flexibility in feed gas pressure and temperature as well as solvent temperature. An  $H_2S$  specification of 10 ppmwt can be achieved, along with a COS specification of 5 ppmwt. For both  $H_2S$  and COS removal, lower specifications are possible in certain cases.

#### Advantages:

- Very low hydrocarbon co-absorption
- No chemical waste generated
- Solvent chemicals can be sourced from the open market
- Easily integrated with other Shell technologies to enable an overall process guarantee for the entire treating complex.



**Installations:** More than 30 ADIP units for liquid treating in operation or under construction worldwide in natural gas/LNG plants, refineries and chemical plants.

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# Shell Claus Offgas Treating (SCOT)

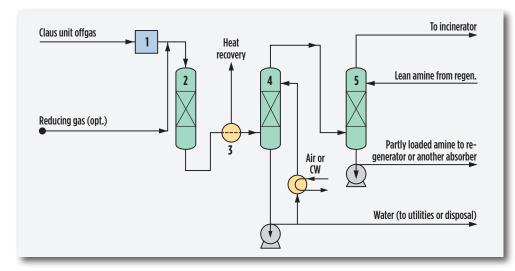
**Application:** The SCOT process is used extensively to clean up Claus sulfur recovery plant tail gas streams to meet environmental requirements where the overall sulfur recovery must exceed 99.8%. The process is insensitive to variations in the upstream SRU, such as in the  $H_2S/SO_2$  ratio, hydrocarbon or ammonia breakthrough.

**Description:** The Claus tail gas feed to the SCOT unit is heated to 220°C-280°C using an inline burner or a heat exchanger (1) with optionally added H<sub>2</sub> or a mixture of H<sub>2</sub>/CO. If reducing gas, H<sub>2</sub> 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, SO<sub>2</sub>, elemental sulfur, COS and CS<sub>2</sub> are converted to H<sub>2</sub>S. The gas is cooled to 40°C in an optional heat-recovery system (3) and a water-quench tower (4), followed by selective H<sub>2</sub>S removal in an amine absorber (5) to 30–100 ppmv H<sub>2</sub>S. The semi-loaded amine is often further loaded in another absorber. The H<sub>2</sub>S 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.

With a standard SCOT unit, overall sulfur recovery efficiency can be maximized to 99.9%, although the standard process can be enhanced to meet more stringent environmental requirements. This enhanced version of the process, known as low-sulfur SCOT, can achieve an  $H_2S$  specification in the SCOT vent gas of less than 10 ppm.

**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%. If required, this can be improved, and an overall sulfur recovery efficiency of 99.95% can be guaranteed.



For new installations, the design of a SCOT unit based on a reactor inlet temperature of 220°C or lower enables the use of a saturated high-pressure steam reheater (1) rather than a superheated steam heater, which results in a less complex system for operations and maintenance. This version of the process is known as the low-temperature SCOT process.

**References:** van den Brand, K., "Shell's low-cost SCOT process," Sulfur Recovery Symposium, Vail, Colorado, September 2002.

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

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

Ito, E., Y. Mirfendereski, K. van den Brand, D. Valenzuela, R. Olgers and K. Smit, "Lower SO<sub>2</sub> Emissions and Energy Requirement by Implementing Process Improvement by Better Understanding of LT SCOT Process and Sulphur Degasser Chemistry," Laurence Reid Gas Conditioning Conference, Norman, Oklahoma, February 2010.

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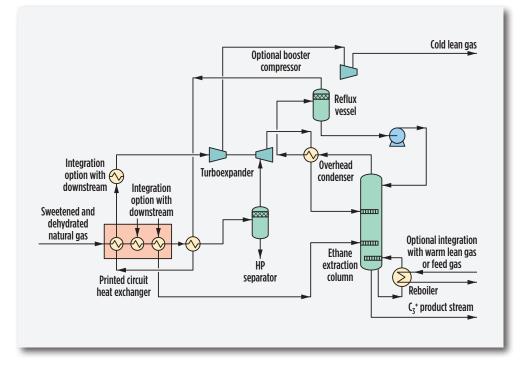
# Shell Deep LPG Recovery Scheme (SHDL)

**Application:** An advanced, turboexpander-based LPG-extraction scheme, designed to efficiently extract LPG from natural gas. The scheme can be optimized further by utilizing available downstream (e.g. LNG) refrigeration duty to enhance LPG recovery.

**Description:** The sweet and dehydrated natural gas feed stream is first cooled in a printed circuit heat exchanger by heat exchange against the cold, lean, treated gas and the flashed liquid from the high-pressure (HP) separator. External refrigerant—e.g. surplus propane from downstream LNG facilities—can also be exchanged against the feed to enhance feed cooling. The cold feed stream is separated in an HP separator. The HP separator overhead vapor is passed through an expander, where the stream is cooled and partially condensed before being fed to the middle of the deethanizer column. The liquid from the HP separator is expanded through a JT valve, exchanged in the printed circuit heat exchanger, and then fed to the deethanizer column bottom. The deethanizer overhead is partially condensed against the middle column feed to provide deethanizer reflux. Cold from the non-condensed deethanizer overheads is recovered by heat exchange against the warm feed stream. The warm, lean gas is then recompressed in the expander recompressor and sent to the downstream unit.

Depending on the required downstream pressure, an additional compression step can be added. Deethanizer column bottoms are partially boiled in a reboiler to generate column-stripping gas, while the remaining liquids, consisting of predominantly LPG and heavier components, are sent to fractionation for further separation.

**Operating conditions:** The application area is preferably in the range of an inlet pressure of natural gas > 60 bar and an inlet temperature between 20°C and 50°C. Considerable concentrations of  $CO_2$  can be toler-



ated (up to 5% mol). The ethane minus/LPG fraction is preferably in the 5–40 molar range. The propane recovery is larger than 99%.

#### Advantages:

- Robust scheme that offers excellent performance over a wide operating envelope (multiple upstream reservoirs, declining well pressures and varying reservoir composition)
- Upstream removal does not require deep treating due to tolerance for  $\mbox{CO}_2$
- Integration, both internally in the schemes and externally with the downstream units, provides an energy-efficient scheme while maintaining an excellent  $C_3$ + recovery

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# Shell Deep LPG Recovery Scheme (SHDL), cont.

- Application of Shell proprietary internals reduces equipment size, enhancing the scheme economics.
- Installations: FEED phase.
- References: US Patent No. WO2007110331
- Licensor: Shell Global Solutions B.V. CONTACT

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# **Shell HCN/COS Hydrolysis**

**Application:** The catalytic conversion of hydrogen cyanide (HCN) and carbonyl sulfide (COS) is a cost-effective process for reducing the harmful effects of these components in gas streams and allowing for their effective removal after conversion. This hydrolysis technology has two main fields of application: Synthesis gas (syngas) treatment upstream of an amine unit for coal or oil gasification processes, and syngas treatment where the presence of HCN or COS is unacceptable to downstream processing units, such as in GTL processes.

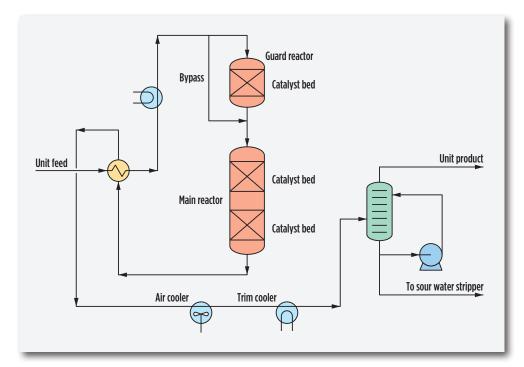
**Description:** HCN and COS in syngas are converted in a fixed-bed reactor filled with a catalyst system, shown below:

 $\begin{array}{l} \mathsf{HCN} + \mathsf{H}_2\mathsf{O} \iff \mathsf{NH}_3 + \mathsf{CO} \\ \mathsf{COS} + \mathsf{H}_2\mathsf{O} \iff \mathsf{H}_2\mathsf{S} + \mathsf{CO}_2 \end{array}$ 

The syngas is fed to the guard reactor, where partial conversion of HCN and COS takes place. The guard reactor's primary functions are to collect soot and debris on top of the bed and to protect the main reactor, where full conversion of HCN and COS occurs.

After passing through the catalyst beds, the syngas is cooled and the water is knocked out. Most of the ammonia ( $NH_3$ ), traces of formate, and some of the carbon dioxide ( $CO_2$ ) and hydrogen sulfide ( $H_2S$ ) will dissolve in the knocked-out water, which is then typically routed to a sour water stripper or other water-treating facility.

**Advantages:** The process enables more selective solvent use for removal of  $H_2S$  in the downstream amine unit. It also can help reduce solvent degradation in the downstream amine process. The process is effective,



with a typical HCN specification of  $\leq$  1–5 ppmv and a typical COS specification of  $\leq$  10 ppmv on a dry basis.

**Installations:** Two units are in operation (NUON IGCC in the Netherlands and Eni S.p.A.'s refinery in Sannazzaro, Italy), and two units are in the design phase.

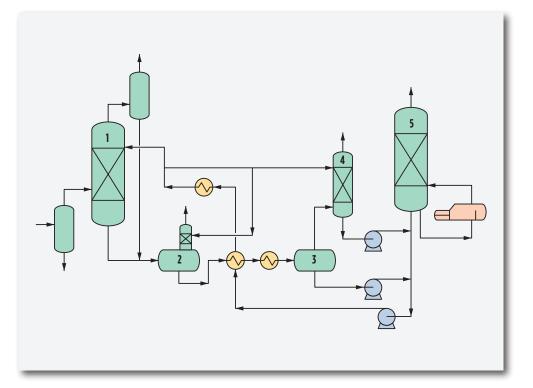
**Licensor:** Shell Global Solutions B.V. Catalysts can be sourced from CRI/Criterion Inc., the global catalyst technology company of Shell Group <u>CONTACT</u>

# Shell Sulfinol processes (Sulfinol-M, Sulfinol-D and Sulfinol-X)

**Application:** This regenerative-hybrid amine process is suitable for bulk and deep removal of hydrogen sulfide (H<sub>2</sub>S), carbonyl sulfide (COS), mercaptans and organic sulfides from natural gas, refinery gases, synthesis gas and other gases. Carbon dioxide (CO<sub>2</sub>) can either be removed or slipped. There are currently three processes offered: Sulfinol-M, when selective H<sub>2</sub>S removal is needed or for bulk H<sub>2</sub>S and CO<sub>2</sub> removal; Sulfinol-D; and the patented Sulfinol-X technology for bulk or deep removal of CO<sub>2</sub>, H<sub>2</sub>S and COS. In all three processes, deep removal of mercaptans, COS and other sulfur species is possible, depending on the operating conditions.

**Description:** The Sulfinol-M and Sulfinol-X processes use a hybrid solution of the tertiary amine, methyl diethanolamine (MDEA), and sulfolane. Sulfinol-X contains a piperazine additive, which is used as a process accelerator in state-of-the-art processes. The Sulfinol-D process uses a hybrid solution of the secondary amine diisopropanolamine (DIPA), and sulfolane. The solvent formulations can be tailored for individual customer requirements. Unlike Sulfinol-D (a first-generation Sulfinol process), Sulfinol-M and Sulfinol-X (which are second-generation Sulfinol processes) do not form oxazolidinones, thereby eliminating the need to remove oxazolidinones by reclaiming.

Various process lineups are available. A patented, highly selective configuration is shown in the diagram. Loaded acid gas from the acid gas absorber (1) is routed to a flash vessel (2) for flashing of hydrocarbons; it is heated up and sent to the hot flash (3). Flashed  $CO_2$  gas is sent to the selective enrichment absorber (4) to remove the remaining  $H_2S$ , and the loaded solvent is then combined with the loaded solvent from the hot flash and sent to the regenerator (5). This allows for considerably higher acid gas enrichment compared with traditional pro-



cesses. Also, total sulfur recovery is enhanced due to additional mercaptan removal in the enrichment unit.

**Economics:** The Sulfinol processes employ a hybrid solvent that allows for some co-absorption of heavier hydrocarbons. Several process features have been integrated to minimize this co-absorption. Depending on the process requirements, either deep or partial removal of mercaptans may be achieved in the Sulfinol unit, while the rest is removed with molecular sieves. The regeneration gas from the molecular sieve unit is then returned to the Sulfinol unit, requiring no separate solvent system for the regeneration gas of the molecular sieve unit.

# Shell Sulfinol processes (Sulfinol-M, Sulfinol-D and Sulfinol-X), cont.

#### Advantages:

- Treating of highly contaminated gases to very low sulfur specifications is possible
- Additional downstream polishing units can be avoided for NGL plants
- Solvent reclaiming is not needed for Sulfinol-M and Sulfinol-X
- Low solvent-foaming tendency in the presence of heavy hydrocarbons
- Solvent chemicals can be sourced from the open market
- Sulfinol-M is highly selective compared to traditional amines, so it can also be used in TGTU (SCOT) applications and for acid gas enrichment
- In sour gas facilities and syngas facilities, Sulfinol-M can often serve as a single-solvent solution for meeting all specifications and SO<sub>2</sub> emissions limits
- Sulfinol-X and Sulfinol-D can be used to achieve low CO<sub>2</sub> specifications for LNG applications (< 50 ppm mol)
- Sulfinol-X has a higher solvent-loading capacity and lower specific energy consumption compared to the first-generation Sulfinol-D process, thus providing an excellent choice for debottlenecking existing Sulfinol-D units.

**Installations:** More than 220 Sulfinol units are in operation or under construction worldwide in natural gas/LNG plants, refineries and chemical plants. Reference plants have capacities of up to 700,000 sfcd and feed gas compositions of up to 15 mol%  $H_2S$  and up to 33 mol%  $CO_2$ .

**References:** "Best practice for deep-treating sour natural gases (to LNG and GTL)," Gastech, Bilbao, Spain, March 2005.

"Sulfinol-X—Leveraging the advantages of well-proven and established technologies in a single acid gas-removal process," GPA Convention, San Antonio, Texas, March 2009.

Van Son, M. and D. L. Nikolic, "Solutions for lean gas applications (case study of Wasit)."

Licensor: Shell Global Solutions B.V. CONTACT

## **Shell Sulfur Degassing Process**

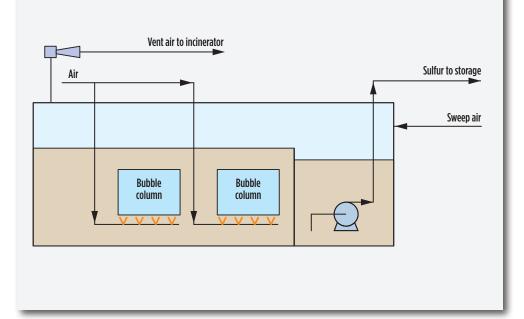
**Application:** To remove dissolved hydrogen sulfide ( $H_2S$ ) and  $H_2S_x$  from liquid sulfur coming from Claus units. Liquid sulfur from Claus units contains approximately 300 ppmw dissolved  $H_2S$  and  $H_2S_x$ . To meet environmental and safety restrictions, the liquid sulfur should be degassed so that less than 10 ppmw  $H_2S$  remains.

**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 gases 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 200 Shell sulfur degassing units in operation, with capacities ranging from 3 tpd-4,000 tpd of sulfur.

**References:** Ito, E., Y. Mirfendereski, K. van den Brand, D. Valenzuela, R. Olgers and K. Smit, "Lower SO<sub>2</sub> Emissions and Energy Requirement



by Implementing Process Improvement by Better Understanding of LT SCOT Process and Sulphur Degasser Chemistry," Laurence Reid Gas Conditioning Conference, Norman, Oklahoma, February 2010.

**Licensors:** Shell Global Solutions B.V. and Jacobs Nederland B.V. CONTACT

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# Shell Sulfur Degassing Process with vent gas recycle option

**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.

When the degasser is placed inside a vessel, it optionally may be operated at elevated pressure (0.5–1.5 barg, typically 1 barg). Then the vent gases can be conveniently recycled to the sulfur recovery plant (Claus furnace).

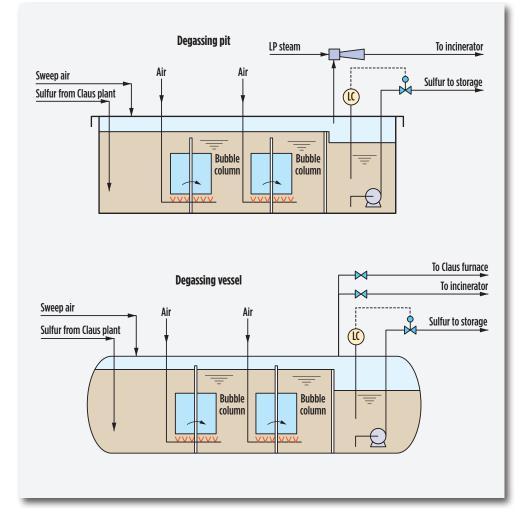
**Description:** Sulfur from the Claus unit is run into either a concrete sulfur pit or a steel vessel. It is then circulated over a stripping (bubble) column by bubbling air through the sulfur. By agitating the sulfur in this way,  $H_2S$  is released. Sweep air is passed over the top of the sulfur to remove released  $H_2S$ . The vent gases are usually sent to an incinerator via an ejector.

In a variation of the process that is operated in a vessel, the degasser may be pressurized to 1 barg outlet pressure. In this way the vent gases have enough pressure to be recycled to the sulfur recovery plant. The degassed sulfur is then pumped into storage.

The major advantage of 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 low, as no catalyst is required.

**Installations:** There are more than 350 Shell sulfur degassing units in operation, with capacities ranging from 5 tpd to 4,000 tpd of sulfur.



Several units operating at elevated pressure have been designed, and first operation is expected in 2013.

**Licensor:** Shell Global Solutions B.V. and Jacobs Comprimo Sulfur Solutions, a member of Jacobs Engineering Group **CONTACT** 

# Small to Mid-Scale LNG (LIMUM)

**Application:** Small- and mid-scale LNG plants are used primarily to meet local or regional energy requirements. Linde specializes in providing pre-engineered solutions adjusted for each customer's individual requirements, offering a full range of liquefaction technologies, including its most recent standardized LNG plant concept, StarLNG<sup>™</sup>.

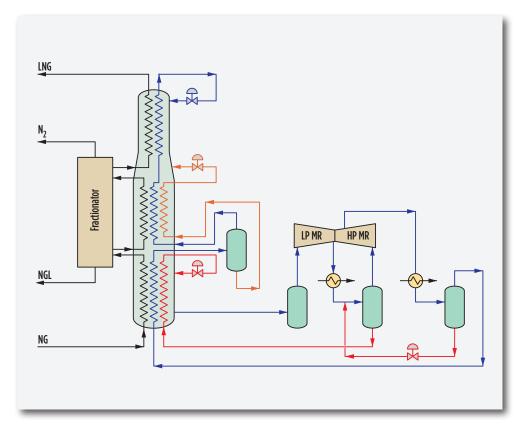
**Description:** StarLNG<sup>™</sup> is a standardized, optimized, small- to mid-scale LNG plant based on a wide set of process variations. This "process toolbox" is designed to cover about 90% of real-life boundary conditions, with the following major benefits:

- Safety features comparable to world-scale LNG
- Fast-tracked EPC time schedule
- Reduction of CAPEX
- Highly efficient and easy-to-operate LIMUM process
- Modularized units for pretreatment, process and main pipe racks
- Toolbox concept with many options.

StarLNG<sup>™</sup> delivers a generic LNG plant design for a 200-tpd (net liquefaction capacity) base case and many alternatives, with pre-engineered documents including a 3D CAD model for a fully modularized plant. StarLNG<sup>™</sup> combines superb safety, reliability, ease of operations and efficiency with competitive prices and a short execution schedule.

The technology has been developed for an LNG capacity range between 100 tpd and 3,000 tpd. The same pre-engineered plant design concept can be used for the above range with a simple adjustment to the actual throughput. For the liquefaction, two proprietary designs (PFHE and CWHE) are available for the main cryogenic heat exchanger. Design selection is based on plant capacity and operational requirements.

**Economics:** The core liquefaction process can be amended by the full range of pretreatment (sour gas and mercury removal, dehydra-



tion) and fractionation facilities (condensate and NGL recovery and nitrogen rejection).

**Installations:** Three in China, two in Norway and one in Australia.

References: US Patent No. 6,334,334

Licensor: The Linde Group CONTACT

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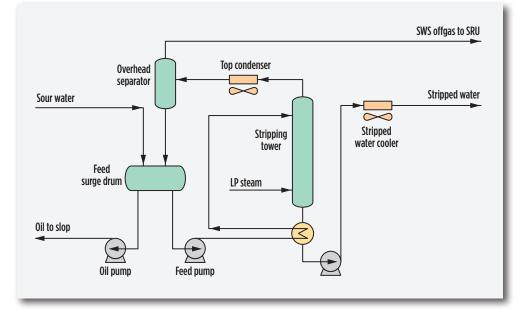
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## Sour water stripper (SWS)

**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 SWSs are designed for feed concentrations 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 2.0, and averages about 1.2. pH is commonly from 7.0 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.

**Description:** SWSs contain 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 unit (i.e., sulfur plant) size and cost. Steam is the most commonly used stripping medium, but flue gas, fuel gas and natural gas also can 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.



**Installations:** More than 30 SWS plants have been constructed globally, with capacities ranging from 1.5 m<sup>3</sup>/h up to 120 m<sup>3</sup>/h. Siirtec Nigi has provided SWS plants to Eni S.p.A., Galp Energia, MOL, IRASCO/IRITEC and others for refineries, gas fields and power facilites.

Contributor: Siirtec Nigi S.p.A. CONTACT

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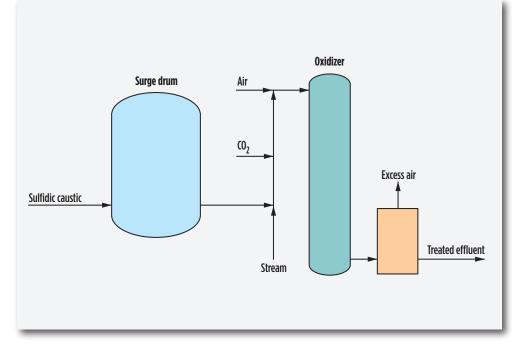
## Spent Caustic Waste Stream Treating

**Application:** Technology to treat spent sulfidic caustic waste streams from gas and LPG-extraction Merox units, and any other  $H_2S$  caustic scrubbers for disposal onsite.

**Product:** A neutral-pH effluent with reduced biological oxygen demand (BOD) and chemical oxygen demand (COD) characteristics that can be sent for further processing within the refinery water treatment facility.

**Description:** Caustic management as well as effluent treating and disposal are areas of growing interest and concern. Spent caustic disposal costs, especially those incurred by waste hauling, are expected to continue to increase. Unfortunately, the excessive pH, BOD and COD of sulfidic caustic can often prohibit direct reuse in process and/or easy disposal.

The process provides a cost-effective solution for refiners to manage disposal of sulfidic caustic streams within the refinery battery limits. The final product has a near-neutral pH, and its COD is reduced by 50% compared to the feed prior to dilution, thus making it easier to handle in downstream treatment facilities.



Installations: Technology has been installed at four refining sites.

Licensor: UOP LLC, a Honeywell Company CONTACT

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# SRU

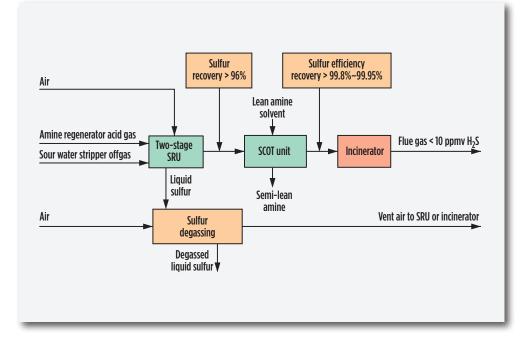
**Application:** To recover liquid sulfur from hydrogen sulfide (H<sub>2</sub>S)-containing gases, such as acid gas from gas sweetening units, acid gas from sour water strippers or offgas from sulfur degassing facilities.

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

The Claus unit is designed to convert  $H_2S$  to sulfur, and the design can be optimized to maximize sulfur recovery. The sulfur complexes, even with  $NH_3$  in the feed, can typically run for three to four years without a maintenance shutdown. The Claus tail gas is routed to a SCOT unit, where the sulfur components are recovered (see "SCOT" for more details).

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 a catalyst, which improves safety during liquid sulfur handling. Offgas from the sulfur stripper can be routed to the Claus unit or to an incinerator.

The incinerator downstream of the Claus/SCOT unit is designed so 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 (SO<sub>2</sub>). 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 catalyst, can be applied if there is the need to take fuel gas consumption into account. The fuel consumption of a catalytic incinerator is considerably lower than that of a thermal incinerator.



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

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

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

Licensor: Shell Global Solutions B.V. CONTACT

## **STAR process (dehydrogenation of light paraffins to olefins)**

**Application:** The Thyssenkrupp Uhde Steam Active Reforming (STAR) process produces (a) propylene as feedstock for polypropylene, propylene oxide, cumene, acrylonitrile or other propylene derivatives, and (b) butylenes as feedstock for methyl tertiary butyl ether (MTBE), alkylate, octanes, polybutylenes, methacrylate (MMA) or other butylene derivatives.

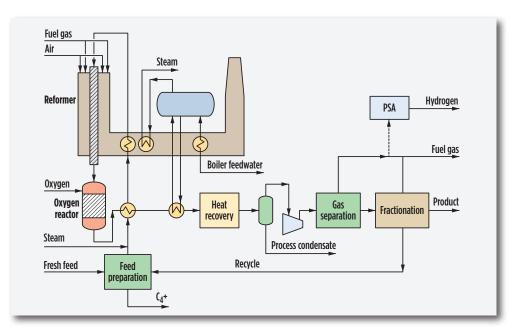
Feed: LPG from gas fields, gas condensate fields and refineries.

**Product:** Propylene (polymer- or chemical-grade), isobutylene and n-butylenes. High-purity hydrogen (H<sub>2</sub>) 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 (Thyssenkrupp Uhde reformer) connected in series with an adiabatic fixed-bed oxyreactor (secondary reformer type). In the reformer, the endothermic dehydrogenation reaction takes place over a proprietary, noble metal catalyst.

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

The reformer is top-fired. Heat recovery utilizes process heat for steam generation, for feed preheat and for heat required in the fractionation section.



After cooling and condensate separation, the product is subsequently compressed, light ends are separated, and the olefin product is separated from unconverted paraffins in the fractionation section.

Apart from light ends, which are internally used as fuel gas, the olefin is the only product. High-purity  $H_2$  may be optionally 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	1,160
Fuel gas, GJ/metric ton	2.4
Circulating cooling water, m <sup>3</sup> /metric ton	45
Electrical energy, kWh/metric ton	130
Steam, ton/metric ton	3.5

Continued **V** 

# STAR process (dehydrogenation of light paraffins to olefins), cont.

**Commercial plants:** The STAR process is being successfully applied in the EPP PDH/PP complex at Port Said for production of 350 ktpy of PP. Futhermore, it has been selected or licensed for a total capacity of 1,500 ktpy of PP to start up between 2014 and 2016.

**References:** Heinritz-Adrian, M., "The EPP PDH-PP Project—Uhde's STAR process for oxydehydrogenation," International Petrochemicals Strategy and Technology Conference, Madrid, Spain, February 2010.

Heinritz-Adian, M., S. Wenzel and I. Youssef, "Advanced propane dehydrogenation," *Petroleum Technology Quarterly,* Q1 2008.

Heinritz-Adrian, M., "STAR Process—Advanced propane dehydrogenation for on-purpose propylene production," Mideast Olefins and Polyolefins Conference, Dubai, November 2007.

Licensor: Thyssenkrupp Uhde GmbH CONTACT

# Substitute natural gas (SNG)

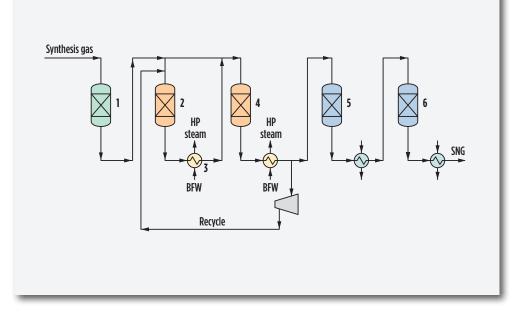
**Application:** To produce substitute natural gas (SNG) from purified synthesis gas produced by coal gasification or coke oven gas sources using shift and methanation reactions.

**Description:** The synthesis gas is fed to a sulfur guard vessel (1) to remove residual catalyst poisons, and it is then split into two parts. Part of the feed is mixed with the recycle gas and passed to the first bulk methanator (2), where shift and methanation reactions take place to produce a methane-rich product in an exothermic reaction. Product from the first bulk methanator is cooled by producing high-pressure (HP) steam (3), and it is then mixed with the remaining feed gas. The gas mixture is passed to the second bulk methanator (4). After cooling to raise additional HP steam, the product stream from the reactor (4) is split, with part providing recycle gas to the first bulk methanator and the remainder passing to the trim methanation stages (5) and (6).

The number of trim methanation stages required depends on the final product specifications. Generally, two trim methanation stages are sufficient to produce a high-methane, pipeline-quality gas.

#### **Economics:**

Steam production Power consumption Feedstock 2 ton/1,000  $\rm Nm^3$  15 kW/1,000  $\rm Nm^3$  Stoichiometric or non-stoichiometric conversion of H\_2 and CO to CH\_4



**Commercial plants:** In the 1960s, over 40 town gas and SNG plants were built in the UK based on naphtha feedstocks. More recently, there has been renewed interest, and seven coal and coke oven gas-based plants have been licensed with a capacity of 7.3 billion Nm<sup>3</sup>/yr of SNG production.

Licensor: Davy Process Technology Ltd. CONTACT

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# **SulFerox**

**Application:** Removal of hydrogen sulfide ( $H_2S$ ) from a large range of gas streams, giving a sulfur production of 0.1–20.0 tpd. Gas applications include natural gas, amine tail gas, enhanced oil recovery CO<sub>2</sub> 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% ppmv 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 Nm<sup>3</sup>/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 fertilizer.

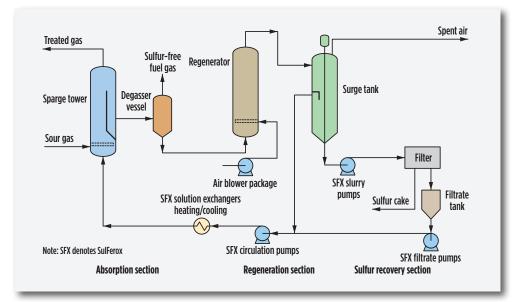
**Description:** SulFerox is a redox-based process that converts the hydrogen sulfide  $(H_2S)$  in sour gas to elemental sulfur through reaction with aqueous ferric iron. The process forms solid sulfur particles that are easily filtered out.

There are three steps in the process: absorption, regeneration and sulfur recovery. During absorption, the sour gas stream comes into contact with a liquid containing soluble iron, and  $H_2S$  is selectively oxidized to form elemental sulfur.

Regeneration involves re-oxidation of the iron to maintain a supply of active iron. To maximize sulfur recovery, the elemental sulfur formed in the first reaction is concentrated in a surge tank and then filtered out. The filtrate is returned to the process for maximum ferric iron solution recovery.

In most cases, filtration and melting produce yellow sulfur of a quality comparable to that of conventional Claus unit sulfur.

**Operating conditions:** Operating pressures vary from just over atmospheric to 28 barg. The SulFerox process itself operates at tempera-



tures of  $43^{\circ}C-60^{\circ}C$ . However, the feed gas temperature can be between  $24^{\circ}C-54^{\circ}C$ . 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 NH<sub>3</sub>, HCN and SO<sub>2</sub>, might affect the economics of the process.

**Installations:** 30 units in operation.

**References:** Smit, C. J. and E. C. Heyman, "Present status SulFerox process," Process GRI Sulfur Recovery Conference, 9th meeting, San Antonio, Texas, October 1999.

Oostwouder, S. P., "SulFerox process update," Process GRI Sulfur Recovery Conference, 8th meeting, Austin, Texas, October 1997.

Licensor: Shell Global Solutions B.V. CONTACT

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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%–99.9%. Different versions of the SULFREEN process are available.

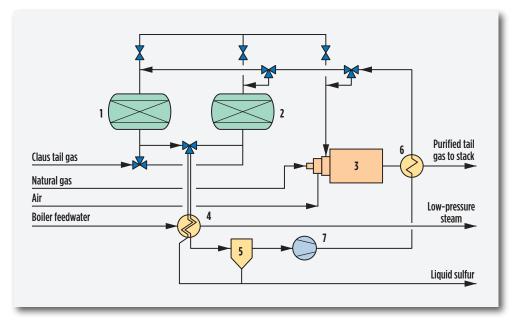
**Description:** The SULFREEN process is based on the well-known Claus reaction in which the components— $H_2S$  and  $SO_2$  in tail gas—are catalytically converted into elemental sulfur. The process occurs in the gas phase; the operating conditions being those at which the tail gas leaves the upstream 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  $120^{\circ}$ C-140°C passes through one of the two reactors (1) (2), where most of the H<sub>2</sub>S and SO<sub>2</sub> are converted into elemental sulfur and adsorbed on the catalyst.

The sulfur-laden catalyst is regenerated 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.



**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 80 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," SULPHUR Conference, Tampa, Florida, November 1994.

Licensor: Lurgi GmbH, Air Liquide Global E&C Solutions, Lurgi Technologies <u>CONTACT</u>

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# **Sulfur Degassing**

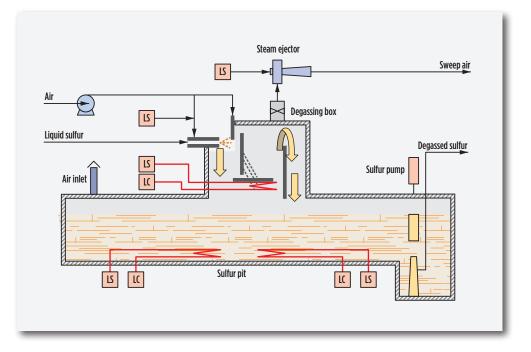
**Application:** Remove hydrogen sulfide ( $H_2S$ ) and hydrogen polysulfides ( $H_2S_x$ ) dissolved in liquid sulfur.

**Safety:**  $H_2S$  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.

**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 with a mixture of air and steam over a mass transfer device. Degassed sulfur is returned to the product section of the sulfur pit. The material for construction is mainly concrete, with internals in stainless steel.

**Economics:** The capital cost is less than 10% of the cost of a two-reactor Claus unit.

**Installations:** Several units are in operation, designed or under construction, with unit capacities of up to 500 mtpd. Siirtec Nigi recently licensed



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the JSC Mozyr refinery with a 240-mtpd unit, and it has provided Galp Energia with a 170-mtpd sulfur degassing unit.

**Reference:** The paper "H<sub>2</sub>S recovery from Claus tail gas treatment and liquid sulfur degassing," is available on request.

Licensor: Siirtec Nigi S.p.A. CONTACT

# Sulfur Pre-Extraction (SPREX)

**Application:** Pre-extraction of hydrogen sulfide ( $H_2S$ ) from sour natural gas streams containing high amounts of  $H_2S$  (typically more than 25 vol%), yielding a treated gas stream with reduced  $H_2S$  content and a liquid  $H_2S$  stream suitable for reinjection.

**Description:** The natural gas feed stream enters into the contactor column (1), where it is contacted with the cold liquid reflux from the lowtemperature 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); it 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 back (5) as a reflux to the top of the contactor (1).

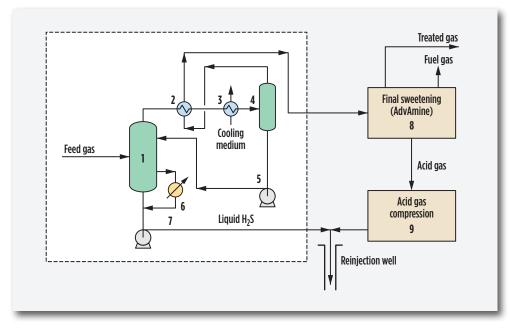
The cold gas from the top of the LTS (4) goes to the gas/gas heat exchanger (2). This gas, which has a reduced  $H_2S$  content of around 10 vol% (depending on the process operating conditions), is then suitable for final purification by an amine process such as AdvAmine (8). The resulting acid gas stream can be compressed (9) and reinjected.

The bottom of the contactor (1) is equipped with a reboiler (6) to minimize hydrocarbon content in the liquid stream from the bottom. This liquid stream, consisting mainly of  $H_2S$  with some carbon dioxide (CO<sub>2</sub>), water and hydrocarbons, is recovered under a pressure similar to the natural gas feed pressure and can easily be reinjected through a pump (7).

SPREX exists in two versions:

• **SPREX:** This version has been developed for bulk  $H_2S$  removal of gases containing 25+ vol%  $H_2S$ . With a temperature of about -30°C (-22°F) in the LTS, no hydrates are formed, and no upstream gas dehydration is required. Treated gas from SPREX typically will contain about 10 vol% residual  $H_2S$ .

• **SPREX CO<sub>2</sub>:** This version is being developed for bulk  $CO_2$  removal and reinjection. Lower LTS temperature is being used, and upstream de-



hydration is required. SPREX  $CO_2$  is best suited for gases containing 40+ vol%  $CO_2$ . Treated gas typically will contain about 20 vol% residual  $CO_2$ .

**Economics:** It has been found that, for a sour gas with 35 vol%  $H_2S$  and 7 vol%  $CO_2$ , combining SPREX with final amine sweetening (8) and acid gas compression (9) allows for a CAPEX reduction of 17% and reduced energy consumption of 35%, when compared to a conventional amine + acid gas compression scheme.

A complete feasibility study comparing SPREX  $CO_2$  + amine to membrane + amine for the treatment of high- $CO_2$  feed gas (60–70 vol%  $CO_2$ ) to meet LNG specifications found a reduction of 17%–20% in overall CA-PEX. Other results were the maximization of gas valorization by halving overall auto-consumption needs, and significantly reducing the overall hydrocarbon losses by using SPREX  $CO_2$ .

# Sulfur Pre-Extraction (SPREX), cont.

**Installation:** One industrial demonstration plant, with a capacity of 70,000  $m^3/d$ , at Total's Lacq field in France.

**Reference:** Deveaux, M., C. Maretto and X. Renaud, "The SPREX CO<sub>2</sub> technology—Optimizing CO<sub>2</sub> separation and management for very acid gas fields," SOGAT, Abu Dhabi, UAE, March 2011.

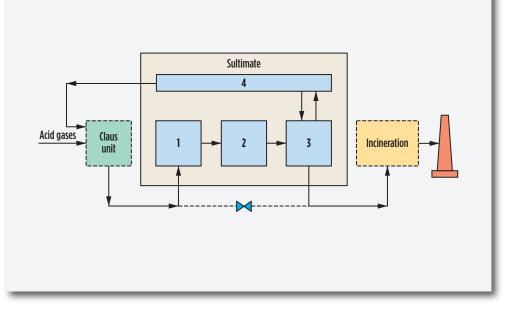
**Licensor:** SPREX was developed jointly by Total, IFPEn and Prosernat, and it is licensed through Prosernat. **CONTACT** 

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### **Sultimate**

**Application:** The Sultimate technology is the most efficient process available to minimize  $SO_2$  emissions from a sulfur recovery unit. This process is based on the hydrogenation of sulfur species and selective amine washing. It is installed downstream of a Claus unit to recover the remaining sulfur species, for a sulfur recovery yield of 99.9+%.

**Description:** The Sultimate unit is a Claus tail gas treatment process based on four steps. In the first step (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 the presence of a reducing gas. This conversion occurs in a reactor filled with efficient hydrogenation catalyst. The second step (2) consists of the saturation of the hydrogenated gas with water, and its cooling to a temperature suitable for the next step. The third step (3) uses a selective amine solution to absorb the  $H_2S$  contained in the gas prior to incineration. For deep sulfur recovery, absorption performances can be lowered to 10 ppm of  $H_2S$  in the gas. The fourth step (4) consists of the separation of the  $H_2S$ contained in the rich amine by thermal regeneration, and its routing to the Claus unit inlet to be transformed into elemental sulfur.



Licensor: Prosernat IFP Group Technologies CONTACT

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### **Super Hy-Pro**

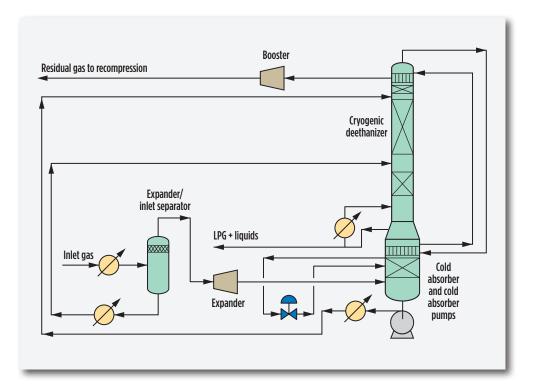
**Application:** The Super Hy-Pro process is a further development of its predecessor—the Hy-Pro process—and is designed for the high recovery of liquid hydrocarbons from natural gas, mainly LPG.

**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 that 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:** An ample range of pressures, temperatures and compositions.



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

Licensors: Randall Gas Technologies CONTACT

## **SUPERCLAUS Process**

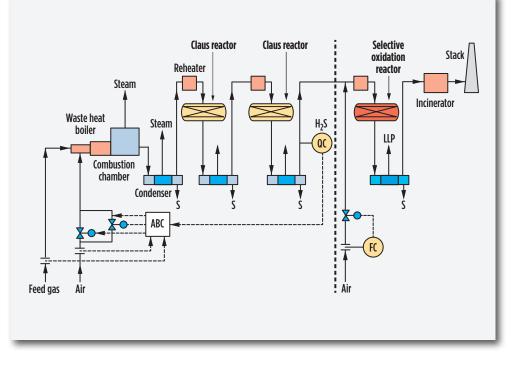
**Application:** The SUPERCLAUS process recovers elemental sulfur from  $H_2S$ -containing gases originating from gas treating plants. SUPERCLAUS plants are able to process  $H_2S$ /ammonia (NH<sub>3</sub>)-containing gases originating from sour water strippers. Yields up to 99.2% overall sulfur recovery, without any further tail gas cleanup, are possible.

**Description:** The SUPERCLAUS process consists of a thermal stage followed by a minimum of three catalytic reaction stages, with sulfur removed between stages by condensers. The first two or three reactors are filled with standard Claus catalyst, while the final reactor is filled with selective oxidation catalyst.

In the thermal stage, the acid gas is burned with a sub-stoichiometric amount of controlled combustion air, such that the tail gas leaving the last Claus reactor contains typically 0.8–1.0 vol% of  $H_2S$ . The selective oxidation catalyst in the final reactor oxidizes the  $H_2S$  to sulfur at an efficiency of more than 85%. However, because the selective oxidation catalyst neither oxidizes  $H_2S$  to  $SO_2$  and water nor reverses the reaction, total sulfur recovery efficiency of up to 99% can be obtained in a three-reactor system. If a sulfur recovery rate of more than 99% is required, one additional Claus reactor stage can be installed upstream of the selective oxidation reactor.

**Utilities:** Basis: 100 t/d, two Claus reactors, one selective oxidation reactor, 71 vol%  $H_2S$  and 11 vol%  $NH_3$  feed gas, thermal incineration with heat recovery, and sulfur recovery of 99%.

		Consumption	Production
4 barg steam	t/h	-	2.7
40 barg steam	t/h	-	12.8
Preheat/reheat 40 barg	t/h	1.7	-



Electricity	kW	310	_
Fuel gas	t/h	0.28	-
Boiler feedwater	t/h	16.4	-
Steam for plant heating	t/h	0.4	-

**Installations:** Since the first commercial demonstration of the SUPER-CLAUS process in 1988, more than 190 units with a total installed capacity of over 48,000 t/d have been licensed. The biggest single unit in operation has a capacity of 1,500 t/d.

**Licensor:** Jacobs Comprimo Sulfur Solutions, a member of Jacobs Engineering Group <u>CONTACT</u>

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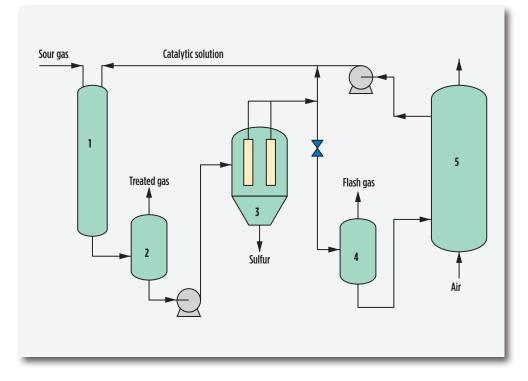
### SweetSulf

**Applications:** SweetSulf is a redox process developed by IFP Energies nouvelles (IFPEn) and commercialized by Prosernat. The goal of the process is to remove  $H_2S$  from a gas at high or low pressure and convert it to elemental sulfur by reaction with a redox solution, which regenerates through contact with air.

**Description:** The natural gas to be treated is co-currently contacted with the SweetSulf solution in the contactor (1). A redox reaction occurs in the contactor, transforming  $H_2S$  into elemental sulfur while reducing the SweetSulf solution. The gas is then separated from the SweetSulf solution in the high-pressure flash drum (2) and can be routed to a sweet gas network. The SweetSulf solution, which contains sulfur particles, is recovered at the bottom of the high-pressure flash drum and routed to the filtration section (3), where the sulfur particles are separated from the SweetSulf Solution under pressure. The SweetSulf solution is then depressurized in the low-pressure flash drum (4) and deoxidized in the oxidizer (5) by contact with air, prior to being recycled back to the contactor.

**Key features:** SweetSulf is based on extensive research, laboratory testing and pilot testing completed over several years by IFPEn. The key features of this process are:

- Selective H<sub>2</sub>S removal from gases, even under high pressure, with direct conversion to elemental sulfur
- Ambient temperature operation
- Very low H<sub>2</sub>S specification (1 ppm or less of H<sub>2</sub>S is achievable)
- Filtration at high pressure; no foaming and no risk of plugging.



**References:** Ballaguet, J. P. and C. Streicher, "Pilot operating experience with a new redox process for the direct, high-pressure removal of  $H_2S$ ," GPA Annual Convention, San Antonio, Texas, March 2001.

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

**Licensor:** SweetSulf was developed by IFPEn, and it is commercialized by Prosernat. <u>CONTACT</u>

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### Syngas (autothermal)

**Application:** Production of carbon monoxide (CO) and hydrogen (H<sub>2</sub>) for petrochemical use. Typical consumers are oxo-alcohol synthesis units and methanol (MeOH) synthesis units.

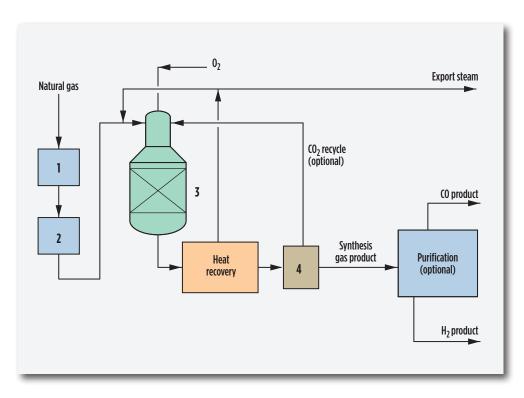
**Products:** Synthesis gas containing CO and  $H_2$ . The synthesis gas can be used directly for chemical production or, alternatively, can be further processed to yield high-purity CO and high-purity  $H_2$ .

**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  $(CO_2)$  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  $(O_2)$  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 a temperature of 1,700°F to 1,900°F, depending on the final product specifications.

The exit gas is cooled and passed through a  $CO_2$  removal unit (4). The resulting process gas consists primarily of CO and  $H_2$  and is available as product synthesis gas. This synthesis gas can be used to make a variety of chemicals, including MeOH and oxo-alcohols. Alternatively, the gas can be further processed (typically by cryogenic separation) to yield high-purity CO and high-purity  $H_2$ .

 $CO_2$  can be recycled to adjust the H<sub>2</sub>/CO product ratio. For natural gas feedstocks, the H<sub>2</sub>/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  $O_2$  is used as feedstock instead of air.  $O_2$  is required since nitrogen would dilute the H<sub>2</sub>/CO product gas purity.



**Economics:** The economics can be favorable for autothermal reforming when  $O_2$  is available at a relatively low cost. For natural gas feedstocks, the optimum  $H_2$ /CO product ratio is 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 CONTACT

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## Syngas (H<sub>2</sub> + CO)

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

Feedstocks: Hydrocarbons ranging from natural gas to naphtha.

**Description:** The generic flowsheet consists of feed pretreatment, 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.

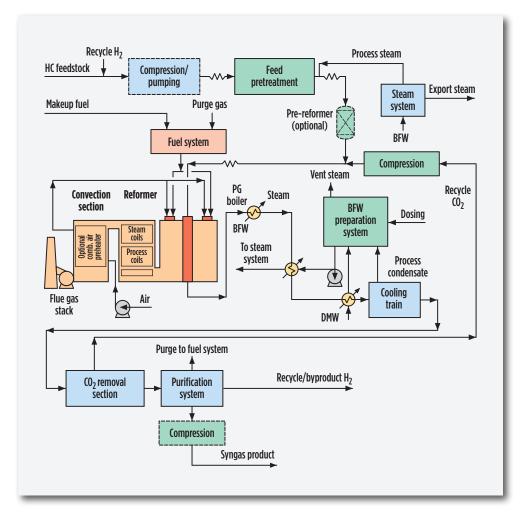
Feed pretreatment normally involves removing sulfur, chlorine and other catalyst poisons after preheating the HC feed to an appropriate level.

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 make-up 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 produce the desired quality of syngas. The entire steam generation is usually on natural circulation, which adds to higher reliability.

**Installations:** Technip has been involved in more than 10 HyCO plants, 25 syngas plants and 50 steam reformers.



Licensor: Technip CONTACT

### Syngas, autothermal reforming

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

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

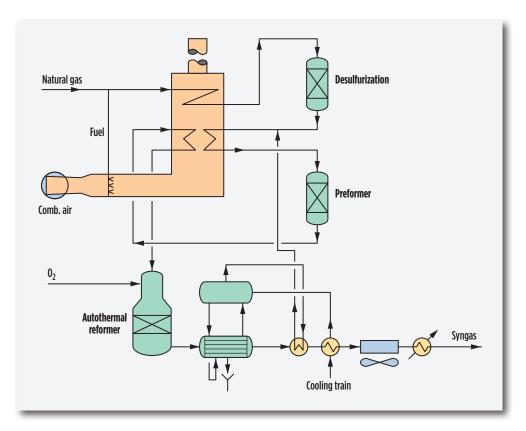
**Product:** Synthesis gas for the production of CO, H<sub>2</sub>, ammonia, methanol, Fischer-Tropsch products, synthetic fuels and oxo-chemicals.

**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 nickel-based catalyst.

The reformed gas leaves the ATR at about 1,000°C–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 ( $CO_2$ ) removal, membrane or cryogenic separation, among others, as requested by the individual application. The process scheme can further include  $CO_2$  addition or recycle to the ATR to further boost the system economics.

**Installations:** ATR technology is derived from Thyssenkrupp Uhde's well-proven secondary reformer design, which has successfully demonstrated its reliability in many ammonia plants worldwide. The water-



cooled burner nozzle arrangements have been operated successfully with O<sub>2</sub> for over 10 years in a 12,000-Nm<sup>3</sup>/h H<sub>2</sub>/CO production unit together with Thyssenkrupp Uhde's proprietary combined autothermal reforming (CAR) technology.

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

Licensor: Thyssenkrupp Uhde GmbH CONTACT

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# Syngas, autothermal reforming (ATR)

Application: Produce CO-rich synthesis gas.

**Products:** Pure carbon monoxide (CO) and hydrogen  $(H_2)$  or synthesis gas for methanol, synthetic fuels, oxo-synthesis or ammonia. Very large-scale production of synthesis gas for GTL plants.

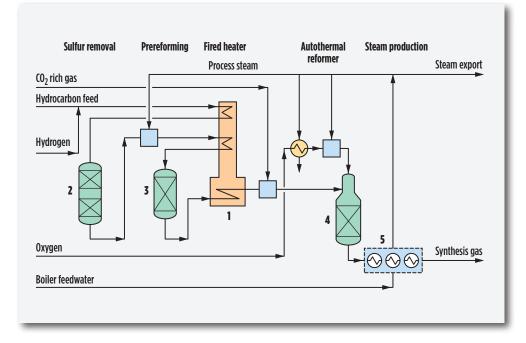
**Description:** The process combines partial oxidation and adiabatic steam reforming using a fixed catalyst bed (nickel catalyst). Soot-free operation is secured by a proprietary burner design. The unit consists of a feed preheater (1); feed desulfurization (2); pre-reforming (optional) (3); an autothermal reformer reactor with a burner, a combustion chamber and catalyst bed (4); a heat-recovery section (5); and, when required, a gas purification section [e.g., CO<sub>2</sub> removal (not shown)].

The autothermal reformer burner features low metal temperatures and high resistance to mechanical wear, thus ensuring a long burner lifetime. The burner is manufactured in commercially available, high-temperature alloys without cooling circuits.

The hydrocarbon feedstock can be natural gas, LPG or naphtha. The oxygen feed can be pure oxygen, air or enriched air.  $CO_2$  recycle or  $CO_2$  import can be applied to adjust synthesis gas composition.

**Operating conditions:** Typically, CO-rich synthesis gas is obtained at feed ratios of  $H_2O:CH_4 = 0.2$  to 1.5 and  $CO_2:CH_4 = 0.0$  to 2.0, resulting in synthesis gas ratios  $H_2:CO$  with 0.8 to 2.5 at reactor exit temperatures of 950°C–1,050°C. Reactor pressure ranges between 20 bar and 70 bar.

**Installations:** Since 1958, 26 complete installations have been licensed. A new burner technology with an improved lifetime was introduced in 1992 and is in operation in 20 autothermal reforming plants, of which six



lines are GTL plants with up to 17,000 bpd of capacity per line. ATR installations for GTL projects are in operation in South Africa and Qatar.

**References:** Ernst, W. S. et al., "Push syngas production limits," *Hydrocarbon Processing*, March 2000.

Christensen, T. S. et al., "Syngas preparation by autothermal reforming for conversion of natural gas-to-liquid products (GTL)," Monetizing Stranded Gas Reserves Conference, San Francisco, California, 1998.

Christensen, T. S. and I. Primdahl, "Improve syngas production using autothermal reforming," *Hydrocarbon Processing*, March 1994.

Christensen, T. S. et al., "Burners for secondary and autothermal reforming—design and industrial performance," Ammonia Plant Safety, Vol. 35, 1994.

Licensor: Haldor Topsøe A/S CONTACT

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# Syngas, steam methane reforming (SMR)

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.

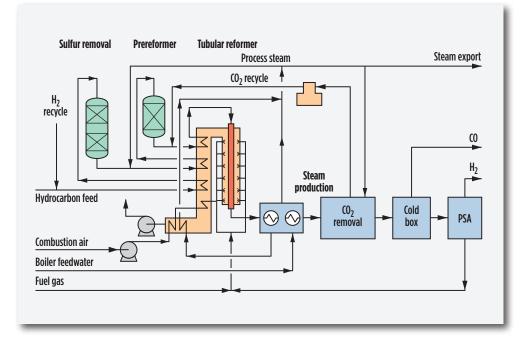
**Description:** Steam reforming in a fired-tubular reformer is the predominant process route for medium-sized synthesis gas plants. The Topsøe radiant-fired reformer and reforming catalysts enable operation at low steam-to-carbon ratios, high reformer outlet temperatures and high heat flux.

The hydrocarbon feedstock can be natural gas, LPG or naphtha. For heavy feedstocks, an adiabatic prereformer 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, prereforming, 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, noble-metal reforming catalyst.

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



**Installations:** Topsøe's reforming technology is in operation in more than 250 industrial plants worldwide.

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

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

Winter Madsen, S. and J.-H. Bak Hansen, "Industrial aspects of CO<sub>2</sub> reforming," AIChE Spring Meeting, Houston, Texas, March 1997.

Licensor: Haldor Topsøe A/S CONTACT

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### 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.

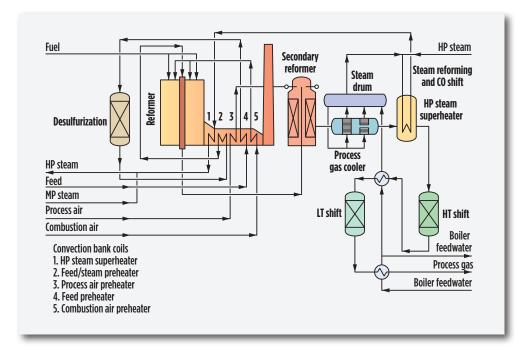
**Product:** Syngas for  $H_2$ , CO, ammonia, methanol, Fischer-Tropsch synfuels, oxo-synthesis products, etc.

**Description:** The steam reforming process comprises high-temperature conversion of desulfurized feed with steam to produce  $H_2$ , CO and carbon dioxide (CO<sub>2</sub>). The design conditions of the steam reformer vary and depend on the application, with discharge temperatures ranging from 740°C-950°C and pressures of 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 steam reformer concept also includes a fully prefabricated 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, CO<sub>2</sub> removal (e.g., MDEA), membrane or cryogenic separation, as required for the desired products.

Other typical process options are feed evaporation, CO<sub>2</sub> recycle, adiabatic feed prereforming and/or HT/LT shift to process—e.g., heavier feeds and/or optimization of feed/fuel consumption and steam production. The



design allows for the combination of maximized process heat recovery and optimized energy efficiency with operational safety and reliability.

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

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

### Syngas, steam reforming, cont.

In 2006, Thyssenkrupp Uhde commissioned the world's largest single-train ammonia plant in Saudi Arabia (3,300 mtpd), using a reformer with 408 tubes. Thyssenkrupp Uhde is presently executing several reformer projects worldwide, including another large-scale ammonia plant in Saudi Arabia and ammonia/urea complexes in Algeria and Egypt.

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

Licensor: Thyssenkrupp Uhde GmbH CONTACT

# **THIOLEX/REGEN**

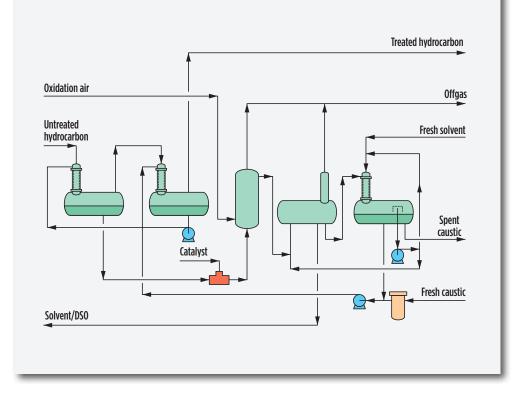
**Application:** The THIOLEX/REGEN systems extract  $H_2S$  and mercaptans from gases and light liquid hydrocarbon streams, including gasolines, with caustic using FIBER FILM Contactor technology. They can also be used to hydrolyze and remove COS from LPG and propane.

**Description:** In a THIOLEX system, the caustic phase flows along the fibers of the FIBER FILM Contactor as it preferentially wets the fibers. Hydrocarbon flows through the caustic-wetted fibers, where the  $H_2S$  and mercaptans are extracted into the caustic phase. The two phases disengage and the caustic flows to the REGEN, where the caustic is regenerated using heat, air and catalyst. The disulfide oil formed in this reaction may be removed via gravity separation, FIBER FILM solvent washing or a combination of the two. The regenerated caustic flows back to the THIO-LEX system for continued reuse.

COS is removed from LPG or propane, either by employing AMINEX technology using an amine solution or by THIOLEX technology using an MEA/caustic solution to hydrolyze the COS to  $H_2S$  and  $CO_2$ , which are easily removed by amine or caustic.

**Economics:** FIBER FILM Contactor technology requires smaller processing vessels, thus saving valuable plant space and reducing capital expenditures.

Installations: 382 licensed units worldwide.



**References:** Oil & Gas Journal, August 12, 1985. Hydrocarbon Engineering, February 2000.

Licensor: Merichem Co. CONTACT

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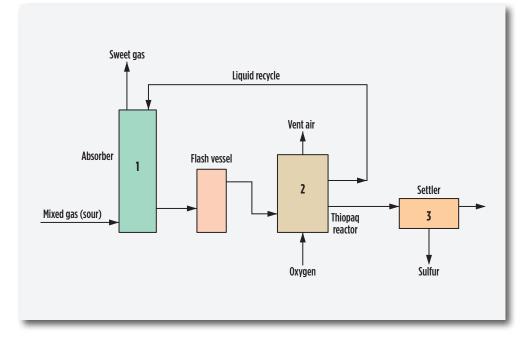
### **Thiopaq O&G process**

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

**Products:** The Thiopaq O&G unit can be designed to treat gas streams containing less than 4 ppmv hydrogen sulfide ( $H_2S$ ) under high pressure above 4 bar, and less than 25 ppmv  $H_2S$  under low pressure below 4 bar. The  $H_2S$  removal efficiency is above 99.99%. The biosulfur produced can be used directly as fertilizer, since it has a hydrophilic character. In combination with the fine particle size, the sulfur is more accessible in the soil for oxidation and subsequent uptake by plants as sulfate. Alternatively, the biosulfur can be washed and melted to produce a final liquid sulfur product that will meet industrial specifications. The hydrophilic character of the biosulfur is lost after melting.

**Description:** In the Thiopaq O&G process,  $H_2S$  is directly oxidized to elemental sulfur 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 sulfur 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 (3) that 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, or it can be processed to high-quality agricultural products.



**Economics:** The Thiopaq O&G 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 replace the combination of an amine/Claus/ TGTU or, for smaller applications, liquid redox processes.

**Installations:** There are eight Thiopaq O&G units in operation, and seven units are in the startup, construction or design phase. These units have capacities ranging from 1 tpd to 50 tpd of sulfur. It compares favorably in terms of capital expenditure 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 lower with decreasing  $CO_2/H_2S$  ratios.

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### Thiopaq O&G process, cont.

**References:** Cline, C. et al., "Biological process for H<sub>2</sub>S removal from gas streams: The Shell-Paques/THIOPAQ gas desulfurization process," Laurence Reid Gas Conditioning Conference, Norman, Oklahoma, February 2003. Janssen, A. J. H. et al., "Biological process for H<sub>2</sub>S removal from high-pressure gas: The Shell-Paques/THIOPAQ gas desulfurization process," *Sulphur*, 2001.

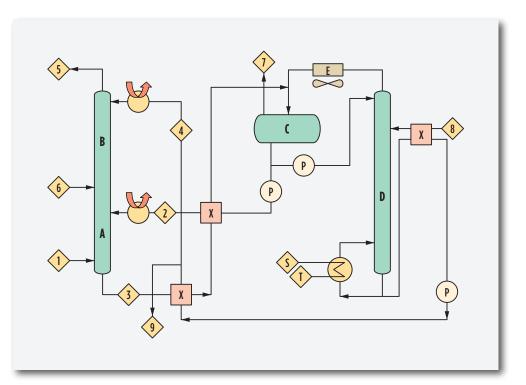
**Licensors:** Paqell B.V., Cameron, Shell Global Solutions B.V., Hofung Technology, and Paques Environmental Technology Shanghai <u>CONTACT</u>

## ThioSolv AMMEX

**Application:** The AMMEX process integrates sour water stripping and sour gas scrubbing in a single, simple process. It can be used without supplemental ammonia (NH<sub>3</sub>) to remove some of the hydrogen sulfide (H<sub>2</sub>S) from a gas stream; for instance, to unload an existing amine unit. Adding a sub-stoichiometric amount of NH<sub>3</sub> allows AMMEX to reduce H<sub>2</sub>S in the scrubbed gas to low concentration, eliminating the need for a separate amine system for gas treating. AMMEX is especially attractive when the sour water stripper gas is converted to ammonium thiosulfate (ATS) in ThioSolv's SWAATS process.

**Description:** ThioSolv developed this process by modeling in PRO/II 8.1 using electrolyte thermo. Water in contact with refining process gases readily dissolves essentially all of the NH<sub>3</sub> from the gas. The NH<sub>3</sub> solution, in turn, dissolves roughly equimolar amounts of H<sub>2</sub>S, which is typically present in excess in the process gas. The molar ratio of H<sub>2</sub>S/NH<sub>3</sub> in the feed to the sour water stripper is, therefore, typically about 1. The vapor pressure of H<sub>2</sub>S over water increases faster with temperature than the vapor pressure of NH<sub>3</sub>, so the ratio of H<sub>2</sub>S/NH<sub>3</sub> in the sour water stripper reflux liquid is about  $\frac{1}{3}$ . When liquid from the stripper reflux drum is cooled, excess NH<sub>3</sub> in the solution allows the liquid to absorb more H<sub>2</sub>S from a gas stream.

Sour feed gas (1) is fed to a first contact zone A, where it is scrubbed with a stream of cooled liquid (2) from the reflux drum C of a sour water stripper D (SWS). The high ratio of  $NH_3$  to  $H_2S$  in the liquid allows it to dissolve  $H_2S$  from the gas. Rich liquid (3) from the bottom of the first contact zone is preheated by exchange (X) and combined with the partially condensed stream from the SWS condenser E. Heat removal from the condenser is modulated to control the temperature of the combined stream to the reflux drum. The gas leaving the first contact zone, containing some  $NH_3$  stripped from the recycle liquid and some  $H_2S$ , enters a second contacting zone B, where it is washed with cooled, recycled sour



water (4), which dissolves some  $H_2S$  and essentially all of the  $NH_3$  from the gas, carrying it into the first zone A. If the intent is to reduce the  $H_2S$ concentration in the scrubbed gas to meet a specification, rather than simply to remove most of the  $H_2S$ , a small amount of  $NH_3$  (6) is added to the second contacting zone B. The refinery sour water (8) feeds the stripper conventionally, with the net stripped water (9) leaving the system. Net  $H_2S$  and  $NH_3$  leave the reflux drum C as SWS gas (7). Heat for stripping is provided by low-pressure steam sulfur.

The SWS acid gas may be fed to a conventional sulfur recovery process, but it would be more favorably converted to ATS fertilizer in Thio-Solv's SWAATS process.

# ThioSolv AMMEX, cont.

**Economics:** AMMEX is highly energy efficient. Most of the  $H_2S$  is removed from the feed gas by the circulation from the reflux drum, using latent heat of condensation that would normally be rejected to atmosphere to reheat the rich liquid and flash out excess  $H_2S$ . Circulation of the reflux liquid costs only pump power and some cooling water. The recycle rate of stripped water required to remove  $NH_3$  from the gas in the second contactor adds only a relatively small load to the sour water stripper. Since the amount of  $H_2S$  in the gas entering the second zone B is small compared to the amount in the feed gas, the moles of  $NH_3$  addition required to reduce the  $H_2S$  concentration to < 100 ppm is less than the total moles of  $H_2S$  captured.

**Example:** A refinery makes 10 tpd of sulfur as  $H_2S$ , 90% in sour fuel gas and 10% in sour water. Sour fuel gas containing 6%  $H_2S$  and 0.6%  $CO_2$  can be treated to < 20 ppm  $H_2S$  using 4.6 tpd of  $NH_3$  addition and recycle of 14 gpm of stripped sour water for washing. By contrast, scrubbing the fuel gas with MDEA would require six times as much circulation.

The SWS gas produced can be converted to ATS in a SWAATS unit at a negligible operating cost.

Installation: None; patent pending

Licensor: ThioSolv LLC CONTACT

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### ThioSolv Sour Water Ammonia to Ammonium Thiosulfate (SWAATS) Process

**Application:** The SWAATS process diverts sour water stripper gas (SWSG) from the Claus unit to convert ammonia (NH<sub>3</sub>) and hydrogen sulfide (H<sub>2</sub>S) to ammonium thiosulfate (ATS) solution, thus freeing up Claus capacity and improving operability. SWAATS can also treat Claus tail gas to low emissions at a low cost. For plants producing small amounts of sulfur, SWAATS can be designed to capture all of the refinery H<sub>2</sub>S. The cost of supplemental ammonia (0.58 ton NH<sub>3</sub>/ton sulfur) is justified by having only one unit that can process both SWSG and amine acid gas (AAG) with low emission rates.

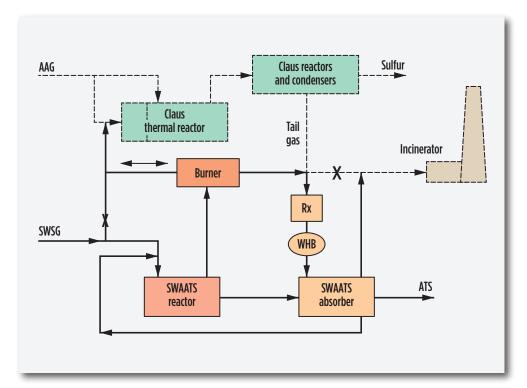
High chemical selectivity of the process enables it to economically remove  $H_2S$  or sulfur dioxide (SO<sub>2</sub>) from gas mixtures, including CO<sub>2</sub>. The process was recognized by the EPA as the best available control technology (BACT) for control of SO<sub>2</sub> emissions.

**Description:** Ammonia and a stoichiometric amount of  $H_2S$  are selectively absorbed from SWSG. The rejected  $H_2S$  and Claus tail gas, if desired, are selectively oxidized to convert all sulfur species to  $SO_2$ , which is then scrubbed from the combustion gas in a low-pressure drop system to yield a vent gas with very low  $SO_x$  concentration and no reduced sulfur requiring incineration:

 $6NH_3 + 4SO_2 + 2H_2S + H_2O \rightarrow 3(NH_4)_2S_2O_3(ATS)$ 

SWAATS may be controlled to import or export  $H_2S$  to balance on the NH<sub>3</sub> available in the SWSG, or supplemental NH<sub>3</sub> may be added to capture additional  $H_2S$ .

The chemistry and internal circulation rates provide for robust operation and resistance to upsets in the feedstreams. They also prevent



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or reverse sulfur precipitation by converting any elemental sulfur in the Claus tail gas to thiosulfate. Control is based on simple inline analyzers (pH, combustion gas  $O_2$ ) and requires little attention.

**Economics:** Each ton of SWSG sulfur diverted from Claus to SWAATS frees up Claus capacity for about three tons of AAG sulfur. Removing  $NH_3$  from the Claus feed also greatly improves Claus operability and extends the service life of the catalyst. The vent gas contains no reduced sulfur compounds that would require incineration. With SWAATS, the SWSG ammonia is an asset; the value of the process increases as higher-severity hydrotreating for ultra-low-sulfur diesel

#### Continued $\mathbf{\nabla}$

### ThioSolv Sour Water Ammonia to Ammonium Thiosulfate (SWAATS) Process, cont.

production increases denitrification to over 90%, greatly increasing ammonia production.

CAPEX for SWAATS to process SWSG and Claus tail gas is about a quarter of the CAPEX for the construction of an equivalent amount of new Claus and tail gas treating capacity. SWAATS OPEX is typically negative due to credit for export of MP steam, and is substantially lower than the OPEX for oxygen enrichment or for an amine-based tail gas treatment. SWAATS consumes no external chemicals or reducing gas. Licensor removes the ATS produced.

An additional advantage to SWAATS is that, because it does not yield elemental sulfur, the US Environmental Protection Agency concluded that SWAATS is not a sulfur recovery process, and the sulfur recovered as ammonium thiosulfate does not count against an existing sulfur recovery permit limit.

**Installations:** The first unit has been operating since June 2007, using supplemental  $NH_3$  to capture all of the refinery sulfur to eliminate the need for a second type of sulfur recovery unit. Three more SWAATS units have been licensed and designed as of April 2009.

**Reference:** US Patent Nos. 6,534,030; 7,390,470; 7,575,732; 7,655,211; other patents pending.

Berry, R., "Treating hydrogen sulfide: When Claus is not enough," *Chemical Engineering*, October 6, 1980.

Anderson, M. C., "Increasing SRU capacity," *Sulphur,* September-October 2007.

Anderson, M. C., "Dealing with increased hydrogen sulfide and ammonia resulting from higher desulfurization severity," *Hydrocarbon Processing*, September 2008.

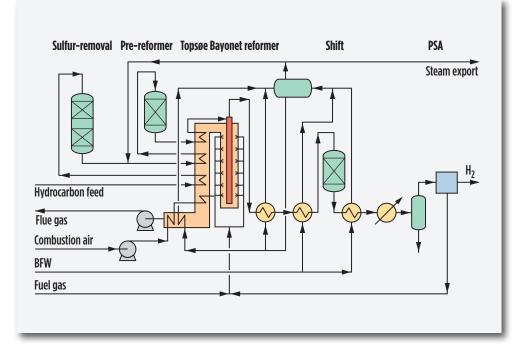
Licensor: ThioSolv LLC CONTACT

## **Topsøe Bayonet Reformer (TBR)**

**Application:** Produce hydrogen (H<sub>2</sub>) from a hydrocarbon feedstock, such as natural gas, LPG, naphtha, refinery offgases, etc., using the Haldor Topsøe Bayonet Reformer (TBR). Plant capacities exceeding 200,000  $\text{Nm}^3/\text{h}$  (200 MMscfd), and H<sub>2</sub> purities from 99.5% to 99.999+% are marketed.

**Description:** The TBR-based H<sub>2</sub> plant combines the flexibility and capacity of the radiant wall reformer with the hydrocarbon efficiency of the Haldor Topsøe Convective Reforming (HTCR) process. The TBR technology consists of a series of double tubes in a single row in a side-fired radiant box. The feed gas flows downward through the catalyst bed located in the annuli between the two tubes. In the bottom of the catalyst bed, the gas turns and continues upward through the inner, empty, bayonet tube. Heat is recovered from the reformed gas to the gas undergoing the reforming reactions, instead of for steam generation. The use of heat exchange tubes in the reformer makes the TBR technology advantageous for plants where steam export should be limited. Furthermore, the TBR plants can be customized to suit the customer's needs with respect to feedstock flexibility.

**Economics:** The TBR-based plant will be highly efficient on hydrocarbon utilization, and can be designed for steam export ranging from medium to low amounts, or even zero. Feed and fuel consumption of about 3.27–3.45 Gcal/1,000 Nm<sup>3</sup> (348–367 Btu/scf) and net energy consumption of about 3.10–3.30 Gcal/1,000 Nm<sup>3</sup> (330–351 Btu/scf) are achieved, depending on layout and feedstock.



**Installations:** One licensed unit with a capacity of  $33,000 \text{ Nm}^3/\text{h}$  (30 MMscfd) under engineering and construction.

**References:** Andersen, N. U. and H. Olsson, "The hydrogen generation game," *Hydrocarbon Engineering*, July 2011.

Hedegaard Andersen, K. and H. Carstensen, "Combining the best of both worlds," *Hydrocarbon Engineering*, November 2009.

Licensor: Haldor Topsøe A/S CONTACT

**COMPANY INDEX** 

# **UOP Amine Guard™ FS Process**

#### Application:

- Removes CO<sub>2</sub> and H<sub>2</sub>S from natural gas
- Removes CO<sub>2</sub> from ammonia syngas
- $\bullet$  Removes  ${\rm H_2S}$  from integrated gasification combined-cycle (IGCC) plant syngas

Amine Guard FS utilizes one of the UCARSOL family of formulated solvents offered by Dow Chemical Co.

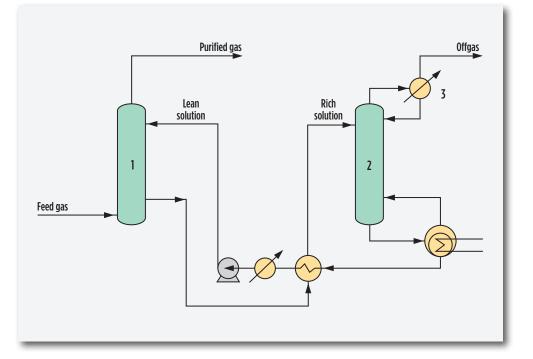
When desired,  $H_2S$  can be removed selectively to provide a superior Claus plant feed and reduce regeneration requirements.

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

**Description:** In a typical flow scheme, the treating solution scrubs acid gases from the feed in an absorber column (1). 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 UCARSOL solvent for the situation, using high-solvent concentrations and proper selection of flow scheme.

**Operating conditions:** Absorption pressure from 25 psi to 1,800 psi, as available. Feed temperature is 60°F to 150°F. Acid gas content may be 0.5% to 20% by volume.



**Installations:** More than 400 units worldwide, mostly treating natural gas, ammonia syngas and hydrogen streams.

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### **UOP Benfield™ Process**

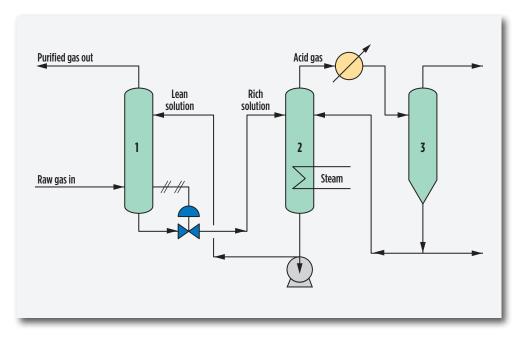
**Application:** Removal of  $CO_2$  and  $H_2S$  from natural and synthesis gases. Removal of  $CO_2$  from ammonia and hydrogen syngas represent the highest number of installations.

**Product:** Purified gas to meet pipeline or LNG plant, ammonia plant or petrochemical plant specifications, and recovery of a high-purity  $CO_2$  stream.

**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 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 60°F to 265°F. If the feed is available at a higher temperature, then that heat will be used to supply regeneration heat. Acid gas content in feed 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.

**Revamps:** UOP offers three revamp options for the Benfield process. The UOP Benfield ACT-1<sup>TM</sup> activator promotes the adsorption of carbon dioxide by hot potassium carbonate solution, by increasing mass transfer rates. It can offer many benefits, including lowering the CO<sub>2</sub> content in the product gas by 25%–85%, lowering regeneration energy requirements by 5%–15%, and lowering the carbonate solvent solution circulation by 5%–15%.



Existing plants can be revamped for capacity increases and/or heat savings of 15%–40% using the UOP Benfield LoHeat<sup>TM</sup> technology.

For systems that have the ability to increase feed gas rates from upstream sources, UOP tower internals can be used to debottleneck the adsorber and regenerator towers to allow higher vapor rates. Depending on the type of packing, capacity increases of 5% to more than 20% can be realized.

Revamp options can be combined to achieve even greater capacity and/or energy savings.

**Installations:** Of the 700+ licensed units worldwide, more than 65 treat natural gas, more than 400 treat ammonia syngas and about 110 are in hydrogen plants. The remainder are in SNG, partial oxidation, coal gasification and petrochemical applications.

### **UOP Merox<sup>™</sup> Process**

**Application:** Extraction of mercaptans from gases, LPG, lower boiling fractions and gasolines, or sweetening of gasoline and distillates by insitu conversion of mercaptans into disulfides.

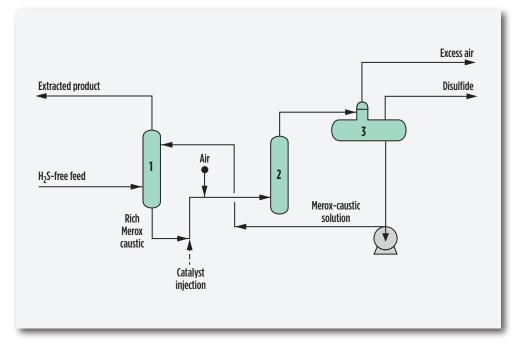
**Products:** Essentially mercaptan sulfur-free (i.e., less than 5 ppmw) and concomitant reduced total sulfur content when treated by Merox extraction technique.

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

**Extraction:** Gases, LPG and light naphtha are counter-currently 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:** Light gasoline and condensate streams can be sweetened using the Minalk process. Conversion of mercaptans into disulfides is accomplished with a fixed bed of Merox catalyst that uses air and a continuous dilute caustic injection. Sweetened gasoline from the reactor is visually clear and typically contains less than 1 ppm of sodium. A Merox Plus reagent can be used within the process to enhance activity and greatly extend catalyst life.

Heavy gasoline, condensates and kerosene/jet fuel streams can be sweetened in a fixed-bed process similar to Minalk by employing addi-



tional processing steps and a stronger caustic solution that is recirculated intermittently over the catalyst bed. A Merox Plus reagent can be used within the process to enhance activity and greatly extend catalyst life.

**Installations:** Capacity installed and under construction exceeds 13 million bpsd. More than 1,700 units have been commissioned to date, with capacities ranging between 100 bpsd and 150,000 bpsd. UOP has licensed Merox gas extraction units for mercaptan control with capacities as high as 83 million scfd.

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### **UOP SELEXOL<sup>™</sup> Process**

#### Application: A process that can:

• Selectively remove  $H_2S$  and COS in integrated gasification combined-cycle (IGCC), with high CO<sub>2</sub> rejection to product gas (95+%) and high-sulfur (25%–80%) feed to the Claus unit

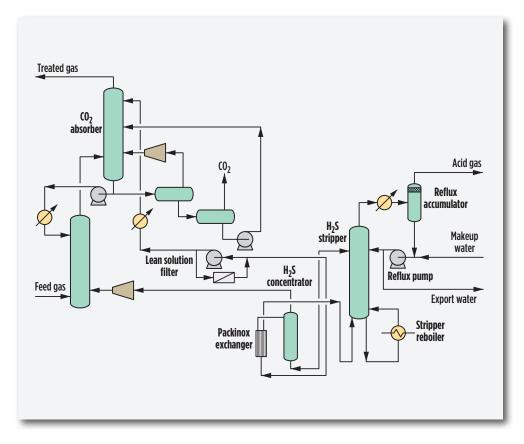
 $\,$  Selectively remove  $\rm H_2S/COS$  plus removal of CO\_2 in gasification for H\_2 generation for refineries, hydroprocessing upgraders, SNG, chemical, fertilizer and liquid fuels production

 $\bullet$  Remove mercaptans, COS and  $\rm H_2S$  from molecular sieve regeneration gas in CNG, LNG and GTL front-end treating.

**Description:** This process uses Dow Chemical Co.'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, metal carbonyls and other trace contaminants. A variety of flow schemes permits process optimization and energy reduction.

Acid gas partial pressure is the key driving force. Typical feed pressure is greater than 350 psia, with an acid gas composition of  $CO_2$  plus  $H_2S$  of 5% or more by volume. The SELEXOL process can treat syngas to less than 1 ppmv of total sulfur and low levels of sulfur in the captured  $CO_2$  product while producing an acid gas with high levels of  $H_2S$ . The process is optimized to produce the targeted quality of all product streams.

**Installations:** More than 110 SELEXOL units have been put into commercial service. The SELEXOL process is used in many applications, ranging



from natural gas to synthetic gas, and it has been the dominant acid gas removal system for gasification project awards.

### **UOP Separex™ Membrane Systems**

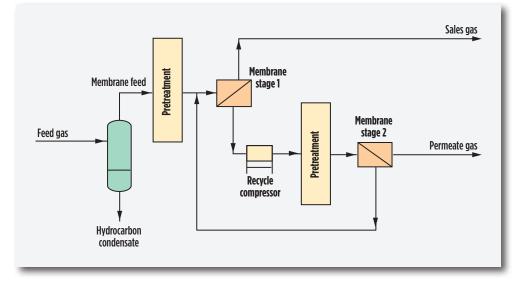
**Applications:**  $CO_2$ ,  $H_2S$  and water vapor removal from natural gas or associated gas to meet pipeline specifications for onshore or offshore locations. Hydrogen and helium purification and upgrading low-GHV gas for fuel. Debottlenecking existing solvent scrubbing systems or providing bulk  $CO_2$  removal upstream of new or existing installations. Hydrocarbon recovery from enhanced oil recovery floods for  $CO_2$  reinjection and landfill gas purification.

**Products:** Purified gas meeting pipeline specifications, high-quality fuel gas for turbine, or high-purity CO<sub>2</sub> 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 stage before being processed in a one- or two-stage membrane system. As the  $CO_2$ -rich feed gas passes over the polymeric membrane at high pressure, it separates into two streams. Carbon dioxide, hydrogen sulfide and water vapor permeate rapidly 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, lowpressure permeate is compressed for further treatment at the secondstage 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 2 million scfd to 1,000 million scfd, with  $CO_2$  levels from 3%–80% and feed pressures from 400 psig–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.

UOP MemGuard<sup>™</sup> Pretreatment Systems are utilized when feed streams are heavy or if dewpoint control is required.

**Economics:** For natural gas upgrading to pipeline specifications, 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. CO<sub>2</sub> 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. More than 130 UOP membrane units have been installed. The largest operating unit processes over 600 million scfd of natural gas.

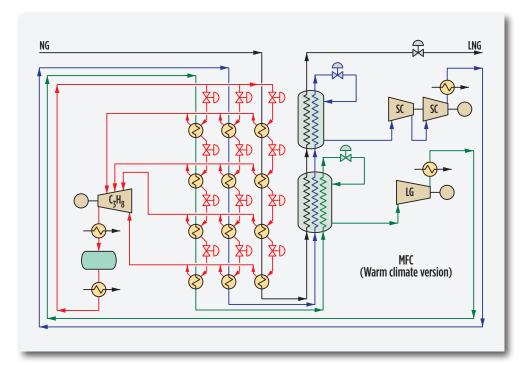
# World-Scale LNG (Mixed Fluid Cascade<sup>®</sup>)

**Application:** The Mixed Fluid Cascade (MFC)<sup>®</sup> process is the most energy-efficient natural gas liquefaction process worldwide (with power consumption of less than 250 kWh/t for the Hammerfest LNG plant in Norway), which has been proven in operation. It can be designed for a capacity range of 3–12 mtpy of LNG.

**Description:** Linde's MFC<sup>®</sup> process, which has been developed jointly with Statoil for baseload LNG plants, is characterized by three independent refrigeration cycles. The intermediate (liquefaction) cycle and the coldest (subcooling) cycle use mixed refrigerants in any case, while the type of refrigerant in the warmest (precooling) cycle depends mostly on the ambient temperature.

The flow chart shows a simplified process sketch for the MFC3<sup>®</sup> process with propane precooling. The load between the three refrigeration cycles can be balanced perfectly. This means the shaft power of all three compressor trains is identical. With such a configuration, which is unique among baseload LNG technologies, the largest LNG capacities can be achieved with a given set of main compressor drives.

In a moderate or cold climate, propane precooling and perfect load balancing among the three refrigeration cycles is no longer feasible. Under these circumstances, the arctic version of the MFC<sup>®</sup> process with three mixed-refrigerant cycles is the preferred solution. The type of heat exchanger in the precooling cycle depends on the selected refrigerant composition. While a pure component like propane can be vaporized efficiently in a kettle with either a tube bundle (TEMA design) or a submerged plate-fin heat exchanger (block-in-shell design), a mixed refrigerant requires a counter-current-type heat exchanger. Here, the choice can be made between plate-fin heat exchangers (PFHE) and coil-wound heat exchangers (CWHE).



**Economics:** The core liquefaction process can be amended by the full range of pretreatment facilities (sour gas and mercury removal, dehydration) and fractionation facilities (condensate and NGL recovery, and nitrogen rejection).

**Installations:** One 4.3-mtpy LNG plant in Hammerfest, Norway for Snøhvit LNG. Several pre-FEED and FEED studies for projects in the Middle East and Latin America are underway.

#### References: US Patent No. 6,253,574.

Bauer, H., "Highly efficient and clean LNG plant concept," World Gas Conference, Kuala Lumpur, Malaysia, June 2012.

Licensor: The Linde Group CONTACT