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- Cleaning Up Gasification Syngas
- Liquid Redox Enhances Claus Process
- The State of Iron-Redox Sulfur Plant Technology: New Developments to a Long-Established Process Technology
- Suncor’s Optimization of a Sulfur Recovery Facility
Devising a comprehensive, flexible hydrogen sulfide (H\textsubscript{2}S) removal/recovery solution requires more than systems, media and equipment – it requires expertise. With more than twenty-five years of experience in H\textsubscript{2}S removal, Gas Technology Products LLC understands the needs of every operator and every plant.

**Gas Technology Products** provides a full line of complementary hydrogen sulfide oxidation products: LO-CAT\textsuperscript{®} and LO-CAT\textsuperscript{®} II, Sulfur-Rite\textsuperscript{®} and The Eliminator\textsuperscript{™} processes, along with its ARI\textsuperscript{®}-100 mercaptan oxidation products and engineering services.

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**ARTICLES**
- The Use of Aqueous Liquid Redox Desulfurization Technology for the Treatment of Sour Associated Gases at Elevated Pressure
- Cleaning Up Gasification Syngas
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- The State of Iron-Redox Sulfur Plant Technology: New Developments to a Long-Established Process Technology
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**PROCESSES**
- Liquid treating
  - AMINEX
  - MERICAT II
  - THIOLEX/REGEN
- Sulfur
  - LO-CAT
**Uhde STAR process (dehydrogenation of light paraffins to olefins)**

**Application:** The steam active reforming (STAR) process produces (a) propylene as feedstock for polypropylene, propylene oxide, cumene, acrylonitrile or other propylene derivatives, and (b) butylenes as feedstock for methyl tertiary butyl ether (MTBE), alkylate, isooctane, polybutylenes or other butylene derivatives.

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

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

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

In the adiabatic oxyreactor, part of the hydrogen from the intermediate product leaving the reformer is selectively converted with added oxygen or air, thereby forming steam. This is followed by further dehydrogenation over the same catalyst. Exothermic selective H₂ conversion in the oxyreactor increases olefin product space-time yield and supplies heat for further endothermic dehydrogenation. The reaction takes place at temperature between 500°C–600°C and at 4 bar–6 bar.

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

After cooling and condensate separation, the product is subsequently compressed, light-ends are separated and the olefin product is separated from unconverted paraffins in the fractionation section. Apart from light-ends, which are internally used as fuel gas, the olefin is the only product. High-purity H₂ may optionally be recovered from light-ends in the gas separation section.

**Economics:** Typical specific consumption figures (for polymer-grade propylene production) are shown (per ton of propylene product):

- **Propane:** 1,200 kg/metric ton
- **Fuel gas:** 6.4 kJ/metric ton
- **Cooling water:** 220 m³/metric ton
- **Electrical energy:** 180 kWh/metric ton

**Installations:** Two commercial plants using the STAR process for dehydrogenation of isobutane to isobutylenes have been commissioned (in the US and Argentina). More than 60 Uhde reformers and 25 Uhde secondary reformers have been constructed worldwide.


**Licensor:** Uhde GmbH, Dortmund, Germany

**Contact:** E-mail: information@tkt-uhde.thyssenkrupp.com
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 natural gas reception terminals, underground gas storage facilities (i.e., salt cavities, aquifers and depleted fields) and prior to LNG production. The process is suitable for prepurification and protection facilities for gas membrane systems.

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

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

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

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

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


Licensor: Advantica Ltd.

Contact: Antony Kane, Holywell Park, Ashby Rd., Loughborough, Leicestershire, UK; E-mail: antony.kane@advantica.biz
Drigas

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

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

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

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

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

Main advantages of the Drigas process are:

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

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

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

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


**Licensor:** SIIRTEC NIGI

**Contact:** SIIRTEC NIGI S.p.A., Via Algardi 2 - 20148, Milano, Italy, Phone: (39) 0 239 2231, Fax: (39) 0 2392 3010, E-mail: marketing@sini.it
Drizo gas dehydration

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

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

**Economics:** Combining very low dew points with low CO₂ and BTEX emissions, Drizo is an environmentally friendly process compared with the other glycol processes. Drizo is very competitive with all dehydration processes at water dew points below –30°C. A Drizo unit would be roughly 20% cheaper than an equivalent glycol stripping unit with recompression of the stripping gas (in addition to the fact that Drizo is able to reach much lower water dew points), and can be 50% cheaper than a mol sieve unit.

**Installations:** More than 45 units.

**References:**

**Licensors:** OPC Drizo, Inc., and Prosernat IFP Group Technologies

**Contact:** Christian Streicher, Marketing Manager, Prosernat, Tour Areva, 92084 Paris La Défense Cedex, France, Phone: (+33) 1 47 96 37 86, Fax: (+33) 1 47 96 02 46, E-mail: cstreicher@prosernat.com
**Ecoteg**

**Application:** Ecoteg is a process that uses triethylene glycol (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 all the outgoing streams of the regenerator.

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

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

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

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

Main advantages of the Ecoteg process are:

- Meet more stringent regulations for disposal without additional facilities
- Low operating cost
- Low gas dew point.

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

**Economics:** Ecoteg is an ecological and cost-effective dehydration process that does not require additional external facilities to meet regulations for effluents. This simplifies the first installation and/or additions to an existing plant. Savings in stripping gas helps the economics and may be a determinant when low gas dew points are required.


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**Return to Gas Processes INDEX**
Ifpexol

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

• Ifpex-1—simultaneous water and hydrocarbon dew pointing (down to −100°C)

• Ifpex-2—removal of acid gases and sulfur compounds (to sales gas specifications).

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

Ifpex-2: The gas from Ifpex-1 (or any other feed gas) is contacted with refrigerated methanol-based solvent in the contactor (3). Acid gases (CO₂, H₂S) 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 dew points below −30°C, Ifpex-1 can compete with glycol processes and offers much reduced (about 30% lower) CAPEX. Ifpex-2 offers significant savings compared to other processes for bulk acid-gas removal with acid-gas reinjection.

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

References: “Methanol treating schemes offers economics, versatility,” Oil & Gas Journal, June 1, 1992, p. 65.


Licensors: Prosernat IFP Group Technologies and Titan SNC Lavalin

Contact: Christian Streicher, Marketing Manager, Prosernat, Tour Areva, 92084 Paris La Défense Cedex, France, Phone: (+33) 1 47 96 37 86, Fax: (+33) 1 47 96 02 46, E-mail: cstreicher@prosernat.com
**AMMOGEN**

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

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

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

**Main advantages include:**
- Gaseous ammonia produced onsite and on demand
- Utmost safety (no governmental reportable amounts or contingency plans)
- Urea feedstock is harmless, easy-to-handle and widely available
- Simple and safe noncatalytic process
- No carryover of compounds that can damage SCR systems
- Very rapid response time and maximum turn-down availability
- Quick startup, shutdown and standby
- Automatic operation and low maintenance
- Limited plant footprint for easier installation; also can be skid-mounted or module
- Low capital and operating cost
- Capacity from several to thousands kg/h of ammonia.

**Installations:** Four plants in the US with design capacity from 270 kg/h to 1,600 kg/h.

**Licensors:** SIIRTEC NIGI and HERA LLC

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[Diagram of the AMMOGEN process]

**Gas Processes 2004**

**Effluent cleanup**
**Application:** Purify tail gas from sulfur recovery units (such as Claus units) and other gas streams containing low concentrations of SO₂. The type of process to be combined with the Beavon treatment depends on the intended disposition of the treated product gas (e.g., additional sulfur recovery, other component recovery, incineration or exhaust, while meeting stringent air pollution standards).

Beavon processing converts sulfur compounds to H₂S.

Beavon-MDEA processing adds H₂S separation.

Beavon-Selectox processing converts H₂S to elemental sulfur.

Beavon-Hi-Activity processing converts H₂S to elemental sulfur.

**Description:** In the Beavon step, essentially all sulfur compounds in the feed gas (SO₂, Sₓ, COS, CS₂) are converted to H₂S. The feed gas is heated (1) to reaction temperature by mixing with the hot combustion products of fuel gas and air. This combustion is carried out with a deficiency of air to provide sufficient H₂ and CO to convert all of the sulfur and sulfur compounds to H₂S. The heated gas mixture is then passed through a catalyst bed (2) where all sulfur compounds are converted to H₂S by hydrogenation and hydrolysis. The hydrogenated gas stream is cooled in a steam generator (3), and then by direct contact (4) with a buffer solution before entering the selected H₂S removal process.

**Beavon-MDEA.** One of several processes used to remove H₂S is by absorption (5) in a solution of MDEA (methyl diethanolamine) or one of the recently developed highly selective amine type solvents. The clean tail gas contains less than 10 ppm H₂S when using the newer solvents. When this combination is operating on a Claus tail gas, the separated H₂S can be recycled to the Claus unit.

**Beavon-Selectox.** An alternative (6) for removing the H₂S is to convert it to elemental sulfur by the Selectox process.

**Beavon-Hi-Activity.** Another alternate for removing the H₂S is to oxidize it directly to elemental sulfur by the Hi-Activity process.

**Operating conditions:** All pressures are near atmospheric. The Beavon hydrogenation/hydrolysis reactor operating temperature is in the range of 550°F to 750°F. Equipment is essentially all carbon steel. Sulfur recovery of Claus plus Beavon-Selectox or Beavon-MDEA is more than 99% or 99.9%, respectively.

**Installations:** There are more than 100 Beavon-type tail gas treating units worldwide. Among these are more than 30 Beavon-MDEA plants operating worldwide. Two Beavon-Selectox plants are operating in the US and Germany; one Beavon-Hi-Activity plant operating in Germany. Two Beavon-Hi-Activity plants to be installed in China and Venezuela.

**Licensors:** Parsons Energy & Chemicals Group, Inc., and UOP LLC.

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**Clauspol**

**Application:** Claus tail-gas treatment with total sulfur recoveries up to 99.9+%. Liquid-phase conversion of H$_2$S and SO$_2$ into liquid elemental sulfur (S).

**Description:** Claus tail gas is contacted counter-currently with an organic solvent in a low-pressure drop packed column (1). Hydrogen sulfide (H$_2$S) and SO$_2$ are absorbed in the solvent and react to form liquid elemental S according to the Claus reaction, which is promoted by an inexpensive dissolved catalyst. The solvent is pumped around the contactor (1), and the heat of reaction is removed through a heat exchanger (3) to maintain a constant temperature slightly above the sulfur melting point. Due to the limited solubility of S in the solvent, pure liquid S separates from the solvent and is recovered from a settling section (2) at the bottom of the contactor (1). This standard Clauspol II flow scheme allows S recovery up to 99.8% (Claus + Clauspol). The recovery level can be customized by adapting the size of the contactor (1).

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

**Economics:** For a Clauspol unit treating a typical Claus tail gas, in the 99.7–99.9% recovery, the CAPEX are typically 60–80% and OPEX 40–60% of those for a conventional hydrogenation/amine plant. Contrarily to the hydrogenation/amine process, Clauspol does not recycle any H$_2$S to the Claus unit, thus saving Claus plant capacity.

**Installations:** More than 40 units.


**Licensor:** Prosernat IFP Group Technologies

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**LTGT (Lurgi tail-gas treatment process)**

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

**Description:** The optimum Claus tail-gas treatment converts sulfur species to H2S and recovers it in a wet-scrubbing process. The Lurgi tail-gas treatment process (LTGT) is an amine treating system with generic MDEA solvent, structured packing and plate heat exchangers when possible. This process enables using smaller diameter columns, plot size, worldwide treating solution availability, proven technology and high selectivity. Installing smaller equipment lowers total investment costs.

Different sulfur species from the incoming Claus tail gas are converted (1) to H2S. Process water formed by the Claus reaction is removed in a direct cooler (2), and H2S is expunged by MDEA solution in an absorber column (3). The amine solution is regenerated in a steam-heated stripper column (4) and produces a H2S gas stream that is recycled back to the Claus section. Due to hydrogenation in the tail-gas treatment, both acid gases—H2S and CO2—are produced and routed to the absorber column.

Tertiary amines like MDEA, which are used in the LTGT, have the ability to selectively absorb H2S due to chemical structure and do not co-absorb CO2. Primary (MEA) and secondary amines (DEA) will absorb H2S along with most of the CO2. In tertiary amine solutions, CO2 can only be absorbed by an indirect acid/base reaction forming bicarbonates; this is a very slow reaction.

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

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


**Licensor:** Lurgi Oel-Gas-Chemie GmbH

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**Resulf**

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

**Products:** Treated vent gas from a Resulf-MM unit typically contains 1,000 ppm H₂S and must be incinerated. Treated vent gas from a Resulf unit typically contains less than 150 ppmv H₂S and is oxidized in an incinerator before venting to the atmosphere. Vent gas from a Resulf-10 unit has a maximum of 10 ppmv H₂S and may not require incineration.

**Description:** SRU tail gas is heated in the feed heater, then mixed with a reducing gas containing H₂. The heated stream passes through the reactor (1), where the SO₂, elemental sulfur and other sulfur-containing compounds, such as COS and CS₂, are converted to H₂S. 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 H₂S and only part of the CO₂. Rich solvent is sent to the regenerator (4) where the H₂S and CO₂ 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 MDEA or formulated MDEA as a solvent. Resulf-10 units are designed using specialty amines such as formulated MDEA. Resulf units use generic MDEA solvents. Resulf-MM units use amine from the primary amine unit (MEA, DEA or MDEA).

**Economics:** Plate and frame heat exchangers have been used to reduce capital costs. Modular designs can also be used to reduce capital costs while maintaining 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 upgrated.

**Installations:** TPA has licensed and designed worldwide:
- Resulf units: 45
- Resulf-10 units: 3
- Resulf-MM units: 2

**Supplier:** CB&I TPA

**Contact:** Mr. Jim E. Lewis, vice president and general manager, CB&I TPA Howe-Baker, 2703 Telecom Parkway, Ste. 150, Richardson, TX 75082, Phone: (972) 773-2257, Fax: (972) 669-3678, E-mail: jlewis@CBIepc.com
SCOT

Application: A low-pressure drop, high-sulfur recovery efficiency process to recover sulfur components from tail gas of sulfur plants. The SCOT process is insensitive to variations in the upstream SRU, such as in the H₂S/SO₂ ratio, hydrocarbon or ammonia breakthrough.

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

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

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

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


Licensor: Shell Global Solutions International B.V.
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**Application:** Catalytic purification of Claus tail gas or lean H<sub>2</sub>S waste gas for an overall sulfur recovery ranging from 99% to 99.9%. Different versions of the SULFREEN process are available.

**Description:** The SULFREEN process is based on the well-known Claus reaction in which the components—H<sub>2</sub>S and SO<sub>2</sub> in tail gas—are catalytically converted into elemental sulfur. The process occurs in the gas phase; the operating conditions being those at which the tail gas leaves the upstream Claus plant. The catalyst, which is arranged in fixed beds, consists of impregnated activated alumina, the properties of which are similar to those of Claus catalysts.

Tail gas leaving the Claus plant at temperatures of 120°C to 140°C passes through one of the two reactors (1) (2), where most of the H<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 by using part of the Claus plant tail gas. The regeneration gas is recovered in the sulfur condenser (4) (5). The desorbed sulfur contained in the hot regeneration gas is recovered in the sulfur condenser. 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<sub>2</sub> concentrations are expected to be present in the tailgas, a modified version of the process, named HYDROSULFREEN, is available. The HYDROSULFREEN process includes a pretreatment of the tail gas in an hydrolysis and oxidation reactor, located upstream of the SULFREEN reactors. For sulfur recoveries up to 99.9%, the DOXOSULFREEN process can be applied. This process includes an additional direct oxidation step downstream of the SULFREEN reactors.

**Economics:** SULFREEN investment amounts to 30–45% of the Claus unit cost for the conventional version, and 50–85% for the improved versions. Operating costs are much lower than for solvent-based processes.

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


**Licensor:** Lurgi Oel-Gas-Chemie GmbH

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DeNO\textsubscript{x} and DeDioxin technology

**Application:** Nitrogen Oxides (NO\textsubscript{x}) and Dioxin removal contained in flue-gas leaving combustion processes, to meet the most stringent environment regulations concerning atmospheric pollution.

**Description:** The De NO\textsubscript{x} and DeDioxin process technologies consist of the selective catalytic reduction (SCR) of NO, NO\textsubscript{2} and dioxin to elemental components air like nitrogen and water (H\textsubscript{2}O) vapor. The reducing agent is ammonia (NH\textsubscript{3}), which is available from anhydrous NH\textsubscript{3}, H\textsubscript{2}O diluted or produced from urea via hydrolysis.

The reaction takes place over a regenerable catalyst based on titanium dioxide (TiO\textsubscript{2}) as a carrier with vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) and tungsten trioxide (WO\textsubscript{3}) as active elements. The catalyst can have either a honeycomb structure with homogeneous pores size distribution and a very active surface or plate structure with a low-pressure drop.

The gas entering the SCR system is heated up to reaction temperature by an inline fuel gas burner. The reducing agent is injected upstream of the SCR reactor by a multiple spray nozzle system or by an injection grid. NH\textsubscript{3} is uniformly distributed and led to intimate contact with the contaminants by a static mixer. Typically, downstream of the SCR reactor, a gas-gas heat exchanger is used to preheat gas entering the DeNO\textsubscript{x} system by cooling down the outlet gas from the reactor routed to the stack.

**Operating conditions:** The SCR system pressure drop ranges from 0.20 bar to 0.30 bar and operating pressure is slightly under atmospheric pressure. Operating temperature can vary between 150°C and 450°C depending on gas composition. Lower limit temperature is dictated by the need to avoid condensation leading to a catalyst deactivation, while the upper limit is to avoid TiO\textsubscript{2} sintering. Catalyst regeneration is performed onsite with a proprietary technology (ReCat). The SCR system can reduce both NO\textsubscript{x} up to 90–95% and dioxin levels down to 0.1ng/Nm\textsuperscript{3}. NH\textsubscript{3} slip in the flue gas to the stack is generally kept below 5 ppm vol.

**Economics:** Technology is based on standard equipment and most are fabricated in carbon steel. Capital cost can range from $1 million for 50,000 Nm\textsuperscript{3}/h to $10 million for 800,000 Nm\textsuperscript{3}/h.

**Commercial plants:** More than 40 units are already in operation worldwide. Recently three plants in Italy and two in France have been built by SIIRTEC NIGI under IUT license. Capacity of DeNO\textsubscript{x} and DeDioxin plants can range from thousands to millions Nm\textsuperscript{3}/h of flue gas.

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

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Fluor CO$_2$LDSep process

**Application:** Modern hydrogen (H$_2$) plants use a pressure swing adsorption (PSA) technology to recover H$_2$ from shifted syngas. PSAs recover between 75% to 90% of the total H$_2$ in syngas. The remaining H$_2$ balance is not recovered; thus is devalued as fuel gas.

In response to growing concerns regarding greenhouse gas emissions, carbon dioxide (CO$_2$) recovery is garnering greater attention. Fluor’s CO$_2$LDSep is a patented process that consists of H$_2$ and CO$_2$ purification and recovery from a H$_2$ plant’s PSA tailgas.

**Description:** The tailgas from the PSA unit, in the existing H$_2$ plant, enters the CO$_2$LDSep plant and is compressed in the feedgas compressor (1). It is then dried (2), further compressed (3), cooled and expanded (4). The compression/expansion services may be accomplished in a single integrally geared package. A portion of the CO$_2$ is removed through liquefaction. Supplemental refrigeration may be used, but is not required in most cases.

If food-grade CO$_2$ production is desired, the liquid CO$_2$ can be purified in a stripper (5) to a purity of 99.99 wt%. The CO$_2$ is available as a pumpable liquid, which allows for low energy consumption when high product pressures are desired for enhanced oil recovery (EOR).

The H$_2$-enriched gas leaving the CO$_2$LDSep unit is sent to the H$_2$ recovery PSA (6), where H$_2$ of 99.9 vol% is separated from CO$_2$, methane and other impurities. The tailgas stream from the new H$_2$ recovery PSA along with the overhead from the stripper, if applicable, is routed to the reformer furnace where it is blended with the natural gas fuel and combusted.

**Operating conditions:** Typical PSA tailgas concentrations are 45% to 55% CO$_2$ and 24% to 26% H$_2$.

**Economics:** When applied to a 65 million scfd H$_2$ plant, the CO$_2$LDSep process is able to recover 7 million scfd of H$_2$ and 440 tpd of CO$_2$ from the PSA tailgas. This plant has an electrical load of 7 MW and requires 4,200 gpm of cooling water in circulation.

**References:** US Patent 6,301,927.

**Licensor:** Fluor Enterprises, Inc.

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Return to Gas Processes INDEX
Shell-Paques process

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

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

**Description:** In the Shell-Paques process, H₂S is directly oxidized to elemental sulfur (S) using colorless sulfur bacteria (Thiobacilli). These naturally occurring bacteria are not genetically modified. Feed gas is sent to a caustic scrubber (1) in which the H₂S reacts to sulfide. The sulfide is converted to elemental S and caustic by the bacteria when air is supplied to the bioreactor (2). Sulfur particles are covered with a (bio-) macropolymer layer, which keeps the sulfur in a milk-like suspension that does not cause fouling or plugging.

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

**Economics:** The Shell Paques/Thiopaq process achieves a very low H₂S content in the treated gas; a very high-sulfur recovery efficiency of 99.99% is achievable. This process can thus replace the combination of an amine/Claus/TGTU or, for smaller applications, liquid redox processes.

**Installations:** There is one Shell-Paques unit in operation with a second license sold. 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 decrease with decreasing CO₂/H₂S ratios.

**Reference:** Cameron Cline et al. “Biological process for H₂S removal from gas streams. The Shell-Paques/THIOPAQ gas desulfurization process” Lawrence Reid, Feb 2003


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

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Thiopaq DeSO\textsubscript{x}

**Application:** The Thiopaq DeSO\textsubscript{x} biological process selectively removes and converts SO\textsubscript{x} in the flue gases to elemental sulfur or H\textsubscript{2}S.

**Product:** The sulfur produced is hydrophilic; thus, it prevents equipment from fouling or blocking. Moreover, this characteristic makes the product sulfur suitable for agricultural use as fertilizer or as an insecticide. Alternatively, the sulfur can be melted to a high-purity product and meet international Claus sulfur specifications. Alternatively, H\textsubscript{2}S can be produced and the gas can be sent to the sulfur treatment unit (amine/Claus).

**Description:** The Thiopaq DeSO\textsubscript{x} is a commercial, two-step biological process. It can convert sulfite and sulfate to elemental sulfur or H\textsubscript{2}S. A sodium biphosphate solution quenches and removes particulates and absorbs SO\textsubscript{x} from the flue gas. The scrubbing liquid is regenerated and recycled to the scrubber.

The heart of the Thiopaq process is the proprietary anaerobic and aerobic bioreactors. In these air-lift-loop reactors, the absorbed sulfite is reduced to sulfide (HS\textsuperscript{−}) inside the anaerobic reactor in the presence of microorganism with hydrogen and could be removed as H\textsubscript{2}S alternatively. The sulfide is oxidized under controlled conditions to elemental sulfur via the microorganisms. The produced elemental sulfur has a hydrophilic nature and is separated from the aqueous effluent in a proprietary three-phase separator.

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

**Installation:** Twenty Thiopaq units operating worldwide to remove sulfur from gas and liquid streams for a variety of industries. Currently, a 13-mtpy unit is in startup phase for refinery service in Egypt.

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

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**Thiopaq—H₂S Removal**

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

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

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

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

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

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

**Installations:** Thirty-one units are operating worldwide to remove sulfur from gas and liquid streams in a variety of industries. Currently, a 13-mtpd unit in startup phase for refinery service in Egypt.

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

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Hydrogen

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

**Feedstock:** Natural gas, refinery gas, liquefied petroleum gas (LPG) and naphtha.

**Product:** High-purity hydrogen and steam.

**Description:** Light hydrocarbon feed (1) is heated prior to passing through two fixed-catalyst beds. Organic sulfur compounds present in feed gas (e.g., mercaptans) are converted to hydrogen sulfide (H$_2$S) and mono-olefins in the gas phase are hydrogenated in the first bed of cobalt molybdenum oxide catalyst (2). The second bed contains zinc oxide to remove H$_2$S by adsorption. This sulfur-removal stage is necessary to avoid poisoning of the reforming catalysts.

Treated feed gas is mixed with steam and heated before passing to the reformer where the hydrocarbons and steam react to form synthesis gas (syngas).

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

Syngas containing hydrogen, methane, carbon dioxide (CO$_2$), carbon monoxide (CO) and water leaves the reformer and passes through the waste-heat boiler to the shift reactor (3) where most of the CO is converted to CO$_2$ and hydrogen by reaction with steam. For heavier feedstocks, prereforming is used for conversion of feedstock upstream of the reformer.

The syngas is cooled through a series of heat-recovery exchangers before free water is recovered in a knockout drum. The resultant raw hydrogen stream passes to the pressure swing adsorption (PSA) unit for purification (4) to typically 99.9% hydrogen product quality. Tail gas from the PSA unit provides a substantial proportion of the firing duty for the reformer. The remaining fuel is supplied from the feed gas or other sources (e.g., refinery fuel gas).

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

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

**Investment:** 10–100 million scfd, 3rd Q 2002, USGC $9–55 million

**Utilities, typical per million scfd of hydrogen produced (natural gas feedstock):**

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed + fuel, lb</td>
<td>960</td>
</tr>
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</tr>
<tr>
<td>Steam, export, lb</td>
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</tr>
<tr>
<td>Water, cooling, US gal</td>
<td>1,180</td>
</tr>
<tr>
<td>Electricity, kWh</td>
<td>12</td>
</tr>
</tbody>
</table>


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

**Licensor:** Foster Wheeler

**Contacts:**

US: 2020 Dairy Ashford, Houston, TX 77077, Phone: (281) 597-3066, Fax: (281) 597-3028

UK: Shinfield Park, Reading, RG2 9FW, Phone: (+44) 118 913 1234, Fax: (+44) 118 913 2333, E-mail: refining@fwc.com

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**Gas Processes 2004**

**Hydrogen**

<table>
<thead>
<tr>
<th>Process</th>
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</tr>
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<tr>
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| Reform | Treated feed gas is mixed with steam and heated before passing to the reformer where the hydrocarbons and steam react to form synthesis gas (syngas). Foster Wheeler supplies proprietary side-fired Terrace Wall reformers, with natural draft mode option for increased reliability, compact plot layout with convection section mounted directly above the radiant section and modular fabrication option. Foster Wheeler supplies top-fired reformer options for large capacity plants. Syngas containing hydrogen, methane, carbon dioxide (CO$_2$), carbon monoxide (CO) and water leaves the reformer and passes through the waste-heat boiler to the shift reactor (3) where most of the CO is converted to CO$_2$ and hydrogen by reaction with steam. For heavier feedstocks, prereforming is used for conversion of feedstock upstream of the reformer. The syngas is cooled through a series of heat-recovery exchangers before free water is recovered in a knockout drum. The resultant raw hydrogen stream passes to the pressure swing adsorption (PSA) unit for purification (4) to typically 99.9% hydrogen product quality. Tail gas from the PSA unit provides a substantial proportion of the firing duty for the reformer. The remaining fuel is supplied from the feed gas or other sources (e.g., refinery fuel gas). Demineralized water makeup is de-aerated, mixed with recovered condensate and preheated through a series of heat-recovery exchangers before passing to the steam drum. Saturated and superheated steam is raised by heat exchange with the reformed gas and flue gas in the convection section of the reformer. Steam export quantities can be varied between 1,250 and 5,750 lb/million scfd of hydrogen produced using air pre-heat and auxiliary firing options. **Economics:** Plant design configurations are optimized to suit the clients’ economic requirements, using discounted cash-flow modeling to establish the lowest lifecycle cost of hydrogen production. **Investment:** 10–100 million scfd, 3rd Q 2002, USGC $9–55 million **Utilities, typical per million scfd of hydrogen produced (natural gas feedstock):**

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</tbody>
</table>

**Reference:** Ward, R. D. and N. Sears, “Hydrogen Plants for the New Millennium,” Hydrocarbon Engineering, Vol. 7, Number 6, June 2002. **Installation:** Over 100 plants, ranging from 1 million scfd to 95 million scfd in a single-train configuration and numerous multi-train configurations. **Licensor:** Foster Wheeler **Contacts:** US: 2020 Dairy Ashford, Houston, TX 77077, Phone: (281) 597-3066, Fax: (281) 597-3028 UK: Shinfield Park, Reading, RG2 9FW, Phone: (+44) 118 913 1234, Fax: (+44) 118 913 2333, E-mail: refining@fwc.com

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Hydrogen

**Application:** Production of hydrogen (H₂) from hydrocarbon (HC) feedstocks, by steam reforming.

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

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

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

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

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

Typical specific energy consumption based on feed + fuel – export steam ranges between 3.0 and 3.5 Gcal/KNm³ (330–370 Btu/scf) LHV, depending upon feedstock, plant capacity, optimization criteria and steam-export requirements. Recent advances include integration of hydrogen recovery and generation, recuperative (post-)reforming also for capacity retrofits.

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

**Licensor:** Technip

**Contact:** Technip Benelux B.V., P.O. Box 86, NL-2700 AB Zoetermeer, The Netherlands, Phone: (31) 79 3293 600, Fax: (31) 79 3522 561, E-mail: tpbenelux@technip.com

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Gas Processes 2004
**Application:** Produce hydrogen for refinery hydrotreating and hydrocracking or other refinery, petrochemical and industrial applications.

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

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

**Description:** The feedstock (natural gas, for example) is desulfurized (1), mixed with steam and converted to synthesis gas in the reformer (2) over nickel catalysts at 20 to 50 bar pressure and temperatures of 800°C to 950°C.

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

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

The Uhde reformer design with the unique proprietary cold outlet manifold system enables construction and operation of world-scale reformers with hydrogen capacities to 290,000 Nm³/h.

**Economics:** Typical consumption figures (feed and fuel) range between 150 and 175 GJ/metric ton of hydrogen, depending on the individual plant concept.

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


**Licensor:** Uhde GmbH, Dortmund, Germany

**Contact:**
E-mail: information@tkt-uhde.thyssenkrupp.com
Hydrogen (Polybed PSA)

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

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

**Product:** Recovery of H₂ varies between 60% and 90%, depending on composition, pressure levels and product requirements. Typical temperatures are 60°F to 120°F. Purity can be +99.9999 mole%.

**Description:** Purification is based on advanced pressure swing adsorption (PSA) technology. Purified H₂ is delivered at essentially feed pressure, and impurities are removed at a lower pressure.

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

All systems use advanced proprietary adsorbents and patented 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 presently produce streams with less than one ppmv impurity from feed concentrations of +40 mole%.

Operation is automatic with pushbutton startup and shutdown. After startup, the unit will produce H₂ 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 x 25 ft to 60 x 120 ft. Units are skid-mounted and modular to minimize installation costs. Material for piping and vessels is carbon steel. Control can be via a local or remote-mounted control panel or by integration into the refinery’s computer control system. Units are designed for outdoor, unattended operation and require no utilities other than small quantities of instrument air and power for instrumentation.

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

**Licensor:** UOP LLC

**Contact:** Anita Black, UOP, 25 E. Algonquin Ave., Des Plaines, IL 60016 USA, Phone: (847) 375-7801, Fax: (847) 391-2253, E-mail: anita.black@uop.com
**Hydrogen (Polysep membrane)**

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

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

**Product:** For typical hydrogen purification applications, recovery varies between 70% and 95% and purity ranges from 70 to 99 mole%, 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 oxo-alcohol plants. Also, a new application is hydrogen recovery from IGCC power generation systems.

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

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

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

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

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

**Licensor:** UOP LLC

**Contact:** Anita Black, UOP, 25 E. Algonquin Ave., Des Plaines, IL 60016 USA, Phone: (847) 375-7801, Fax: (847) 391-2253, E-mail: anita.black@uop.com
Hydrogen (steam reform)

**Application:** Production of hydrogen 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 and light naphtha.

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

**Description:** The feed is heated in the feed preheater and passed through the hydrotreater (1). The hydrotreater converts sulfur compounds to H2S and saturates any unsaturated hydrocarbons in the feed. The gas is then sent to the desulfurizers (2). These adsorb the H2S from the gas. The desulfurizers are arranged in series and designed so that the adsorbent can be changed while the plant is running.

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

Gas leaving the reformer is cooled by the process steam generator (4). Gas is then fed to the shift converter (5), which contains a bed of copper promoted iron-chromium catalyst. This converts CO and water vapor to additional H2 and CO2. Shift converter effluent gas is cooled in a feed preheater, a BFW preheater and a DA feed water preheater. Hot condensate is separated out. Process gas is then cooled in a gas air cooler and a gas trim cooler. The cooled stream flows to a cold condensate separator where the remaining condensate is separated and the gas is sent to a PSA hydrogen purification system (6).

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

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

**Installations:** Over 170 plants worldwide-ranging in size from less than 1 million scfd to over 90 million scfd capacities. Plant designs for capacities from 1 million scfd to 280 million scfd.

**Supplier:** CB&I Howe Baker

**Contact:** Mr. Craig E. Wentworth, vice president of sales, CB&I Howe-Baker, 3102 East Fifth St., Tyler, TX 75701, Phone: (903) 595-7911, Fax: (903) 595-7751, Email: cwentworth@CBIepc.com
**Hydrogen (steam reform)**

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

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

The desulfurized feed is mixed with process steam at an optimized steam/carbon ratio, superheated to 500–650°C and fed to the Lurgi Reformer. The feed/steam mixture passing the reformer tubes is converted at 800–900°C by presence of a nickel catalyst to a reformed gas containing H₂, CO₂, CO, CH₄ and undecomposed steam. The reformed gas is cooled to approximately 33°C in a reformed gas boiler.

The Lurgi Reformer is a top-fired reformer with a low number of burners and low heat losses, almost uniform wall temperature over the entire heated tube length and low NOₓ formation by very accurate fuel and combustion air equipartition to the burners. An adiabatic pre-reformer operating at an inlet temperature of 400–500°C (dependent on feedstock) may be inserted upstream of the feed superheater as a process option. Feedgas is partly converted to H₂, CO and CO₂ with high-activity catalyst; all hydrocarbons are totally converted to methane. The pre-reformer limits steam export to maximize heat recovery from the process and increases feedstock flexibility.

The CO in the reformed gas is shift-converted with an iron-chromium catalyst, increasing hydrogen yield and reducing CO content to below 3-vol.%. The shift gas is cooled to 40°C and any process condensate is separated and recycled to the process. The gas is then routed to the PSA unit, where pure hydrogen is separated from the shift-gas stream. Offgas is used as fuel for steam reforming.

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

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

**Economics:** Consumption figures based on light natural gas feedstock/1 million scfd of H₂:

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<thead>
<tr>
<th>Item</th>
<th>Consumption</th>
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<tr>
<td>Feed + fuel, million scfd</td>
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<tr>
<td>Demineralized water, t</td>
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<td>Cooling water, m³</td>
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<td>Electricity, kWh</td>
<td>19</td>
</tr>
<tr>
<td>Export steam, t</td>
<td>0.7</td>
</tr>
</tbody>
</table>

**Installations:** More than 105 gas reforming plants, 25 being hydrogen plants, with single-train capacities ranging from 1 million scfd to 200 million scfd.

**Licensor:** Lurgi Oel-Gas-Chemie GmbH

**Contact:** Ulrich Wolf, Lurgi Oel-Gas-Chemie GmbH, Lurgiallee 5, D-60295 Frankfurt am Main, Germany, Phone: (49) 69 5808 3238, Fax: (49) 69 5808 2639, E-mail: Ulrich_Wolf@lurgi.de
**Hydrogen and liquid hydrocarbon recovery—cryogenics**

**Application:** Recover high purity hydrogen and $C_2^+$ liquid products from refinery offgases.

**Description:** Cryogenic separation of refinery offgases and purges containing from 10% to 80% hydrogen ($H_2$) and 15% to 40% hydrocarbon liquids such as ethylene, ethane, propylene, propane and butanes. Refinery offgases are optionally compressed and then pretreated (1) to remove sulfur, carbon dioxide ($CO_2$), $H_2O$ and other trace impurities. Treated feed is partially condensed in an integrated multi-passage exchanger system (2) against returning products and refrigerant.

Separated liquids are sent to a demethanizer (3) for stabilization while hydrogen is concentrated (4) to 90% to +95% purity by further cooling. Methane, other impurities, and unrecovered products are sent to fuel or optionally split into a synthetic natural gas (SNG) product and low-Btu fuel. Refrigeration is provided by a closed-loop system (5). Mixed $C_2^+$ liquids from the demethanizer can be further fractionated (6) into finished petrochemical feeds and products such as ethane, ethylene, propane and propylene.

**Operating conditions:** Feed capacities from 10 to 150+ million scfd. Feed pressures as low as 150 psig. Ethylene recoveries are greater than 95%, with higher recoveries of ethane and heavier components. Hydrogen recoveries are better than 95% recovery.

**Economics:** Hydrogen is economically co-produced with liquid hydrocarbon products, especially ethylene and propylene, whose high value can subsidize the capital investment. High hydrocarbon liquid products recovery is achieved without the cost for feed compression and subsequent feed expansion to fuel pressure. Power consumption is a function of hydrocarbon quantities in the feed and feed pressure. High-purity hydrogen is produced without the investment for a “back-end” PSA system. Project costs can have less than a two-year simple payback.

**Installations:** Five operating refinery offgas cryogenic systems processing FCC offgas, cat reformer offgas, hydrotreater purge gas, coker offgas and refinery fuel gas. Several process and refrigeration schemes employed since 1987 with the most recent plant startup in 2001.

**Reference:** US Patents 6,266,977 and 6,560,989.


**Licensor:** Air Products & Chemicals Inc.

**Contact:** Joanne Trimpi, Marketing Manager, Energy & Process Industries, 7201 Hamilton Blvd., Allentown, PA 18195-1501, Phone: (610) 481-7326, Fax: (610) 706-2982, E-mail: trimpijl@apci.com
Hydrogen recovery (cryogenic)

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

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

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

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

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

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

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

Economics: Cryogenic recovery of hydrogen is economically favored by the ability to recover other valuable products, e.g., olefins and LPG. Compared with alternative technologies, cryogenic processing is the most efficient and has the lowest utilities cost. Cryogenic recovery has been used to treat gases with hydrogen feed concentrations as high as 80% and pressures up to 80 barg.

Installations: Fourteen.


Licensor: Costain Oil, Gas & Process Ltd.

Contact: Adrian Finn, Technology Development Manager, Costain Oil, Gas & Process Ltd., Costain House, Styal Road, Manchester, UK, Phone: (44) 161 910 3227, Fax: (44) 161 910 3256, e-mail: Adrian.Finn@cogap.com
Hydrogen, HTCR based

**Application:** Produce hydrogen ($H_2$) from hydrocarbon feedstocks such as: natural gas, LPG, naphtha, refinery offgases, etc., using the Haldor Topsøe Convective Reformer (HTCR). Plant capacities range from 200 Nm$^3$/h to 20,000 Nm$^3$/h (200,000 scfd to 20 MMscfd) and hydrogen purity ranges from 99.5% to 99.999+% without steam export.

**Description:** The HTCR-based hydrogen plant can be tailor-made to suit the customer’s needs with respect to feedstock flexibility. In a typical plant, feedstock is first desulfurized. Subsequently, process steam is added, and the mixture is fed to the HTCR. Process gases are reacted in a water-shift reactor and purified by pressure swing absorption (PSA) unit to obtain product-grade hydrogen. PSA offgases are used as fuel for the HTCR. Excess heat is efficiently used for process heating and steam generation.

A unique technology feature is high thermal efficiency. Product gas and flue gas are both cooled to about 600°C (1,100°F) to recover heat for the reforming reaction. Energy-efficient hydrogen plants based on the HTCR use high thermal efficiency and have no steam export.

**Economics:** HTCR-based plants provide the customer with a low-investment cost and low operating expenses. The plant can be supplied skid-mounted providing a short erection time. The plants have high flexibility, reliability and safety. Fully automated operation, startup and shutdown allow minimum operator attendance. Net energy efficiency of about 3.4–3.6 Gcal/1000 Nm$^3$ is achieved depending on size and feedstock (360–380 Btu/scf).

**Installations:** Twenty-one licensed units.


**Licensor:** Haldor Topsøe A/S

**Contact:** Jørgen N. Gøl or Michael Agertoft, Nymollevej 55, DK-2800 Lyngby, Denmark, Phone: (45) 45 27 2000, Fax: (45) 45 27 29 99, E-mail: JNG@topsoe.dk or MCA@topsoe.dk
**Hydrogen, steam methane reform (SMR)**

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

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

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

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

**References:**

**Licensor:** Haldor Topsøe A/S

**Contact:** Jørgen N. Gøl, Nymollevej 55, DK-2800 Lyn- gby, Denmark, Phone: (45) 45 27 2000, Fax: (45) 45 27 29 99, E-mail: JNG@topsoe.dk
Hydrogen-methanol decomposition

**Application:** Produce hydrogen (H₂) in the capacity range of 100–1,000 Nm³/h of H₂ for usage by the chemical industry and the manufacture of electronics.

**Description:** Feed methanol and water are mixed, evaporated and superheated before being sent to the methanol decomposition reactor. In this reactor, the methanol is reacted to form H₂, CO and CO₂. The reaction is endothermic and requires energy by heat transfer from externally heated oil or by steam.

The raw gas from the reactor is cooled, and the process condensate is separated. The separated gas is further purified by a pressure swing adsorption (PSA) unit; startup, operation and shutdown are automatic.

**Features:** Utility requirements per Nm³ of H₂ are:

<table>
<thead>
<tr>
<th>Utility</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol, kg</td>
<td>0.63</td>
</tr>
<tr>
<td>Fuel, kcal</td>
<td>320</td>
</tr>
<tr>
<td>Demineralized water, kg</td>
<td>0.37</td>
</tr>
<tr>
<td>Electricity, kWh</td>
<td>0.06</td>
</tr>
<tr>
<td>Additional utilities required</td>
<td>Cooling water, instrument air and nitrogen</td>
</tr>
</tbody>
</table>

The hydrogen plant construction is compact and can be skid-mounted.

**Economics:** Features include:
- Low investment cost
- Low operating costs
- Low maintenance cost
- Short delivery time
- Fast installation of the skid-mounted unit.

**Installations:** Ten plants are in operation worldwide.

**Licensor:** Haldor Topsøe A/S

**Contact:** Jørgen N. Gøl, Nymollevej 55, DK-2800 Lyngby, Denmark, Phone: (45) 45 27 2000, Fax: (45) 45 27 29 99, E-mail: JNG@topsoe.dk
Hydrogen—PRISM membrane

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

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

The hydrocarbon-rich nonpermeate product is returned at nearly the same pressure as the feed gas for use as fuel gas, or in the case of synthesis gas applications, as a carbon monoxide (CO) enriched feed to oxo-alcohol, organic acid, or Fisher-Tropsch synthesis.

**Description:** Typical PRISM membrane systems consist of a pretreatment (1) section to remove entrained liquids and preheat feed before gas enters the membrane separators (2). Various membrane separator configurations are possible to optimize purity and recovery, and operating and capital costs such as adding a second stage membrane separator (3). Pretreatment options include water scrubbing to recover ammonia from ammonia synthesis purge stream.

Membrane separators are compact bundles of hollow fibers contained in a coded pressure vessel. The pressurized feed enters the vessel and flows on the outside of the fibers (shell side). Hydrogen selectively permeates through the membrane to the inside of the hollow fibers (tube side), which is at lower pressure.

PRISM membrane separators’ key benefits include resistance to water exposure, particulates and low feed to nonpermeate pressure drop.

Membrane systems consist of a pre-assembled skid unit with pressure vessels, interconnecting piping, and instrumentation and are factory tested for ease of installation and commissioning.

**Economics:** Economic benefits are derived from high-product recoveries and purities, from high reliability and low capital cost. Additional benefits include relative ease of operation with minimal maintenance. Also, systems are expandable and adaptable to changing requirements.

**Installations:** Over 270 PRISM H₂ membrane systems have been commissioned or are in design. These systems include over 54 systems in refinery applications, 124 in ammonia synthesis purge and 30 in synthesis gas applications.

**Licensor:** Air Products and Chemicals, Inc.

**Contact:** Joanne Trimpi, Marketing Manager, Energy & Process Industries, 7201 Hamilton Blvd., Allentown, PA 18195-1501, Phone: (610) 481-7326, Fax: (610) 706-2982, E-mail: trimpijl@apci.com
**Hydrogen—PRISM PSA**

**Application:** Purify hydrogen from dedicated H₂-production equipment and a wide range of offgas streams from refineries and hydrocarbon processing industries (HPI) to produce 95–99.999+% H₂ purity.

**Feed:** Wide range of H₂-containing streams, typically with feed H₂ greater than 50%, pressure from 70 psi to 600 psi (5–40 bar), and temperature from 60°F to 110°F. Examples of dedicated H₂-production units include steam-methane reformers, naphtha-fired reformers and gasifiers. Hydrogen can be recovered from ethylene, propylene, styrene, and coke oven offgases; and various refinery streams such as cat reformer, hydrotreater/hydrocracker offgases.

**Products:** Hydrogen recovery is 83–90% for SMR applications, with CO from 1 ppm to 50 ppm. Purity is typically 95–99.9% for offgas plants, with recovery dependent on operating conditions. Integrated processes producing multiple products are practiced. For example, gasifier or refinery offgas pressure swing absorption (PSA) can be integrated with cryogenic processes for co-recovery of H₂ with CO or hydrocarbons, respectively. PSAs are typically integrated with membranes in gasifier installations to co-produce high-purity H₂ and a wide range of syngas compositions.

**Description:** PSA purifies H₂ by sequentially adsorbing impurities in multiple layers of adsorbents within a single PSA vessel. Adsorbent selection is critical, and is based on extensive R&D with verification from frequent plant performance tests. Hydrogen is produced from vessel(s) in their feed step, while other vessels are regenerated.

The number of vessels depends on the system capacity and the desired H₂ recovery. For example, 4-bed PSA typically produces up to 15 million scfd H₂. As capacity increases, it is generally economical to increase the recovery and number of beds. A 10-bed PSA unit can produce over 120 million scfd H₂ at up to 90% recovery. Single-train capacities exceed 200 million scfd.

The systems are skid-mounted, requiring minimal fieldwork. These PSAs include all control valves, switch valves and instrumentation required. Feed, product, and tail gas monitoring, isolation, and venting systems can be integrated into the skid design to further minimize field piping associated with the PSA. The system can be controlled using any commercial PLC or DCS products. Average reliabilities exceed 99.9%.

**Economics:** PSA costs vary with capacity and recovery. When compared to the other hydrogen recovery technologies (cryogenics and membranes), hydrogen PSAs fall in the medium-capital cost range and have moderate scaling economics. Using a PSA, H₂ can typically be recovered for about 1.2-2X fuel value from offgas plants. When ultra-high-purity is required (e.g., ppm levels of CO, CO₂ or other contaminants), PSA is typically the best technical and economic choice.


**Installations:** Over 50 operating units, including the world’s largest operating PSA installation.

**Licensor:** Air Products and Chemicals, Inc.

**Contact:** Joanne Trimpi, Marketing Manager, Energy & Process Industries, 7201 Hamilton Blvd., Allentown, PA 18195-1501, Phone: (610) 481-7326, Fax: (610) 706-2982, E-mail: trimpijl@apci.com
MEDAL membrane (hydrogen)

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

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

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

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

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

Consistent H₂ recovery and product purity can be maintained through wide fluctuations in feed composition, operating pressures and feed flow rates. The systems are skid-mounted for compactness, 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 hydrogen membrane systems are characterized by low capital and operating costs, and a high return on capital.

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

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

Contact: David Marchese, Sales and Marketing Manager, Phone: (302) 225-1100, E-mail: info.medal@airliquide.com
AMINEX

**Application:** Extract H₂S, COS and CO₂ from gases and light liquid streams with amine solution using FIBER-FILM contactor technology.

**Description:** The amine phase flows along the FIBER-FILM contactor fibers, which are continuously renewed, as the wet fibers are preferentially wetted by the amine phase in the AMINEX process. Hydrocarbons flow through the shroud parallel to the amine-wetted fibers where the H₂S, COS, and/or CO₂ are extracted into the amine phase. The two phases disengage in the separator vessel where the rich amine flows to the amine regeneration unit and the treated gas or light liquids goes to storage.

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

**Installations:** Ten worldwide.


**Licensor:** Merichem Chemicals & Refinery Services LLC

**Contact:** Tara Johnson, Media Relations Manager, Merichem Chemicals & Refinery Srvs, 5450 Old Spanish Trail, Houston, TX  77023, Phone: (713) 428 5280, Fax: (713) 921-4604, E-mail: tjohnson@merichem.com

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MERICAT II

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

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

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

Installations: Twenty-eight worldwide.


Licensor: Merichem Chemicals & Refinery Services LLC

Contact: Tara Johnson, Media Relations Manager, Merichem Chemicals & Refinery Srvs, 5450 Old Spanish Trail, Houston, TX 77023, Phone: (713) 428 5280, Fax: (713) 921-4604, E-mail: tjohnson@merichem.com

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THIOLEX/REGEN

Application: Extract H₂S, COS and mercaptans from gases and light liquid streams, including gasoline, with caustic using FIBER-FILM contactor technology. It can also be used to hydrolize COS contained in LPG.

Description: The caustic phase flows along the FIBER-FILM contactor fibers, which is continuously renewed, as the wet fibers are preferentially wetted by the caustic phase in the THIOLEX process. Hydrocarbons flow through the shroud parallel to the caustic phase where the H₂S and mercaptans are extracted into the caustic phase. The two phases disengage and the caustic flows to the REGEN system. The spent caustic is regenerated using air and catalyst in the oxidizer for reuse, which converts the extracted mercaptans to disulfides. The disulfides are removed from the caustic by a FIBER-FILM contactor solvent wash system.

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

Installations: Over 200 worldwide.

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

Licensor: Merichem Chemicals & Refinery Services LLC

Contact: Tara Johnson, Media Relations Manager, Merichem Chemicals & Refinery Srvs, 5450 Old Spanish Trail, Houston, TX 77023, Phone: (713) 428 5280, Fax: (713) 921-4604, E-mail: tjohnson@merichem.com

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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 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 NGLs overhead and lean solvent at the bottom. After heat recuperation, the lean solvent is presaturated with absorber overhead gases. The chilled solvent flows into the top of the absorber column. The separated gases from the presaturator separator form the pipeline sales gas.

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

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

Installations: Two units operating successfully.


Licensor: Advanced Extraction Technologies, Inc., 2 Northpoint Dr., Houston, TX 77060; e-mail: seekinfo@aet.com.
AET Process NRU

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

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

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

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

**Installations:** Two commercial.

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


**Licensor:** Advanced Extraction Technologies, Inc., 2 Northpoint Dr., Houston, TX 77060; e-mail: seekinfo@aet.com.
**CO₂ recovery and purification**

**Application:** Purification and liquefaction of carbon dioxide (CO₂) from process gases to remove small traces of light hydrocarbons, e.g., amine stripper off-gases. Purification of natural gas containing high levels of CO₂ and separation of ethane/CO₂, via a hybrid membrane/cryogenic process.

**Products:** Carbon dioxide of purities up to 99.998%. Gaseous CO₂ for use in applications such as enhanced oil recovery (EOR).

**Description:** Impure CO₂-rich feed (typically 90% + CO₂) is compressed and cooled to remove water (1). The gas is dried by molecular sieve driers (2) before entering the low-temperature section, where the gas is used to reboil the distillation column (3) before entering the column. The condenser is usually a reflux exchanger. Vapor rising through the exchanger passages is cooled, and the resulting liquid flows back down the same passages and has intimate contact with the rising vapor. The cold reflux to the column is provided by an external refrigeration cycle (4), typically ammonia evaporating at −28°C. The bottoms product from the column is pure liquid CO₂.

For recovery from lean-CO₂ streams, a hybrid membrane/cryogenic process can produce pure CO₂. Typically, the membrane concentrates the CO₂ content from 30% to 90%. The concentrated stream passes to a low-temperature unit for further purification. This method enables ethane/CO₂ mixtures to be separated to pure products without multiple distillation columns.

For recovery from rich-CO₂ streams, enhanced recovery can be achieved with a membrane to process the distillation column overheads and recycling of the CO₂-rich permeate into the cryogenic process.

**Operating conditions:** Plants from 5-tpd to 1,200-tpd pure CO₂. Virtually any feed-gas pressure can be handled. Compression is required for feed-gas pressures below 14 barg.

**Economics:** Typical power requirements for a cryogenic plant with a feed-gas at atmospheric pressure and producing liquid CO₂ are 0.15 kWh/kg.

**Installations:** Seven.

**References:**

**Licensor:** Costain Oil, Gas & Process Ltd.

**Contact:** Adrian Finn, Technology Development Manager, Costain Oil, Gas & Process Ltd., Costain House, Styal Road, Manchester, UK, Phone: (44) 161 910 3227, Fax: (44) 161 910 3256, e-mail: Adrian.Finn@cogap.com
**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 bars is cooled to –30°C in E1 and enters V1 where liquid and gas are separated. The cold high-pressure gas is expanded to 30 bars in expander T1, and the resulting stream feeds the purifier C1. Liquid from V1 is sent to the purifier bottom. The liquid from the purifier is pumped to 33 bars and is reheated to 20°C to feed the deethanizer. The deethanizer C2 produces a vapor distillate that is ethane-rich. This stream is liquefied in E1 and sent to C1 as reflux. The treated gas at 30 bars is reheated and compressed to sales-gas pressure. Approximately 99.5% propane recovery can be reached when propane value is high.

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

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

**Reference:** US Patents 4 690 702 and 5 114 450.

**Licensor:** Technip

**Contact:** La Defense 12, 9273 Paris La Defense Cedex, France; E-mail: grenaudin@technip.com
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 turbo-expander. Multi-stream plate-fin heat exchangers increase efficient heat integration of the process.

Description: The high-pressure, dry feed gas at 25°C, 70 bars is cooled to –40°C in E1 and enters V1 where the liquid and gas are separated. The cold high-pressure gas is divided in two streams—the main cut (85%) is sent to the expander and to the demethanizer C1 that operates at 30 bars. The small segment (15%) is liquefied and sent as second reflux to C1. The liquid pressure is reduced to 50 bars, and the liquid is partially vaporized in E1. Liquid and vapor are separated in V2. The vapor is liquefied in E2, used as third reflux and liquid is sent to C1.

The demethanizer overhead is reheated and compressed to sales gas pipeline specifications. A portion of the stream (10%) is recycled, cooled, liquefied and sent as first reflux. Approximately 99% ethane recovery can be reached when CO$_2$ content of feed gas is low.

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

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


Licensor: Technip

Contact: La Defense 12, 9273 Paris La Defense Cedex, France; E-mail: grenaudin@technip.com
Fluor Cryo-Gas process

**Application:** The Fluor Cryo-Gas process for natural gas liquids (NGL) recovery is a complete portfolio of patented or patent pending turbo-expander-based NGL recovery processes. It is tailored to meet a wide variety of feed gases and NGL recovery requirements.

**Description:** The Cryo-Gas process presented in the diagram is the vapor reflux absorption process (VRAP). VRAP is a two column process that can achieve 99.9% propane recovery without external refrigeration. It features low capital cost, weight and footprint and has low energy and utility requirements.

Four additional Fluor Cryo-Gas process schemes are:

- Fluor's patent pending two columns, high-pressure absorber process (TCHAP) is the most energy efficient NGL recovery process for feed gas pressures exceeding 1,000 psig. TCHAP achieves up to 85% ethane recovery with propane recovery in excess of 99%. Alternately, the process can achieve propane recoveries exceeding 99% while rejecting ethane. It is resistant to carbon dioxide (CO2) freezing and requires 30% less residue gas compression hp than competing processes. TCHAP can produce product quality ethane with <500 ppmv CO2 without treating.
- The stabilizer expander process (STEP) is specifically designed for rich feed gases that also vary in composition over time. STEP is capable of 88% ethane recovery with 97% propane recovery. It also has a high C2 and C3 recovery under a wide variation of feed gas compositions.
- The twin-reflux absorption process (TRAP) achieves greater than 90% ethane recovery with more than 99% propane recovery. It is ideal for revamping existing NGL plants. The process can completely reject ethane without loss in propane recovery. TRAP can also be used for ethane recovery at feed pressures as low as 300 psig. When used in an existing plant retrofit, TRAP usually does not require re-wheeling the existing turbo-expander.
- The subcooled absorption reflux process (SARP) is designed for rich feed gases with a high CO2 content. SARP can achieve ethane recoveries exceeding 90% with propane recoveries of more than 99%. SARP minimizes CO2 removal requirements and freezing problems while maintaining ethane recovery exceeding 90%.

**Installations:** More than 50 turbo-expander plants designs with single train capacities as high as 2,500 million scfd

**References:** US Patent 6,601,406 (VRAP).

**Licensor:** Fluor Enterprises, Inc.

**Contact:** Dick Nielsen, One Fluor Daniel Dr., Aliso Viejo, CA 92698, Phone: (949) 349-2000, Fax: (949) 349-2585, E-mail: dick.nielsen@fluor.com

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Fluor LNG utilization technology 1 (FLUT 1)

**Application:** Liquefied natural gas (LNG) often has a higher heating value and is richer in heavier hydrocarbons than is permitted by typical natural gas pipeline specifications. The FLUT 1 regasification configuration, for which patents are pending, processes a wide range of LNG compositions to produce natural gas meeting pipeline standards. Thus, allowing importers to purchase LNG from the most economical source. Electric power, LPG, and LNG and CNG vehicle fuels can be produced.

**Description:** LNG from storage is pressurized by LNG pump P1 to about 500 psig. Approximately 50% of this LNG is sent to the demethanizer (V1) as reflux. LNG power cycle pump P2, pressurizes the remaining LNG. This high-pressure LNG is used as a working fluid to recover low level heat from the power plant flue gas. High-pressure LNG from P2 is heated in two heat exchangers, E1 and E2. The reflux condenser E1 in the deethanizer (V2) overhead increases the LNG temperature to –190°F. Using LNG to satisfy the fractionation process refrigeration requirement eliminates a costly propane refrigeration system.

LNG leaving the reflux condenser is heated to 300°F and vaporized in glycol-water exchanger E2, using waste heat from the power plant flue gas. A glycol-water heat medium is used to transfer heat between the power block and the LNG regasification facility. This indirect heat exchange system isolates the LNG from direct heat exchange with the power block. A backup heat source can use this heat transfer fluid to vaporize the LNG if the power plant is not in operation. Possible backup heat sources include a fired heater or duct firing of the waste heat recovery units. Hot LNG vapor is then expanded in EP1 to produce power. The low temperature of the LNG working fluid results in a highly efficient power cycle.

The process can recover up to 99% of the propane and over 90% of the ethane in LNG. For a 1.2 billion scfd integrated LNG regasification power plant facility, the total power produced is 541 MW vs. 474 MW for a non-integrated power plant. 37,700 bpd of ethane, 51,200 bpd of LPG, and 1,070 million scfd of 999 Btu/scf HHV pipeline gas are also produced.

Fluor also has a process option, FLUT 2, that produces low cost vehicle grade LNG and CNG along with additional power.


**Licensor:** Fluor Enterprises, Inc.

**Contact:** Dick Nielsen, One Fluor Daniel Dr., Aliso Viejo, CA 92698, Phone: (949) 349-2000, Fax: (949) 349-2585, E-mail: dick.nielsen@fluor.com
Gas-to-liquids (GTLs)

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

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

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

The streams of synthetic crude are combined and refined into ultra-clean diesel, kerosene, naphtha and LPG. Compared to conventional crude oil, refining FT crude is less severe, i.e., lower H₂ consumption, lower temperature and pressure, and longer catalyst life, due to the absence of sulfur, aromatics and heavy metals.

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

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

**Reference:** Patent 6,265,453

**Licensor:** Syntroleum Corp.

**Contact:** Ken Roberts, Senior Vice President, Business Development, 4322 S 49th W. Ave., Tulsa, OK 74107, Phone: 918-592-7900, Fax: 918-592-7979, Email: kroberts@syntroleum.com

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**Gas Processes 2004**

- **Synthesis gas**
- **LPG**
- **Naphtha**
- **Kerosene/jet**
- **Diesel**
- **Air**
- **Compression**
- **Gas treating**
- **Steam**
- **Fischer-Tropsch reactors**
- **Product upgrading**
- **Syngas production (ATR)**
- **Return to Gas Processes INDEX**
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\textsubscript{3}+ liquid at the bottom and a C\textsubscript{2} top stream. The tower is generally provided with an external heat source for bottom reboiling.

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

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


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**Liquefin**

**Application:** Natural gas liquefaction (LNG) process.

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

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

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

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

**Economics:** Detailed studies by international petroleum and E&C companies comparing conventional 4.5 to 8 MMtpy propane-plus-mixed refrigerant liquefaction trains with Liquefin LNG installations have shown a 15–20% specific investment cost advantage for the LIQUEFIN train.


**Licensor:** Axens

**Contact:** Pierre-Yves Martin, 89, bd Franklin Roosevelt-BP 50802, 92508 Rueil-Malmaison Cedex, France, Phone: (33) 1 47 14 24 62, E-mail: pierre-yves.martin@axens.net

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**Gas Processes 2004**

**NGL and LNG**

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**LNG Dual Expander Cycle**

**Application:** LNG production for either offshore or onshore

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

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

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

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

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

**Contact:** Jorge Foglietta, 3010 Briarpark Drive, Houston, TX 77042, Phone: 713-821-4313, Fax: 713-821-3538, E-mail: jorge.h.foglietta@us.abb.com

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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 T1 turbine to produce electric power. It is mixed with liquefied fuel gas recycle before entering the LNG flash drum V1 at 1.2 bars. The LNG is pumped to storage tank through P1.

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

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

**Installations:** None with turbo-expander T2/K2.

**Reference:** US patent application and LNG 13 conference, Seoul, paper PS2-1.

**Licensor:** Technip

**Contact:** La Defense 12, 9273 Paris La Defense Cedex, France; E-mail: grenaudin@technip.com
**Application:** Liquefaction of natural gas for plant capacities ranging from small peak shaving applications, up to mid-size plants (4,000 tpd, 1.4 million tpa) using a mixed refrigerant cycle.

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

**Description:** Pretreated natural gas is cooled and condensed by a multi-stage 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 is cooled (2) in the main exchanger (3), which normally consists of multiple, brazed aluminum plate-fin heat exchangers, against returning low-pressure mixed refrigerant (4). The subcooled refrigerant is then let down in pressure and evaporated to provide cooling. Liquids from refrigerant compression are cooled separately (5) in the main exchanger, let down in pressure and evaporated to provide increased process efficiency.

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

- The subcooled LNG then enters a two-stage flash system (9) where it is let down in pressure before being pumped to storage at near atmospheric 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 a 1.4 million tpy-facility, a total installed cost of $300 per tpy is feasible.

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

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


**Licensor:** Costain Oil, Gas & Process Ltd.

**Contact:** Adrian Finn, Technology Development Manager, Costain Oil, Gas & Process Ltd., Costain House, Styal Road, Manchester, UK, Phone: (44) 161 910 3227, Fax: (44) 161 910 3256, e-mail: Adrian.Finn@cogap.com

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**Gas Processes 2004**

**NGL and LNG**

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**Return to Gas Processes INDEX**
**LNG-Pro**

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

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

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

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

**Performance index**

<table>
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<th>Relative hp/lb LNG</th>
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<tr>
<td>Cascade refrigeration</td>
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<tr>
<td>Mixed refrigerants</td>
<td>1.15–1.4</td>
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<tr>
<td>Turboexpander cycle</td>
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<tr>
<td>High-efficiency cycles</td>
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**Utilities**

<table>
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<td>Recycle compr.</td>
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**Cooling duty**

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<tr>
<td>Refrig. condenser</td>
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<tr>
<td>Fuel gas usage</td>
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</tbody>
</table>


**Licensors:** Randall Gas Technologies, ABB Lummus Global Inc.

**Contact:** Jorge Foglietta, 3010 Briarpark Drive, Houston, TX 77042, Phone: 713-821-4313, Fax: 713-821-3538, E-mail: jorge.h.foglietta@us.abb.com
LPG recovery

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

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

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

Installation: First unit under construction for Pertamina.


Licensor: Black & Veatch Pritchard, Inc.

Contact: Robert Mortko, 11401 Lamar, Overland Park, KS 66211 USA, Phone: (913) 458-6058, Fax: (913) 458-6098, E-mail: mortkora@bv.com
Natural gas sweetening—MEDAL membrane (CO₂ removal)

**Application:** Selectively removing carbon dioxide (CO₂) and water (H₂O) vapor from raw natural gas or associated gas to meet pipeline specifications for both onshore and off-shore locations. Upgrade low Btu gas (e.g., landfill gas) for fuel. Debottleneck existing solvent-based CO₂ removal systems. Recover valuable hydrocarbons from enhanced oil recovery floods for CO₂ reinjection.

**Product:** Purified natural gas, predominantly methane, meeting pipeline specifications; high Btu fuel gas; high-purity CO₂ for reinjection.

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

The feed stream (from which CO₂ needs to be removed) passes over the membrane module feed chamber at high pressure. Carbon dioxide, H₂O vapor and hydrogen sulfide (H₂S) pass through the membrane from the high-pressure chamber to the low-pressure chamber (the permeate). Methane, ethane, nitrogen and other hydrocarbons are enriched into high-pressure residual gas.

Typically, a two-stage design is used to limit the hydrocarbon losses to less than 1%. In a single stage, between 2% and 5% losses are typical. Typical feed rates vary from less than 1 million scfd to as high as 1,000 million scfd with CO₂ content varying between 3% and 70%. Typical feed pressure varies between 100 to 1,500 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—making them the ideal choice for remote locations.

**Economics:** Typical processing cost for CO₂ removal using MEDAL natural gas membranes varies between $0.05 and $0.15 per 1,000 scf of feed gas depending on feed composition, temperature and pressure.

**Installations:** Several references processing up to 300 million scfd of natural gas.

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

**Contact:** Charlie Anderson, Director of CO₂ Activity,
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Return to Gas Processes INDEX
NGL from LNG

**Application:** Natural gas liquids (NGL) separation from liquefied natural gas (LNG) for Btu control of LNG and for enhanced product value. Primary application is for LNG import terminals.

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

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

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

**References:** US Patent 6,564,579, “Method for Vaporizing and Recovery of Natural Gas Liquids from Liquefied Natural Gas.”


**Licensor:** Black & Veatch Pritchard Inc.

**Contact:** Brian Price, 11401 Lamar, Overland Park, KS 66211 USA, Phone: (913) 458-6151, Fax: (913) 458-6098, E-mail: pricebc@bv.com
NGL recovery

Application: Deep recovery of NGL from natural gas.

Products: Sales gas and stable NGL, with a propane recovery as high as 99%. For an ethane-extraction plant, ethane recovery can be over 95%, with a propane recovery of essentially 100%.

Description: With high feed-gas pressure and particularly with dense-phase operation (above the cricondenbar), two expanders used in series enables the design pressure of the gas/gas exchanger to be reduced significantly. It also enables a plate-fin heat exchanger to be used, thus improving process efficiency as compared to using a shell and tube exchanger.

For very high-pressure ratios across the plant, two expanders in series avoid very high liquid flows in the expander exhaust, thus improving the performance and reliability of the turboexpander system.

Dehydrated feed gas is let down in pressure by the first expander (1), and the exhaust is passed to the first separator (2). Vapor from the first separator is cooled and condensed in the gas/gas exchanger (3) and let down in pressure by the second expander (4). The exhaust is passed to the second separator (5). Unstable liquids recovered from both separators are sent on to be stabilized. Cold vapor from the second separator is rewarmed and recompressed in the brake ends of the expanders to sales gas pressure.

Operating conditions: A very high propane recovery of 99% can be achieved by using a pre-absorber column and optimizing thermal integration with multistream heat exchangers.

Improved energy integration enables NGL recovery to be increased to very high levels with similar power consumption to conventional technology. Very high ethane recovery, of over 95%, can be achieved by using a portion of the sales gas for demethanizer refluxing and by utilizing refrigeration efficiently with good thermal integration.

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


US patent no. 6581410 (Propane-plus)
US patent no. 6363744 (Ethane-plus).

Contributor: Costain Oil, Gas & Process Ltd.

Contact: Adrian Finn, Technology Development Manager, Costain Oil, Gas & Process Ltd., Costain House, Styal Road, Manchester, UK, Phone: (44) 161 910 3227, Fax: (44) 161 910 3256, e-mail: Adrian.Finn@cogap.com
NGL-MAX

**Application:** Ethane/ethylene and heavier hydrocarbons recovery, from natural gas or refinery off gas feed streams, using a cryogenic turboexpander process. High ethane recovery (99%) is achievable with essentially complete C3+ recovery. Lower ethane recoveries are possible with the same process while maintaining C3+ 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 concentration is large enough to produce freezing in the plant’s cryogenic section.

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

The demethanizer produces at the top, a methane and lighter stream, and at the bottom a C2+ stream containing the desired components to be recovered. Cold residue gas (10) is warmed up in exchangers and boosted in pressure by a compressor (11). The warm and intermediate pressure residue gas is boosted to pipeline pressure by residue compressors (12) and sent for further processing. A part of the high-pressure residue gas (13) is cooled, condensed and sent to the demethanizer as top feed. This top feed is very low in C2+ thereby enabling very high C2+ recovery levels.

**Operating conditions:** Due to the presence of two reflux streams, the scheme is able to process feed gases with a wide range of liquid content in the feed gas. The scheme requires the demethanizer tower to run at a somewhat higher pressure than a single tower system. This higher pressure will make the process more CO2 tolerant, and hence simplify or eliminate inlet gas treating.


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

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


**Licensors:** Randall Gas Technologies, ABB Lummus Global Inc.

**Contact:** Jorge Foglietta, 3010 Briarpark Drive, Houston, TX 77042, Phone: 713-821-4313, Fax: 713-821-3538, E-mail: jorge.h.foglietta@us.abb.com

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**Diagram:**

- Inlet gas from dehydration
- Residue gas compressor and aftercooler
- Gas/gas-reflux exchanger
- Reflux subcooler
- Demethanizer
- Booster
- Expander
- Cold separator
- NGL pump
- Residue to pipeline
- Side reboilers
- UMB

**Legend:**

- U
- M
- B
- NGL

**Return to Gas Processes INDEX**
Nitrogen removal (reject)

Application: Remove 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 expanded 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 purge stream containing helium 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 against the natural gas feed to provide refrigeration to the process.

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

Operating conditions: The double-column process is sufficiently flexible to handle natural gas with nitrogen concentrations varying from 5 mol% to 80 mol%, and can be a good choice for variable content streams associated with enhanced oil recovery (EOR). Feed gas above 27 bar can be processed without any compression. For feed gas containing heavy hydrocarbons or a low-nitrogen content, a three-column process is more efficient. The third column also improves plant tolerance to CO₂, which may simplify gas pretreatment requirements.

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

Installations: Five, with capacities from 80,000 Sm³/h to 350,000 Sm³/h.


Licensor: Costain Oil, Gas & Process Ltd.

Contact: Adrian Finn, Technology Development Manager, Costain Oil, Gas & Process Ltd., Costain House, Styal Road, Manchester, UK, Phone: (44) 161 910 3227, Fax: (44) 161 910 3256, e-mail: Adrian.Finn@cogap.com
**PetroFlux**

**Application:** Recovery of light olefins—typically ethylene, propylene or butylene—from offgases using reflux exchanger technology as part of a low-temperature recovery system (LTRS). Reflux exchanger technology can also be applied to ethylene chill trains and to NGL recovery from refinery and petrochemical offgases, as well as from natural gas.

**Products:** Olefins with a typical recovery of 99%. For NGL recovery: 95+% recovery of propane and 100% recovery of heavier hydrocarbons.

**Description:** After removal of water and freezable components in the molecular sieves (1), the gas is partially liquefied in the plate-fin heat exchanger (2) and separated in the feed separator (3). The vapor formed passes upward through the passages of a refluxing plate-fin heat exchanger (4) where it is cooled and condensed. Condensed liquids flow countercurrently to the gas down the heat exchanger passages and are fractionated before collecting in the feed separator. The resulting gas is then rewarmed and sent to product/fuel gas while the liquids collected are stabilized. Refrigeration (5) may be provided by a separate refrigeration cycle or by work expansion of the product/fuel gas. The choice of refrigeration scheme depends on both feed and product/fuel gas pressures.

**Operating conditions:** Typically, feed gas flows of up to 100,000 Sm³/h can be processed. Feed gas pressure is typically between 10 barg and 70 barg.

**Economics:** The PetroFlux process offers high recoveries and significant savings in refrigeration costs, giving attractive returns on investment. It has been used widely for plant debottlenecking and to make more effective use of existing refrigeration systems.

**Installations:** The basic refluxing heat exchange system has been used worldwide on 28 plants.

**References:**

**Licensor:** Costain Oil, Gas & Process Ltd.

**Contact:** Adrian Finn, Technology Development Manager, Costain Oil, Gas & Process Ltd., Costain House, Styal Road, Manchester, UK, Phone: (44) 161 910 3227, Fax: (44) 161 910 3256, e-mail: Adrian.Finn@cogap.com

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*Gas Processes 2004*
Phillips optimized cascade LNG process

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

**Feedstock:** Naturally occurring hydrocarbon gas pretreated to remove contaminants such as moisture, H₂S, CO₂, 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 system (2) consisting of two or more stages. Ethane may be substituted for ethylene. A combination of brazed aluminum and core-in-kettle exchangers are utilized for heat exchange. Feed is routed successively through each stage of propane and ethylene. Air or cooling water removes process heat and condenses propane, while propane removes heat and condenses ethylene.

Heavier products are typically removed (3) after one or more stages of ethylene refrigeration. Fractionation design is highly dependant on feed composition and desired product recovery. Efficient designs with high ethane and propane (>95%) recovery 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 recycle 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 process offers a well-established, reliable, efficient and low-cost LNG solution. Overall facility EPC costs utilizing the technology have been at or under $200 per mtpy. 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 mtpy are available in multiple turbine/driver configurations with even larger train sizes in development.

**Installations:** The first installation was the Kenai, Alaska facility, brought online in June 1969. The facility has demonstrated over 34 years of reliable uninterrupted LNG supply. Efforts to commercialize the technology began in 1993. Since that time, three trains using the technology have been successfully brought online in Trinidad with a fourth in construction. Additional licenses have been signed for two trains in Idku, Egypt, one train in Darwin, Australia, and one train for a confidential LNG project. Other projects are in various stages of commercial development.

**Licensor:** ConocoPhillips

**Contact:** Rick Hernandez, LNG Technology licensing manager, Phone: (281) 293-5698, E-mail: Rick.Hernandez@ConocoPhillips.com

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**Gases Processes 2004**

**NGL and LNG**

**Feed:**

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<tr>
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<td>421</td>
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</table>

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**PRICO (LNG)**

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

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

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

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

Natural gas feed is pretreated for removal of carbon dioxide (CO₂) to less than 50 ppmv and dried to less than 1 ppmv water by conventional methods. Natural gas liquids (NGL) from the natural gas feed are separated in (8). The NGLs may then be separated by subsequent fractionation into desired products. Nitrogen in the natural gas feed is dealt with according to the LNG product specification requirements by adjusting the liquefaction conditions. The process matches well with gas turbine, steam turbine or electric motor-driven compression systems.

**Installations:** Eight peak-shaving units up to 16 million scfd each are now being successfully operated. Three 180 million scfd base load plants with ethane and heavier hydrocarbons extraction as separate products also use the process.

**References:**


**Licensor:** Black & Veatch Pritchard Inc.

**Contact:** Brian Price, 11401 Lamar, Overland Park, KS 66211 USA, Phone: (913) 458-6151, Fax: (913) 458-6098, E-mail: pricebc@bv.com
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 is used in the Hy-Pro process.

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

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

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

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

Licensors: Randall Gas Technologies, ABB Lummus Global Inc.

Contact: Jorge Foglietta, 3010 Briarpark Drive, Houston, TX 77042, Phone: 713-821-4313, Fax: 713-821-3538, E-mail: jorge.h.foglietta@us.abb.com

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CRG processes—
pre-reforming, derichment, methanation

**Application:** Adiabatic steam reforming of hydrocarbon from natural gas through LPG to naphtha feeds. May be used for the derichment of natural gas (LNG plants), as an adiabatic pre-reformer or in the methanation of H₂/CO-rich streams in SNG manufacture.

**Description:** Fixed bed of nickel-based catalyst converts hydrocarbon feeds in the presence of steam to a product stream containing only methane together with H₂, CO, CO₂ and unreacted steam. This stream may be exported as product, used as feed for further processing in a conventional fired reformer or as feed to additional CRG processing steps when the methane content of the product can be further enhanced.

Using a CRG pre-reformer enables capital cost savings in primary reformer as a result of reduction in radiant box heat load and allows high-activity gas reforming catalyst to be used. The ability to increase preheat temperatures and transfer radiant duty to the convection section of the primary reformer can minimize involuntary steam production.

**Operating conditions:** CRG processes operate over a wide range of temperatures from 250°C to 650°C, and at pressures up to 75 bara.

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

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

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

**Contact:** 20 Eastborne Terrace, London W2 6LE, UK; e-mail: dpt@davyprotech.com
**AQUISULF**

**Application:** Decrease H$_2$S content in liquid sulfur condensed in SRUs and routed to sulfur degassing facilities. Maximum H$_2$S content is 10 ppm.

**Description:** A degassing unit is required to achieve 10 ppm H$_2$S in liquid sulfur. The degassing is done in a concrete pit or sulfur degassing vessel that is divided into two compartments. The first compartment (1) is equipped with a recirculation and cooling pump (3) and a spraying system. The second (2) is equipped with a recirculation and transfer pump (4) also with a spraying system. A partition wall separates the two areas.

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

The optimal temperature for degassing is reached by cooling the sulfur (5). The heat generates LP steam that is condensed in the air cooler (6). The pit vapor phase is swept with atmospheric air sucked in by a steam ejector. Sweeping gas flows from the second compartment to the first through a hole located at the top of the partition wall. The gas and H$_2$S are sent to the incinerator through a steam ejector.

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

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


**Licensor:** Lurgi Oel-Gas-Chemie GmbH

**Contact:** Wolfgang Nehb, Lurgi Oel-Gas-Chemie GmbH, Lurgiallee 5, D-60295 Frankfurt am Main, Germany, Phone: (49) 69 5808 1530, Fax: (49) 69 5808 3115, E-mail: Wolfgang_Nehb@lurgi.de
**CAP-compact alkanolamine plant**

**Application:** Selective hydrogen sulfide (H$_2$S) removal in the presence of carbon dioxide (CO$_2$), based on the novel co-current ProPure gas-liquid contactor and a regenerative solvent.

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

CAP’s H$_2$S-selectivity is achieved by a short retention time combined with the high gas-solvent exposure area throughout the contactor. Compared to counter-current contactors the gas residence time is considerably shorter, typically 30–60 times shorter. Therefore, CO$_2$ co-absorption is significantly reduced, allowing higher solvent H$_2$S-loading capacity. Tertiary amines such as MDEA yield selective H$_2$S-removal, as the solvent proton reaction with H$_2$S is instantaneous whereas the reaction with CO$_2$ undergoes several (slow) intermediate reactions. The higher the ratio between CO$_2$ and H$_2$S concentrations, the more competitive CAP becomes as compared to conventional counter-current contactor technology.

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

**Economics:** For a case with inlet concentrations of 5% CO$_2$, 10–20 ppmv H$_2$S and H$_2$S-outlet specification of 2 ppmv, a reduction in installed weight of 60% is estimated compared to conventional technology. This is mainly due to the reduced amine circulation rate. The limited foot-print requirement makes CAP feasible for retrofit installations on existing offshore fields.

**Installations:** Extensive tests have been carried out at the Statoil Mongstad refinery and at ProPure’s test facility. During 2004, CAP will undergo a technology qualification program with sour hydrocarbon gas at 80–100 bar. The program is supported by a JIP (Total, Statoil, ConocoPhillips and Gaz de France) joint venture, and the tests will be run at Gaz de France’s gas processing and distribution plant at Chemery, France.


**Licensor:** ProPure AS, Contact: Harald Linga, ProPure AS, Ytrebygdsvien 215, 5 etg. Floy 6, P.O.Box 7150, N-5020 BERGEN, Phone: (47) 55 52 94 20, Fax: (47) 55 52 94 01, E-mail: harald.linga@propure.com
Claus, modified

**Application**: Recover sulfur from acid-gas streams that contain hydrogen sulfide (H₂S) and ammonia (NH₃).

**Product**: Bright yellow sulfur with 99.9 % purity and less than 10 ppmw of dissolved H₂S after degassing. Front-end Claus tail gas is either processed in a tail gas clean-up (TGCU) unit for further sulfur recovery, or routed to the Claus incinerator where residual H₂S is oxidized to SO₂.

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

**Operating conditions**: The temperature inside the combustion chamber depends upon the type and quantities of species accompanying the H₂S and O₂. Generally, the operating temperature ranges between 925°C–1,200°C, but can be increased to 1,450°C if NH₃ is present in the feed gas. Total pressure drop of the process gas depends upon the numbers of converter stages. Typically, pressure drop can vary between 0.3 bar and 0.5 bar.

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

**Economics**: Capital cost is approximately U.S.$10 million/100-tpd sulfur recovery unit designed to achieve 95% recovery efficiency from typical amine off gas. Operating costs can be considered negligible if credit for steam generation is taken into account.

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

**Licensor**: BP AMOCO through SIIRTEC NIGI

**Contact**: SIIRTEC NIGI S.p.A., Via Algardi 2 - 20148, Milano, Italy, Phone: (39) 0 239 2231, Fax: (39) 0 2392 3010, E-mail: marketing@sini.it
Claus, oxygen-enriched

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

**Product:** Bright yellow, high-purity sulfur. Claus tail gas is either processed in a tail gas clean-up unit (TGCU), or routed to the Claus incinerator where residual hydrogen sulfide (H₂S) is oxidized to SO₂.

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

**Process variations:**
- Up to about 30% oxygen, only minor modifications to the plant would be expected.
- Above 30% oxygen concentration, a proprietary oxygen-compatible burner would be required using the SURE burner. Some limited modifications could be expected.
- For capacity increases in excess of about 100%, the SURE double combustion process could be used to achieve the desired expansion.

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

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

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

**Licensor:** SIIRTEC NIGI (up to 30% O₂), SURE Parsons/BOC through SIIRTEC NIGI

**Contact:** SIIRTEC NIGI S.p.A., Via Algardi 2 - 20148, Milano, Italy, Phone: (39) 0 239 2231, Fax: (39) 0 2392 3010, E-mail: marketing@sini.it
Cold Bed Adsorption (CBA)

**Application:** Recover elemental sulfur from acid-gas streams that contain hydrogen sulfide (H₂S), or treat Claus tail gas for additional sulfur recovery. CBA beds can be retrofitted in existing units to increase the sulfur recovery.

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

**Description:** The CBA is a dry-bed catalytic process which extends and enhances the characteristics of the Claus reaction in two ways:
- Operating the CBA reactors near the sulfur dew point extends the Claus reaction equilibrium and can achieve higher sulfur conversion
- Using the catalyst as an in-situ capture point for the produced sulfur drives the reaction to completion.

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

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

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

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

**Licensor:** BP AMOCO through SIIRTEC NIGI

**Contact:** SIIRTEC NIGI S.p.A., Via Algardi 2 - 20148, Milano, Italy, Phone: (39) 0 239 2231, Fax: (39) 0 2392 3010, E-mail: marketing@sini.it
**COPE**

**Application:** Increase capacity and recovery of existing Claus sulfur recovery/tail gas cleanup units, provide redundant sulfur processing capacity, and improve combustion performance of units processing lean acid gas through oxygen (O\(_2\)) enrichment.

**Description:** The sulfur processing capacity of typical Claus sulfur recovery units can be increased to more than 200% of the base capacity through partial to complete replacement of combustion air with pure O\(_2\). SRU capacity is typically limited by hydraulic pressure drop. As O\(_2\) replaces combustion air, the quantity of inert nitrogen is reduced allowing additional acid gas to be processed. The process can be implemented in two stages.

As the O\(_2\) enrichment level increases, the combustion temperature (1) increases. COPE Phase I, which does not use a recycle stream, can often achieve 50% capacity increase through O\(_2\) enrichment to the maximum reaction furnace refractory temperature limit of about 2,700–2,800°F. Higher O\(_2\) enrichment levels are possible with COPE Phase II which uses an internal process recycle stream to moderate the combustion temperature allowing enrichment up to 100% O\(_2\).

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

**Operating conditions:** Combustion pressure from 6 psig to 12 psig; combustion temperature up to 2,800°F. Oxygen concentration from 21% to 100%. SRU sulfur recovery is 95% to 98%.

**Economics:** Expanded SRU and tail gas unit retrofit sulfur processing capacity at capital cost of 15–25% of new plant cost. New plant savings of up to 25%, and redundant capacity at 15% of base capital cost. Operating costs are a function of O\(_2\) cost, reduced incinerator fuel, and reduced operating and maintenance labor costs.

**Installations:** Nineteen COPE trains in operation at 11 locations. Two additional trains are in engineering and/or the construction phase of projects.

**Reference:** US Patents 4,552,747 and 6,508,998.

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

**Contact:** Steve Fenderson, Goar, Allison & Associates, Inc., 1902 Sybil Lane, Tyler, Texas 75703, Phone: (903) 561-8456, Fax: (903) 561-7692, e-mail: sfenderson@goarallison.com
**Application:** Removes hydrogen sulfide (H₂S) from gas streams such as natural gas, refinery fuel gas, hydrogen recycle stream in refinery HDS, high-carbon dioxide (CO₂) streams in EOR plants and geothermal vent gas. Also removes H₂S, sulfur dioxide (SO₂) and elemental sulfur vapor from Claus tail gas in natural gas processing plants and petroleum refineries. Can treat any high- or low-pressure gas stream. CrystaSulf is the most economical choice for H₂S removal from gas streams containing between 0.2 and 25 long tons per day (ltpd) of sulfur (S).

**Description:** Gas phase H₂S is converted to elemental sulfur in a single process step using a proprietary nonaqueous sorbent. The sulfur formed remains dissolved in the solution; thus, no solids are present in the circulating scrubbing liquor. Sulfur is removed from the system by cooling in a crystallizer/filter system. No surfactants, wetting agents or antifoams are needed.

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

**Operating conditions:** Atmospheric to 2,000+ psi; 120°F to 180°F. CO₂, COS and CS₂ in the inlet gas do not react and do not affect the system. Inlet gas hydrocarbons do not cause foaming or sulfur settling problems for CrystaSulf.

**Installations:** Eighteen months of pilot plant testing was conducted on a 300-psig CO₂ stream. Two licenses sold. First commercial unit startup is expected mid-2004.

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

**Licensor:** CrystaTech is the Gas Technology Institute’s (GTI) exclusive licensor of CrystaSulf. The Hanover Company and GTI are investors in CrystaTech and provide engineering and research support to CrystaTech. Hanover provides detailed design and fabrication of CrystaSulf units and can offer turnkey projects.

**Contact:** Bryan Petrinec, Director of Operations, CrystaTech, Inc., 4616 W. Howard Lane, Suite #2500, Austin, TX 78759, Phone: (512) 248-6317, Fax: (509) 696-2939, E-mail: bryan.petrinec@crystatech.com

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**D’GAASS**

**Application:** Removal of dissolved H$_2$S and H$_2$S$_x$ from produced liquid sulfur. Undegassed sulfur can create odor problems and poses toxic and explosive hazards during the storage and transport of liquid sulfur.

**Description:** Degasification is accomplished in a pressurized vertical vessel where undegassed sulfur is efficiently contacted with pressurized process air (instrument or clean utility air). The contactor vessel may be located at any convenient location. The undegassed sulfur is pumped to the vessel and intimately contacted with air across special fixed vessel internals. Operation at elevated pressure and a controlled temperature accelerates the oxidation of H$_2$S and polysulfides (H$_2$S$_x$) to sulfur.

The degassed sulfur can be sent to storage or directly to loading. Operation at elevated pressure allows the overhead vapor stream to be routed to the traditional incinerator location, or to the SRU main burner or TGTU line burner—thus eliminating the degassing unit as an SO$_2$ emission source.

**Economics:** D’GAASS achieves 10 ppmw combined H$_2$S/H$_2$S$_x$ in product sulfur without use of 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:** Sixteen units in operation. Fourteen additional trains in engineering and construction phase with total capacity over 17,000 ltpd.

**Reference:** US Patent 5,632,967.


**Licensor:** Goar, Allison & Associates, Inc.

**Contact:** Steve Fenderson, Goar, Allison & Associates, Inc., 1902 Sybil Lane, Tyler, Texas 75703, Phone: (903) 561-8456, Fax: (903) 561-7692, e-mail: sfenderson@goarallison.com
EUROCLAUS process

Applications: The EUROCLAUS process recovers elemental sulfur from hydrogen sulfide (H₂S) containing gases, which originate from gas treating plants such as alkanolamine units or physical solvent plants. Yields up to 99.7% overall sulfur recovery without any further tail gas clean up are possible.

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

In the thermal stage, acid gas is burned with a substoichiometric amount of controlled combustion air such that, the tail gas leaving the second reactor contains typically 0.8 vol.% to 1.0 vol.% of H₂S and 100–200 ppmv sulfur dioxide (SO₂). The low SO₂ content, produced with a hydrogenation catalyst, converts SO₂ to H₂S in the reactor bottom. The last reactor oxidizes H₂S to sulfur at more than 85% efficiency. However, because this catalyst neither oxidizes H₂S to SO₂ nor reverses the reaction: total sulfur recovery up to 99.3% efficiency can be obtained. If more than 99.3% sulfur recovery is required, one additional Claus reactor stage may be installed upstream of the selective oxidation reactor.

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

<table>
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<th>Utility</th>
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<tr>
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</tbody>
</table>

Installations: Since the first commercial demonstration of the EUROCLAUS process in 2000, more than 12 plants are in operation or under construction in the first quarter of 2003.

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

Contact: Juste Meijer, Plesmanlaan 100, 2332 CB, P.O. Box 141, 2300 AC, Leiden, The Netherlands, Phone: (31) 71 582 7887, Fax: (31) 71 528 7079, E-mail: juste.meijer@jacobs.com
Fluor hydrogenation/amine 
Claus tail gas treating process

**Application:** The Claus sulfur conversion process recovers up to 97% of the sulfur from acid gas streams. The Fluor hydrogenation/amine process converts sulfur dioxide (SO₂), COS, carbon disulfide (CS₂), elemental sulfur and other sulfur species in the Claus tail gas to hydrogen sulfide (H₂S). The H₂S is then removed via selective amine treating to achieve a total sulfur recovery efficiency of up to 99.99%.

**Description:** Air and natural gas are combusted under substoichiometric conditions in a reducing gas generator (1). The hot combustion product reducing gases, carbon monoxide (CO) and hydrogen (H₂), are mixed with the Claus tail gases in a mixing chamber (2) integral with the reducing gas generator. The cobalt molybdenum (CoMo) catalyst in the reactor (3) hydrogenates/hydrolyzes all the sulfur species in the gas mixture to H₂S. The hydrogenated tail gas is then cooled in the effluent cooler (4), generating steam in the process. The effluent gas is further cooled in a direct contact quench tower (5) to condense and remove water. The condensed water, which contains a small amount of H₂S, is treated in a sour-water stripper where the H₂S is removed and returned to the Claus unit.

The Fluor design optionally uses a desuperheating section with an alkaline circulation to remove any potential SO₂ breakthrough from the hydrogenation reactor. This design feature is especially useful when the downstream amine unit operates with an expensive proprietary amine.

After quench cooling, the hydrogenated tail gas is then treated by a highly efficient selective amine to remove H₂S. In the absorber (6), the H₂S is selectively absorbed in the amine while rejecting as much CO₂ as possible. The rich amine solution is then regenerated in the stripper (7) and circulated back to the absorber. Acid gas from the stripper is recycled back to the upstream Claus unit. The process can achieve a total sulfur recovery efficiency of up to 99.99%.

**Installations:** Three plants engineered or constructed.


**Licensor:** Fluor Enterprises, Inc., Contact: Thomas Chow, One Fluor Daniel Dr., Aliso Viejo, CA 92698, Phone: (949) 349-4247, Fax: (949) 349-2898, e-mail: thomas.chow@fluor.com

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HCR—High Claus Ratio

**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, CS₂, Sₓ and SO₂). Tail gas is heated to about 300°C and, without hydrogen addition, is treated with Co/Mo catalyst. Gas passes through a waste-heat boiler (WHB) and is cooled to approximately 40°C in a direct contact tower.
- H₂S removal and recycle of acid gas to a Claus plant. The gas is washed in a carefully designed amine absorber, and the treated gas is incinerated. Rich amine is processed and recycled.

The process requires adjusting the operating criteria for the Claus unit by increasing the H₂S/SO₂ tail gas ratio. The operation is very steady and has high service factors that are achieved during upset conditions from upstream units. Hydrogen or reducing gas from external sources are not required in the hydrogenation reactor.

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

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

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

**Installations:** The first commercial HCR plant was started up in November 1988 at Agip Plas’s facility (an affiliate of Agip Petroli S.p.A.) in Robassomero, Italy. Since then, more than 10 HCR plants are under construction with capacities ranging from 1.5 tpd up to 270 tpd.

**Licensor:** SIIRTEC NIGI

**Contact:** SIIRTEC NIGI S.p.A., Via Algardi 2 - 20148, Milano, Italy, Phone: (39) 0 239 2231, Fax: (39) 0 2392 3010, E-mail: marketing@sini.it
**Application:** Removal of H₂S and the production of high-purity sulfur from both anaerobic and aerobic gas streams including wellhead gas, fuel gas, acid gas, natural gas, carbon dioxide, Claus tail gas, synthesis gas and ventilating-air streams. Infinite turndown with respect to H₂S concentration, sulfur loading and gas rate with sulfur capacities ranging from a few pounds per day to greater than 25 ltpd. Recovery of the sulfur product as a slurry, a filter cake or as high-purity, molten sulfur. In most cases, sulfur cake can be deposited in a non-hazardous landfill. Autocirculation configuration when treating amine acid gas allows for remote or unattended operation typical for gas field operation.

**Description:** Three processing configurations are available depending on the type of gas and final use of the sweet gas. The conventional scheme, shown above, is used to process both combustible gas streams and product gas streams. The sour gas contacts a dilute, proprietary, iron chelate catalyst solution in an absorber (1), where the H₂S is absorbed and oxidized to solid sulfur. The sweet gas leaves the absorber for use by the client. The reduced catalyst solution returns to the oxidizer (2), where sparged air reoxidizes the catalyst solution. The catalyst solution is then returned to the absorber. The continuous regeneration of the catalyst solution allows for very low chemical operating costs.

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

The third processing scheme sweetens air streams contaminated with H₂S. The absorption and oxidation of H₂S to sulfur, as well as the regeneration of the catalyst solution, occur in one vessel. The air in the gas stream is used to regenerate the catalyst, eliminating the oxidizer air blowers.

**Operating conditions:** Operating pressures from vacuum conditions to several hundred psi. Operating temperatures range from 40°F to 140°F. Hydrogen sulfide concentrations from a few ppm to 100%. Sulfur loadings from a few lb/d to 25+ ltpd. No restrictions on type of gas to be treated; however, some contaminants such as SO₂ may increase operating costs.

**Installations:** 119 operating, 3 under construction and 151 under license.


**Licensor:** Gas Technology Products LLC, a Merichem Co.

**Contact:** William Rouleau, applications engineering manager, Gas Technology Products LLC, 846 E. Algonquin Rd. Ste. A100, Schaumburg, IL 60173, Phone: (847) 285-3865, Fax: (847) 285-3888, E-mail: wrouleau@merichem.com

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**Merox**

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

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

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

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

**Sweetening:** Minalk is now the most prevalent Merox gasoline and condensate sweetening scheme. Conversion of mercaptans into disulfides is accomplished with a fixed bed of Merox catalyst that uses air and a continuous injection of only minute amounts of alkali. Sweetened gasoline from the reactor typically contains less than one ppm sodium. A new additive, Merox Plus reagent, can be used to greatly extend catalyst life.

Heavy gasoline and condensate may be sweetened in a fixed-bed unit that closely resembles Minalk, except that a larger amount of more concentrated caustic is recirculated intermittently over the catalyst bed.

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

**Licensor:** UOP LLC
**Contact:** Anita Black, UOP, 25 E. Algonquin Ave., Des Plaines, IL 60016 USA, Phone: (847) 375-7801, Fax: (847) 391-2253, E-mail: anita.black@uop.com
**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 combustion. By using a proprietary thermal reactor burner (1), levels of 80–90% net oxygen can be utilized. Combustion temperature moderation is achieved without the need for any type of gas recycle. Oxygen is combusted with the acid gas in the center of an extremely hot flame core, while air is introduced around the outside of this flame, combusting the balance of the acid gas. Considerable cracking of H₂S to hydrogen and sulfur occurs in the hot flame core as thermodynamic equilibrium is approached. Carbon dioxide is also reduced to carbon monoxide. These endothermic reactions provide proven temperature moderation consistent with conventional refractory/insulating brick materials. The level of produced hydrogen then decreases in the waste-heat boiler as the hot gas is cooled, since equilibrium of the H₂S-cracking reaction is favored by high temperatures. Heat generated by the exothermic reverse reaction is removed in the waste-heat boiler (2). Downstream recovery of elemental sulfur is accomplished by the conventional modified Claus process using a series of catalytic reactors (3) and sulfur condensers (4). No specialized equipment or changes to conventional design practices are required.

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

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

**Economics:** For a reference 200-tdp sulfur recovery unit (Claus and tail gas unit) requiring 99.9% overall sulfur recovery, capital cost savings of $1.6 million to $2.5 million are achievable with oxygen enrichment as compared to an air-only design.

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

**Installations:** More than 30 Claus sulfur recovery units with OxyClaus are in operation or under design worldwide.


**Licensors:** Lurgi Oel-Gas-Chemie GmbH and The Pritchard Corporation (US only)

**Contact:** Wolfgang Nehb, Lurgi Oel-Gas-Chemie GmbH, Lurgiallee 5, D-60295 Frankfurt am Main, Germany, Phone: (49) 69 5808 1530, Fax: (49) 69 5808 3115, E-mail: Wolfgang_Nehb@lurgi.de
**Application:** To recover liquid sulfur from hydrogen sulfide (H₂S)-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 (NH₃), present in the sour-water stripper offgas, is processed in the main burner (1) directly with other feed gas streams. Practical complete NH₃ destruction is ensured by choosing the proper high-intensity burner and preheating feed gas. The Claus unit is designed to suppress SO₃ formation at the reaction furnace and subsequent line burners. The sulfur complexes, even with ammonia in the feed, can typically run for 3 to 4 years without a maintenance shutdown.

The Claus tail gas is routed to a SCOT unit, where the sulfur components are recovered (see SCOT). Upsets, such as those based on partial oxidation, usually pass almost unnoticed in the SCOT unit. For example, a hydrocarbon upset in the feed to the Claus will not have any other effect on the SCOT, other than a slight increase in H₂S content from the SCOT.

The incinerator downstream the Claus/SCOT unit is designed such that a maximum of 10 ppmv H₂S can slip through, the remainder of the H₂S and any other sulfur component are oxidized to SO₂. A thermal incinerator can be designed with a heat-recovery section for superheating steam produced in the Claus unit or gas preheating. A catalytic incinerator, using propriety catalyst, more selectively oxidizes sulfur compounds, thus significantly reducing the risk from temperature runaways.

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


**Contact:** Henk Grootjans, Shell Global Solutions International B.V., P.O. Box 3800, 1030 BN, Amsterdam, The Netherlands, Phone: (31) 20 630 2859, Fax: (31) 20 630 2900, E-mail: Henk.Grootjans@shell.com

**Licensor:** Shell Global Solutions International B.V.

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**SulFerox**

**Application:** Removal of hydrogen sulfide (H$_2$S) from a large range of gas streams giving a sulfur production of 0.1–20 tpd. Gas applications include: natural gas, amine tail gas, enhanced oil recovery CO$_2$ recycle, refinery gases, geothermal, syngas, offshore production gas, digester offgas and offgas from wastewater treatment plants. The full range of H$_2$S concentrations (from a few ppmv to almost 100%v of H$_2$S) can be treated to 1 ppmv H$_2$S. Turndown properties—both on H$_2$S 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$^3$/d) the combination of an amine unit coupled to a SulFerox unit becomes more economical. The sulfur product can be obtained as a filter cake or alternatively as molten sulfur of high quality. The sulfur cake can be land filled as a nonhazardous waste or—depending on local regulations—directly used as a fertilizer.

**Description:** SulFerox is a redox-based process that converts H$_2$S in sour gas to elemental sulfur (S) in the contacotor through reaction with a proprietary aqueous ferric iron chelate solution. Various contacotor types are available, such as sparged towers, spray towers and pipeline contactors. The sparged tower is the most versatile contacotor and will be selected whenever pressure drop allows. After contacting the sour gas and SulFerox solution in the (sparged tower) contacotor, the gas/liquid mixture is separated. In the separator, the solution and treated gas is separated yielding the treated sweet gas—leaving the unit via an optional knockout vessel—and the depleted SulFerox solution.

After optional degassing, the reduced iron chelate solution is regenerated via reaction of Fe$_2^+$ back to Fe$_3^+$ with oxygen from an air source in the regenerator vessel. Via a thickener vessel, part of the solution is sent for filtration and sulfur recovery; the major portion of the stream is returned to the contacotor.

In addition, the resulting filtrate is returned to the process for maximum solution recovery, thus, optimally using the chelate solution. Depending on the feed gas conditions, the contacotor and separator can be combined in one vessel as can be done with the regenerator and surge vessel. This gives a two-vessel configuration suited for amine regenerator offgas.

**Operating conditions:** Operating pressures vary from just over atmospheric to 500 psig. The SulFerox process itself operates at temperatures of 110°F–140°F. However, the feed gas temperature can be between 75°F–130°F. The feed gas must be free of hydrocarbon liquids. Gas at other conditions may need pretreatment first (cooling, dew pointing). Although the applicability of the SulFerox process is very wide, some feed gas contaminants such as high levels of NH$_3$, HCN and SO$_2$ might affect the economics of the process.

**Installations:** Thirty units in operation.


**Licensor:** Shell Global Solutions International B.V.

**Contact:** Henk Grootjans, Shell Global Solutions International B.V., P.O. Box 3800, 1030 BN, Amsterdam, The Netherlands, Phone: (31) 20 630 2859, Fax: (31) 20 630 2900, E-mail: Henk.Grootjans@shell.com
**Sulfint HP**

**Application:** Selective hydrogen sulfide (H₂S) removal from high-pressure gases with direct conversion of H₂S into elemental sulfur (S). Residual H₂S levels in the treated gas can be lower than 1 ppm vol.

**Description:** The Sulfint HP uses the well-known concept of redox desulfurization. However, this process has been specifically designed to treat high-pressure gases. The feed gas is contacted with the redox catalytic solution (aqueous iron chelate based solution) in a co-current absorber (1). The H₂S is absorbed by the catalytic solution, reacts with the catalyst and is converted into elemental S. Desulfurized gas is recovered from the top of the separator vessel (2). The sulfur-loaded solution is then pumped through a multi-cartridge, high-pressure filter (3). The filtered solution can be partly recycled to the absorber (1) and partially expanded for regeneration.

The expanded solution, after separation of the dissolved gases (4) is regenerated with air in the oxidizer vessel (5). The whole process operates at near-ambient temperature, and no thermal regeneration nor chilling is needed. High-pressure filtration mitigates foaming/plugging problems, especially after the expansion of the solution. Due to direct recycle of the filtered solution to the absorber, pumping costs are minimized. This process is highly selective; only H₂S is removed (no CO₂ co-absorption and very little hydrocarbons co-absorption).

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

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


**Licensors:** Prosernat IFP Group Technologies and Le Gaz Integral

**Contact:** Christian Streicher, Marketing Manager, Prosernat, Tour Areva, 92084 Paris La Défense Cedex, France, Phone: (+33) 1 47 96 37 86, Fax: (+33) 1 47 96 02 46, E-mail: cstreicher@prosernat.com
**Application:** Hydrogen sulfide (H₂S) removal from sulfur.

**Description:** Sulfur, as produced by the Claus process, typically contains from about 200–500 ppmw H₂S. The H₂S may be contained in the molten sulfur as H₂S or as hydrogen polysulfides (H₂Sₓ). The dissolved H₂S separates from the molten sulfur readily, but the H₂Sₓ does not.

The sulfur degassing process accelerates the decomposition of hydrogen polysulfides to H₂S and elemental sulfur (S). The dissolved H₂S gas is released in a controlled manner. Sulfur temperature, residence time, and the degree of agitation all influence the degassing process. Chemical catalysts, including oxygen (air) that accelerate the rate of H₂Sₓ decomposition, are known to improve the degassing characteristics.

In fact, the majority of successful commercial degassing processes use compressed air, in some fashion, as the degassing medium. Research performed by Alberta Sulphur Research Ltd. has demonstrated that air is a superior degassing agent when compared to nitrogen, steam or other inert gases. Oxygen present in air promotes a level of direct oxidation of H₂S to elemental S, which reduces the gaseous H₂S partial pressure and increases the driving force for H₂Sₓ decomposition to the more easily removed gaseous phase H₂S.

The MAG degassing system concept was developed to use the benefits of degassing in the presence of air without relying on a costly compressed air source. With the MAG system, motive pressure from a recirculated degassed sulfur stream is converted to energy in a mixing assembly within the undegassed sulfur. The energy of the recirculated sulfur creates a high air-to-sulfur interfacial area by generating intense turbulence within the jet plume turning over the contents many times, thus exposing the molten sulfur to the sweep air. Intimate mixing is achieved along with turbulence to promote degassing. This sulfur degassing system can readily meet a 10 ppmw total H₂S (H₂S + H₂Sₓ) specification.

Tests show degassing rate constants nearly identical to traditional air sparging for well-mixed, air-swept degassing systems. Thus, comparable degassing to air sparging can be achieved without using a compressed air source. The assemblies are designed to be self-draining of molten sulfur and to be easily slipped in and out for maintenance through the pit nozzles provided. The mixing assemblies require no moving parts or ancillary equipment other than the typical sulfur-product-transfer pump that maximizes unit reliability and simplifies operations.

The process is straightforward; it is inherently safer than systems using spray nozzles and/or impingement plates because no free fall of sulfur is allowed.

**Economics:** Typically does not require changes to existing sulfur processing infrastructure.

**Installation:** Several units are in design.


**Licensor:** Black & Veatch Pritchard, Inc.

**Contact:** David K. Stevens, Vice President, Sulfur Technology, 11401 Lamar, Overland Park, KS 66211 USA, Phone: (913) 458-6068, Fax: (913) 458-6098, Email: stevensdk@bv.com
**Sulfur degassing**

**Application:** Remove hydrogen sulfide (H\textsubscript{2}S) and hydrogen poly-sulfides (H\textsubscript{2}S\textsubscript{x}) dissolved in liquid sulfur.

**Safety:** Hydrogen sulfide is a highly toxic and potentially explosive gas. A concentration of 600 ppmv is lethal and is explosive at approximately 3.5% vol. Dissolved H\textsubscript{2}S\textsubscript{x} is decomposed, and H\textsubscript{2}S is released in storage, during loading and unloading and also during transportation, thus leading to potentially dangerous conditions.

**Product:** Liquid sulfur containing 10 ppmw of H\textsubscript{2}S or less.

**Description:** Liquid sulfur flowing from the Claus plant to the sulfur pit contains typically 250–350 ppmw of H\textsubscript{2}S + H\textsubscript{2}S\textsubscript{x}. Sulfur is degassed using an active gas-liquid contacting system to release dissolved gas. Adding chemicals is not required. Sulfur from the pit is pumped into the degassing tower where it is contacted counter-currently with hot compressed air over a fixed catalyst bed. Degassed sulfur is returned to the product section of the sulfur pit.

**Operating conditions:** The operating temperature in the sulfur degassing tower can vary from 125°C to 150°C depending on the temperature in the sulfur pit. The operating pressure drop is around 0.3–0.5 bar. Treated sulfur has a residual H\textsubscript{2}S level in the range of 5–10 ppmw.

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

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

**Licensor:** BP AMOCO through SIIRTEC NIGI

**Contact:** SIIRTEC NIGI S.p.A., Via Algardi 2 - 20148, Milano, Italy, Phone: (39) 0 239 2231, Fax: (39) 0 2392 3010, E-mail: marketing@sini.it
SUPERCLAUS process

Application: The SUPERCLAUS process recovers elemental sulfur from hydrogen sulfide (H₂S) containing gases originating from gas treating plants such as alkanolamine units or physical solvent plants. Modern SUPERCLAUS plants should be able to process H₂S/ammonia (NH₃) containing gases as well, originating from sour water strippers, to yield up to 99.4% overall sulfur recovery without any further tail gas clean-up.

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

In the thermal stage, the acid gas is burned with a substoichiometric amount of controlled combustion air such that the tail gas leaving the second reactor contains typically 0.8 vol.% to 1.0 vol.% of H₂S. The catalyst in the third reactor oxidizes H₂S to sulfur at more than 85% efficiency.

However, because the new catalyst neither oxidizes H₂S to SO₂ and water nor reverses the reaction; total sulfur recovery up to 99% can be obtained. If sulfur recovery more than 99% is required, one additional Claus reactor stage will be installed upstream of the selective oxidation reactor.

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

<table>
<thead>
<tr>
<th>Utility</th>
<th>Consumption</th>
<th>Production</th>
</tr>
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<tbody>
<tr>
<td>Steam, LP, tph</td>
<td>—</td>
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</tr>
<tr>
<td>Steam, MP, tph</td>
<td>—</td>
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<td>Electricity, kW</td>
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<td>—</td>
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<tr>
<td>Boiler feed water, tph</td>
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<td>—</td>
</tr>
<tr>
<td>Steam, LP (plant heating), tph</td>
<td>0.4</td>
<td>—</td>
</tr>
</tbody>
</table>

Installations: Since the first commercial demonstration of the SUPERCLAUS process in 1988, more than 110 plants with a capacity up to 1,165 tpd are in operation or under construction in the first quarter of 2003.

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

Contact: Juste Meijer, Plesmanlaan 100, 2332 CB, P.O. Box 141, 2300 AC, Leiden, The Netherlands, Phone: (31) 71 582 7887, Fax: (31) 71 528 7079, E-mail: juste.meijer@jacobs.com

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Sure

**Application:** Oxygen-enhanced recovery of sulfur from H₂S-containing gas streams. Products are bright yellow sulfur (99.9% pure) and clean tail gas for further recovery or incineration.

**Description:** The capacity of a Claus-type sulfur recovery unit can be increased by thermal combustion of H₂S in two or more stages with an oxidant which is an oxygen-rich gas stream comprised of pure oxygen or a mixture of air and oxygen. A portion of the oxidant is fed to a first combustion zone (1) with all or a portion of the acid gas or ammonia-containing acid gas. The reacted mixture is cooled (2) and the remaining gas streams are fed to a second combustion zone (3). After condensing sulfur, the remaining gas stream is then fed to one or more Claus converters (4).

**Operating conditions:** Pressures are near atmospheric. Oxygen concentration in oxidant is 21% to 100%. Sulfur recovery is 90% to 98%.

**Economics:** Replacing air with oxygen will more than double the capacity of a Claus-type sulfur plant and subsequent tail gas treating unit. Use of the Sure process is particularly attractive for revamping existing Claus and tail gas units to substantially increase the acid gas removal and for intermittent operation of such units at higher throughputs. Using the Sure process in new installations significantly reduces capital investment.

**Installations:** One in Japan, one in the UK, eight in Italy and six in the US. Twelve more plants in various engineering and design phases.

**Licensors:** BOC Gases and Parsons Energy & Chemicals Group, Inc.

**Contact:** Arif Habibullah, P.E., Senior Technical Director & Manager, Process Technology, Parsons E&C, 125 W Huntington Drive, Arcadia, CA 9100, Phone: (626) 294-3582, Fax: (626) 294-3311, E-mail: arif.habibullah@parsons.com

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Gas Processes 2004
ACORN methane wash

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

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

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

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

**Installations:** Six.

**Licensor:** Air Products and Chemicals, Inc.

**Contact:** Joanne Trimpi, Marketing Manager, Energy & Process Industries, 7201 Hamilton Blvd., Allentown, PA 18195-1501, Phone: (610) 481-7326 , Fax: (610) 706-2982 , E-mail: trimpijl@apci.com

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ACORN partial condensation

**Application:** To produce a high-purity carbon monoxide (CO) stream, and a moderate-purity hydrogen (H₂) stream, plus a ratio adjusted synthesis gas stream for use as a chemical feedstock. The synthesis gas stream is typically the product of partial oxidation reaction (POX).

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

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

Variations on this basic cycle are possible depending on feed gas pressure and gas composition, and desired product purity. The H₂ product is delivered at high pressure, but the CO exits the process at low pressure. Therefore, a CO-product compressor is usually required to deliver the product to a downstream process.

**Installations:** Eleven.

**Licensor:** Air Products and Chemicals, Inc.

**Contact:** Joanne Trimpi, Marketing Manager, Energy & Process Industries, 7201 Hamilton Blvd., Allentown, PA 18195-1501, Phone: (610) 481-7326, Fax: (610) 706-2982, E-mail: trimpijl@apci.com
**Gas-to-liquids (GTL)**

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

**Description:** The front-end process (1) is based on ConocoPhillips’ unique and highly proprietary COPox catalytic partial oxidation syngas technology. The hydrocarbon feed conversion and selectivity to carbon monoxide (CO) and hydrogen (H₂) is higher than conventional equilibrium syngas production methods. The ConocoPhillips reactors have a high throughput and operate at relatively mild conditions.

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

The FT product is finished in a back-end Product Upgrading Unit (3) that includes Hydro Processing using both conventional and ConocoPhillips proprietary technology.

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

**Operating conditions:** The ConocoPhillips COPox syngas process operates within a range of conditions depending on inlet gas composition. Typical operating temperature range is 600–1,000°C. The ConocoPhillips FT process operates within a typical temperature range of 200–250°C.

**Installations:** ConocoPhillips is currently starting up a 400 barrel per day (bpd) demonstration plant in Ponca City, Oklahoma. Plans are to have the first commercial plant operating in 2010.

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

**Contact:** Jim Rockwell, Manager Gas to Liquids, E-mail: Jim.L.Rockwell@ConocoPhillips.com
Gas Processes 2004

Gas-to-liquids (GTL)

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

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

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

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

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

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

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

**Licensor:** Davy Process Technology

**Contact:** 20 Eastborne Terrace, London W2 6LE, UK; e-mail: dpt@davyprotech.com

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![Diagram of Gas-to-liquids (GTL) process]

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**MegaSyn**

**Application:** Large-scale syngas production, essentially hydrogen (H₂) and carbon monoxide (CO), from natural gas or other gaseous hydrocarbons for methanol, ammonia, Fischer-Tropsch and other synthesis plants in one train.

**Description:** The hydrocarbon feedstock is preheated and desulfurized. The gas is then saturated with water by a circulation loop fed by process condensate. Before routing the feedgas to the autothermal reformer (prereforming is optional), this gas is preheated by a fired heater. Superheated gas is then sent to the autothermal reformer. If required carbon dioxide (CO₂) can be fed to the prereformed gas.

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

**Economics:** Typical figures are presented for a syngas generation plant delivering syngas to Fischer-Tropsch synthesis. Consumption per 1 million scfd syngas:
- Natural gas (feed + fuel): 441 million Btu; oxygen: 0.22 million scfd (over the fence); CO₂: 0.09 million scfd; demineralized water: 0.98 tons; cooling water: 11.5 tons; electricity: 22.4 kWh; export steam: 18.5 tons; specific investment: €224,000/million scfd syngas.

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

**Licensor:** Lurgi Oel-Gas-Chemie GmbH

**Contact:** Dr. Thomas Wurzel, Lurgi Oel-Gas-Chemie GmbH, Lurgiallee 5, D-60295 Frankfurt am Main, Germany, Phone: (49) 69 5808 2490, Fax: (49) 69 5808 3032, E-mail: Dr._Thomas_Wurzel@lurgi.de

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![Diagram of the MegaSyn process](image)
**Multipurpose gasification**

**Application:** Production of synthesis gas, essentially H₂ and CO, from a wide range of gaseous to extra heavy liquid hydrocarbons, as well as emulsions and slurries. Recent new applications are in (chemical) waste gasification. The main advantage over comparable processes is its extreme feedstock flexibility in the quench mode. A boiler mode for highest efficiency is also available.

**Description:** Continuous noncatalytic partial oxidation process. The quench mode is shown above: hydrocarbon feedstock, moderator (H₂O, CO₂ or N₂) and oxidant (pure or diluted O₂, 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 value. Quench water washes out most particulates as unconverted carbon (soot) and ash.

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

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

**Economics:** Characteristic consumption and production rates per ton of heavy residue feedstock: 1 to 1.1 t O₂ (100%), export 0.5 t MP steam to 2.2 t HP steam, 2.2 t raw syngas (dry) equiv. to 2,600 Nm³ H₂ + CO. Cold gas efficiency is 82% to 85%. In boiler mode, thermal efficiencies including HP steam generated are about 95% based on feedstock HHV. This makes the process attractive for syngas production and for an IGCC power plant. A highly integrated and efficient power complex will be in the range of $800/kW total invested cost.

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


**Licensor:** Lurgi Oel-Gas-Chemie GmbH

**Contact:** Dr. Holger Schlichting, Lurgi Oel-Gas-Chemie GmbH, Lurgiallee 5, D-60295 Frankfurt am Main, Germany, Phone: (49) 69 5808 1418, Fax: (49) 69 5808 2639, E-mail: Dr_Holger_Schlichting@lurgi.de

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**Gas Processes 2004**

**Synthesis gas**

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**Syngas (ATR)**

**Application:** Produce CO-rich synthesis gas.

**Products:** Pure carbon monoxide (CO) and hydrogen (H₂) 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 proprietary burner design and application.

The unit consists of a feed preheater (1), feed desulfurization (2), pre-reforming (optional) (3), autothermal reformer reactor with burner, combustion chamber and catalyst bed (4), heat-recovery section (5) and, when required, gas purification section, e.g., CO₂ removal (not shown).

The autothermal reformer burner features low metal temperatures and high resistance to mechanical wear, thus ensuring 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. CO₂ recycle or CO₂ import can be applied to adjust synthesis gas composition.

**Operating conditions:** Typically, CO-rich synthesis gas is obtained at feed ratios of H₂O/CH₄ = 0.2 to 1.5 and CO₂/CH₄ = 0.0 to 2.0, resulting in synthesis gas ratios H₂/CO = 0.8 to 2.5 at reactor exit temperatures of 950°C to 1,050°C. Reactor pressure ranges between 20 bar and 70 bar.

**Installations:** Since 1958, 26 complete installations have been licensed. New burner technology with improved lifetime was introduced in 1992 and is in operation in 20 autothermal reforming plants and 8 secondary reforming plants. Six burners are on order for GTL plants with up to 17,000-bpd capacity per line. Recently, LOIs have been obtained for ATR installations for GTL projects in South Africa and Qatar.

**References:**


**Licensor:** Haldor Topsøe A/S

**Contact:** Jørgen N. Gel or Peter Soegaard-Andersen, Nymollevej 55, DK-2800 Lyngby, Denmark, Phone: (45) 45 27 2000, Fax: (45) 45 27 29 99, E-mail: JNG@topsoe.dk or PSA@topsoe.dk
Syngas (autothermal)

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

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

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

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

Carbon dioxide can be recycled to adjust the H₂/CO product ratio. For natural gas feedstocks, the H₂/CO product ratio ranges from about 2.7 (for no CO₂ recycle) to 1.6 (for full CO₂ recycle).

Autothermal reforming technology is similar to secondary reforming for ammonia production, except that oxygen is used as feedstock instead of air. Oxygen is required since nitrogen would dilute the H₂/CO product gas purity.

**Economics:** The economics can be favorable for autothermal reforming when oxygen is available at relatively low cost. For natural gas feedstocks, the optimum H₂/CO product ratio is about 1.6 to 2.7.


**Supplier:** CB&I Howe Baker

**Contact:** Mr. Craig E. Wentworth, vice president of sales, CB&I Howe-Baker, 3102 East Fifth St., Tyler, TX 75701, Phone: (903) 595-7911, Fax: (903) 595-7751, Email: cwentworth@CBIepc.com
Syngas-advanced SMR

**Application:** Produce a CO-rich synthesis gas.

**Products:** Pure CO and H₂, or mixtures of CO and H₂ (synthesis gas), are used to manufacture many chemicals, e.g., acetic acid, oxo-alcohols and isocyanates.

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

The hydrocarbon feedstock can be natural gas, LPG or naphtha. For heavy feedstocks, an adiabatic pre-reformer is needed upstream of the tubular reformer. Carbon dioxide (CO₂) import and/or CO₂ recycle is applied to produce CO-rich synthesis gas.

The unit typically consists of a feed desulfurization, pre-reforming, tubular reforming, CO₂ 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 H₂O/CH₄ = 1.5 to 2.0 with CO₂ recycle and/or CO₂ import. This results in H₂/CO ratios down to 1.8 at reformer exit temperatures of 950°C (1,740°F). Even lower H₂/CO ratios can be obtained by CO₂ reforming using the SPARG process or by applying a high-activity, noble-metal reforming catalyst.

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

**References:**

**Licensor:** Haldor Topsøe A/S

**Contact:** Jørgen N. Gøl, Nymollevej 55, DK-2800 Lyngby, Denmark, Phone: (45) 45 27 2000, Fax: (45) 45 27 29 99, E-mail: JNG@topsoe.dk

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**Syngas-autothermal reforming**

**Application:** Carbon monoxide (CO)-rich synthesis gas production.

**Feedstock:** Natural gas, multiple feedstock and naphtha.

**Product:** Synthesis gas for the production of carbon monoxide, hydrogen (H₂), ammonia, methanol, Fischer-Tropsch synthetic fuel and oxo-chemicals.

**Description:** Autothermal reforming can be used as an alternative to conventional steam reforming. Feedstock is preheated and subsequently desulfurized before entering the adiabatic reactor (ATR) combustion chamber. At the ATR top, the feed mixture is burned with oxygen in a partial oxidation chamber. The main feature of the ATR design is the unique arrangement of water cooled oxygen nozzles in the ATR dome. This method allows for complete mixing without any metal internals in the combustion zone, thus ensuring a long burner life.

After entering a nickel-based catalyst bed where the steam reforming reactions occurs, the reformed gas leaves the ATR at about 1,050°C. The gas passes the cooling train before entering the required purification section, e.g. carbon dioxide (CO₂) removal, cryogenic separation, etc.

**Installation:** Uhde's autothermal reforming technology is derived from the secondary reformer used in the ammonia technology, except that oxygen instead of air is applied. The water cooled burner nozzles arrangement has been tested successfully over ten years in a 12,000 Nm³/h H₂/CO demonstration unit based on Uhde's proprietary combined autothermal reforming (CAR) technology.


**Licensor:** Uhde GmbH, Dortmund, Germany

**Contact:**
E-mail: information@tkt-uhde.thyssenkrupp.com
**Application:** Produce hydrogen and/or \( \text{H}_2/\text{CO} \)-rich gas using advanced steam-reforming methods.

**Feedstock:** Natural gas, refinery offgas, LPG/butane and light naphtha.

**Product:** Synthesis gas for hydrogen, ammonia, methanol, Fischer-Tropsch-synfuel, oxo-synthesis products, etc.

**Description:** The steam-reforming process comprises the high-temperature reaction of methane or light hydrocarbons over a nickel catalyst that produces hydrogen and carbon monoxide (CO). The reforming occurs in tubes packed with catalyst and arranged vertically in gas-fired steam reformers. A nickel catalyst is used and applied to a supporting structure. The operating conditions of the steam reformer vary and depend on the application, with discharge temperatures ranging from 740°C to 950°C and pressures up to 50 bar. This wide range of operating conditions necessitates a versatile reformer design.

The Uhde steam reformer is a top-fired reformer which has tubes made of centrifugally cast alloy steel and a proprietary “cold” outlet manifold system. The reformer and outlet system design have proved its suitability over the past decades. It satisfies the demands of various applications and permits constructing and operating world-scale reformers with unrestricted reliability. The largest reformer, based on Uhde technology, consisted of 960 tubes.

**Installations:** More than 60 Uhde reformers exist worldwide. The first Uhde reformer with a cold outlet manifold went onstream in 1966. In 1977 and 1984, two large Uhde steam reformers with 540 reformer tubes each were commissioned, and these units are still in operation today. The company has recently commissioned two large ammonia/urea complexes based on natural gas in Qatar and Egypt with ammonia syngas capacities of 96,000 Nm\(^3\)/h of \( \text{CO} + \text{H}_2 \) and 81,000 Nm\(^3\)/h of \( \text{CO} + \text{H}_2 \), respectively. A plant for oxo-chemicals supplied by Uhde to South Korea has an oxo-syngas production capacity of 9,700 Nm\(^3\)/h of \( \text{CO} + \text{H}_2 \). Uhde has recently commissioned two world-scale hydrogen plants for SINCOR C.A., Venezuela (2 \times 98,000 Nm\(^3\)/h) and Shell Canada Ltd., Canada (2 \times 130,000 Nm\(^3\)/h).


**Licensor:** Uhde GmbH, Dortmund, Germany

**Contact:**
E-mail: information@tkt-uhde.thyssenkrupp.com
**ADIP**

**Application:** The regenerative-amine process removes hydrogen sulfide (H₂S) and carbon dioxide (CO₂) from natural gas, refinery gases and synthesis gas. Hydrogen sulfide can be reduced to low sulfur levels. The process can also be applied to remove H₂S, CO₂ and carbonyl sulfide from liquefied petroleum gas or natural gas liquids (NGL) to low levels. Bulk CO₂ removal from synthesis gas with flash regeneration is another application.

The process sequence-ADIP/Claus/SCOT-can be used advantageously with an integrated ADIP system that handles selective H₂S removal upstream and the SCOT process treating the Claus offgas.

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

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

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

For a typical design, the co-absorbed hydrocarbons from the absorber (1) are flashed (2) from the solvent and used as fuel gas after treatment (3). The solvent is flashed again (4) to release CO₂ from the enrichment absorber (5), thereby improving the acid-gas composition from the regenerator (6) to the Claus unit.

**Operating conditions:** A very wide range of treating pressures and contaminant concentrations can be accommodated. Sulfur specifications of 100 mbara H₂S in gas and 10 ppmw in liquid hydrocarbon streams can be met. In liquid hydrocarbon, COS can be removed down to 5 ppmw. Improved Claus feed gas quality can be met by improving the H₂S/CO₂ ratio in the acid gas. Bulk CO₂ removal from a high percentage to several percentage points is easily attained.

**Installations:** More than 400 ADIP units are in operation or under construction.

Applications include: natural gas, liquefied natural gas, refinery gases and liquefied petroleum gases and synthesis gases.

**References:**
- “ADIP as the preferred solvent for amine treatment in refinery applications,” Laurance Reid Conference, March 1999.
- “Process applications of the ADIP and Sulfinol process,” Gas Processing Symposium, Dubai, United Arab Emirates, April 1999.

**Licensor:** Shell Global Solutions International B.V.

**Contact:** Henk Grootjans, Shell Global Solutions International B.V., P.O. Box 3800, 1030 BN, Amsterdam, The Netherlands, Phone: (31) 20 630 2859, Fax: (31) 20 630 2900, E-mail: Henk.Grootjans@shell.com
**ADIP-X**

**Application:** This regenerative-amine process is highly suitable for bulk and deep carbon dioxide (CO₂)-removal from gas streams. It also removes hydrogen sulfide (H₂S), some COS and mercaptans from natural gas, refinery gas, and synthesis gas. Hydrogen sulfide can be reduced to low-sulfur levels. This process achieves a higher loading capacity and reduced equipment size compared to general aqueous amine solvents.

**Description:** The ADIP-X process uses aqueous solutions of the tertiary amine, methyl diethanolamine, and an additive. Amine concentrations up to 50%wt can be applied. The process has low observed corrosion rates and a controllable foaming tendency of the solvent due to an optimized design. Its lineup can be very diverse, depending on the application. High integration of separate process units is possible. The simplest system resembles those of other amine processes.

**Operating conditions:** A very wide range of treating pressures and contaminant concentrations can be accommodated. Carbon dioxide specifications below 50 ppmv in gas streams can be met. Hydrogen sulfide specifications down to 100 mbar are also achievable. Bulk CO₂ removal from a high percentage to several percentage points is easily attained.

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

**References:**

**Licensor:** Shell Global Solutions International B.V.

**Contact:** Henk Grootjans, Shell Global Solutions International B.V., P.O. Box 3800, 1030 BN, Amsterdam, The Netherlands, Phone: (31) 20 630 2859, Fax: (31) 20 630 2900, E-mail: Henk.Grootjans@shell.com
Advanced amines

Applications: Advanced Amines is a complete portfolio of amine (DEA, MDEA and activated MDEA) based processes to sweeten natural gases. The Advanced Amines processes cover all types of acid gas removal applications, for any feed gas composition and product specifications as low as hydrogen sulfide (H$_2$S) <1 ppm and carbon dioxide (CO$_2$) <50 ppm.

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

- High load DEA: based on using high concentration (4 mol DEA/l) and high loading (mol acid gas/mol DEA) DEA, for high performance complete deacidification.
- Selective MDEA: based on using pure MDEA aqueous solution for selective H$_2$S removal or H$_2$S enrichment applications.
- Activated MDEA: for all complete deacidification and bulk CO$_2$ removal applications, with a range of patented activators. Activated MDEA offers specific advantages like partial/total flash regeneration of the solvent for CO$_2$ 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 requirements. It uses a flow of semi-lean amine, withdrawn from the thermal regenerator’s (3) intermediate level and sent back at the absorber’s (1) intermediate level. Energy requirements can also be minimized by using activated MDEA, with flash regeneration of the solvent. With high load DEA, a proprietary absorber design is also available which allows high COS hydrolysis levels (up to 95% COS removal).

Installations: More than 120 units, among which about one fifth operated by TOTAL, with unit capacities between 0.3 and 25.2 Nm$^3$/d.

References: “MDEA based solvents used at the Lacq processing plant,” Elgue J. and F. Lallemand, GPA Europe meeting, January 18, 1996.

Licensor: Prosernat–IFP Group Technologies

Contact: Christian Streicher, Marketing Manager, Prosernat, Tour Areva, 92084 Paris La Défense Cedex, France, Phone: (+33) 1 47 96 37 86, Fax: (+33) 1 47 96 02 46, E-mail: cstreicher@prosernat.com
aMDEA process

**Application:** Removal of carbon dioxide (CO₂), hydrogen sulfide (H₂S), COS and RSH from synthesis gas, natural gas or other gases.

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

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

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

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

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

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

**Licensor:** BASF AG

**Contact:** aMDEA Team, Carl Bosch Str. 38, D-67056 Ludwigshafen, Germany, Phone: (49) 621 60 40937, Fax: (49) 621 60 21033, E-mail: Info.aMDEA@BASF-AG.de.
Amine Guard FS

Application: Remove CO₂ and H₂S from natural gas; CO₂ from ammonia syngas, etc., with a solution containing one of the UCARSOL family of formulated solvents offered by Dow. When desired, H₂S can be removed selectively to provide a superior Claus plant feed and reduce regeneration requirements.

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

Description: 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 process parameters.

Operating conditions: Absorption pressure is atmosphere to 1,800 psi, as available. Feed temperature is 85°F to 150°F. Acid gas content may be 5–35%.

Economics: For a 500-million scfd natural gas unit having a feed gas containing 6% CO₂ and 1% H₂S, typical costs are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Pipeline</th>
<th>LNG feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment, $million</td>
<td>14.0</td>
<td>17.0</td>
</tr>
<tr>
<td>Operating costs, $million/y</td>
<td>6.0</td>
<td>7.0</td>
</tr>
</tbody>
</table>

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

Licensor: UOP LLC

Contact: Anita Black, UOP, 25 E. Algonquin Ave., Des Plaines, IL 60016 USA, Phone: (847) 375-7801, Fax: (847) 391-2253, E-mail: anita.black@uop.com
Ammonia Claus technology—ACT

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

**Product:** Bright yellow high-purity sulfur and NH₃ decomposition in elemental species like nitrogen and water (H₂O).

**Description:** Conventional straight-through Claus plant configuration applying a single zone reactor furnace that can operate when NH₃ volume concentration in the feed gas is lower than a few tenths of a percent. At higher NH₃ concentrations, especially from a SWS gas stream, which is mainly NH₃, H₂S and H₂O, it becomes necessary to destroy NH₃ in order to avoid severe operational problems that may occur in the sulfur recovery units (SRU).

In fact, NH₃ in the presence of H₂S forms ammonium (poly) sulfide, which solidifies at temperatures below 150°C and tends to plug sulfur condensers, sulfur run-down lines and seal pots. In addition to plugging problems, NH₃ in sulfur recovery gas feeds increases plant size, related cost and decreases sulfur recovery.

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

**Operating conditions:** The operating temperature in the ACT “two zone furnace” configuration can vary between 1,350°C and 1,650°C and the ACT pressure drop is around 0.3 bar. By adopting ACT, an NH₃ bearing feed can be treated up to a level of NH₃ concentration in the furnace effluent gas that is not harmful for regular SRU operation.

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

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

**Contact:** SIIRTEC NIGI S.p.A., Via Algardi 2 - 20148 , Milano, Italy, Phone: (39) 0 239 2231, Fax: (39) 0 2392 3010, E-mail: marketing@sini.it

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Ammonia Claus Technology

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**Description:** Conventional straight-through Claus plant configuration applying a single zone reactor furnace that can operate when NH₃ volume concentration in the feed gas is lower than a few tenths of a percent. At higher NH₃ concentrations, especially from a SWS gas stream, which is mainly NH₃, H₂S and H₂O, it becomes necessary to destroy NH₃ in order to avoid severe operational problems that may occur in the sulfur recovery units (SRU).

In fact, NH₃ in the presence of H₂S forms ammonium (poly) sulfide, which solidifies at temperatures below 150°C and tends to plug sulfur condensers, sulfur run-down lines and seal pots. In addition to plugging problems, NH₃ in sulfur recovery gas feeds increases plant size, related cost and decreases sulfur recovery.

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

**Operating conditions:** The operating temperature in the ACT “two zone furnace” configuration can vary between 1,350°C and 1,650°C and the ACT pressure drop is around 0.3 bar. By adopting ACT, an NH₃ bearing feed can be treated up to a level of NH₃ concentration in the furnace effluent gas that is not harmful for regular SRU operation.

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

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

**Contact:** SIIRTEC NIGI S.p.A., Via Algardi 2 - 20148 , Milano, Italy, Phone: (39) 0 239 2231, Fax: (39) 0 2392 3010, E-mail: marketing@sini.it

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**Gas Processes 2004**

**Ammonia Claus technology—ACT**

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

**Product:** Bright yellow high-purity sulfur and NH₃ decomposition in elemental species like nitrogen and water (H₂O).

**Description:** Conventional straight-through Claus plant configuration applying a single zone reactor furnace that can operate when NH₃ volume concentration in the feed gas is lower than a few tenths of a percent. At higher NH₃ concentrations, especially from a SWS gas stream, which is mainly NH₃, H₂S and H₂O, it becomes necessary to destroy NH₃ in order to avoid severe operational problems that may occur in the sulfur recovery units (SRU).

In fact, NH₃ in the presence of H₂S forms ammonium (poly) sulfide, which solidifies at temperatures below 150°C and tends to plug sulfur condensers, sulfur run-down lines and seal pots. In addition to plugging problems, NH₃ in sulfur recovery gas feeds increases plant size, related cost and decreases sulfur recovery.

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

**Operating conditions:** The operating temperature in the ACT “two zone furnace” configuration can vary between 1,350°C and 1,650°C and the ACT pressure drop is around 0.3 bar. By adopting ACT, an NH₃ bearing feed can be treated up to a level of NH₃ concentration in the furnace effluent gas that is not harmful for regular SRU operation.

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

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

**Contact:** SIIRTEC NIGI S.p.A., Via Algardi 2 - 20148 , Milano, Italy, Phone: (39) 0 239 2231, Fax: (39) 0 2392 3010, E-mail: marketing@sini.it
**Application:** Removal of CO₂ and H₂S from natural gas, syngas, etc. Removal of CO₂ from ammonia syngas, ethylene oxide recycle gas, etc.

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

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

**Operating conditions:** Absorption pressure is 150 to 1,800 psi, as available. Feed temperature is about 150°F to 250°F. If the feed is available at a higher temperature, that heat will be used to supply regeneration heat. Acid gas content may be 5–35%. Heavy hydrocarbons are easily handled. If no H₂S is present, oxygen contents of several percent are handled without difficulty or solvent degradation.

**Economics:** The extensive use of carbon steel, the elimination of a rich/lean solution heat exchanger, the heat recovered by LoHeat and the low cost of the solution chemical make the process attractive for a wide range of applications. For a 500-million scfd natural gas unit having a feed gas containing 6% CO₂ and 1% H₂S, typical costs are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Pipeline</th>
<th>LNG feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment, $\text{million}$</td>
<td>14.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Operating costs, $\text{million}/y</td>
<td>5.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

**Installations:** Of the more than 700 units worldwide, more than 65 treat natural gas, over 200 treat ammonia syngas and about 110 are in hydrogen plants. The remainder are in SNG, partial oxidation, coal gasification and petrochemical applications.

**Licensor:** UOP LLC

**Contact:** Anita Black, UOP, 25 E. Algonquin Ave., Des Plaines, IL 60016 USA, Phone: (847) 375-7801, Fax: (847) 391-2253, E-mail: anita.black@uop.com
CO₂ recovery

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

Description: CO₂-containing feed gases are first cooled and scrubbed (1), if necessary, to reduce SO₂ levels. The gases are boosted slightly in pressure before entering the recovery system.

The system is based on absorption/stripping using a monoethanolamine (MEA) solution. Feed gases are sent to an amine absorber (2) where they are scrubbed with MEA to recover CO₂. The scrubbed gases are vented to the atmosphere after water washing in the absorber’s top to minimize MEA losses. Rich solution from the MEA absorber is preheated in an exchanger (3), flashed and sent to a stripper (5) where CO₂ is recovered overhead. Condensate from the stripper overhead is returned to the system.

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

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

Operating conditions: Operating units have exhibited availability factors in excess of 98%. Absorption and stripping operations take place at slightly above atmospheric pressure. Moderate levels of SO₂ and NOₓ in the feed are acceptable. SO₂ prescrubbing is required only with SO₂ levels higher than 25 ppmv.

Economics: Typical capital investment for a 200-tpd CO₂ plant is $9 million. Liquefaction facilities would add roughly $4 million to the capital investment. Utility consumptions used in a design are determined from utility costs and availability. Typical utility and chemical requirements per ton of CO₂ recovered are as follows (for the recovery section only):

<table>
<thead>
<tr>
<th>Utility</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam, LP</td>
<td>1.9 to 2.7 t</td>
</tr>
<tr>
<td>Water, cooling, gal</td>
<td>23,000</td>
</tr>
<tr>
<td>Power, kWh</td>
<td>100</td>
</tr>
<tr>
<td>Chemicals, $</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Installations: Four units are operating on coal-fired boiler flue gases. Two plants produce gaseous chemical-grade CO₂ and two produce food-grade liquid. Capacities range from 150 tpd to 800 tpd. Maximum train capacity for high CO₂ content feeds is approximately 2,700 tpd.

Licensors: Randall Gas Technologies, ABB Lummus Global Inc.

Contact: Jorge Foglietta, 3010 Briarpark Drive, Houston, TX 77042, Phone: 713-821-4313, Fax: 713-821-3538, E-mail: jorge.h.foglietta@us.abb.com
**CO₂ removal—Molecular Gate**

**Application:** Simultaneously removes carbon dioxide (CO₂) and water from contaminated natural gas. Feedstocks include coalbed methane and natural gas. Water-saturated feeds and CO₂ levels of 3% to 40% can be treated. Product is pipeline-quality natural gas with characteristic CO₂ levels of less than 2%. The process uses a specialty adsorbent for CO₂ removal in a patent-pending, proprietary, pressure swing adsorption (PSA) system.

**Description:** Water-saturated feed, at pressure levels between 100 psig and 800 psig, is routed through a series of adsorber vessels. One or more vessels are removing the water and CO₂ while pipeline-quality natural gas flows through the adsorbent bed at essentially feed pressure. Typically, between three and eight adsorber vessels are used. When the adsorbent is saturated with water and CO₂, 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 CO₂ to be rejected. To maximize adsorbent capacity, impurities are removed through a single-stage vacuum blower. If the feed contains C₃+ components in large quantities an NGL recovery section can be added to produce a mixed NGL product containing these components at high recovery rates. The system is flexible for a wide range of CO₂ concentrations and has turndown capability to 30%. Modular construction facilitates installation.

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

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


**Licensor:** Engelhard Corp.

**Contact:** Michael Mitariten, Business Manager, Molecular Gate, Phone: (732) 205-6979, Fax: (732) 205-5915, E-mail: michael.mitariten@engelhard.com

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**Gas Processes 2004**

**Treating**

**Molecular gate adsorbers**

**Feed gas**

**CO₂ 3% to 40%**

**Methane recycle**

**Product natural gas CO₂ < 2%**

**Fuel**

**Water-saturated feeds and CO₂ levels of 3% to 40% can be treated.**

**Matterien, M. J., “Eliminating carbon dioxide from coalbed methane using the Molecular Gate adsorption process,” Third Annual Coalbed and Coal Mine Methane Conference, Denver, March 2002.**

**Engelhard Corp.**

**Michael Mitariten, Business Manager, Molecular Gate, Phone: (732) 205-6979, Fax: (732) 205-5915, E-mail: michael.mitariten@engelhard.com**

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**CYNARA membrane technology**

**Application:** Carbon dioxide (CO₂) removal from hydrocarbon gas streams such as produced natural gas, associated gas and associated natural gas liquids recovery. The systems are used for high CO₂ gas bulk removal as in offshore applications and onshore EOR, and to remove CO₂ to meet pipeline gas specifications in low CO₂ gas streams onshore.

CYNARA membranes can also be applied to create a high quality CO₂ product (+95% CO₂) for reinjection. The unique hollow fiber design allows condensation of liquid hydrocarbons from rich gas streams (i.e., EOR) during separation.

**Description:** Systems use CYNARA asymmetric, hollow membrane fibers to selectively separate CO₂ from hydrocarbon streams. The membrane is a polymeric material that, unlike filters, molecularly interacts with the gas components to transport them through the membrane wall.

CYNARA membrane modules contain thousands of hollow fibers bundled to maximize surface area.

Membrane modules are housed in vertical cases and skid packaged to reduce installation and site work costs. System configurations (i.e., staged units, primary/secondary units, and parallel units) are quite flexible to meet various process objectives.

**Economics:** CYNARA membrane systems range from 5 to 750 million scfd and process various feed compositions. Generally, economics favor feed streams containing 15% to 85% CO₂, but CYNARA membranes have been successfully applied in lower CO₂ streams to polish gas to pipeline specifications. Liquids recovery and environmental factors also favor CYNARA membrane systems over solvents and other membranes. Secondary membrane systems can be designed to further recover hydrocarbons from the primary permeate stream.

**Operating conditions:** CYNARA membranes can process a variety of gas compositions from 5% to 90% CO₂ in the inlet to outlets of 1.5% to 23% CO₂. Systems are designed with an application specific pretreatment process that removes harmful contaminants while optimizing feed temperature and pressure for membrane selectivity and efficiency. CYNARA membranes typically operate with CO₂ partial pressure less than 500psi.

**Installations:** Over 30 installations including the first large scale commercial CO₂ membrane facility (SACROC, 367 million scfd with >98.6% availability for 20 years), and the world’s largest offshore membrane plant (750 million scfd).

**Licensor:** NATCO Group Inc.

**Contact:** Gary Blizzard, NATCO Group, 2950 N. Loop West, Suite 700, Houston, TX 77092, Phone: (713) 975-6121, E-mail: gblizzard@natco-us.com

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**Gas Processes 2004**

**Treating**

[Return to Gas Processes INDEX]
**FLEXSORB solvents**

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

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

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

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

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

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

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

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

- Flexsorb SE—28 plants operating, one in design
- Flexsorb SE Plus—15 plants operating, two in design
- Hybrid Flexsorb SE—two plants operating, two in design
- Flexsorb PS—four plants operating.


**Licensor:** ExxonMobil Research and Engineering Co.

**Contact:** Dr. Girish Chitnis, ExxonMobil Research and Engineering Company, 3225 Gallows Road, Fairfax, Virginia 22037-0001 USA, Phone: (703) 846-2724, Fax: (703) 846-2725, E-mail: girish.k.chitnis@exxonmobil.com

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**Gas Processes 2004**

**Sulfur**

**Return to Gas Processes INDEX**
**Fluor ammonia destruction process**

**Application:** Ammonia (NH₃) and hydrogen sulfide (H₂S) are usually encountered in refinery sour water stripper offgas. This gas is often processed in a Claus sulfur plant prior to venting to atmosphere. Ammonia must be completely destroyed in the Claus plant reaction furnace to prevent deposition of ammonia salts in the downstream equipment.

**Description:** The process utilizes a split-flow reaction furnace to destroy NH₃. All the NH₃ containing sour water acid gases from the sour water stripper (SWS), and all the combustion air is mixed with a controlled portion of the amine acid gas stream from the amine treating units.

The furnace is divided into two zones. The NH₃-rich stream combustion occurs in the first zone at 2,650°F to 2,800°F. This temperature is sufficiently high to ensure complete NH₃ destruction. Zone 1 temperature is controlled by the amine acid gas amount diverted to that zone. The balance is sent to the reaction furnace's Zone 2 and mixed with the combustion products from Zone 1.

**Installations:** Five plants engineered or constructed.


**Licensor:** Fluor Enterprises, Inc.

**Contact:** Thomas Chow, One Fluor Daniel Dr., Aliso Viejo, CA 92698, Phone: (949) 349-4247, Fax: (949) 349-2898, E-mail: thomas.chow@fluor.com
**Flour Econamine FG Plus process**

**Application:** Econamine FG Plus is an energy efficient, patents pending process used to recover carbon dioxide (CO₂) from low-pressure, oxygen (O₂) containing streams, such as burner flue gas, combined cycle gas turbine flue gas and coal-fired power plant flue gas streams.

**Description:** Flue gas is cooled in a direct contact cooler (1) and is sent to a blower to overcome pressure losses though the system. It then enters the absorber (2) bottom and flows upward through random dumped packing where the CO₂ reacts chemically with the lean and semi-lean monoethanolamine (MEA) solvent to remove most of the CO₂. MEA concentration is at least 30%.

Treated gas is passed through a water wash and vented through the top of the absorber. Solvent intercooling in the absorber may be utilized to reduce absorber size and solvent circulation rates.

The CO₂-rich solution is split into two streams, heated and regenerated, utilizing two schemes: flash regeneration and steam stripping. Steam stripping takes place in the stripper (3) where energy is provided through the reboiler (5), producing a lean solution. Flash regeneration is conducted in the semi-lean flash drum (4) where a semi-lean solution is produced without additional external energy. The overhead gas produced is sent to the stripper top. The gas is cooled and condensate is routed back to the column to generate CO₂ product. This may be compressed for sequestration or liquefied to produce a saleable product. The lean and semi-lean solutions are pumped, cooled and filtered before being sent back to the absorber. The reclaimer (6) is operated intermittently to recover amine from heat stable salts and to remove degradation products.

**Operating conditions:** The feed gas may contain 3 to 25+ mol% CO₂ and up to 15 mol% O₂. The feed gas pressure may be near atmospheric. Due to the addition of an inhibitor that retards decomposition and corrosion, the majority of the plant may be constructed using carbon steel.

**Economics:** Typical US Gulf Coast investment (ISBL) for a 300 tpd plant is approximately $10.4 million. For a typical flue gas from a steam methane reformer, the energy consumption is approximately 1395 Btu/lb CO₂. Solvent replacement costs approximately equal $2.09/ton CO₂.

**Installations:** Twenty-four Econamine FG plants have been built worldwide.


**Licensor:** Flour Enterprises, Inc.

**Contact:** Satish Reddy, One Fluor Daniel Dr., Aliso Viejo, CA 92698, Phone: (949) 349-2000, Fax: (949) 349-2585, E-mail: satish.reddy@fluor.com
Fluor ECONAMINE/Fluor improved ECONAMINE

**Application:** Amine plants where stringent gas specifications must be met and cooling water is not available. Carbon dioxide (CO₂) removal down to 50 ppmv (liquefied natural gas (LNG) specification) and hydrogen sulfide (H₂S) removal down to 4 ppmv at treating pressures as low as 50 psig.

**Description:** Feed gas is contacted with a diglycolamine (DGA) solution in the contactor (1) where acidic impurities react with the amine. The rich solution is flashed to recover hydrocarbons (2), heated by exchange with the hot lean solution (3), and then flows to the solvent regenerator (4). Acid gases and water vapor pass overhead to the condenser (5). Condensed water is returned to the regenerator while the acid gases go to flare, sulfur recovery or further processing. Regenerator heat can be furnished by suitable heat media or direct firing. Lean solution is pumped from the regenerator through the exchangers and coolers to the contactor. Amine degradation by COS and carbon disulfide (CS₂) is completely reversible by reclaiming (5) at elevated temperatures. The reclaimer provides part of the regenerator heat.

The Fluor improved ECONAMINE process is designed for plants using all air cooling in a hot environment. The process adds a side cooler (6) to the absorber to remove a significant portion of the reaction heat. Amine circulation is reduced, which results in lower capital costs in the plant’s regeneration section.

The Fluor ECONAMINE process uses an aqueous DGA solution. Solution concentrations up to 65 wt% DGA result in appreciably lower circulation rates and steam consumption, which in turn, results in substantial savings in both capital and operating costs when compared to other amines. Aqueous DGA has a very low freezing point, below –40°F, making it suitable for Arctic climates where winterization is an issue.

**Installations:** More than 55 ECONAMINE plants, ranging in size from 3 to 400 million scfd. There are 7 Improved Econamine plants, each sized for 547 million scfd.


**Licensor:** Fluor Enterprises, Inc.

**Contact:** Dick Nielsen, One Fluor Daniel Dr., Aliso Viejo, CA 92698, Phone: (949) 349-2000, Fax: (949) 349-2585, E-mail: dick.nielsen@fluor.com
Fluor oxygen enrichment process

**Application:** Oxygen (O₂) enrichment technology is one of the most economical routes for achieving incremental sulfur recovery unit/tail gas treating unit (SRU/TGTU) capacity.

**Description:** Fluor offers two levels of O₂ enrichment technologies—low and medium. The process can increase a sulfur plant's capacity up to 175% of the original design capacity depending on the enrichment level and acid gas composition.

Pure O₂ is injected into combustion air or fed directly into the reaction furnace burner. Installing a new O₂ line, supply system, compatible burner and management system is required depending on the enrichment level and the chosen technology.

The Fluor oxygen enrichment process provides a unique control and burner management scheme ensuring safe and smooth operation.

**Installations:** Five plants engineered or constructed.


**Licensor:** Fluor Enterprises, Inc.

**Contact:** Thomas Chow, One Fluor Daniel Dr., Aliso Viejo, CA 92698, Phone: (949) 349-4247, Fax: (949) 349-2898, E-mail: thomas.chow@fluor.com

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**Diagram:**

- **Acid gas** flows into the burner, where it mixes with air and O₂.
- **Furnace** processes the mixture, generating waste heat.
- Process gasses exit to catalytic stages.
- Wastewater is directed to the catalytic stages.
Fluor Solvent process

Application: The Fluor Solvent process is a physical solvent process to remove bulk carbon dioxide (CO₂) and trace hydrogen sulfide (H₂S) amounts from various gas streams. The process can remove CO₂ to less than 1.0 mol% and H₂S to 4 ppmv for natural gas. CO₂ removal down to 1,000 ppmv is possible for synthesis gas. The process is particularly suited for feed gases with a CO₂ partial pressure above 70 psia, H₂S levels below 50 ppmv and <0.5 mol% C₅⁺.

Description: Feed gas is dried with TEG (1) and chilled (2, 3) to remove heavy hydrocarbons. Liquids formed are removed in a knock-out (KO) drum (4) and the gas enters the absorber (5). The gas is contacted with Fluor Solvent and propylene carbonate to remove acid gases. Acid gas desorption is accomplished without heat.

The rich liquid passes through three pressure flashes (6), an atmospheric flash (7) and a vacuum flash (8). The gas from the first three flash stages (6) containing significant volumes of hydrocarbons, is compressed (9) and recycled to the absorber. Hydraulic turbines between the absorber and the first stage flash and the first and second stage flashes recover energy and reduce refrigeration requirements. Patents are pending.

Since the solvent loading increases with decreasing temperature, the absorber is operated below 0°F to reduce the circulation rate. The solvent is non-hazardous, biodegradable and freezes at –57°F, making the process suitable for Arctic environments. It is usually the most economic choice for CO₂ bulk removal when CO₂ partial pressure is high and H₂S concentration is low.

Process configurations for feed gas H₂S concentrations up to 200 ppmv or for producing a liquid CO₂ stream are also available.

Installations: 13 plants (8 natural gas, 2 ammonia, 1 synthesis gas, 2 hydrogen) with feed gas rates up to 220 million scfd and pressures up to 2,000 psig.


Licensor: Fluor Enterprises, Inc.

Contact: Dick Nielsen, One Fluor Daniel Dr., Aliso Viejo, CA 92698, Phone: (949) 349-2000, Fax: (949) 349-2585, E-mail: dick.nielsen@fluor.com
Gas contaminants removal—Multibed

Application: Remove mercury (Hg), arsenic, water, CO₂, other oxygenates, tertiary butyl catechol (TBC), NH₃ and sulfur species from natural gas, industrial gases and petrochemical streams using Axens Multibed technology.

Description: This technology uses combinations of special aluminas and zeolite molecular sieve adsorbents that are installed as beds in the same or separate vessels. (The configuration will depend on the specific application.) The aluminas function as catalysts or adsorbents for chemical or physical removal of contaminants such as HCl, Hg, AsH₃, TBC and water. The molecular sieves remove contaminants by physical adsorption.

In multibed processing, Hg can be removed either upstream or downstream of the gas dehydration step. The treated gas can contain less than 0.01µg/Nm³ Hg and less than 1 ppmv of other contaminants. Most adsorbents are thermally regenerated with nitrogen or light-hydrocarbon streams.

Operating parameters: Operating conditions are:
- Inlet temperature, °F: 40–140
- Inlet pressure, psig: 40–1,400
- Regeneration gas temperature, °F: 350–600
- Phase: liquid or vapor

Installations: Currently, over 60 installations worldwide are treating natural and industrial gases and other hydrocarbon streams from refining, gas and petrochemical sectors.


Licensor: Axens

Contact: Laurent Savary, 89, bd Franklin Roosevelt-BP 50802, 92508 Rueil-Malmaison Cedex, France, Phone: (33) 1 47 14 25 55, Fax: (33) 1 47 14 24 98, E-mail: laurent.savary@axens.net
IRON SPONGE

Application: To remove hydrogen sulfide (H₂S) and mercaptans from natural gas streams at low- or high-pressure conditions at or near the well head.

Process description: Iron sponge (iron oxidized onto wood shavings) uses a simple packed tower (3) on a flow-through support (4). After liquid separation (1), the deflected (2) sour gas flows down to contact with the reactive iron oxide, simply and effectively converting H₂S into a solid. The iron sulfide stays in the packed tower, effectively removing it from the gas stream. Iron sponge also removes mercaptans, the malodorous sulfur compounds found in some gas, producing a deodorized, sweet gas.

For iron sponge to effectively perform, it must be maintained within a range of water levels. This requirement is usually satisfied if the gas is saturated with water vapor, as is frequently the case. If it is not the case, a simple water spray will correct it. An excess of water is tolerated very well by iron sponge as long as the excess is drained off (5), so as not to flood the bed. Because the reaction of iron oxide with H₂S produces a small quantity of water, monitoring the drip water volume is an effective method of confirming the presence of sufficient moisture. Since the iron oxide is impregnated onto the wood, it will not wash off or migrate with the gas.

Operating conditions: The process should be located as close to the source of gas as possible, to eliminate as many corrosion problems as possible caused by the H₂S. The process should be used after a gas/liquid separator and before the dehydration process. The maximum temperature should not exceed 120°F, and the minimum of 50°F, or whatever is necessary to avoid hydrate formation for the system pressure and composition of the gas.

The gas purification is not pressure sensitive, and is not affected by other gas constituents. Carbon dioxide levels are not a problem for treatment, but liquid hydrocarbons should be removed before the IRON SPONGE process.

Since the process is so simple, minimum operator time is required. It runs unattended for days at a time.

Manufactured and supplied by: Connelly-GPM, Inc.
Contact: Galen Dixon, 3154 S. California Ave., Chicago, IL 60608-5176, Phone: (773) 247-7231, Fax: (773) 247-7239, E-mail: Connellygpm@aol.com

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LRS 10—CO₂ removal

**Application.** Remove CO₂ from natural gas, SNG or ammonia syngas. The purification process is applicable in facilities for LNG plants and petrochemical applications.

**Description.** Rich-CO₂ feed gas is passed to the absorber column containing potassium carbonate solutions and LRS10 additives. The used solution goes through the regeneration system and purified gas exits the top of the absorber. The rich solution is regenerated either in a re-boiler facility or directly with steam. The recovered potassium carbonate/LRS10 solution is pumped back to the absorber for further reaction. Feed gas containing about 20% CO₂ has been treated successfully, typically to CO₂ levels of 1% in the processed gas, depending on process arrangement. Process configuration changes can lower CO₂ slippage levels from 500 ppm to 1,000 ppm in some designs.

**Economics.** A plant utilizing typically 3% LRS10 in a potassium carbonate system has been shown to offer improved performance over CO₂-removal systems such as Benfield (DEA promoted potassium carbonate) by up to 10%. OPEX savings are realized through:
- Increasing gas throughput of typically 10%
- Lower regeneration energy by about 10%
- Reduce CO₂ slippage in the outlet gas by up to 50%
- Improve column operations by moving away from column constraints.

**Installations.** Thirty plants worldwide, mainly retrofits, in the ammonia, hydrogen, natural gas and chemicals industries.

**Licensor.** Advantica Ltd.

**Contact:** Antony Kane, Holywell Park, Ashby Rd., Loughborough, Leicestershire, UK; E-mail: antony.kane@advantica.biz
Morphysorb (acid gas removal from natural gas)

**Application:** Hydrogen sulfide (H₂S), carbon dioxide (CO₂), COS and RSH removal from natural gas or syngas by physical absorption. Bulk-acid gas removal with simple flash regeneration. Removes impurities to pipeline specification with additional thermal regeneration step. Highly selective H₂S removal, even at high CO₂ partial-pressures. Simultaneous dehydration and BTEX removal.

**Description:** For bulk acid gas removal the Morphysorb process simply requires solvent flash regeneration as the acid gas compounds are physically dissolved. Applications vary from product gas specifications of several percent for the acidic components down to about 2% for CO₂ alone. Additional thermal regeneration is required for H₂S removal down to pipeline specification (4 ppmv H₂S, 2% CO₂) or removal of CO₂ to liquefied natural gas (LNG) specification (50 ppmv CO₂, 4 ppmv H₂S).

The process flow diagram shows a bulk-acid gas removal unit as an example. The feed gas enters the absorber bottom, flows upward through a packed bed, where it is treated with the regenerated solvent, and leaves the absorber at the top.

The enriched solvent exits the absorber bottom and is flashed consecutively into the recycle flash drums. The offgas from these drums is recycled to the absorber feed by a two-stage compressor minimizing methane losses. The solvent is further flashed into the acid gas flash drums for regeneration. The acid gas is produced at two pressure levels for high-pressure downhole reinjection or for further processing in a sulfur recovery unit. The regenerated Morphysorb solvent is pumped back to the absorber.

Due to the solvent’s specific nature (low co-absorption of C₁ to C₅ hydrocarbons, high acid gas capacity, non-corrosive, low-vapor pressure and non-toxic) the process exhibits the following features: low recycle gas flow and higher hydrocarbon product yield, low solvent circulation rate, extensive carbon steel usage as construction material and low solvent losses in the product and acid gas.

**Operating conditions:** Typical feed conditions range from 400 psi to 1,300 psi with a 5% to 70% acid gas content (CO₂ and H₂S). Depending on the process application, product specifications vary from a few ppmv to several percent for bulk removal.

**Installations:** Two plants: A 300 million-scfd feed gas capacity commercial plant, removing 1,000 tpd of acid gas for downhole reinjection. A pilot plant installation with a 1 million-scfd feed gas capacity.

**References:**

- “Performance of Morphysorb solvent in a commercial acid gas treating plant,” 53rd Annual Laurance Reid Gas Conditioning Conference, February 23–26 2003, Norman, OK, USA.

**Licensor:** Uhde GmbH, Dortmund, Germany

**Contact:**

E-mail: information@tkt-uhde.thyssenkrupp.com
**N₂ rejection—Molecular Gate**

**Application:** Remove nitrogen (N₂) from contaminated natural gas. Feedstocks include N₂ contamination from 5% to 30%. Product is pipeline quality natural gas with typical N₂ levels of 3% to 4% using the Molecular Gate process and a patented proprietary adsorbent in a pressure swing adsorption (PSA) system.

**Description:** Natural gas at pressure levels between 100 psig and 800 psig is routed through a series of adsorber vessels. One or more vessels remove N₂, 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 N₂, 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 N₂ to be rejected. To maximize adsorbent capacity, N₂ is typically removed through a single-stage vacuum blower. The process is based on an adsorbent that is size selective and allows smaller N₂ molecules to fit in adsorbent pores, while the larger methane molecule is unaffected. Carbon dioxide is also completely removed with the N₂ and oxygen is removed at N₂ levels. The system is flexible for a wide range of N₂ concentrations and has turndown capability to 30%. 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 ft³ of feed processed. This is decreased to less than $0.30/thousand ft³ for a 10-million scfd design. Modular construction allows low-cost installation and equipment relocation flexibility.

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


**Licensor:** Engelhard Corp.

**Contact:** Michael Mitariten, Business Manager, Molecular Gate, Phone: (732) 205-6979, Fax: (732) 205-5915, E-mail: michael.mitariten@engelhard.com
Nitrogen rejection

**Application:** Reject nitrogen from natural gas to increase heating value.

**Description:** Natural gas feed to the nitrogen rejection unit (NRU) is partially condensed and fed to the top of the high-pressure (HP) column. A reboiler driven by condensing the feed provides stripping vapors in the column. The bottoms from the first stripping column are enriched in hydrocarbons and depleted in nitrogen. This HP residue is boiled in the warm NRU exchanger and sent to residue gas compression. Enriched in nitrogen, the overhead vapor from the column is sent to the cold end of the NRU.

Vapor from the HP column is partially condensed against returning residue streams. The vapor and liquid are separated in a vertical separator drum. The vapor stream, enriched in nitrogen, from the drum is further condensed and is fed as reflux to the low-pressure (LP) column.

Liquid from the drum is the feed to the LP column. Vapor generated in the reboiler strips the descending liquid of nitrogen creating the remainder of the residue product. The liquid flowing down the column scrubs the methane from the vapor, creating a high-purity nitrogen vent stream from the top of the column. Liquid product from the LP column is pumped to LP residue pressure. This stream is boiled against the condensing HP vapor from the overhead of the first stripping column. The nitrogen vent stream and LP residue stream are warmed in both exchangers in the NRU along with the HP residue gas stream. The residue streams are sent to recompression for export to pipeline systems. Nitrogen is vented to the atmosphere or recompressed for reinjection.

**Operating conditions:** The dual-column NRU process has good CO₂ tolerance and feed flexibility, handling feeds from 5 to 80 mol% nitrogen and pressures as low as 250 psig (17 barg).

**Economics:** The dual-column NRU has high hydrocarbon recovery (>99.9%). This process is particularly well-suited for streams with less than 20% nitrogen in the feed, and is easily adapted to recover helium (HeRU) as well. The hydrocarbons are recovered at two pressure levels, reducing recompression requirements. The amount of hydrocarbons recovered from the second column is greatly reduced requiring a smaller cryogenic pump.

**Installations:** Eight NRU and HERU installations, with three using the dual-column process with capacities from 30 million scfd to 70 million scfd.


**Licensor:** Air Products and Chemicals, Inc.

**Contact:** Joanne Trimpi, Marketing Manager, Energy & Process Industries, 7201 Hamilton Blvd., Allentown, PA 18195-1501, Phone: (610) 481-7326, Fax: (610) 706-2982, E-mail: trimpijl@apci.com
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 from trace contaminants such as COS, mercury and specifically, mercaptans is becoming evermore important; aside from classic hydrogen sulfide (H$_2$S), carbon dioxide (CO$_2$) and water removal task.

**Description:** The OmniSulf concept encompasses the following proprietary key processes: Acidic components are eliminated using BASF’s aMDEA process (AGR). The cleaned gas is routed to a DMR unit that removes moisture and mercaptans with Zeochem’s special 13X zeolite technology. Where necessary, the sweet gas can be routed further to a mercury removal unit operated with impregnated activated carbon. The DMR is thermally regenerated at regular intervals. Mercaptans are recovered from the regeneration gas using Purisol technology. The gas can then be fed to the fuel gas system.

All gas streams containing sulfur are routed to a sulfur recovery unit (SRU). Elemental sulfur is produced in the Claus process (equipped with Lurgi Multi-Purpose Burner). A Lurgi tail gas treating and acid gas enrichment (LTGT) system is combined with the Claus unit to boost sulfur recovery. The sulfur product is then treated further applying an AQUISULF degassing process (AQU) which removes H$_2$S concentrations below 10 ppm. Vent gases are incinerated (INC) before being released to the atmosphere.

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

**Installations:** A contract for the OmniSulf process was signed in 2003 for a plant in the Middle East.


**Licensor:** Lurgi Oel-Gas-Chemie GmbH

**Contact:** Wolfgang Nehb, Lurgi Oel-Gas-Chemie GmbH, Lurgiallee 5, D-60295 Frankfurt am Main, Germany, Phone: (49) 69 5808 1530, Fax: (49) 69 5808 3115, E-mail: Wolfgang_Nehb@lurgi.de
PURASPEC

Application: PURASPEC processes remove low levels of sulfur and mercury compounds from hydrocarbon gases and liquids to meet pipeline, chemical grade or environmental specifications.

Description: PURASPEC uses absorbent fixed beds to irreversibly react with impurities to be removed. There are no feedstock losses; only the impurity binds within the absorbent. The process is flexible to accommodate changes in throughput. There is no operator intervention required to run the process and change-out can be done by contract labor.

During operation, there are no vents, flares or noise sources. Used absorbent can be reprocessed and disposed in an environmentally friendly manner. A typical lead-lag configuration is shown. However, single vessels are operated and have been used to phase expenditure. Axial and radial flow reactor designs are available. Radial flow reactors have been used in duties where a very low-pressure drop is required.

Hydrogen sulfide (H₂S) removal from natural and associated gas can achieve impurity levels a low as ppbv at the bed exit. In liquid duties (propane and liquefied petroleum gas), H₂S is removed to meet copper strip 1A quality.

Mercury can be removed from natural gas to levels below 10 ng/Nm³ (liquefied natural gas quality). In liquid duties (propane, butane, naphthas) mercury can be reduced to <1 ppbw.

Operating conditions: PURASPEC operates effectively over wide temperature and pressure ranges from 20°F to 400°F and atmospheric to 2,000 psi. No heat input is required.

Installations: There are over 100 operating units worldwide treating natural gas rates up to 2 billion scfd and NGLs up to 5,000 tpd for major oil and gas companies.


Licensor: Johnson Matthey Catalysts

Contact: Andréa Foster, Technical Sales Manager, Johnson Matthey Catalysts, Phone: 44 (0) 1642-523377, E-mail: andrea.foster@matthey.com
**Purisol**

**Application:** Removal of acid gases from natural gas, fuel gas and syngas by physical absorption in NMP (N-methyl-pyrrolidone). Typical cases: 1. High CO₂ contents to low residual level, 2. Bulk acid gas removal to moderate purity by simple flash regeneration, 3. Selective H₂S removal. Ideally suited for (3) in an IGCC based on POX of coal or oil, as NMP is the most selective solvent on the market. 4. Selective removal of mercaptans from gas streams, e.g., from spent regeneration gas coming from a molecular sieve mercaptan removal unit from natural gas. It is a cheap, stable, noncorrosive and easily available solvent with a broad range of further industrial applications.

**Description:** Raw gas from a POX of heavy residue is cooled; HCN and organic sulfur compounds are removed in prewash (1). H₂S is removed in main absorber (2) by hot-regenerated, lean solvent cooled slightly below ambient temperature. NMP traces are backwashed on top of (1) with H₂O. Laden solvent from (1) is flashed at medium pressure in a reabsorber (2). H₂S 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 reabsorber (2). Solvent from (3) is finally hot-regenerated in (4). The resulting, cooled acid gas, very rich in H₂S, is processed in an OxyClaus unit, the tail-gas is hydrogenated, formation water is removed by quenching, recompressed to reabsorber (2) for desulfurization and finally ending 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%**

<table>
<thead>
<tr>
<th>Raw gas</th>
<th>Fuel gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>43.12</td>
</tr>
<tr>
<td>N₂ + Ar</td>
<td>1.49</td>
</tr>
<tr>
<td>CO + CH₄</td>
<td>45.9</td>
</tr>
<tr>
<td>CO₂</td>
<td>8.27</td>
</tr>
<tr>
<td>H₂S + COS</td>
<td>1.20</td>
</tr>
<tr>
<td>Flow, kmol/h</td>
<td>18,666.3</td>
</tr>
<tr>
<td>Pressure, bar</td>
<td>52.0</td>
</tr>
</tbody>
</table>

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

**Installations:** Seven units in operation or under construction.

**Licensor:** Lurgi Oel-Gas-Chemie GmbH

**Contact:** Ulrich Koss, Lurgi Oel-Gas-Chemie GmbH, Lurgiallee 5, D-60295 Frankfurt am Main, Germany, Phone: (49) 69 5808 3740, Fax: (49) 69 5808 2645, E-mail: Ulrich_Koss@lurgi.de
**Rectisol**

**Application:** Acid gas removal using an organic solvent at low temperatures. In general, methanol is used for \( \text{H}_2\text{S} \), \( \text{COS} \) and bulk \( \text{CO}_2 \) removal, whereby organic and inorganic impurities are also removed. It is possible to produce a clean gas with less than 0.1 ppm sulfur and a \( \text{CO}_2 \) content down to the ppm range. The main advantage over other processes is the use of a cheap, stable and easily available solvent, a very flexible process and low utilities.

**Description:** Rectisol unit for the selective desulfurization and \( \text{CO}_2 \) removal in the production of methanol synthesis gas. Raw gas (from SGP-POX) is cooled and trace components are removed in the prewash (1) with cold methanol. Prewashed gas is desulphurized (1) by using \( \text{CO}_2 \)-laden solvent down to 0.1 ppm. \( \text{H}_2\text{S} \)-laden solvent is regenerated first by flashing to medium pressure (4) to recover \( \text{H}_2 \) and \( \text{CO} \), and second, by heating to boiling temperature and stripping with methanol vapors (3). The stripped \( \text{H}_2\text{S} \)-enriched gases are sent to a Claus unit. The portion of the desulfurized gas which has been shifted in the CO-shift conversion unit (6) has a typical \( \text{CO}_2 \) content of 33%. Shifted gas re-enters the Rectisol unit, is cooled and the \( \text{CO}_2 \) is removed in a two-stage absorber (2). In the lower section, the gas \( \text{CO}_2 \) content is reduced to about 5% using flash-regenerated methanol (5). Remaining \( \text{CO}_2 \) is removed using hot regenerated (3), cold methanol in the upper section; thus, about 3% \( \text{CO}_2 \) is contained in the synthesis gas. The flashed \( \text{CO}_2 \) is free of sulfur and can be discharged to atmosphere or used further. The refrigeration balance of the system is maintained by a conventional refrigeration unit. Methanol is injected in the raw gas cooling to prevent icing. The condensed methanol/water mixture is separated in a methanol/water column (not shown).

**Material balance for a 2,000-tpd methanol plant in mol%**

<table>
<thead>
<tr>
<th>Component</th>
<th>Raw gas</th>
<th>Syngas</th>
<th>Claus gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>43.80</td>
<td>67.69</td>
<td>0.59</td>
</tr>
<tr>
<td>( \text{N}_2 + \text{Ar} )</td>
<td>0.25</td>
<td>0.25</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>( \text{CO} + \text{CH}_4 )</td>
<td>52.57</td>
<td>29.03</td>
<td>0.26</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>2.30</td>
<td>3.03</td>
<td>99.15</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} + \text{COS} )</td>
<td>1.08</td>
<td>&lt; 0.1 ppm</td>
<td>traces</td>
</tr>
</tbody>
</table>

**Flow, kmol/h**

- 8,482.5
- 8,415.0
- 1,868.7
- 193.5

**Pressure, bar**

- 56
- 48.5
- 1.2/Ambient
- 2.5

**Utilities:**

- Power (shaft) (without power recovery): 1,640 kW
- Steam, low-pressure: 5.5 tph
- Refrigerant at 242°K: 4,200 kW
- Water, cooling (\( \Delta t = 10^\circ \text{C} \)): 133 m³/h
- Methanol vapor loss: 40 kg/h

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

**Licensor:** Lurgi Oel-Gas-Chemie GmbH and Linde AG

**Contact:** Ulrich Koss, Lurgi Oel-Gas-Chemie GmbH, Lurgiallee 5, D-60295 Frankfurt am Main, Germany, Phone: (49) 69 5808 3740, Fax: (49) 69 5808 2645, E-mail: Ulrich_Koss@lurgi.de

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**Return to Gas Processes INDEX**
SELEXOL

Application: A process that can:
- Selectively remove H₂S and COS in integrated gasification combined cycle (IGCC), with high CO₂ rejection to product gas (+85%) and high sulfur (25% to 80%) feed to the Claus unit
- Selectively remove H₂S/COS plus bulk removal of CO₂ in gasification for high-purity H₂ generation for refinery or fertilizer applications, and
- Treat natural gas to achieve either LNG or pipeline specification with dew-point reduction

Description: This process uses Dow’s SELEXOL solvent—a physical solvent made of a dimethyl ether of polyethylene glycol, which is chemically inert and not subject to degradation. The process also removes COS, mercaptans, ammonia, HCN and metal carbylons.

A variety of flow schemes permits process optimization and energy reduction. Carbon steel can be used for the construction materials of equipment and piping due to the process’s non-aqueous nature and inert chemical characteristics.

Acid gas partial pressure is the key driving force. Typical feed conditions range between 300 and 2000 psia, with acid gas composition (CO₂ + H₂S) from 5% to more than 60% by volume. The product specifications achievable depend on the application and can range from ppmv up to percent levels of acid gas.

Installations: More than 55 SELEXOL units have been put into commercial service. The SELEXOL process is used in many applications, ranging from natural gas to synthetic gas, and has been the dominant acid-gas removal system for gasification project awards.

Licensor: UOP LLC

Contact: Anita Black, UOP, 25 E. Algonquin Ave., Des Plaines, IL 60016 USA, Phone: (847) 375-7801, Fax: (847) 391-2253, E-mail: anita.black@uop.com
**Selexsorb**

**Application:** Purify ethylene feed stream to polyethylene production processes. Treated ethylene gas contains less than 0.2 ppmv CO₂ and H₂O and less than 1.0 ppmv oxygenates.

**Description:** Upstream of Selexsorb towers, the feed ethylene stream is prepurified via acetylene converter (1), tower (2) of reduced copper catalyst and bed (3) of CuO. Water and oxygenates are removed by combination bed (4) of 3A molecular sieve (H₂O adsorption) and Selexsorb CD selective adsorbent (oxygenate adsorption). Final treating step involves adsorption of CO₂ with bed (5) of Selexsorb COS selective adsorbent. Selexsorbs are thermally regenerated with nitrogen or light hydrocarbon streams. The selective adsorbents will purify: comonomer, fresh diluent, recycle diluent and reaction controlling gas (hydrogen, nitrogen) to polyethylene processes. In ethylene treating service (CO₂ adsorption), Selexsorb COS has proven its value in protecting Ziegler-Natta type catalysts in polyethylene plants worldwide.

**Operating conditions:** (typical)
- Inlet ethylene temperature, °F: 40 to 120
- Inlet pressure, psig: 50 to 1,500
- Inlet contaminant, ppmv:
  - CO₂: 0.5 to 50
  - H₂O: 0.5 to saturated
  - Oxygenates: 2.0 to 50
- Regeneration gas temperature, °F: 450 to 600
- Regeneration gas pressure, psig: 10 to 200

**Installations:** More than 200 installations worldwide for the treatment of ethylene and propylene feed streams to polymer plants.


**Contributor:** Alcoa Inc., Alcoa World Chemicals

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Return to Gas Processes INDEX
Separex membrane systems

Applications: CO2 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 CO2 removal upstream of new installations. Hydrocarbon recovery from enhanced oil recovery floods for CO2 reinjection and landfill gas purification.

Products: Purified gas meeting pipeline specifications, high-quality fuel gas for turbine, reformer, or power generation or high-purity CO2 gas for reinjection.

Description: Separex membrane systems are simple, dry systems requiring minimal moving parts. Feed gas, after liquids separation, is conditioned at the pretreatment before being processed in a one- or two-stage membrane system. As the CO2-rich feed gas mixture passes over the polymeric membrane at high pressure, it separates into two streams. Carbon dioxide, hydrogen sulfide and water vapor permeate readily through the membrane collecting on the low-pressure permeate side. The high-pressure residual retains most of the methane, ethane, other hydrocarbons and nitrogen. In a two-stage system, the first stage low-pressure permeate is compressed for further treatment at the second-stage membranes to recover hydrocarbons.

Hydrocarbon recovery can be as high as 99% for a two-stage design, and 95% for a single stage without compression, depending upon feed composition, pressure levels, system configuration and product requirements. Feedrates vary from 1 million scfd to 1,000 million scfd, with CO2 levels from 3% to 70% and feed pressures from 400 to 1,400 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.

Separex membrane systems offer two membrane module configurations, spiral wound and hollow fiber, to satisfy the varied CO2 removal requirements.

Economics: For natural gas upgrading to pipeline specification, the processing costs are lower than, or comparable to, an amine unit. However, the Separex membrane system eliminates the need for the glycol dehydration unit found in typical treating plants. The economics of smaller installations or remote operations favor membrane systems over traditional treatment options. CO2-removal costs range between $0.05 to $0.15 per 1,000 scf of feed gas, depending on removal requirements, feed pressure, system configuration and product specifications.

Installations: Separex membrane systems have been successfully used in gas field operations since 1981. Over 50 units have been built or are in construction. The largest operating unit processes over 260 million scfd of natural gas.

Licensor: UOP LLC

Contact: Anita Black, UOP, 25 E. Algonquin Ave., Des Plaines, IL 60016 USA, Phone: (847) 375-7801, Fax: (847) 391-2253, E-mail: anita.black@uop.com
Shell HCN/COS hydrolysis technology

**Application:** The catalytic conversion of HCN and COS is a cost effective technology to abate the harmful effects these components have in gas streams.

This hydrolysis technology has three main fields of application:

1. Syngas treatment upstream of an amine unit for coal or oil gasification processes.
2. Other syngas treatments where HCN and/or COS presence is not acceptable to downstream processing units such as gas-to-liquid processes, e.g., the Shell middle distillate synthesis process.
3. FCC dry gas treatment to avoid problems in downstream treating units.

**Description:** In the gasification process, for example, syngas is produced, which is mainly comprised of hydrogen and carbon monoxide. However, contaminants such as COS and HCN are also formed. A deep removal of both these contaminants is not possible using “conventional” amine treating solvents. However, catalytic HCN/COS hydrolysis technology is a cost effective alternative to avoid the harmful effects of these compounds downstream of the process.

Syngas is water scrubbed for soot removal. Consequently, the water saturated gas is heated to a desired temperature before the syngas enters a HCN/COS hydrolysis reactor. In this reactor, catalytic hydrolysis of HCN and COS takes place to produce CO, H₂S, CO₂ and ammonia.

After the HCN/COS reactor, the syngas is first cooled and then fed into an ammonia scrubber to remove the water-soluble components. The condensed water is sent to water treatment and the syngas is routed to downstream processing units.

**Installations:** At present one unit is in operation and license agreements have been signed to supply the technology to two other companies.

**Licensor:** Shell Global Solutions International B.V.

**Contact:** Henk Grootjans, Shell Global Solutions International B.V., P.O. Box 3800, 1030 BN, Amsterdam, The Netherlands, Phone: (31) 20 630 2859, Fax: (31) 20 630 2900, E-mail: Henk.Grootjans@shell.com
Shell sulfur degassing process

**Application:** To remove dissolved hydrogen sulfide (H₂S) and H₂Sₓ from liquid sulfur coming from Claus units. Liquid sulfur from Claus units contains approximately 300 ppmw dissolved H₂S and H₂Sₓ; to meet environmental and safety restrictions the liquid sulfur should be degassed such that less than 10 ppmw H₂S remains.

**Description:** Sulfur from the Claus unit is rundown 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, H₂S is released. Sweep air is passed over the top of the sulfur to remove released H₂S. The vent gasses are usually sent to an incinerator via an ejector. The degassed sulfur is then pumped into storage. The advantage to this process is that there are no moving parts and no catalyst is required, consequently, the process is easy to operate.

**Economics:** The Shell sulfur degassing process has been developed to decrease residence time and consequently capital expenditure. Operational costs are kept low as no catalyst is required.

**Installations:** There are currently more than 150 Shell sulfur degassing units in operation with capacities varying from 3 to 4,000 tpd of sulfur.

**Licensor:** Shell Global Solutions International B.V. and Jacobs Nederland B.V.

**Contact:** Henk Grootjans, Shell Global Solutions International B.V., P.O. Box 3800, 1030 BN, Amsterdam, The Netherlands, Phone: (31) 20 630 2859, Fax: (31) 20 630 2900, E-mail: Henk.Grootjans@shell.com
**SORDECO**

**Application:** The SORDECO process applies Sorbead adsorbent beads packed into an adsorber column. It selectively removes water (H₂O) 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 H₂O and heavy hydrocarbons.

**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 H₂O, the attainable dew point specification is virtually independent of the natural gas pressure. This is a major advantage over low temperature separation technology when natural gas is available at a relatively low-pressure (<100 Bar, <1,500 psi) or when only limited pressure drops over the treating unit is allowed.

The process is very flexible with respect to feed gas and turndown ratio; this only influences the cycle time, which is an operational variable. The excellent turndown capabilities and short startup time make the process ideal for peak shaving and underground storage facilities. The process can be designed to selectively remove aromatics for membrane protection applications.

**Installations:** Shell Global Solutions has provided its operating companies with design support and operational advice since the early 1990s. Engelhard was involved with over 200 Sorbead based dew pointing units.


Brands, D.S. and J.B. Rajani, “Comparison between low temperature separation (LTS) and SORDECO process for hydrocarbon dew pointing”, GPA Europe Meeting, Amsterdam, September 2001.

**Licensor(s):** Shell Global Solutions International B.V. and Engelhard Process Chemicals GmbH

**Contact:** Henk Grootjans, Shell Global Solutions International B.V., P.O. Box 3800, 1030 BN, Amsterdam, The Netherlands, Phone: (31) 20 630 2859, Fax: (31) 20 630 2900, E-mail: Henk.Grootjans@shell.com
**Sour water stripper (SWS)**

**Application:** Remove dissolved hydrogen sulfide (H₂S) and ammonia (NH₃) from sour water (H₂O) before conveying it to waste H₂O treatment. Sour H₂O comes from many sources such as catalytic cracking units, hydrocrackers, flare seal drums, etc. Normally, refinery SWS are designed for feed concentration ranging from 500 to 15,000 ppmw each of NH₃ and H₂S. The molar ratio of NH₃ to H₂S generally ranges between 0.75 to 2, and averages about 1.2. pH is commonly from 7 to 9.3. The process can also be designed to take account of mercaptans, phenols and some aromatics. There are several SWSs types, all of them operate by passing sour H₂O through a multi-stage stripping tower.

**Description:** SWS contains a fractionating tower, which removes H₂S and NH₃ from sour H₂O along with some mercaptans, aromatics and phenols. The tower is normally refluxed to reduce H₂O in the overhead offgas and reduce downstream processing units (i.e. sulfur plants) size and cost. Steam is the most commonly used stripping medium, but flue gas, fuel gas and natural gas can also be used.

Typically, the sour H₂O feed stream is preheated by heat exchange with hot stripped H₂O prior to tower entry. Stripping steam is introduced into the tower bottom. H₂S and NH₃ are stripped out by counter-current contact with the steam. Typically, H₂S and NH₃ are stripped to ppm level.

**Operating conditions:** Operating pressure is generally set at a level to provide enough pressure to deliver offgas to its destination. A tower top pressure of 1.3–1.7 barg is typically enough when the offgas is sent to a sulfur recovery plant.

Overhead separator operating temperature should be set in the range of 82°C–90°C. A lower temperature can lead to plugging problems due to the formation of ammonium hydrosulfide, while a higher temperature results in more H₂O vapor in the offgas affecting downstream equipment size. Fluids handled in SWS facilities are corrosive. Proper construction materials selection is an important aspect in SWS design.

**Commercial plants:** More than 25 SWS plants have been built globally with capacities ranging from 1.5 m³/h up to 120 m³/h. Recently a SWS plant was designed for AGIP GAS BV LIBYAN BRANCH consisting of two units whose capacity is 25 m³/h sour H₂O each.

**Licensor:** SIIRTEC NIGI

**Contact:** SIIRTEC NIGI S.p.A., Via Algardi 2 - 20148, Milano, Italy, Phone: (39) 0 239 2231, Fax: (39) 0 2392 3010, E-mail: marketing@sini.it
SulfaClean–HC

**Application:** SulfaClean–HC is a granular material that is used to remove aggressive sulfur compounds, primarily hydrogen sulfide (H₂S), in a variety of clear liquid streams. Propane/propylene, butane, LNG, NGL, gasoline and other light liquid hydrocarbon streams treatment reduces corrosion to pass copper strip testing and meet H₂S limits. Dry or water-saturated liquid hydrocarbon can be treated, as well as water or brines for removal of dissolved H₂S prior to disposal.

**Description:** Liquids flow upward through the SulfaClean–HC media. Flow rates and system designs depend on fluid type and contaminants quantity. Systems range from single vessels or multiple parallel flow to lead/lag style applications. A properly designed system can adapt to variable flow rates without loss in treating efficiencies.

**Economics:** The SulfaClean–HC media removes up to 7.5 wt% H₂S. Its costs are often one-fourth the cost of zinc oxide products. It is competitive with caustic systems when accounting for regulatory, personal safety and disposal issues. The vessels are simple and inexpensive. Converted mole sieve, zinc oxide or iron sponge units can usually be used without modification.

**Installations:** This system has numerous placements worldwide. This process is currently being qualified for treatment of diverse streams such as MTBE and iso-octane.

**Licensor:** SulfaTreat, a Business Unit of M-I L.L.C.

**Contact:** June Weible, SulfaTreat, a Business Unit of M-I LLC, 17998 Chesterfield Airport Rd., Suite 215, St. Louis, Missouri 63005 USA, Phone: (800) 726-7687, Fax: (636) 532-2764, E-mail: jweible@midf.com
**SulfaTreat—Gas or air H₂S removal**

**Application:** Various SulfaTreat processes treat contaminated gas and air with a granular media that selectively removes hydrogen sulfide (H₂S) and some light mercaptans.

**Description:** Gas or vapor flows through the media, reacting with H₂S forming a stable and environmentally compliant byproduct at any point in its life cycle. Product consumption is not adversely affected by other gas components. The media prefers high humidity levels to fully water-saturate gas. Computer-assisted design matches operating conditions with desired results, such as maximum outlet allowed pressure drops (needs only a few inches W.C.) and long bed life. It works in any gas pressure or vacuum, inlet H₂S concentration and at temperatures up to 300°F. System sizes range from removing a few pounds up to over a ton H₂S daily, and to as low as 0.1-ppm maximum outlet, depending on system design.

**Products:**
- **SulfaTreat:** media removes H₂S in fully water-saturated gas.
- **SulfaTreat–HP:** media removes H₂S and light mercaptans in under-saturated gas and is faster than SulfaTreat in fully water-saturated gas.
- **SulfaTreat–410HP:** media performs like SulfaTreat-HP but with a low pressure drop required. It is faster reacting and has twice the H₂S loading capacity in gas or air streams containing oxygen.
- **SulfaTreat–XLP:** is a concentrated high-capacity product that lasts 2 to 4 times longer in the same vessel. It extends the operating period and reduces operating costs.

**Economics:** Operating costs are less than liquid reactants and have greater reliability. Operator attention is minimal. Vessels are simple and non-proprietary in design, thus lowering installation cost. Products can be used alone or may be combined with other processes that remove contaminants other than H₂S.

**Installations:** Over 2,000 applications globally.

**Licensor:** SulfaTreat, a Business Unit of M-I L.L.C.

**Contact:** June Weible, SulfaTreat, a Business Unit of M-I LLC, 17998 Chesterfield Airport Rd., Suite 215, St. Louis, Missouri 63005 USA, Phone: (800) 726-7687, Fax: (636) 532-2764, E-mail: jweible@midf.com

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**Return to Gas Processes INDEX**
Sulfinol

Application: Removal of hydrogen sulfide (H₂S), COS, RSH, other organic sulfur compounds and bulk or deep removal of carbon dioxide (CO₂) from natural, synthetic and refinery gases. Total sulfur compounds in the treated gas can be reduced to ultra-low ppm levels, as required for refinery-fuel and pipeline-quality gases.

An improved application is to selectively remove H₂S, COS, RSH and other organic sulfur compounds for pipeline specification, while co-absorbing only part of the CO₂. Deep CO₂ removal for LNG plants is another application, as well as bulk CO₂ removal with flash regeneration of the solvent. The process sequence—Sulfinol/Claus/SCOT—can be used advantageously with an integrated Sulfinol system that handles selective H₂S removal upstream and the SCOT process that treats the Claus offgas.

Description: The mixed solvent consists of a chemical-reacting alkanolamine, water and physical solvent Sulfolane (tetra-hydrothiophene dioxide). The actual chemical formulation is customized for each application. Unlike aqueous amine processes, Sulfinol removes COS, RSH and other organic sulfur compounds to stringent total sulfur specifications. The process achieves 4 ppm H₂S pipeline specification at low stream consumption. Observed corrosion rates are low and very little foaming is experienced, both are controlled through the application of optimized design.

The system line-up resembles that of other amine processes. In most applications, co-absorbed hydrocarbons from the absorber (1) are flashed (2) from the solvent and used as fuel gas after treatment in a fuel-gas absorber (3). Loaded solvent is regenerated (4).

Operating conditions: Very wide ranges of treating pressures and contaminant concentrations can be accommodated. Refinery-fuel gas and gas pipeline specifications, such as 40 ppmv total sulfur and 100 ppmv H₂S, are readily met. Removal of organic sulfur compounds is usually done for the circulation set by H₂S and CO₂ removal. In LNG plants, a 50 ppmv CO₂ specification is easily attained.

Installations: Over 200 units have been licensed worldwide, covering natural gas treating, synthesis gas and refinery gases.


Licensor: Shell Global Solutions International B.V.

Contact: Henk Grootjans, Shell Global Solutions International B.V., P.O. Box 3800, 1030 BN, Amsterdam, The Netherlands, Phone: (31) 20 630 2859, Fax: (31) 20 630 2900, E-mail: Henk.Grootjans@shell.com
ThioSolv SWAATS process
(sour water ammonia to ammonium thiosulfate)

**Application:** Converts ammonia (NH₃) and sulfur in sour water stripper gas (SWSG) to low-toxicity ammonium thiosulfate (ATS) solution. The process can also oxidize all sulfur species in Claus tail gas and scrub sulfur dioxide (SO₂) from that or other dilute streams to achieve low sulfur oxide (SOₓ) emissions.

**Description:** Ammonia and a stoichiometric amount of hydrogen sulfide (H₂S) are selectively absorbed from the SWSG. Unabsorbed H₂S is burned to SO₂. Claus tail gas is combined with the burner outlet and all sulfur species therein are oxidized to SO₂, which is scrubbed by reaction to thiosulfate with negligible pressure drop.

\[
6 \text{NH}_3 + 4 \text{SO}_2 + 2 \text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow 3(\text{NH}_4)_2\text{S}_2\text{O}_3 \quad (\text{ATS})
\]

SWAATS converts the NH₃ in the SWSG; no purchased NH₃ is required. The process prevents and reverses equipment plugging by converting any elemental sulfur in Claus tail gas to soluble thiosulfate. The process is highly selective for H₂S and SO₂ vs. CO₂.

**Economics:** For each ton of sulfur in SWSG diverted to SWAATS, about 2.5 tons of capacity for amine acid gas (AAG) sulfur is freed up in Claus. The value of the effect will increase as deeper desulfurization increases NH₃ production. Avoids CAPEX to expand SRU capacity or OPEX for oxygen enrichment. Claus operability and catalyst life are greatly improved by removing NH₃ from its feed. OPEX <$100/ton of sulfur captured from SWSG and tail gas. CAPEX to convert SWSG and scrub tail gas is less than for SCOT alone. Consumes no external chemicals, reducing gas or steam. Operational simplicit reduces overall cost of operation and maintenance for the combined SRU. Licensor removes ATS produced.

**Installations:** SWAATS process was developed from the Coastal ATS process that has been successfully desulfurizing acid gas and Claus tail gas in a Coastal plant since 1980. No units incorporating the improvements have been built.

**References:** US Patent No. 6,534,030

**Licensor:** ThioSolv, LLC

**Contact:** Mark C. Anderson, Principal, ThioSolv, LLC, 8911 Kennet Valley Road, Spring, TX 77379, Phone: (281) 320-7570, E-mail: manderson6@houston.rr.com
**Twister supersonic gas conditioning**

**Application:** Twister is a gas conditioning technology. Applications include natural gas dehydration, hydrocarbon dewpointing, natural gas liquids (NGL)/liquefied petroleum gas (LPG) extraction, heating value reduction and bulk hydrogen sulfide (H₂S) removal.

Condensation and separation at supersonic velocity is the key to unique benefits. An extremely short residence time prevents hydrate problems, eliminating chemicals and associated regeneration systems. The simplicity and reliability of a static device, with no rotating parts and operating without chemicals, ensures a simple facility with a high availability, suitable for unmanned operation.

**Description:** Feed gas is cooled using a combination of air/seawater coolers (1) and gas/gas cross-exchange (3). In case of deep NGL extraction, upstream dehydration will be required (2). Inlet cooling is operating just outside the hydrate regime. Condensed liquids are removed in an inlet separator (4). The gas is directed through Twister tubes (5). The tubes (5) expand the gas isentropically to supersonic velocity, cooling the gas to cryogenic temperatures and condensing water and NGLs, which are then separated using an in-line cyclone separator.

The separate product streams are recompressed using a diffuser, reducing the velocity. The gaseous liquid stream contains slip gas, which is removed in either a two- or three-phase liquid degassing vessel (6) and recombined with the dry gas stream. Dry export gas is directed through the exchanger (3) to cool the feed stream. In case the operating conditions of the degassing vessel (6) are within the hydrate regime, Twister BV proprietary LTX technology is used to melt the hydrates. Depending on the application, water and condensate from the separators (4,6) is treated, processed, re-injected and/or disposed (7,8).

**Economics:** Typical capital investment for a 100 million scfd package is $2 million.

- Footprint: 4m x 3.5m x 4.5m (LxWxH)
- Weight: 25 metric tons
- Power: 2 kW, excluding power for tracing and LTX heating (75 kW)
- Pressure drop: 25%–35%

**Installations:** Two 300-million scfd trains including 12 Twister tubes on Sarawak Shell Berhad/Petronas B11 platform offshore Malaysia. One 35-million scfd train for Shell SPDC Utorogu field onshore Nigeria.

**Licensor:** Twister BV

**Contact:** Twister BV, Einsteinlaan 10, 2289 CC, Rijswijk (ZH), Netherlands, Phone: 31 (70) 300 2222, Fax: 31 (70) 300 2200, E-mail address: office@twisterbv.com
The Use of Aqueous Liquid Redox Desulfurization Technology for the Treatment of Sour Associated Gases at Elevated Pressure

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Abstract

The use of aqueous, liquid redox desulfurization technology for the direct treatment of sour associated and process gas streams at elevated operating pressure and relatively high CO$_2$ partial pressure presents unique design and operational challenges. The LO-CAT II ®process, an aqueous liquid redox process that utilizes a ferric (Fe $^{+3}$)/ferrous (Fe $^{+2}$) amino-carboxylate redox couple, installed at the MOL Gas Plant in Szeged, Hungary has performed to specification. However, to achieve this goal, resolution of technological challenges related to the solution circulation pump; absorber pluggage with associated high system pressure drop; liquid hydrocarbon influx; foaming with associated liquid entrainment; and corrosion were required.

The design and operational history of the facility is presented, and the aforementioned technological challenges and their resolution are discussed.

Background

ARI Technologies, the developer of the LO-CAT® and LO-CAT II processes; and the predecessor of USF/Gas Technology Products, supplied a LO-CAT II desulfurization system to MOL Hungarian Oil and Gas Company for operation at the Szeged Production Unit. Szeged is located in southern Hungary, approximately 100 miles southeast of Budapest. This unit was placed in service in late 1992, was only the
third of the LO-CAT II units produced, and was the first to treat gas at elevated pressure. Furnished at the same time by others were auxiliary operations such as the water removal system downstream of LO-CAT.

![Figure 1. Process Flow Diagram of LO-CAT II® Unit at MOL, Hungary](image)

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LO-CAT and LO-CAT II are registered trademarks of Gas Technology Products.

The LO-CAT II unit was designed to treat natural gas, however the actual gas is a blend of recycled process gas and associated gas collected from the oilfields around the plant. Both oil and gas from the oilfields are simultaneously transported to the plant via a mixed-phase transport pipeline, followed by separation in a bank of gas-liquid separators. After the separators, the associated gas is combined with
the recycled process gas stream, compressed to approximately 250 psig, and then sent to the LO-CAT II unit.

Figure 1 is the flow diagram of the LO-CAT II unit. As the design team anticipated some liquid entrainment in the sour gas, the first two unit operations are a knockout pot and a coalescing filter. The knockout pot had a liquid surge volume of approximately 35 ft³. After the coalescing filter, the sour gas is routed to the LO-CAT II static mixer absorbers where it is contacted with oxidized LO-CAT catalyst solution. (Two static mixers had been provided with the forethought that they would probably plug with sulfur and would therefore require periodic cleaning). Exiting the static mixer absorber is a two-phase stream consisting of sweet gas and reduced LO-CAT solution, which then enters the absorber separator. In the separator, the gas and liquid are allowed to separate. The treated gas exits the LO-CAT II unit after passing through a mist eliminator. Downstream of the unit, the gas is then cooled to remove water, and then compressed to 925 psig in the third stage compressor.

The reduced solution from the separator passes through a pressure reducing valve and flash drum, then gravity drains to the oxidizer, where the iron is regenerated for re-use in the absorber. A slipstream of this oxidized solution is then sent to the settler where sulfur is allowed to settle and subsequently transferred as slurry to the belt filter. Filtrate from the filter is returned to the oxidizer while sulfur cake is discharged after washing. A small quantity of flash gas is vented to the flare header.

**LO-CAT @II Chemistry**

The LO-CAT II process utilizes a ferric (Fe +3 )/ferrous (Fe +2 ) amino-carboxylate redox couple as a catalyst to absorb H₂S from sour gas and to oxidize it to elemental sulfur in the absorber according to reactions (1) through (3):

\[
\begin{align*}
\text{H}_2\text{S (gas)} + \text{H}_2\text{O (liq)} & \leftrightarrow \text{H}_2\text{S (aq)} \\
\text{H}_2\text{S (aq)} & \leftrightarrow \text{H}^+ + \text{HS}^- \\
\text{HS}^- + 2\text{Fe}^{3+} & \rightarrow \text{S}^0 + 2\text{Fe}^{2+} + \text{H}^+ 
\end{align*}
\]

The ferrous ion that is produced is then recycled to the oxidizer where it is regenerated by oxygen according to reactions (4) and (5):
The overall reaction (6) is therefore:

\[
\frac{1}{2}O_2 \text{(gas)} + H_2O \text{(liq)} \leftrightarrow \frac{1}{2}O_2 \text{(aq)}
\]  

Equation (5) is recognized as the overall Claus reaction, and it can be seen that the role of iron is catalytic since it is not consumed. Chelating agents, represented by "L" in the above equations, while not partaking in any role in the above reactions, serve to maintain the ferric and ferrous ions in solution.

**Design Parameters**

The LO-CAT II unit was designed as outlined in Table 1.

<table>
<thead>
<tr>
<th>Gas to be treated</th>
<th>Natural gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum anticipated gas flow, SCFM</td>
<td>47,000</td>
</tr>
<tr>
<td>Design gas flow, SCFM</td>
<td>58,000</td>
</tr>
<tr>
<td>Inlet gas pressure, psig</td>
<td>260-275</td>
</tr>
<tr>
<td>Allowable gas pressure drop through LO-CAT, psi</td>
<td>14.5</td>
</tr>
<tr>
<td>Inlet (H_2S) concentration, ppmv</td>
<td>100</td>
</tr>
<tr>
<td>Outlet (H_2S) concentration, ppmv</td>
<td>3</td>
</tr>
<tr>
<td>Inlet (CO_2) concentration, %</td>
<td>1.2</td>
</tr>
<tr>
<td>Sulfur load, LTPD</td>
<td>1/3</td>
</tr>
<tr>
<td>Make-up alkali</td>
<td>NaOH</td>
</tr>
</tbody>
</table>

**Start-Up Challenges**

During the initial start-up and subsequent restarts of the unit, problems arose in several areas including:

- Liquid entrainment in sweet gas, thus limiting gas flow
- Foaming and floating sulfur
- Chronic failure of the catalyst recirculation pump
- High system pressure drop
- Poor \(H_2S\) removal efficiency

To answer these challenges, modifications to equipment, procedures and chemistry were required. A discussion of the challenges and the countermeasures are discussed below.

**Discussion**

**Liquid Entrainment**
During the initial start-up, liquid entrainment was seen to be excessive whenever the sour gas flow exceeded 35,000 SCFM. This was attributed, at that time, to the absorber separator vessel being undersized. As a result, not only was it difficult for the gas and liquid to separate, but sulfur particles were also entrained, thus causing the mist eliminator to foul, resulting in further aggravation of the entrainment issue.

To remedy the situation, the separator was resized and a new separator, complete with modified mist eliminator, was retrofitted into the plant. As a result, gas flow up to 58,000 SCFM was achieved without excessive liquid entrainment.

**Foaming and Floating Sulfur**

Foaming and floating sulfur are typical start-up problems that oftentimes are remedied in short order. However, such was not the case with this unit.

Foaming and sulfur settling problems usually go hand-in-hand and are a result of condensed hydrocarbons and/or an imbalance in the use of surfactant and anti-foam additives. When condensed hydrocarbons are present, sulfur particles become coated. These hydrocarbon-coated particles cannot be wetted and can trap air or gas bubbles, so they float on free liquid surfaces such as in the absorber separator, oxidizer, and settler and therefore cannot be removed from the system via settling. When surfactant is added in an attempt to wet the sulfur, foam can be created. Further, if anti-foam is added to control the resultant foam, this could actually aggravate the foaming situation.

Eventually, it was determined that there were excessive liquid hydrocarbons entering the LO-CAT II unit. At one point, a sample of solution was found to contain solid wax-like material. Additionally, stable emulsions were forming among the aqueous LO-CAT solution, sulfur particles, and hydrocarbon condensate. In retrospect, hydrocarbon induced foaming may have aggravated the entrainment situation in the absorber separator as well.

If the condensate could have been prevented from entering the system, this entire problem would not have existed. However, it was determined that considerable condensate was frequently being introduced from both the process gas and also as a result of operation of the two-phase oil/gas pipeline. Consequently, it was deemed not possible to easily keep the condensate out. Therefore, a multi-faceted
approach to the problem was undertaken. To reduce the quantity of condensate and to provide immediate, short-term relief, modifications were made to the sour gas transfer line to allow condensate to be trapped out. Fortunately, the main line was high on the pipe rack and a simple drainage boot could be retrofitted to catch the condensate. In addition, the knockout pot that was furnished with the unit was replaced with a larger one.

At the same time, MOL’s R&D group went about to develop a new additive, which would allow the stable emulsions to be broken and the sulfur to be wetted. Their goal was met by the formulation of what is termed "B-3". B-3 has replaced ARI-600 and anti-foam in this unit, and has allowed the plant to operate in spite of continued hydrocarbon influx.

**Catalyst Recirculation Pump**

The catalyst recirculation pump in this plant was a six stage progressive cavity pump. This type of pump was selected as it best fit the hydraulic specifications and had operated successfully in many previous units, albeit at lower pressure. However, during the several attempts to start the plant, it became apparent that this pump would not be dependable in the long-term, even though a larger, slower running pump was installed as recommended by the manufacturer. As a result of the failure of the larger pump on Christmas Eve, 1997 and the need to keep the plant running, plant maintenance personnel retrofitted a scavenged multi-stage centrifugal pump. This style pump had never been used in LO-CAT units before due to fear of erosion and inter-stage plugging. However, there were no options available on Christmas Eve. A year later, this pump was still operational but the capacity of the unit had been compromised, as the volumetric capacity of this pump was less than that required. As a result, in December of 1998, a new pump with the required capacity was installed. Emboldened by the lack of erosion and inter-stage plugging in the multi-stage pump, but not wanting to chance inter-stage plugging in the long-term, MOL selected a Durco, Mark III pump. This pump is a centrifugal pump with an open impeller, and operates at 3160 rpm. So far, the new pump has performed satisfactorily, having operated successfully for 9 months.

**High System Pressure Drop**

High system pressure drop was caused by absorber fouling and back-pressure in the water removal train downstream of the LO-CAT unit.
Absorber pluggage had been expected; therefore the two static mixers were furnished with flushing connections. Unfortunately, the planned cleaning procedure was not effective, possibly due to the stickiness of hydrocarbon-coated sulfur. An alternate cleaning procedure, using steam, was implemented by the operators, but the pressure drop was never reduced to the as-clean condition. In September of 1998, a revised steaming procedure was implemented that allowed recovery to the as-clean condition. However, to implement this procedure, the absorber required isolation by blinds, as the original isolation valves were not rated for steam service. Replacement of these valves is scheduled shortly. When replaced, more frequent steam outs will be possible, thus allowing low absorber pressure drop and increased gas throughput to be maintained.

Modifications to the water separation train downstream of LO-CAT are also planned for the future and will permit a further increase in gas flow.

**H₂S Removal Efficiency**

From the onset, H₂S removal efficiency had been less than designed for. This was largely due to the CO₂ concentration of the sour gas being higher than the design, thus greatly reducing the solution pH at the discharge of the static mixer (where liquid and gas emerge as a two-phase stream). To remedy this, it was recognized that additional solution buffering (i.e. more bicarbonate ion) was required beyond that designed for. Unfortunately, increasing the buffer when NaOH is used as alkali supply can cause precipitation of NaHCO₃. Usually, KOH is used for higher buffering capacity but it is more expensive. Operators at MOL decided to supplement the NaOH feed with NH₄OH. This worked insofar as the solution buffer capacity was increased, but there was a continuous NH₃ loss from the oxidizer vent. A packed column scrubber was added to the vent, using oxidizer make-up water as the absorbent. This had some beneficial effect, however ammonia losses continued. Further, a review of solution chemistry in September of 1998 revealed that the solubility product of NaHCO₃ was being approached. This prompted a switch to KOH and the discontinuance of NH₄OH in December of 1998.

**Present Situation**

At present, the plant has been operating with a gas flow of 35,000 to 58,000 SCFM, averaging about 38,000 SCFM, with a sulfur load of about 0.05 LTPD (due to low H₂S concentration in the gas). The
improvements that were made in the hydrocarbon collection system, coupled with improvements in operating procedures have greatly reduced the ingress of hydrocarbon condensates into the unit. In turn, this has reduced the difficulties associated with floating sulfur, foaming, and absorber fouling. The development of B-3 has further improved hydrocarbon-induced problems.

The recently replaced recirculation pump, the switch to KOH, and improved absorber cleaning procedures have combined to permit higher gas flow (58,000 SCFM when clean) and greater H₂S removal efficiency (averaging 90%).

Table 2 summarizes the present operating conditions of the unit.

Table 2 -- Present Operating Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual gas flow, SCFM</td>
<td>58,000 (clean)/35,000 (dirty)</td>
</tr>
<tr>
<td>Inlet gas pressure, psig</td>
<td>230-250</td>
</tr>
<tr>
<td>Gas pressure drop, LO-CAT, psi</td>
<td>6 (clean)/9 (dirty)</td>
</tr>
<tr>
<td>Gas pressure drop, system, psi</td>
<td>10 (clean)/22 (dirty)</td>
</tr>
<tr>
<td>Inlet H₂S concentration, ppmv</td>
<td>40-50</td>
</tr>
<tr>
<td>Outlet H₂S concentration, ppmv</td>
<td>4-5</td>
</tr>
<tr>
<td>Inlet CO₂ concentration, %</td>
<td>3.25</td>
</tr>
<tr>
<td>Sulfur load, LTPD</td>
<td>0.08</td>
</tr>
<tr>
<td>Make-up alkali</td>
<td>KOH</td>
</tr>
</tbody>
</table>

Corrosion is not considered to be a problem at this time, but an inspection of the oxidizer and settler is planned during the next turnaround. Replacement of the EPDM sleeves by polyurethane is a possibility at that time as well.

ANTICIPATED FUTURE CONDITIONS

It is anticipated that when final modifications to the absorber isolation valves and water separation train are made, a sustained gas flow of 58,000 SCFM, meeting pipeline H₂S specification of less than 4 ppmv will be achieved (static mixer efficiency improves with increased gas flow). Table 3 summarizes the anticipated future conditions.

Table 3 -- Anticipated Future Operating Conditions
CONCLUSION

After a difficult, extended start-up period, modifications to equipment, procedures, and chemistry has permitted the LO-CAT II unit to operate close to expectations in spite of the continuing ingress of hydrocarbon condensate and higher than designed for CO$_2$ partial pressure. It is anticipated that design gas load and efficiency will be achieved shortly.

The experiences gained in this first LO-CAT II elevated-pressure application, a subsequent 4 LTPD unit operating at 500 psig, and a high pressure pilot plant operating at nearly 1000 psig have been invaluable and will serve as a guide to the design and operation of future units of this nature.

As demonstrated at the MOL site, the impediments to the use of aqueous liquid redox technology for direct treat applications have been resolved. This achievement, when combined with over 20 years of experience in other LO-CAT/LO-CAT II applications, makes LO-CAT II the technology-of-choice for the direct treatment of sour gases at elevated pressure.
Cleaning Up Gasification Syngas

**Introduction**

By definition, gasification is the art of changing a non-gaseous substance, such as a liquid or a solid, into a gas. By this definition, processes such as combustion, anaerobic digestion and pyrolysis would be classified as gasification. However, in today’s world, gasification is defined as any process, which produces a "synthesis gas" or a "syngas", which is a gas consisting mainly of CO and H\textsubscript{2}. With this definition, the substance to be gasified may be a gas. The syngas can be used for producing power and/or hydrogen, methanol, Fischer-Tropsch liquids, etc. Gasification is extremely environmentally friendly in that if properly designed, gasification systems produce very minimal pollution even when processing dirty feedstocks, such as high sulfur coals. In addition, gasification can effect large volume reductions in solid wastes while producing an environmentally friendly slag-type byproduct. Also as the prices of natural gas and crude oil continue to increase, gasification can be economically attractive even without governmental subsidies.

In a gasification process, a feedstock is heated to very high temperatures (1000°C to 1500°C) under pressure (20 bar to 85 bar) in the presence of controlled amounts of steam and pure oxygen. As indicated below, two sets of reactions occur in the gasifier. First, partial oxidation (Equation 1) occurs, which is exothermic and provides the heat required for the second set of pyrolysis reactions (Equations 2 through 4), which are endothermic.

\[
\begin{align*}
C_nH_m + (n2) O_2 & \rightarrow nCO + (m/2) H_2 \quad (1) \\
CO_2 + C & \rightarrow 2CO \quad (2) \\
C + H_2O & \rightarrow CO + H_2 \quad (3) \\
CO + H_2O & \rightarrow CO_2 + H_2 \quad (4)
\end{align*}
\]

In addition to CO, H\textsubscript{2} and CO\textsubscript{2}, small amounts of CH\textsubscript{4}, HCl, HF, COS, NH\textsubscript{3} and HCN are also formed. H\textsubscript{2}S is also formed with the amount dependent on the sulfur content of the feedstock.

Gasification feedstocks can consist of anything organic-based such as coal, petroleum coke, biomass, wood-based materials, agricultural wastes, tars, coke oven gas and asphalt. Gasification provides a means of upgrading the value of very low or even negative value...
materials. In refineries, cokers use to provide the same function; however, the fuel market for petroleum coke is disappearing, and petroleum coke is becoming a waste product in and of itself.

Gasifiers are classified into three different types - fixed bed units, fluidized bed units and entrained flow units. The best known fixed bed unit is the British Gas / Lurgi process as shown in Figure 1. In this unit, the feedstock is fed into the gasifier from the top and is deposited on the top of a fixed bed of material, which is maintained in the vessel. Steam and oxygen is fed into the bottom of the unit. As the feedstock is consumed, all inorganic materials melt and are removed from the bottom of the vessel where the molten material is fused into a non-leachable, non-hazardous slag. Syngas is removed from the top of the vessel. The best known entrained flow gasifier is the Texaco downflow gasifier as shown in Figure 2. In this process, the material to be gasified is slurried with water and fed into the top of the gasifier along with oxygen. Slag and syngas are removed from the bottom of the gasifier. A fluidized bed gasifier is shown in Figure 3. In this type of unit, the material to be gasified along with steam and oxygen are fed into the bottom of the gasifier and the velocities are such that a percolating bed of material is maintained in the vessel. Syngas is removed form the top of the vessel and slag is removed from the bottom.
In all of these processes, essentially all of the organic material is gasified, and the only solid material remaining is the inorganic slag, which can be used as road base and other building material. This tremendous volume reduction in solid wastes is extremely attractive, especially in Europe where it is becoming very difficult and very expensive to dispose of solid wastes.
Combining a gasification process with power generation is called "Integrated Gasification Combined Cycle" or IGCC. As shown in Figure 4, a typical IGCC facility combines the gasification process with a Brayton cycle (gas turbine/generator) and a Rankine cycle (steam turbine/generator). In petroleum refinery applications, a pressure swing adsorption unit (PSA) can be added to produce hydrogen for use in the refinery.

IGCC's generally consists of four processing blocks or "islands" - an air separation unit (ASU), the gasifier, the syngas purification island and finally the power generation island. These islands are generally designed and furnished by totally different vendors. The air separation unit is provided by a merchant gas company, which sometimes owns and operates the ASU. The ASU may be sized to provide other customers in the area with oxygen and nitrogen. As previously mentioned, there are many suppliers of gasifiers and the number of suppliers and types of gasifiers are increasing as the global gasification market expands. The power generation equipment is supplied by the same vendors as conventional power plant equipment. And finally, there are many approaches and consequently, many suppliers of purification equipment, which is the main focus of this article.
SynGas Purification

In an IGCC plant (Figure 4), the feedstock generally needs to be processed to make it suitable to feed to the gasifier. Generally, feed preparation consists of milling and screening, and in the case of the Texaco gasifier, the feed needs to be slurried with water.

The feed is then fed to the gasifier where it is combined with oxygen and steam. Two streams exit the gasifier, a molten slag stream which is composed of all the inorganic material in the feed and a syngas stream consisting mainly of CO and H\textsubscript{2} but also containing entrained soot and ash, various amounts of H\textsubscript{2}S depending on the sulfur content.
of the feed, and trace quantities of CO\(_2\), NH\(_3\), COS, HCl and HCN. Various treatment processes are required to remove the H\(_2\)S and other trace contaminants. A description of these processes follows. The clean syngas from the purification island is then saturated with water prior to be combusted in a gas turbine. The moisture reduces NO\(_x\) formation in the gas turbine. The chemical energy contained in the syngas is recovered as both power and steam generation via a gas turbine/generator set followed by a waste heat boiler/steam turbine/generator set.

The gas exiting the gasifier is hot and contains fine soot and ash particulate. The particulate is removed by either hot, dry candle filters located upstream of the high temperature heat recovery devices or by water scrubbers located downstream of the cooling devices. Hot candle filters are advantageous since the particulate is removed as a dry solid; however, these filters are subject to blinding and breakage. In water scrubbers, the particulate is removed as a slurry which must be dewatered; however, the water scrubber also removes the trace quantities of chlorides which may be present in the syngas and which if not removed will poison the hydrolysis catalyst and cause metallurgy problems in downstream equipment. In both cases, the recovered particulate is recycled back to the gasifier.

The high temperature heat recovery is generally accomplished by a firetube or radiant boiler followed by water tube boiler. Both boilers produce high pressure steam while reducing the syngas temperature to approximately 425°C.

The next step in the purification process is to remove the carbonyl sulfide (COS) from the gas stream; otherwise, SO\(_2\) emission limits may be exceeded after combustion in the gas turbine. There are two means of accomplishing this removal. The more conventional means is to pass the syngas through a fixed bed, catalytic hydrolysis reactor, which will hydrolyze the COS to CO\(_2\) and H\(_2\)S and the HCN to NH\(_3\) and CO. Activated alumina type catalysts are generally employed for these applications, and COS concentrations approaching equilibrium levels (1 - 10 ppm) can be achieved.

When hydrolysis reactors are employed, the reactor effluent gas is cooled and then processed through an acid gas removal system to separate the H\(_2\)S from the syngas. In syngas applications, physical solvent systems are generally more economical than chemical solvent systems, and the processes of choice are either Rectisol or Selexol. Rectisol tends to remove all of the acid gas components while Selexol
is more selective for sulfur compounds. However, chemical solvents such as MDEA are also in use in gasification facilities.

A different approach to removing the COS and the other acid gas compounds from the syngas, is to process cooled (<50°C) digester gas, free of particulate, through a diglycolamine® (DGA) unit. In the process, the DGA reacts with COS as follows,

\[ 2R\cdot NH_2 + COS \rightarrow R\cdot N\cdot C\cdot N\cdot R + H_2O + H_2S \uparrow \quad (5) \]

In the above equation R is HO-CH 2-CH 2-O-CH 2-CH 2- and R-NH 2 is DGA.

The degradation product, R-N-C-N-R, is converted back to DGA in a reclaimer which operates at of temperature of approximately 190°C. The reclaimer reaction is as follows,

\[ R\cdot N\cdot C\cdot N\cdot R + 2H_2O \rightarrow 2R\cdot NH_2 + CO_2 \uparrow \quad (6) \]

In addition to removing COS, DGA also removes H 2S and CO 2to very low levels.

An economic comparison should be done for each application to determine which acid gas removal scheme should be employed - Hydrolysis/Rectisol, Hydrolysis/Selexol or DGA.

For straight IGCC applications, the effluent syngas from the acid gas removal step is ready to be processed in the power generation island of the facility. The gas is first combusted in a gas turbine/generator set. Usually steam is injected into the combustion zone of the gas turbine to decrease NOx formation. The effluent gas from the gas turbine is then directed through a high pressure, waste heat recovery boiler. The high pressure steam is directed through a steam turbine/generator set. Low pressure steam from the turbine is directed to export, and the effluent gas from the waste heat boiler is exhausted to atmosphere.

For some refinery applications, it may be advantageous to separate some or all of the hydrogen from the syngas for use in the refinery. This is accomplished by passing the syngas through a pressure swing adsorption unit. In this type of unit, the syngas is passed through a bed of adsorbent in which all components other than hydrogen are adsorbed onto a molecular sieve at relatively high pressure. Thus producing a very pure hydrogen stream. The adsorbent bed is then isolated and depressured which releases the CO and other impurities. A water gas shift reactor may also be installed to increase the yield of H 2.
Sulfur Recovery

As previously stated, in a gasification process an acid gas stream consisting primarily of CO\textsubscript{2} and H\textsubscript{2}S is produced from whichever acid gas removal process (DGA, hydrolysis/Rectisol, hydrolysis/Selexol, etc.) is employed. It is imperative that the H\textsubscript{2}S contained in the acid gas stream be recovered in a safe and efficient manner to ensure that the entire process remains "Clean." Consequently, the selection of the sulfur recovery technology or technologies is an extremely important step in the design process of a gasification facility.

Since essentially all of the sulfur in the gasifier feedstock is converted to H\textsubscript{2}S, the amount of H\textsubscript{2}S produced is totally dependent on the sulfur content of the feedstock. As a point of reference, coal has a relatively high sulfur content while biomass has a relatively low sulfur content. Generally, the acid gas removal processes will lower the H\textsubscript{2}S content of the syngas to less than 4 ppm, which means that, in essence, all of the H\textsubscript{2}S produced in the gasifier must be processed in the sulfur recovery system.

The type of sulfur recovery system required is dependent on the required sulfur recovery efficiency, the quantity of sulfur to be removed and the concentration of the H\textsubscript{2}S in the acid gas. The required sulfur removal/recovery efficiency will vary depending on location; however, the gasification industry claims that the technology has "near zero" pollution, so it behooves the industry to install the best available control technology. Currently, H\textsubscript{2}S removal efficiencies of 99.9+\% can be economically achieved.

The Claus process has been the sulfur recovery workhorse for applications with large amounts of sulfur (>20 LTPD), relatively high H\textsubscript{2}S concentrations (>15\%) and consistent inlet conditions. However, the Claus process is limited by chemical equilibrium to removal efficiencies of approximately 98\% if three catalytic reactor stages are employed. To achieve higher removal efficiencies, a tail gas treating unit is required.

For over 30 years, the tail gas treating process of choice has been the SCOT process. A simple schematic flow diagram of the SCOT process is shown in Figure 5. In the process, the tail gas from the Claus unit is heated to approximately 300°C in an in-line burner, which serves the dual purpose of heating the gas stream and producing a reducing gas, which is needed in the downstream reactor. The effluent from the
burner is then passed over a cobalt-molybdenum catalyst. In the reactor, all of the SO$_2$, COS, and CS$_2$ are converted to H$_2$S by a combination of hydrogenation and hydrolysis reactions. The reactor effluent gas is then cooled and processed through a typical amine unit, which is selective to the absorption of H$_2$S. The recovered H$_2$S is then recycled back to the Claus unit, and the remaining gas is sent to an incinerator prior to exhausting to atmosphere.

It is important to select the proper amine and to design the absorber in such a manner to minimize the absorption of CO$_2$. Otherwise, a large CO$_2$ recycle stream will develop in through the Claus unit. Since the rate of absorption of H$_2$S in alkanolamines is much quicker than CO$_2$, absorbers should be designed to minimize gas-liquid contact. Regarding amine selection, MDEA is a good selection for syngas. If the absorber is designed properly and the correct amine is chosen, CO$_2$ absorption can be limited to between 10% and 40% of the CO$_2$ in the feed gas to the absorber(1).

In some cases, the SCOT unit can be integrated with the upstream amine unit, which is treating the syngas and producing the acid gas for the Claus unit. For instance, if the syngas is being treated with an MDEA amine unit, the system can be designed with two absorbers, one for the syngas and one for the Claus tailgas; however, only one regenerator would be required.

When using MDEA, the sulfur content of the treated effluent gas will be less than 250 ppm, and the overall sulfur recovery of a Claus/SCOT system is typically 99.8%(2). The treated effluent gas is always processed through an incinerator prior to exhausting to atmosphere.

Another method of increasing the overall sulfur recovery of a Claus unit is to replace the amine portion of the SCOT process with a liquid redox process such as LO-CAT® as illustrated in Figure 6. This approach differs from that of SCOT because 99.9+% of the H2S in the effluent gas from the hydrolysis/hydrogenation unit is converted directly to sulfur in the redox process(3) without having to recycle gas back to the inlet of the Claus unit. Because the liquid redox system is so efficient in removing H$_2$S, overall (Claus + tail gas cleanup) sulfur recoveries of 99.9+% can be easily realized. Thus, incineration of the liquid redox effluent gas is not required prior to exhausting to atmosphere; consequently, the capital and operating cost of the incineration system are removed from the project economics. In addition, by operating the Claus unit at high H$_2$S:SO 2ratios (sub-stoichiometric oxygen), it is possible to eliminate the
hydrolysis/hydrogenation unit and still maintain overall sulfur recoveries of 99.9+%. This approach is shown in Figure 7.

Another unique feature of employing a liquid redox system as a tail gas treating unit is that the turndown capability of the Claus/tail gas system can approach 100% if the system is design properly. The liquid redox system differs from SCOT in that the liquid redox process is a sulfur recovery process in and of itself, which has 100% turndown capability. Consequently, by correctly sizing the liquid redox unit, the acid gas feed to the Claus unit can be routed directly to the liquid redox unit when the turndown capability of the Claus unit is reached.

For syngas applications in which the sulfur capacity is less than 20 LTPD and/or the \( \text{H}_2\text{S} \) in the acid gas is less than 15% and/or a great deal of turndown is required, Claus units may not be a good choice due to difficulties in keeping the unit running. However, these are ideal conditions for a liquid redox process.

**Conclusions**

Cleaning up syngas from gasification units is not a straightforward proposition. Each application must be investigated in regards to both the technical and economic aspects of the specific requirements of the application. Feedstock variability is also an important characteristic, which must be evaluated since many of the cleanup requirements will be dependent upon the nature of the feedstock. In addition, great care should be taken in the selection of the sulfur recovery portion of the system, since the sulfur recovery unit will determine how really "Clean" the system is.

**References**

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Throughout the years, the Claus process has undergone a continuous evolution in attempts to increase the sulphur recovery efficiency of the process. In the 1930s, a thermal stage was added to the two catalytic stages, which increased the recovery efficiency from 95% to approximately 97%. In the 1970s, the SCOT process was introduced which added hydrogenation/hydrolysis plus amine separation to treat the tail gas from the Claus process. In 1988, SuperClaus was introduced, which added a selective oxidation reactor to the end of the Claus process, increasing the efficiency to approximately 99%. And just recently, EuroClaus was introduced, which replaced the second Claus reactor in the SuperClaus process with a selective hydrogenation catalyst increasing the efficiency to 99.5%.

It is obvious that the trend is to achieve higher and higher sulphur recovery efficiencies. It is anticipated that in the near future Claus units installed in developed nations will required sulphur recovery efficiencies of 99.5% or better. Coupling a Claus unit and a liquid redox process, such as the LO-CAT either directly or indirectly in combination with a hydrogenation/hydrolysis reactor, can reliably achieve 99.9+% sulphur recovery.

**Direct tail gas treatment**

When considering liquid redox to treat Claus tail gas without the inclusion of a hydrogenation/hydrolysis reactor, the amount of SO₂ in the tail gas is an important operating parameter. Liquid redox units operate at alkaline pHs in the range of 8 to 9, any SO₂ in the tail gas will be easily absorbed, and form sulphates in accordance with reaction 1:

\[
\text{SO}_2 + 2\text{NaOH} + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \quad (1)
\]

It is important to note that SO₂ does not interfere with the liquid redox chemistry and consequently does not affect the H₂S removal efficiency of the process. However, reaction 1 does affect the operating cost of the process in two ways. First, two moles of caustic are consumed for each mole of SO₂ absorbed, which increases the operating cost of the unit. Secondly, the resultant sulphate product accumulates in the liquid redox solution, and eventually a blowdown is required resulting in loss of valuable catalyst solution. Replacing lost solution adds further to operating costs. Consequently, if this process configuration is to be employed, it is advantageous to minimise the formation of SO₂ in the Claus unit.

The first LO-CAT unit to treat Claus tail gas was recently installed at the Western Gas/Anadorko Bethel plant in Texas, USA.
The SO\textsubscript{2} formation rate can be minimised by operating the Claus unit with sub-stoichiometric quantities of oxygen, thus increasing the H\textsubscript{2}S:SO\textsubscript{2} ratio in the unit. The effect of this mode of operation can be seen by analysing the Claus reactions.

\[
\begin{align*}
H_2S + 1\frac{1}{2}O_2 & \rightleftharpoons SO_2 + H_2O \quad (2) \\
2H_2S + SO_2 & \rightleftharpoons 3S + 2H_2O \quad (3)
\end{align*}
\]

The conventional mode of operation for a Claus unit is to convert one third of the H\textsubscript{2}S to SO\textsubscript{2}, which then reacts with the remaining H\textsubscript{2}S to form elemental sulphur. This is accomplished by carefully controlling the quantity of oxygen entering the system. Due to equilibrium limitations, some of the SO\textsubscript{2} leaves the system with the tail gas.

If the unit is operated in a manner such that there is insufficient oxygen to complete reaction 2, then there will be insufficient SO\textsubscript{2} produced to complete reaction 3, and the H\textsubscript{2}S removal efficiency will be reduced. However, the amount of unreacted SO\textsubscript{2} in the tail gas will also decrease. The effects of H\textsubscript{2}S:SO\textsubscript{2} ratio on the H\textsubscript{2}S and SO\textsubscript{2} contents in the tail gas and the overall removal efficiency are illustrated in Figs 1-3.

A flow diagram of a typical LO-CAT liquid redox unit for treating Claus tail gas directly is shown in Fig. 4. Since the liquid redox system is aqueous-based, elevated temperatures will cause water balance problems; consequently, the tail gas is first passed through a cooler where the gas temperature is reduced from approximately 135°C to 50°C. The cooled gas then enters a knockout pot where any condensate is separated. Depending on the amount of condensate and sulphur tonnage, this sour condensate may be employed as make-up water to the liquid redox process. If it cannot all be used as make-up water, the remaining sour water will need to be processed through a sour water stripper with the sour gas being directed back to the liquid redox unit.

For direct treatment of Claus tail gas, the LO-CAT process would employ a proprietary Mobile Bed Absorber (MBA) because of its low, inherent pressure drop (approximately 500 mm of WC). For contacting media, the MBA uses hollow, ping-pong-like spheres which, when fluidised, are
self-cleaning. Within the MBA, the H₂S and the SO₂ are absorbed into the circulating solution, and the sulphide ions are converted to elemental sulphur in accordance with the Reaction 4 while the SO₂ is converted to sulphate as indicated by reaction 1.

\[
H_2S + \frac{1}{2}O_2 \rightarrow H_2O + S \quad (4)
\]

As indicated in Reaction 4, the reaction is catalysed by a proprietary chelated-iron catalyst.

MBA’s are normally designed to reduce the H₂S concentration in a gas to approximately 10 ppm. For tail gas applications with H₂S:SO₂ ratios of greater than 2.0, this would result in overall removal efficiencies of 99.99+. Even if the ratio were maintained at 2.0, the removal efficiency would be 99.7%; however, the caustic consumption would be much higher as indicated in Figure 3.

The solution exiting the MBA is directed to an Oxidiser where air is injected to regenerate the iron catalyst. If there is insufficient pressure available for moving the tail gas through the MBA, a blower can be supplied or an eductor may be installed as shown in Fig. 4.

LO-CAT systems are designed with very ample liquid inventories. Although this increases the capital cost slightly, there is sufficient capacitance in these systems to render them very insensitive to sudden changes in feed conditions. Thus, fluctuations in the H₂S:SO₂ ratio in the Claus unit will essentially have no effect on the overall removal efficiencies of the system as long as the Claus unit continues to run. In the event that the Claus unit is unable to operate due to turn-down requirements beyond its capabilities, the system can be designed to bypass the Claus unit entirely and route the acid gas directly into the LO-CAT unit. This mode of operation (Fig. 5) will still yield H₂S removal efficiencies of 99.99+. The versatility of the liquid redox system will ensure that the overall system will achieve 99.9+% removal efficiencies at all times. This inherent feature of the system is well accepted by regulators. In addition, the effluent from the liquid redox unit will not require incineration since it will only contain a very small amount of H₂S and essentially no SO₂.

**Indirect tail gas treating**

In this processing scheme (Fig. 6) all sulphur compounds in a Claus tail gas
are converted to $\text{H}_2\text{S}$ by passing the tail gas through a hydrogenation/hydrolysis, catalytic reactor at elevated temperatures. Reactions 5 and 6 (hydrogenation) and reactions 7 and 8 (hydrolysis) represent the major reactions, which occur in the reactor.

\begin{align*}
\text{SO}_2 + 3\text{H}_2 & \rightleftharpoons \text{H}_2\text{S} + 2\text{H}_2\text{O} \quad (5) \\
\text{S}_2 + 2\text{H}_2 & \rightleftharpoons 2\text{H}_2\text{S} \quad (6) \\
\text{CS}_2 + 2\text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{S} \quad (7) \\
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2\text{S} \quad (8)
\end{align*}

In this processing scheme, a fuel gas is subjected to partial oxidation, which not only generates sufficient heat to raise the tail gas to reaction temperatures but also generates sufficient hydrogen (reaction 9 shown below) to satisfy the requirement of reactions 5 and 6.

$$\text{CH}_4 + \text{O}_2 \rightleftharpoons 2\text{H}_2 + \text{CO}_2 \quad (9)$$

After passing through the reactor, the effluent gas must be cooled to approximately 50°C. This can be accomplished by employing a direct contact condenser as shown in Figure 6. Alternatively, an indirect condenser can be employed.

In either case, sour cooling water or sour condensate will be generated. Again a portion of the sour condensate or water may be used as makeup water for the liquid redox unit; however, some of it will need to be sent to a sour water stripper with the vapor being routed back to the liquid redox unit.

This processing scheme will be even more forgiving to changes in the operations of the upstream Claus unit, since the hydrogenation/hydrolysis unit will act to muffle any compositional changes from the Claus unit. Consequently, the amount of $\text{SO}_2$ entering the liquid redox unit will remain fairly constant, and the operating cost of the system will remain constant.
Sulphur disposal

Because of its poor quality, sulphur produced from liquid redox processes has a bad reputation, which in some cases is well earned. However, due to the relatively small quantities of sulphur produced in liquid redox installations, most liquid redox sulphur has been either landfilled or disposed of as solid, agricultural sulphur; hence, not a lot of effort has been exerted to improve its quality. However, great progress has been made in improving the quality of sulphur produced in LO-CAT units.3

Sulphur is produced as a solid in a liquid redox unit. Since the reactions are not gas phase, there is no dissolved H$_2$S in liquid redox sulphur; thus sulphur degassing is never required. The sulphur is normally filtered and washed to produce a filter cake, which is 65% to 85% sulphur depending on the type of filter used, with the remainder being water and dissolved salts. It is not possible to simply dump this cake into the Claus sulphur pit, since there is insufficient heat in the pit to evaporate the water and to melt the sulphur. And even if the moisture is removed prior to dumping the sulphur in the pit, the solid particles have a tendency to float on top of the molten sulphur thus making heat transfer and consequently melting very difficult. Due to these problems, the sulphur from the liquid redox system must be disposed of as a solid3 or melted prior to being introduced into the sulphur pit.

Melting of liquid redox sulphur can be accomplished in either batch type melters or continuous melters. As a rule of thumb, sulphur production rates of greater than 5 tons per day (TPD) warrant continuous melting while rates less than 5 TPD generally require batch melting due to economics. However, continuous melters can be installed on any LO-CAT system regardless of size. A typical melter system for a LO-CAT system is shown in Fig. 7.

The change in quality of the Claus sulphur due to the addition of molten, liquid redox sulphur will be as indicated in Figure 8. As a matter of comparison, specifications for sulphuric acid plant grade sulphur are less than 1000 ppm carbon and less than 250 ppm ash. This suggest that adding molten, liquid redox sulphur to a Claus sulphur pit can be done without degrading the Claus sulphur to any great degree. However, the overall quality of the sulphur mix can be further improved by processing the liquid redox sulphur through a diatomaceous earth filter prior to directing it to the sulphur pit.

Costs

Budgetary capital costs of direct-treat, liquid redox, tail gas units complete with coolers and sour water strippers are contained in Fig. 9. For comparison purposes, the capital costs4 of amine-based, tail gas cleanup units (TGCUs) are also contained Fig. 9. It is obvious that considerable capital cost savings can be realized by utilizing liquid redox systems as tail gas treating units. With regard to operating costs, the liquid redox system will increase the operating cost of the Claus unit by approximately $14 per long ton of sulphur entering the Claus unit. For an amine-based TGCU this figure will be approximately $8 per long ton. Consequently, each application needs to be analysed to see if the
savings in operating cost of the amine-based system justifies the higher capital cost.

Field experience

The direct contact, tail gas treating scheme described above has never been demonstrated commercially; however, the two processes comprising the scheme are commercially proven. The HCR² process, which is a Claus unit operating with sub-stoichiometric oxygen, is well proven while the LO-CAT liquid redox process has been in commercial operation for over 20 years with 150 licensed units. In addition, approximately 50 of these units are treating acid gas streams (CO₂ and H₂S). Consequently, there is no reason to believe that the proposed arrangement would not operate satisfactorily.

Variations of the indirect, tail gas treating scheme employing an intermediate hydrogenation/hydrolysis step have been in commercial operation since the early 1970s when the Beavon Sulphur Removal Process was introduced. This process consisted of a hydrogenation/hydrolysis reactor followed by a Stretford unit. Approximately 30 of these units were installed. The process fell out of favour due the potential toxicity problem with the vanadium catalyst employed in the Stretford process. Due to this problem, iron-based, liquid redox processes such as the LO-CAT process has since replaced the Stretford process.

Recently, Western Gas installed the first LO-CAT unit in a Claus tail gas application at their natural gas production field in Palestine, Texas, USA. Initially, the LO-CAT unit was treating amine acid gas; however, as the processing and the sulphur capacities of the facility increased, a 2-stage Claus unit and a hydrogenation/hydrolysis reactor were installed, and the LO-CAT unit treated the reactor effluent. This system is yielding over 99.9+% sulphur removal.

Conclusions

Claus units can easily achieve hydrogen sulfide removal efficiencies exceeding 99.9+% by employing a liquid redox system such as LO-CAT as a tail gas treating unit. The combination of Claus and liquid redox has a significantly lower capital cost than conventional amine-based tail gas units which offsets its higher operating costs. In addition, the liquid redox unit will significantly reduce the inherent sensitivity of the Claus unit to changes in feed gas composition and flow rate. And if designed properly, the turndown capability of a system employing a Claus unit with a LO-CAT tail gas unit can be approximately 100%.

References

The State of Iron-Redox Sulfur Plant Technology
New Developments to a Long-Established Process Technology

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Abstract
The iron-redox process has enjoyed commercial success for over 25 years, generally in applications requiring sulfur removal capacity below 20 tons per day. Key process benefits include high H₂S conversion efficiency, significant turndown flexibility, and ability to treat a wide range of gas compositions, and environmentally innocuous process and products. The process has also been known to consume expensive chemicals, produce “low-value” sulfur, and plug. This paper reviews the status of the technology, explains how the operating issues are being addressed in commercial practice, and provides a glimpse of improvements that are in the final stages of development.

Introduction
The family of liquid redox processes that has been developed since the 1920’s is best represented, currently, by the “iron-redox process” or “chelated-iron” process. This technology has served its clients well for more than 25 years. Units typically achieve 99.9+ % H₂S removal efficiency, treat a wide variety of gas types over a wide variety of operating conditions, have substantial turndown capability on H₂S concentration and gas flow and produce innocuous products and by-products. No wonder more than 200 such units have been licensed around the world – a technical and commercial success by almost any definition!

The iron-redox technology is typically applied to gas streams requiring less than 20 tons per day sulfur removal capacity, unless operating conditions limit use of other sulfur plant technologies, such as Claus. In such cases, Iron-redox may still be the best sulfur removal technology. Highly variable gas and low H₂S concentration are examples. Iron-redox plants as large as 80 tons per day are in
Also well known are the operating issues that have been associated with this process, such as high chemical cost, chemical degradation, plugging, foaming, production of “low-value” sulfur, inability to treat high-pressure applications.

How are the leading developers of this technology addressing these operating issues? What improvements are on the horizon? With 25 years of commercial application, is iron-redox technology still competitive in today’s commercial environment?

The answers are clear. The iron-redox process technology has been improved continuously over the last 25+ plus years. Numerous testimonials confirm that the technologies/solutions described in this paper are being successfully applied in commercial applications. As further evidence, there continues to be significant commercial activity for this well-developed, well-proven technology in applications for natural gas and associated gas processing, geothermal plants, refinery fuel gas, municipal odor control, landfill gas, and recently, municipal waste gasification, as well as a host of others. Furthermore, improvements in the final stages of development will benefit the users of this process technology in the near-term future, and ensure its long-term commercial viability.

This paper will discuss the benefits of H₂S removal, provide a basic description of iron-redox technology, a description of the solutions being commercially employed to successfully address past and current operating issues, and, finally, explore the innovations that are on the horizon.

**Background**

Removal of hydrogen sulfide (H₂S) from gas streams has been an issue for the energy industry since its inception. Hydrogen sulfide is an extremely toxic, corrosive and odorous gas, causing safety and materials issues in its unaltered form. After burning, the H₂S is oxidized to sulfur dioxide (SO₂), a major player in acid rain and greenhouse gas emissions for the downwind neighbors. So, while sulfur removal from gas streams has been an issue since the inception of the hydrocarbon-based energy industry, it also continues to get ever-increasing attention as an environmental issue. Iron is an excellent oxidizing agent for the conversion of H₂S to elemental sulfur. However, due to the very low solubility of iron in commercial use.
aqueous solutions, the iron had to be present in the dry state (iron sponge) or in suspensions (the Ferrox process) or compounded with toxic materials such as cyanides. In the 1960’s development work was begun in England to increase the solubility of elemental iron in aqueous solutions. This work led to the introduction of CIP (Chelated Iron Process). However, it wasn’t until the late 1970s that a system of chelates was developed that had sufficient oxidative resistance to be sufficiently stable and be commercially successful. This development work led to the successful commercialization of the iron redox process.

**Iron-redox process**

In this process, iron, in its ferric state (+3), is held in solution by chelating agents. The intent of the process is to oxidize hydrosulfide (HS-) ions to elemental sulfur by the reduction of the ferric (Fe+3) iron to ferrous (Fe+2) iron, and the subsequent reoxidation of the ferrous ions to ferric ions by contact with air. The chemistry of all chelated iron processes is summarized as follows with (l) and (v) representing the liquid and vapor states, respectively;

\[
\begin{align*}
H_2S (v) + H_2O (l) & \rightarrow H_2S (l) \quad (1) \\
H_2S (l) & \rightarrow H^+ + HS^- \quad (2) \\
HS^- + 2Fe^{+3} & \rightarrow S^0 + 2Fe^{+2} + H^+ \quad (3) \\
\frac{1}{2}O_2 (air) + H_2O (l) & \rightarrow \frac{1}{2}O_2 (l) \quad (4) \\
2Fe^{+2} + \frac{1}{2}O_2 (l) + H_2O & \rightarrow 2Fe^{+3} + 2OH^- \quad (5) \\

\text{Overall Reaction} \\
H_2S (v) + \frac{1}{2}O_2 (v) & \rightarrow S^0 + H_2O \quad (Fe) \quad (6)
\end{align*}
\]

Equations 1 and 2 represent the absorption of H$_2$S into the aqueous, chelated iron solution and its subsequent ionization, while equation 3 represents the oxidation of hydrosulfide ions to elemental sulfur and the accompanying reduction of the ferric iron to the ferrous state. Equations 4 and 5 represent the absorption of oxygen into the aqueous solution followed by oxidation of the ferrous iron back to the ferric state.
Equations 3 and 5 are very rapid. Consequently, iron-based systems generally produce relatively small amounts of by-product thiosulfate ions, and, in properly designed units, air streams can actually be processed. However, equations 1 and 4 are relatively slow and are the rate controlling steps in all chelated iron processes.

It is interesting to note that the chelating agents do not appear in the process chemistry, and in the overall chemical reaction, the iron cancels out. So why is chelated iron required at all, if it doesn’t take part in the overall reaction? The iron serves two purposes in the process chemistry. First, it serves as an electron donor and acceptor, or in other words, a reagent. Secondly, it serves as a catalyst in accelerating the overall reaction. Because of this dual purpose, the iron is often called a “catalytic reagent”. The chelating agent(s) do not take part at all in the process chemistry. The sole purpose of the chelating agents is to solubilize iron in water, thus making it possible to have a solution of iron.

Iron-based, liquid oxidation has developed into a very versatile processing scheme for treating gas streams containing moderate amounts of H₂S. Advantages of these systems include the ability to treat both aerobic and non-aerobic gas streams, removal efficiencies in excess of 99.9%, essentially 100% turndown on H₂S concentration and quantity, and the production of innocuous products and by-products.

The two most common processing schemes encountered in iron-based, liquid oxidation systems are illustrated in Fig. 1 and 2. Fig. 1 shows a “conventional” unit, which is employed for processing gas streams, which are either combustible or cannot be contaminated with air such as carbon dioxide, which is being treated for beverage purposes. In this scheme, equations 1 through 3 are performed in the Absorber while equations 4 and 5 are performed in the oxidizer. Fig. 2 illustrates an “autocirculation” unit, which is used for processing acid gas (CO₂ and H₂S) streams or for other non-combustible streams, which can be contaminated with air. In this scheme, equations 1 through 3 are performed in the “centerwell” which is nothing more than a piece of pipe open on each end. The purpose of the centerwell is to separate the sulfide ions from the air to minimize by-product formation. The volume within the centerwell is essentially the same as the absorber in a conventional unit. The other unique feature of the autocirculation scheme is that no pumps are required to circulate solution between the centerwell (absorber) and the oxidizer. In these units there is a larger volume of air than acid gas; consequently, the aerated density
on the outside of the centerwell is less than on the inside resulting in a natural circulation from the oxidizer into the centerwell.

The sulfur product is typically a sulfur “cake”, with entrained water and catalyst solution. The entrained catalyst solution is effectively a “blowdown” stream for the aqueous process. (The catalyst solution is itself non-toxic and non-hazardous.) Depending on the type of sulfur filter used, the sulfur cake can have a sulfur concentration between 30% (bag filter) to 90% (filter press). The vacuum belt filter is quite common, and produces a sulfur cake that is 60-65% sulfur.
Developments in Iron-Redox Technology

Practitioners of iron-redox technology have as many as 25 years of experience designing process solutions for a wide variety of applications. That can be a very good thing, but it also means that a lot that is “known” about iron-redox characteristics is 25 years old. However, this technology has, indeed, continued to evolve to address the issues of high chemical costs, chemical degradation, plugging,
foaming, production of “low-value” sulfur, and an “inability” to treat high-pressure gas.

**High Chemical Cost**

It is not a simple matter of expensive catalysts used in the process. Rather, chemical costs in the iron-redox process are a function of several variables: catalyst concentration, chemical degradation and chemical recycle.

**Catalyst Concentration**

Chemical concentration is an issue because the sulfur produced from the process is in the form of a sulfur “cake,” which has significant amount of entrained liquid. The filtered sulfur product exiting the process typically runs between 60% and 80% sulfur, but can run as low as 30% sulfur. The remaining amount is a combination of wash water and catalyst solution. Clearly, the more concentrated the catalyst solution, the more chemical is likely to leave the process with the sulfur.

The main licensees of the iron-redox technology practice two very different philosophies regarding catalyst concentration. The difference in catalyst concentration between the two philosophies is on the order of 20-40x, depending on actual configurations and applications. This difference in chemical concentration has aspects of a capital/operating trade-off, as the more concentrated solution clearly has benefits in vessel and pump size (capital cost), at the expense of operating cost (chemicals). However, that analysis very much understates the impact of the catalyst concentration issue.

The scale factor on capital cost is moderated by several factors. 1) Vessel size is moderated by circulation rates, and 2) there are significant elements of the capital cost that are not affected significantly by this relative equipment size, such as license fee, engineering design, project management, start-up, commissioning, and to a lesser degree, installation. So, while there is likely to be a difference in capital cost between the two philosophies, it will be significantly moderated.

Chemical cost difference will be moderated by the effectiveness of the sulfur wash and chemical recycle. The catalyst cost difference won’t be 20-40x, but it is likely to be at least several multiples. Current practice suggests that a chemical cost difference of 2 to 3 times exists between
Looking at catalyst concentration as solely a cost issue overlooks the operating benefits with the more dilute system, namely:

- Higher capacity to solubilize products and by-products, and
- Moderated response to process changes.

Depending on the feed gas composition, the iron-redox catalyst solution will have varying amounts of thiosulfates, carbonates and bicarbonates and oxalates, in addition to the iron and chelates. It is reasonable that the more dilute catalyst solution will have higher capacities to keep these other chemical species in solution, with less likelihood of creating precipitates, and less likelihood of operating problems resulting from precipitation. In fact, it is these solubility limits and the resulting operating problems that often limit the amount of chemical recycle that can be achieved in efforts to reduce chemical loss. (This issue will be covered in more detail in the following two sections on chemical degradation and chemical recycle.)

The larger catalyst volumes and lower chemical concentrations combine to create a “fly wheel” effect, so that changes to the inlet gas conditions result in greatly moderated changes to the sulfur plant operating conditions, and a commensurate reduction in operator attention.

There are iron-redox clients that operate the two different systems side-by-side that can and have testified to the difference in operating cost and operability between the two systems.

**Chemical Degradation**

The catalyst regeneration process requires oxidation of the iron catalyst. Unfortunately, chelates are oxidized at the same time. This creates two issues: the need to replace the degraded chelates and the existence of the products of the degradation reaction, which tend to be oxalates. The build-up of the oxalates in the system will limit the amount of chemical recycle that can be achieved before precipitation of the oxalates occurs.

However, there has been significant development work to control the rate of chemical degradation.

Although the iron-redox process is about 25 years old, research to understand and reduce chelate degradation has been ongoing for more than 40 years and continues today. The catalyst systems employed by
the leading licensors tend to be proprietary, some are patented. For example, one technology supplier has used a patented blend of chelates to improve stability over a broader range of operating conditions, offering better oxidative resistance than can be accomplished by a catalyst system that is based on only one type of chelate.

In addition, there is significant work done on identifying oxygen scavengers. One elegant solution is the controlled production of thiosulfate ions, which act as an oxygen scavenger in the system and effectively reduces chelate degradation rates.

The chemical equation for the production of thiosulfate (potassium thiosulfate, assuming potassium hydroxide is used to maintain pH) is shown in equation 7.

\[
2 \text{HS}^- + 2 \text{KOH} + 3/2 \text{O}_2 \rightarrow \text{K}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \tag{7}
\]

The trick is to produce thiosulfate in the right amount. Over production of thiosulfate will over consume the caustic used to maintain pH. Underproduction will result in excessive chelate degradation. Controlled thiosulfate production can make a significant contribution to lowering chemical cost and improving process performance.

In summary, prospective buyers of iron-redox processes should ask their supplier about their chelate degradation control mechanism. Best practice includes both oxidation resistant chelates and controlled production or introduction of an effective oxygen scavenger.

Chemical Recycle

The ability to recycle chemicals reduces chemical cost. The more concentrated catalyst system requires more chemical recycle to be economic. However, too much recycle leads to a build-up of unwanted oxalates and other chemicals, which can lead to precipitation and operating problems. Thus, there is a limit to how much chemical recycle can close the chemical cost disparity associated with a large difference in catalyst concentration.

Summary of Catalyst Concentration-Related Issues:

The dilute catalyst system offers significant operating cost benefits, as there are fewer chemicals leaving the system and fewer barriers to recycling chemicals. In addition, there are significant operating benefits, as there is a significantly lower amount of oxalates and other
salts being recycled back into a catalyst solution that has a higher capacity for the recycled salts. This means that they dilute system is far less likely to incur operating and maintenance problems associated with precipitates. Also, the relatively large volume attributed to the dilute catalyst system creates a “fly wheel” effect that moderates the impact of variations in the inlet gas on the operation of the sulfur unit.

So, while chemical costs can vary significantly, depending on gas to be treated and sulfur wash and recycle designs, chemical costs for many systems employing the dilute catalyst concentration are in the range of $175-$250/ton. Comparable costs for the more concentrated system, in similar applications, tend to be a factor of 2-3 times that cost.

In conclusion, prospective buyers of modern iron-redox systems should insist in good chemical cost guarantees with his unit. The reputable and experienced firms in this area offer good experience, can estimate chemical usage based on feed gas and equipment configuration with reasonable accuracy, and will back their analysis with good guarantees.

**Plugging**

Plugging problems have been solved by eliminating packed towers, and by incorporating standard piping designs that limit dead spots and areas of restricted flow—not rocket science, just good basic design discipline.

Some iron-redox suppliers insist sulfur is formed in the oxidizer, and the return catalyst stream can run through a filter to prevent sulfur from going into the absorber to prevent plugging. This design will plug. The sulfur reaction is fast: sulfur will form in the absorber, and the packed tower will plug, regardless of the effectiveness of any filter in the catalyst return line. Prospective customers of this technology need to insist that their design be void of any fixed surfaces that can offer sites for sulfur build-up, or alternatively, insist on good sulfur clean-out provisions as part of the design.

Additional steps to prevent plugging include proprietary heat exchanger designs that minimize plugging. Newly designed absorber spargers and improved oxidizer spargers have significantly improved maintenance requirements and decreased plugging in the oxidizer. Oxidizer vessels and/or separator vessels now have cone-shaped bottoms with additional air injection systems to maintain fluidity in the cone.
For absorber designs that include counter-current gas/liquid flow in which the catalyst solution is sprayed into the column, plugging due to sulfur carryover is being controlled with properly designed and positioned spray nozzles and knockout pots.

**Foaming**

Chelated-iron systems can foam when two conditions are present: during the initial plant start-up and when a large amount of heavy hydrocarbons enter the system.

In the first case, the surface tension properties of the fresh catalyst solution can lead to foaming issues in the first few days of operation. This is an issue only with the initial start-up with fresh solution, and can easily be handled by following the start-up procedures. This will not be an issue with subsequent start-ups with aged solution.

Continuous incursions of small amounts of liquid hydrocarbons are frequently experienced with no adverse effect on the operation of a unit; however, the introduction of large amounts of liquid hydrocarbons can present foaming problems. The good news is that the unit will continue to operate and treat the gas, but the operation will be “messy”. It is unlikely the plant will need to shut down. (This is in contrast to most Claus-type reactor systems with fixed catalyst beds that would likely experience catalyst fouling, and be forced to shut down and replace catalyst following a similar process upset.) Where this is seen to be a possibility, suitably designed knockouts and separators should be incorporated into the gas inlet piping design. However, should foaming occur, “designer” surfactants have been developed, which alleviate the foaming symptoms caused by the introduction of large amounts of liquid hydrocarbons.

**Production of “low-value” sulfur**

In this world of excess sulfur production due to the large amount of by-product sulfur being produced, when was the last time anyone produced “high-value” sulfur?

It is true that typical iron-redox sulfur has entrained water and residual catalyst in sulfur cake form. The sulfur content of the cake can range from 30% sulfur to 90% sulfur depending on the type of sulfur filter incorporated. Though sulfur in this unmelted “cake” form is typically undesirable as a chemical feedstock; it actually has superior
properties as a sulfur fertilizer when compared to typical “pure” sulfur produced by more traditional processes.

One California chemical manufacturer typically handles 20,000 tons of iron-redox sulfur per year, and would like more. The fact that iron-redox sulfur was formed in the liquid phase at low temperature means that the sulfur particle is amorphous (softer) than solidified molten sulfur, and has a smaller particle size, for faster reaction in the soil. In addition, the other catalyst elements in the iron-redox solution, and present in the sulfur “cake” (iron, chelates), are micronutrients in their own right and sold as such by several suppliers of agricultural products.

In order to ensure a market for iron-redox-produced sulfur, commercial proposals have been made that include concurrent fertilizer market development activity.

Commercial sulfur purification systems can convert iron-redox sulfur to molten sulfur of 99.9% purity. However, the appearance (color) will still be slightly degraded due to the presence of iron polysulfides. Where development of a fertilizer market is an option, it is preferable to develop that opportunity rather than install equipment to purify the sulfur, as the cost incurred is generally not matched by a corresponding increase in sulfur value in this market of excess sulfur.

**Inability to treat high-pressure gas**

Operation of aqueous-based liquid redox systems at high pressure has been a problem due to difficulties with keeping the liquid circulation pumps running. Circulation pumps were always specified as ANSI, open-impeller centrifugal pumps. The logic being that closed-impeller pumps would plug with sulfur particles or possibly erode. Consequently, for high head applications in which open impeller pumps would not apply, plunger type pumps were chosen. The plunger pumps had no difficulty supplying the required head, however, seal rings had extremely short lives. To solve this problem, a multi-staged, closed-impeller, centrifugal pump was installed in one high-pressure application with excellent results. The pump has been in continuous operation for approximately 4 years without any signs of plugging or erosion. Since that installation, similar installations at even higher pressure (as high as 1,000 PSI) have had similar success. For all future high-pressure applications, closed-impeller single or multi-stage centrifugal pumps will be specified. Obviously, the original concern about plugging had no basis.
While iron-redox systems can now be designed to direct treat high pressure gas streams, there will still be occasions where it will make sense to direct treat the high pressure gas with a conventional amine unit and treat the resulting acid gas with an iron-redox autocirculation unit (Figure 2). In applications that benefit from the additional absorption capabilities of a conventional amine unit, such as removal of CO₂, along with the required infrastructure, utilities, and experience to run a conventional amine unit, the simplicity of the iron-redox autocirculation can be an advantageous process solution. About 30% of the installed iron-redox plants are this configuration.

**The Future of Iron-Redox Systems**

While many of the operating issues associated with iron-redox systems have been successfully addressed in current designs, significant advances are being made in the state of the technology which will ensure a bright future well into the next century. Development activities are focusing on improved capital cost and design flexibility, focused on development of improved mass transfer devices in the oxidizer, and improved iron-redox sulfur market development.

An improved mass transfer device in the oxidizer is scheduled for commercial demonstration in early 2003. Successful demonstration of this technology will result in reducing the size of the oxidizer by as much as a factor of ten, creating significant cost, space and weight differences relative to current systems and provide significant design flexibility. Also, the ability to modularize portions of the plant should also create economies in the design and installation of the new units.

Finally, expansion of the successful marketing of iron-redox sulfur can pay large dividends to the operator of the iron-redox plant. In addition to the significant agricultural benefits available to the surrounding agriculture industry, the successful market development of this sulfur should reduce sulfur transport and disposal costs, reduce future liability from disposal issues, and improve plant-permitting prospects for new and/or expanded facilities.

**Summary**

In summary, the iron-redox technology has been continuously improved over 25 years of successful commercial application. Solutions to most of the “operating issues” associated with the technology have been developed and are being successfully practiced in commercial
applications. The most robust iron-redox plant operations will incorporate, as part of the design:
- low concentration iron catalyst (around 1,000 PPM)
- catalyst solutions that incorporate “chelate blends” for enhanced stability and oxidative resistance
- avoidance of “packed” columns for gas-liquid contacting
- “slurry-friendly” piping designs.

New developments on the horizon promise improvements in design flexibility and reduced capital cost.

The implication for operators that must remove sulfur from gas streams is that the iron-redox technology offers a unique combination of proven experience and continuous improvement. It is a technology that is commercially and technically attractive, and in which the operator can have a high degree of confidence.
Suncor’s Optimization of a Sulfur Recovery Facility

By Dean Freeman, Suncor, Jackie Barnette, GTP LLC, Gary Nagl, GTP LLC

Introduction

Suncor Incorporated Resources Group acquired the 7-22 Progress Gas Plant, located in Spirit River, Alberta, Canada, in 1996. Due to the extremely competitive nature of the natural gas business, all gas processors, including Suncor, are obsessed with reducing operating costs. As part of Suncor’s cost reduction program, a close examination of their sulfur recovery unit by Suncor and Gas Technology Products LLC resulted in significant cost savings by optimizing the method of operation.

The Facility

The 7-22 Progress Gas Plant processes 20 MMSCFD of natural gas at approximately 950 psig. As shown in Figure 1, the processing train consists of an MDEA amine unit for removing CO₂ and H₂S, a glycol dehydrator and an Autocirculation LO-CAT® unit for removing the H₂S in the amine acid gas prior to exhausting to the atmosphere.

![Figure 1](image)

The LO-CAT® process is a proprietary process, which converts H₂S to elemental sulfur by employing a patented, environmentally safe, multichelate, iron catalyst. The overall reaction (Rx 1) of the process is
the modified Claus reaction; however, the mechanism for achieving this reaction is much different than that which occurs in the Claus process.

\[ \text{H}_2\text{S} + \text{O}_2 \rightleftharpoons \text{H}_2\text{O} + \text{S} \]  

The LO-CAT® process is a liquid phase, ambient temperature process, which is in contrast to a Claus unit, which is a gas phase, elevated temperature process. The LO-CAT® reactions can be separated into the Absorption Section and the Regeneration Section. In the Absorption Section, the H\(_2\)S is absorbed (Rx 2) from the gas stream into the circulating aqueous (aq.) LO-CAT® solution. Once absorbed, the H\(_2\)S ionizes (Rx 3) into hydrogen and hydrosulfide ions, and the hydrosulfide ions then react (Rx 4) with ferric ions to form elemental, solid sulfur and ferrous ions.

**ABSORPTION SECTION**

- **Absorption**
  \[ \text{H}_2\text{S} \text{ (gas)} + \text{H}_2\text{O} \text{ (aq.)} \rightleftharpoons \text{H}_2\text{S} \text{ (aq.)} + \text{H}_2\text{O} \text{ (aq.)} \]  

- **Ionization**
  \[ \text{H}_2\text{S} \text{ (aq.)} \rightleftharpoons \text{HS}^- \text{ (aq.)} + \text{H}^+ \text{ (aq.)} \]  

- **Oxidation**
  \[ \text{HS}^- \text{ (aq.)} + 2 \text{Fe}^{3+} \text{ (aq.)} \rightarrow \text{S} \text{ (solid)} + 2 \text{Fe}^{2+} \text{ (aq.)} + \text{H}^+ \text{ (aq.)} \]  

The ferrous ions are not capable of being reduced any further; consequently, to have a continuous process they must be oxidized back to the ferric state. This is accomplished by sparging air through the effluent solution from the Absorption Section of the process. Oxygen is absorbed (Rx 5) into the solution, which then oxidizes the ferrous ions (Rx 6) back to the ferric state.

**REGENERATION SECTION**

- **Absorption**
  \[ \_\text{O}_2 \text{ (gas)} + \text{H}_2\text{O} \text{ (aq.)} \rightleftharpoons \_\text{O}_2 \text{ (aq.)} + \text{H}_2\text{O} \text{ (aq.)} \]  

- **Oxidation**
  \[ \_\text{O}_2 \text{ (aq.)} + \text{H}_2\text{O} \text{ (aq.)} + \text{Fe}^{3+} \text{ (aq.)} \rightarrow 2 \text{OH}^- \text{ (aq.)} + \text{H}^+ \text{ (aq.)} + \text{Fe}^{3+} \]  

Adding reactions 2 through 6 yields reaction 1 with all components in the gaseous phase with exception of the sulfur, which is in the solid phase.

The LO-CAT® unit employed at the Suncor plant was installed in 1990 and is of the patented Autocirculation design, which is shown in Figure 2. In this configuration, the Absorption and Regeneration Sections of the process are located within the same vessel. The acid gas from the
Amine unit is sparged into a centerwell (Absorber), which is nothing more than an open-ended pipe located within a cone-bottom tank. The Absorption reactions (Rx 2 – 4) occur within the centerwell. The regeneration air is sparged into the solution outside of the centerwell where the regeneration reactions (Rx 5 & 6) occur. Since there is considerably more regeneration air than acid gas, the solution outside of the centerwell is more aerated (less dense) than the solution inside of the centerwell. Consequently, this density difference creates a natural liquid circulation from the Regeneration Section of the vessel to the Absorption Section. Thus liquid circulation is established without the need of pumps.

Sulfur settles out of solution into the cone section of the Autocirculation Vessel where it is removed as a 10 wt% to 15 wt% slurry. The sulfur slurry is heated to approximately 120o C by heat exchange with hot oil, and the solid sulfur is melted. The molten sulfur and LO-CAT® solution are then separated, with the solution being returned to the process. The melter system operates under approximately 3.5 barg pressure to prevent the aqueous solution from boiling. The molten sulfur is allowed to solidify, and is then hauled to a landfill. Due to the remoteness of the plant and the relatively small amount of sulfur being produced (2.2 MTPD), it is more economical to dispose of the sulfur at the local landfill than to sell it to a remote user. Trucking the sulfur to a remote user will cost more than what the sulfur is worth.

Even though water is produced in the process, a small amount of makeup water is still required for the LO-CAT® unit to compensate for the moisture consumed in saturating the regeneration air. The plant originally used well water for this purpose; however, the plant personnel discovered that some of the problems they were experiencing in the unit, such as occasional foaming, disappeared when they switched to deionized water. Obviously, the well water contained surface active components which were conducive to foaming. In general, LO-CAT® units only require water of potable quality.

An Autocirculation LO-CAT® unit is an extremely simple system to operate. In essence, the unit consists of a cone-bottom tank through which air and acid gas are sparged through an aqueous solution of chelated iron. A small slip stream of concentrated sulfur slurry is pumped through a hot oil heat exchanger with molten sulfur being withdrawn from the system, and solution being returned to the cone-bottom tank. Operators’ attention is only required to test the solution
for pH and Redox potential once or twice a day.

**Operating Costs Associated with the LO-CAT® Unit.**

There are two major sources of operating costs associated with a liquid redox process such as LO-CAT®. They being the costs related to chemical makeup and those related to power consumption. The major components of the power costs for the Suncor unit involved two, rotary lobe blowers (65 KW/each) used for blowing air into the process, and the major components of the chemical makeup costs are associated with iron and chelate makeup’s and caustic addition to the unit.

Chelates are water soluble, organic compounds which hold the iron in solution. By employing the proper chelate, the solubility of iron in water can be increased from a few parts per million to the 5 wt% range. The chelates will, over time, oxidize by a free radical mechanism and require replacement. The rate at which they oxidize can be controlled by utilizing a stabilizing agent, which acts as a free radical scavenger.

The LO-CAT® process utilizes a proprietary means of reducing chelate degradation. Within the process, a small portion of the H₂S is deliberately converted to thiosulfate ions (S₂O₃=), which are excellent free radical scavengers. In fact, many years of research by Gas Technology Products have failed to result in a better free radical scavenger. By being able to generate thiosulfate within the process, chelate replacement costs can be held to a minimum with minimal effort.

Iron is lost from the system by physically removing solution from the unit. For LO-CAT® systems with sulfur melters, the major means of iron lost is by the blowdown of solution from the unit to control solution specific gravity.
The specific gravity of a LO-CAT® solution is dependent upon the amount of salts, which are dissolved in the solution. Since LO-CAT® operates at relatively low iron concentrations, the chelated iron is not a major contributor to the density of the solution. This is in sharp contrast to other redox processes. In a LO-CAT® unit, the major contributors to solution density are carbonate/bicarbonate salts and thiosulfate/sulfate salts. Carbonate/bicarbonate salts are formed when gas streams containing CO$_2$ are being processed. Depending on the CO$_2$ partial pressure and the desired pH of the solution, CO$_2$ will develop equilibrium concentrations of carbonate and bicarbonate as follows:

\[
\begin{align*}
\text{CO}_2(\text{gas}) + H_2O(\text{aq.}) & \rightleftharpoons H_2CO_3(\text{aq.}) \\
H_2CO_3(\text{aq.}) & \rightleftharpoons H^+(\text{aq.}) + HCO_3^-(\text{aq.}) \\
HCO_3^-(\text{aq.}) & \rightleftharpoons CO_3^{2-}(\text{aq.}) + H^+(\text{aq.})
\end{align*}
\]

The equilibrium constants for each reaction are pH dependent, increasing with increasing pH. Although the Suncor LO-CAT® unit is
processing an acid gas stream containing a high concentration of CO₂, the system is operating at atmospheric pressure, which yields a relatively low CO₂ partial pressure. Consequently, the carbonate/bicarbonate concentrations in the solutions are also low.

As previously discussed, thiosulfate formation is desirable as a means of controlling chelate degradation. However, if solutions become too oxidizing (high oxidation/reduction potential), thiosulfate can be oxidized to sulfate, which has no beneficial value in the process. The formation of thiosulfate and sulfate occur as follows:

\[
\begin{align*}
2\text{HS}^{\text{aq.}} + 2\text{O}_2^{\text{aq.}} & \rightleftharpoons \text{S}_2\text{O}_3^{\text{aq.}} + \text{H}_2\text{O} & (10) \\
\text{S}_2\text{O}_3^{\text{aq.}} + 2\text{O}_2^{\text{aq.}} + \text{H}_2\text{O} & \rightleftharpoons 2\text{SO}_4^{\text{aq.}} + 2\text{H}^+^{\text{aq.}} & (11)
\end{align*}
\]

It is important to note that the above reactions (Rx 7 – 11) all produce acidic products (H⁺). Consequently, to maintain the solution in the slightly alkaline range, which is required to promote good absorption of H₂S, caustic in some form (KOH, NaOH or NH₃) must be added to the solution. The thiosulfate/sulfate salts also contribute to increasing the specific gravity of the solution.

If the concentrations of dissolved salts are allowed to increase unabated, a point will eventually be reached when one or both of two things will occur. First, the solution will become less capable of absorbing oxygen and H₂S, which will affect the ability of the process to remove H₂S from a gas stream, and second, the solution will eventually become saturated and salts will actually start precipitating from the solution resulting in plugging problems. To prevent this from happening, a small blowdown stream is taken. For systems, which have a filter for removing sulfur from the unit, a sulfur cake is produced, which usually contains sufficient solution to compensate for salt formation; however, in a system, which produces molten sulfur such as Suncor’s, a liquid blowdown stream is usually required. These blowdown streams represent a loss of iron from the process, which require makeup iron to be added.

Unless there is a hazardous or toxic component in the gas stream being treated, which is soluble in aqueous solutions, the blowdown liquid will be merely water containing dissolved salts; however, it will have a chemical and biological oxygen demand due to the chelates. Consequently, there is a cost associated with treating the blowdown stream. In Suncor’s case the blowdown is hauled away for remote treatment since there are no onsite wastewater treatment facilities.
**Suncor’s Optimization**

Prior to Suncor’s purchase of the Spirit River facility, little attention was given to the LO-CAT® unit. In general, over injecting chemicals into a LO-CAT® unit will not result in operating problems, just higher than required operating costs. Consequently, in remote gas plants such as Spirit River, it is sometimes difficult to convince operators to change operating conditions if the unit is not presenting any operating problems. However, this is not Suncor’s operating philosophy.

Upon taking ownership of the facility, Suncor contacted Gas Technology Products and stated that the operating costs associated with the LO-CAT® unit were not cost effective and something had to be done about chemical consumption, power consumption and the disposal cost of blowdown liquid or the unit would be shutdown. At this point, Suncor and Gas Technology Products started working closely together to optimize the system.

The Suncor LO-CAT® unit is operating at close to the design conditions of 123.4 Nm3/Hr of acid gas containing 57.5% H₂S (2.19 MT/day of sulfur). As suspected, an initial examination of the unit and a review of historical operating data show that the chemical addition rates were much higher than the original design rates, and that the operators were maintaining a lower solution specific gravity than required by maintaining a higher than normal blowdown rate. For example, the iron concentration was being maintained at more than twice the design level while the chelate concentration was more than three times the design level. In addition, the system was designed to operate with one air blower in operation; however, the unit was being operated with both air blowers in operation. These conditions resulted in a very positive, solution oxidation-reduction potential (redox potential), which promoted the formation of sulfate rather than thiosulfate resulting in a relatively high chelate oxidation rate. Consequently, this highly oxidized solution state resulted in high salt formation and thus a high blowdown rate to maintain the less than design solution specific gravity. Consequently, the high blowdown rate resulted in a high iron replacement rate and higher than required solution disposal costs. The unit was also experiencing symptoms such as occasional sparger plugging, which indicated that the solution was close to saturation.

The obvious remedy to Suncor’s problems was to get the solution chemistry back to a normal state. This was accomplished by discontinuing the chemical addition of the makeup chelate and the
makeup iron. In addition, one air blower was shutoff, thus immediately reducing power consumption by 50%. During this period, GTP monitored the solution chemistry on a biweekly basis. Over a relatively short period of time, the iron, chelate, and stabilizer concentrations and the solution specific gravity were bought into line. At this time, the chemical addition and blowdown rates were re-established, but at rates corresponding to actual processing conditions of the unit. When the unit was operating at design conditions, power consumption, chemical costs and disposal costs were reduced by approximately 50%, thus achieving operating costs, which were in line with Suncor’s requirements. In addition, problems with sparger plugging were greatly reduced. All of these reductions were achieved while maintaining an H₂S removal efficiency of greater than 99.99+%. Table 1 summarizes the before and after operating costs.

<table>
<thead>
<tr>
<th>Table 1 OPERATING CHANGES</th>
<th>Before changes</th>
<th>After changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas to plant, MMCFD</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Sulfur removed, metric ton (MT)/day</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Operators</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Blowers operating</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Chemical use, $US/MT sulfur</td>
<td>~300</td>
<td>~150</td>
</tr>
<tr>
<td>Power, kW</td>
<td>139.7</td>
<td>74.7</td>
</tr>
</tbody>
</table>

It is important to note that these cost savings were obtained by simply turning pumps and blowers off. No daily detailed chemical analyzes were required, just simple redox potential, pH and specific gravity readings. And although it took years to get the LO-CAT® solution in a state of near saturation, the situation was remedied in a matter of weeks.

Although dramatic reductions in chemical costs were achieved at the Suncor facility, even more chemical savings can be realized in more modern LO-CAT® units due to the ability to more accurately control thiosulfate concentrations.

**Conclusions**

A determined commitment to teamwork by Suncor and Gas Technology Products has resulted in a significant reduction in plant operating costs in the LO-CAT® unit while maintaining high H₂S removal efficiency and ease of operation. As summarized by the plant
operation staff—“Chemical consumption and cost savings are important to Suncor. The ultimate is to remain emission free while running as economical as possible. This process can run emission free which will in turn guarantee the safety of the plant operators and our environment.”
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Products: Gas Technology Products provides a full line of complementary hydrogen sulfide oxidation products: LO-CAT® and LO-CAT® II, Sulfur-Rite® and The Eliminator™ processes, along with its ARI®-100 mercaptan oxidation products and engineering services. GTP offers both liquid and solid media desulfurization technologies to sweeten gas streams and ventilation air containing virtually any levels of hydrogen sulfide or mercaptans – for systems of widely ranging capacities. For any size or type application, GTP offers complete turnkey systems and can take total system responsibility. As a wholly owned subsidiary of Merichem Chemicals & Refinery Services LLC, Gas Technology Products LLC is a part of a fully integrated organization with unmatched technical knowledge, applications expertise, and worldwide service coverage.