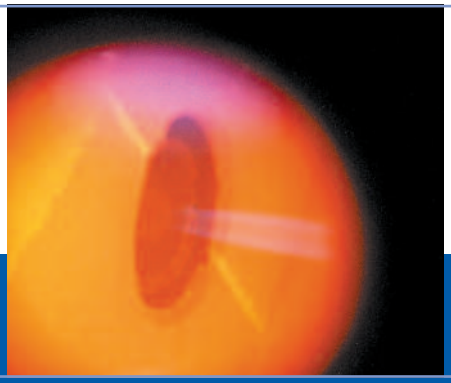
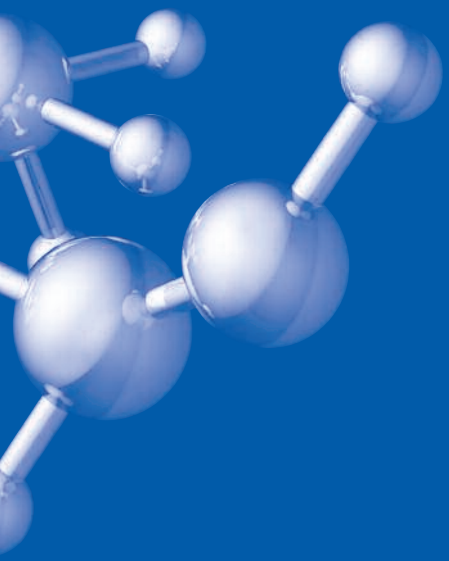
AIR LIQUIDE

Lurgi





The Rectisol® Process

Lurgi's leading technology for purification and conditioning of synthesis gas

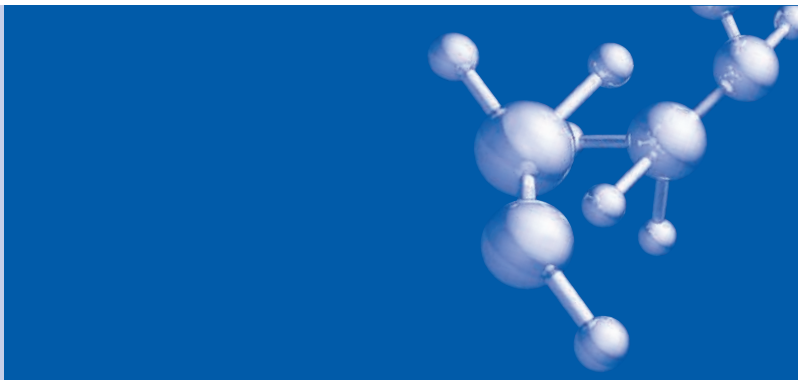
History

In 1955 Rectisol® began its first commercial-scale installation in Sasolburg, Republic of South Africa. During the following decades, Rectisol® paved the way for huge-scale ammonia and Fischer-Tropsch synthesis. In the 1970s and 80s, oil residue gasification was added as yet another field of application. Today, more than half a century later, Rectisol® is still unique worldwide in obtaining synthesis gas quality using a single process. A series of new, alternative technologies have now appeared on the market for the "easy" removal of sulfur compounds and CO_2. However, Rectisol® is still the only process that deals with all the raw gas contaminants related to coal and oil gasification. These are sometimes present in very small quantities such as parts per billion (ppb) in raw syngas.

Because of this, the comeback of coal gasification technology in the last decade corresponds with an impressive boost in performance of Rectisol® plants: nearly all coal gasification units used in the production of ammonia, methanol, hydrogen or synfuels are or will be equipped with a Rectisol® gas purification system.

As we begin the new millennium, the purification of syngas produced by the gasification of heavy oil residue from oil shale or oil sands represents a new field of application alongside the "classics" coal, lignite and refinery residue gasification.

Through continuous improvement, Lurgi Rectisol today is here to serve your needs in the most competitive way ever and is working to maintain its outstanding position in the future!



Performance

The main useful components of a raw syngas gas produced by heavy oil or coal gasification are H_2 and CO. Depending on the feedstock and type of gasification process, this raw gas may contain 3–40 % CO_2 as well as smaller proportions of CH_4, H_2O, N_2 and Ar. H_2S, COS, HCN, NH_3, nickel and iron carbonyls, gum formers, CS_2, mercaptans, naphthalene, thiophenes, organic sulphides, and higher hydrocarbons may all be present as trace contaminants.

In order to obtain the gas quality needed for use as a feedstock for a synthesis process (e.g. ammonia synthesis, methanol synthesis, Fischer-Tropsch synthesis, oxo-alcohol synthesis or simply as a hydrogen product, reduction gas or town gas), these impurities must be removed. This is especially true for the trace contaminants which have to be eliminated.

Typical purity requirements for synthesis gas:

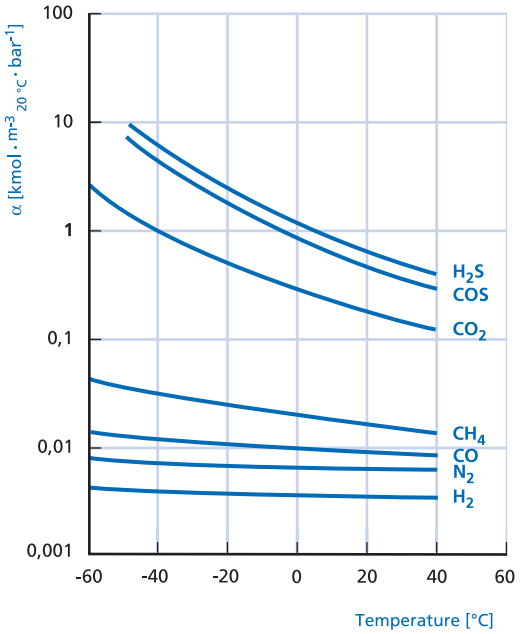
- Total sulfur — less than 0.1 ppm by volume
- CO_2 — 2 ppm to 3 % by volume depending on the type of synthesis

Sulfur compounds, HCN and NH_3 should be discharged in a stream as concentrated as possible so as to improve the economics of subsequent treatment. The CO_2 must be sufficiently clean to allow it to be discharged directly into the atmosphere or even used as a product.

The CO_2 separated from the gas may be a mixture with nitrogen when it is vented into the atmosphere. If the CO_2 is used as a feedstock for another process (e.g. in a urea synthesis or for the production of food grade CO_2), the CO_2 must be partially or completely recovered as a highly concentrated, pure and dry product stream. The permissible residual H_2S content for both cases typically varies in a range of 5–25 ppmV.
To summarize, the following functions must be met by the gas purification system:

- Trace contaminant removal
- Deep de-sulfurization incl. COS (no hydrolysis needed)
- Drying
- Bulk CO_2 removal
- CO_2 purification
- Acid gas enrichment

Where other approaches may have a number of separate processes, Rectisol technology provides an excellent option to use only one integrated technology and plant which yields excellent results in performance and reliability. Lurgi's outstanding track record and experience offers a broad range to help optimise your gas cleaning problems with CAPEX and OPEX.



Absorption coefficient α a of various gases in methanol (partial pressure: 1 bar)

Rectisol has been successfully applied for purifying syngas produced by:

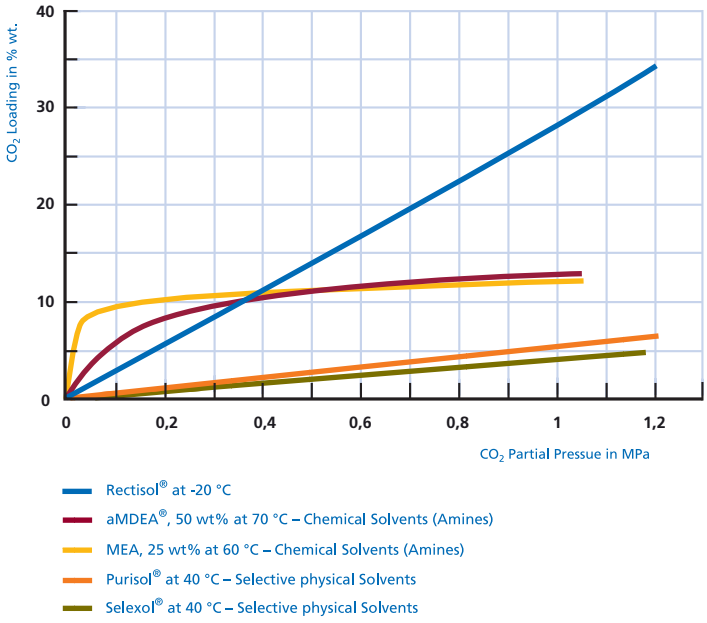
- Sasol/Lurgi Fixed Bed Dry Bottom Coal and Lignite Gasification
- Lurgi British Gas BGL Coal gasification
- Lurgi MPG Heavy Oil Gasification
- Shell Oil Gasification
- Shell Coal Gasification
- GE (former Texaco) Oil & TAR Gasification
- GE (former Texaco) Petcoke Gasification
- Reformed gas from natural gas reformers

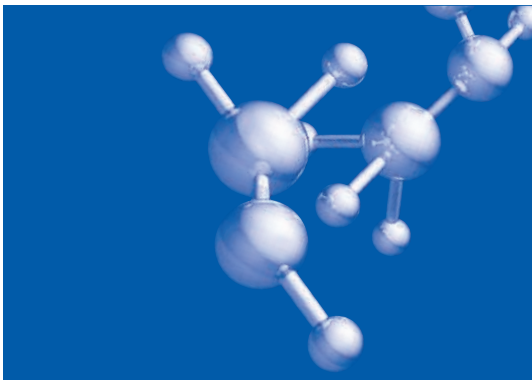
Process Principle

Rectisol uses refrigerated methanol as the solvent for physical absorption. Unwanted raw gas components, such as CO_2, H_2S, COS and the remaining sulfur compounds, HCN, NH_3, as well as nickel and iron carbonyls are physically absorbed from the raw gas by the solvent. These components are then desorbed by reducing the pressure of the solvent, stripping and, if required, reboiling the solvent. The higher hydrocarbons so absorbed are recovered in an additional extraction stage, if needed.

The solubility of the different components to be removed, varies considerably. This also applies to H_2S and CO_2 and allows selective removal of these components. The solubility data of the various gases in methanol is illustrated above.

Since the solubility data of H_2S and the organic sulfur compounds is appreciably higher than that of CO_2, the H_2S concentration in the Claus gas can be increased to accept-



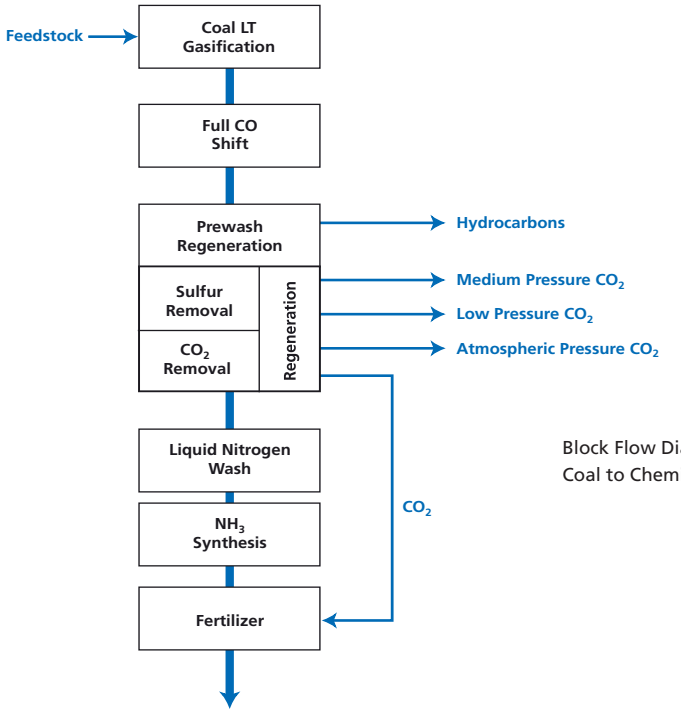


CO_2 Bulk Removal capacity of different types of solvents

able levels even if the H_2S to CO_2 ratio in the raw gas is unfavourable. The solubility of the trace components HCN, NH_3 and sulfur compounds like mercaptans is much higher than that of H_2S. This makes it possible to remove them separately using a very low solvent rate in a prewash stage. The rich methanol from this prewash stage is regenerated by integrating this loop into the H_2S hot regeneration system so that these trace components are routed directly to the Claus gas. Rectisol is also excellent in separating large amounts of CO_2 from the gas. At CO_2 partial pressures – due to high concentration in the feed gas and/or due to high gasification pressure – the absorption capacity of low temperature methanol exceeds that of any alternative solvent.

The process is extremely flexible – a feature that permits it to be tailored to a large number of different individual applications.

One possible arrangement starts with the gasification of heavy oil using the Lurgi Multi Purpose Gasification Process (MPG®). The example focuses on the production of methanol. On page 8, we show a simplified process flow chart for this method. In this example, the gas train is equipped with a clean gas shift, integrated in the Rectisol system. Methods where a raw gas shift is installed upstream of the Rectisol unit are also possible and demonstrated in various ways.



Block Flow Diagramm
Coal to Chemicals

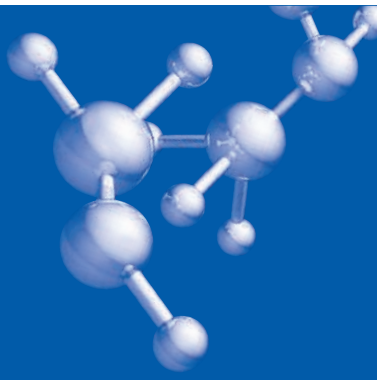
Process Description

The raw gas entering the plant is cooled. The trace components like HCN and NH_3, are removed in the prewash stage with cold methanol.

Next the sulfur is removed from the gas using CO_2-loaded solvent resulting in a residual sulfur content of below 0.1 ppm. The solvent from the H_2S absorber is regenerated first by flashing at medium pressure to recover the useful gases (H_2 and CO) and then by heating to boiling temperature and stripping with methanol vapour. In cases where there is sufficient H_2S in the raw gas, hot regeneration produces a Claus gas with adequate H_2S content for further treatment without any additional measures needed. Where the H_2S content of the raw gas is lower or the CO_2 content higher, an additional stage, stripping and reabsorption, must be carried out.

The portion of the clean gas which has been shifted in the CO shift conversion unit exhibits a typical CO_2 content of 33 %. This gas re-enters the Rectisol unit, is cooled, and the CO_2 is removed in a two-stage CO_2 absorber. In the lower section, the CO_2 content of the gas is reduced to about 5 % using flash-regenerated methanol. The remaining CO_2 is removed using hot regenerated, cold methanol in the upper section so that about 3 % CO_2 is contained in the synthesis gas.

The flashed CO_2 is free from sulfur and may be discharged directly into atmosphere. Under certain circumstances a water wash system may be necessary to further reduce the residual content of methanol in the CO_2 for environmental reasons. The system's refrigeration balance is maintained by the refrigeration unit.



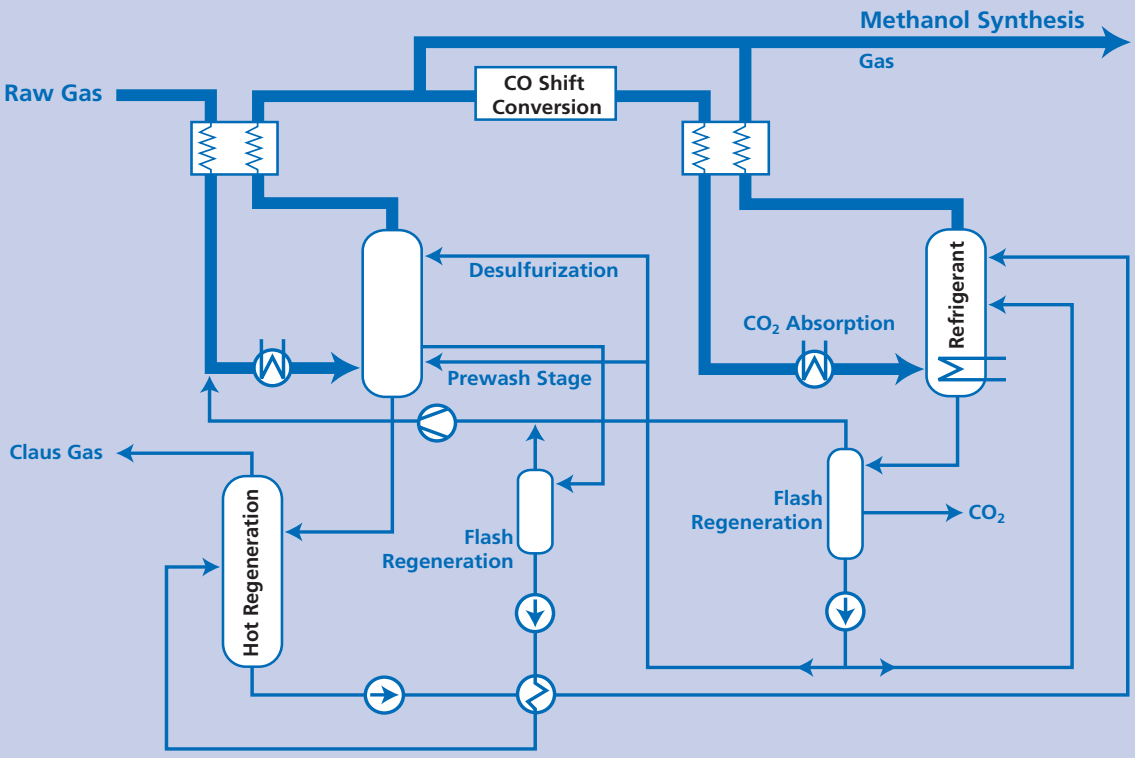
As the raw gas usually is saturated with water, a small portion of water is fed to the plant and is also completely absorbed by the solvent. The water content of the solvent is kept at the desirable low level by continuously distilling a small side stream of the solvent circulation in a methanol/water distillation column. This step is not illustrated in the chart. An important feature of Rectisol is that this water leaves the distillation as the bottom product, carrying heavy boiling trace contaminants, salts, other trace contaminants and/or even Ni and Fe sulphides formed through decomposition of carbonyls, if present, into the raw gas. Nevertheless, as the concentration of such components is small, the water can be routed directly to a biological treatment.

Utility Consumption (typical)

Reference is made to a 2,000 metric tons per day methanol plant.

- Electric power (without refrigeration unit) 990 kW
- Low pressure steam 5,100 kg/h
- Cooling water 275 m^3/h
- Refrigeration duty (boiling temperature: –38 °C) 1,5300 kWth

Selective desulfurization and CO_2 removal to produce methanol synthesis gas



Other applications

This method can be modified for the production of pure gas streams meeting other product requirements. This could primarily be the stoichiometric ratio between H_2 and CO in the product gas, required the type of downstream synthesis process, or purity requirements for certain components. Basically, one single Rectisol method could provide the complete product range simultaneously, although usually only one or two products are needed.

Clean Coal Technologies, Carbon Capture & Storage

In the last decade, the world has experienced a revival of coal as a raw material. It is used for the production of chemicals, petrochemicals and even substitute natural gas (SNG). Clean coal technology (CCT) allows for the processing of coal in an environmentally-friendly manner, thereby challenging the general perception of coal being a source of "dirty" energy.

As a major consequence of the Kyoto protocol, CO_2 emission reduction will be a vital issue – talking about coal, Carbon Capture and Storage (CCS) is the key here. On one hand, CCS has the potential to solve the controversy caused by the trend back to coal and on the other, the possibility of reducing global CO_2 emissions suggested in the Kyoto protocol.

Rectisol is a key technology for both CCT as well as CCS: The most promising course for the CO_2 emission-free production of electricity from coal, lignite, oil residue, biomass and waste is a Zero Emission Integrated Gasification Combined Cycle (ZE IGCC). In a ZE IGCC, CO_2 can be separated in a neat manner and easily prepared for underground storage so that the efficiency can be increased.

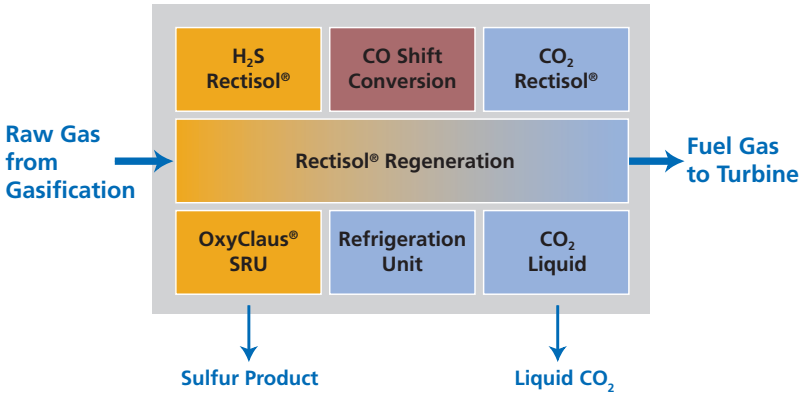
In the COORIVA project, founded by the BMWA, a consortium of leading German utilities and engineering companies, develops the German ZE IGCC, fuelled with lignite or hard coal. It will enable to generate CO_2 emission-free power from coal in a very efficient and environmentally friendly manner. Contributing its excellent capabilities with respect to trace contaminants, bulk CO_2 removal and overall reliability, Lurgi Rectisol is the key technology in the "Fuel Gas Conditioning", provided by Lurgi, allowing to produce the CO_2 in the purity and quality needed for safe storage or other usage, as for example, the Enhanced Oil Recovery (EOR). The Lurgi OxyClaus® sulfur plant is integrated in such a way with the Rectisol system that no further source of emission exists apart from the nearly CO_2-free exhaust gas of the power island. Aside from the hydrogen fuel gas fed to the gas turbine and the pure, dry, liquid CO_2 produced, the only co-product is saleable "bright yellow" sulfur.

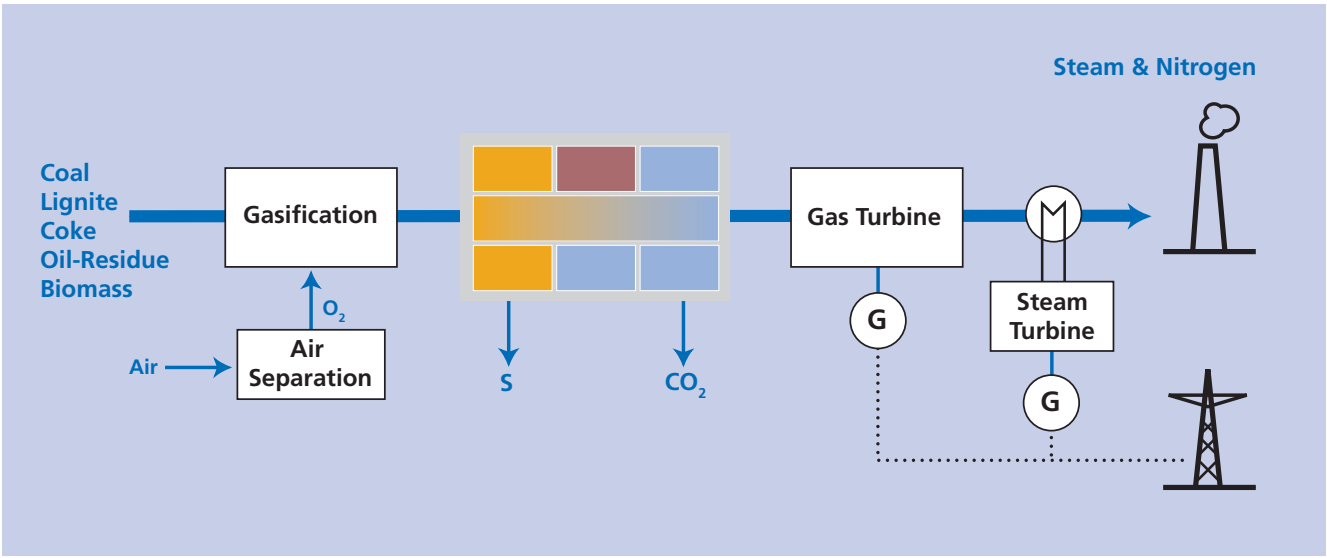
The emission-free gas conditioning concept of the COORIVA ZE IGCC can be easily transferred to every coal or oil residue gasification based project, whatever the usage of the purified syngas. Thus, the ZE IGCC is only one example of a whole family of Zero Emission Syngas Technologies (ZEST), taking care of today's energy and product demands and tomorrow's climate.

Technological Highlights of Rectisol

- Track record of <85 plants, proven reliable since 1949
- Removal of all impurities and trace contaminants in one single absorption process
- Ultra-pure product gas: e.g. total sulfur <0.1 ppmV, CO_2 <2 ppmV
- Tailor-made stoichiometrics for any kind of synthesis either with raw gas shift or integrated clean gas shift
- Multi-product application possible in one single unit, e.g. methanol-syngas plus ammonia syngas plus hydrogen plus IGCC fuelgas
- All gaseous products are completely dry
- Optimised energy consumption by cheap flash regeneration and/or nitrogen stripping to the extent possible
- Production of suitable Claus-gas possible with CO_2/H_2S ratio in the raw syngas up to 700
- A pure CO_2 product stream, ready for Enhanced Oil Recovery, underground storage or chemical usage can be produced
- Inexpensive, thermally and chemically-stable solvent available worldwide anywhere

No degradation, no corrosion, no disposal problems.





Zero Emission IGCC with integrated Rectisol based "fuel gas conditioning"

Lurgi is a leading technology company operating worldwide in the fields of process engineering and plant contracting. Based on syngas, hydrogen production and clean conversion technologies for fuels or chemicals Lurgi offers innovative solutions that allow the operation of environmentally compatible plants with clean and energy-efficient production processes.
Its technological leadership is based on proprietary and exclusively licensed technologies which aim to convert all carbon energy resources (oil, coal, natural gas, biomass, etc.) in clean products.

Lurgi is a member of the Air Liquide Group.

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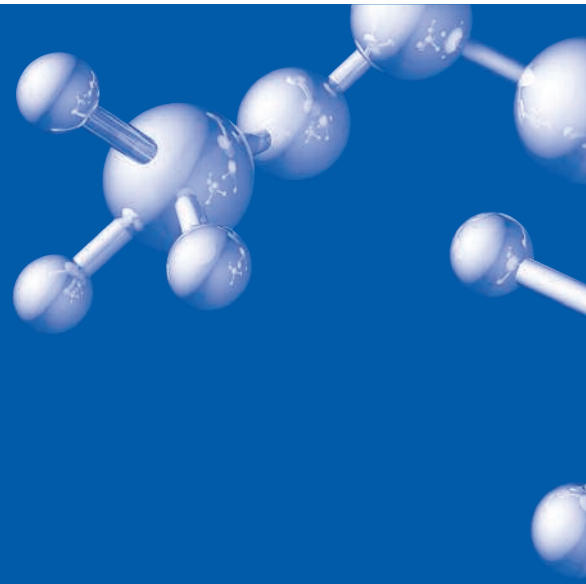

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