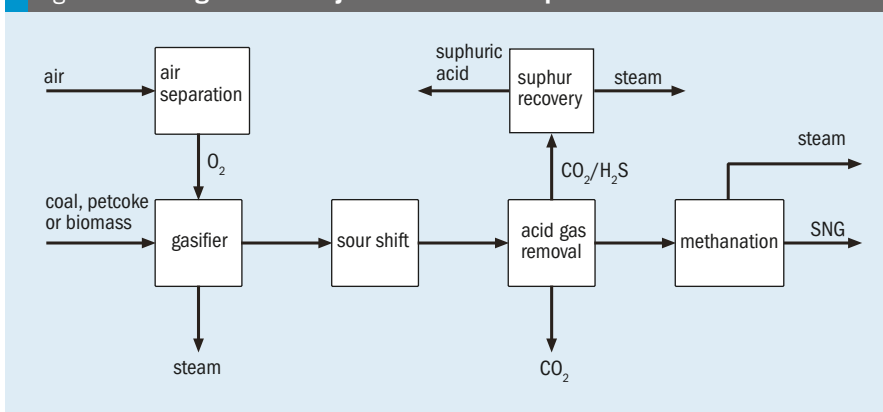


Fig 1: Block diagram with major units of the SNG plant



From coal to clean energy

Converting even low grade coal to clean Substitute Natural Gas (SNG) is not only feasible but highly attractive from the perspectives of the environment, security of energy supply, use of available (domestic) resources and economics.

J. H. Jensen, J. M. Poulsen and N. U. Andersen of Haldor Topsøe A/S highlight the inherent challenges in SNG methanation and suggest solutions to them.

As the world economies recover from the downturn, the energy demand equally grows. Natural gas is an attractive energy source, being clean and easy to distribute, and natural gas demand is predicted to grow at a higher pace than general energy demand growth.

Natural gas production has been increasing in some regions through advances in technology. However, some of these unconventional methods are expensive, and not all countries can increase supply sufficiently. They become increasingly dependent on pipeline supplies and expensive LNG, which raise questions not only regarding cost, but also in terms of energy independence and security of supply.

Coal is abundant, easy to ship, and some countries with few natural gas resources are rich in coal.

Modern coal gasification and SNG methanation technologies constitute an excellent opportunity to address energy and environmental challenges in an economically attractive way.

Two SNG plants based on coal gasification are currently under construction using Haldor Topsøe technology: POSCO in Korea and Qinghua in China. Additionally, two plants based on biomass gasification are currently in progress based on Haldor Topsøe technology: GoBiGas is under construction and EON is in study phase. Both plants are located in Sweden. More plants based on coal, biomass and other feeds are in the pipeline.

Fundamentally the technology is not new. Haldor Topsøe initiated research and development in this field back in the 1970s. Political changes led to a long dormant period but within the last five years, the interest in substitute natural gas has become strong. Haldor Topsøe has reinitiated its efforts in the technology, and the knowledge gained over the years has been used to refine the tried and tested technology and catalyst. As a result, an updated version with improved efficiencies and lower investment cost is now being offered to the market.

SNG plant overview

Figure 1 shows a block diagram with major units of the SNG plant.

Gasification, at least from coal, is not new. The feedstock is initially gasified in the presence of O₂ and H₂O. The gas is then cooled and cleaned for tars, salts and dust. Different types of gasifiers exist, and basically three different types are available for syngas generation for SNG plants: fixed beds, fluid beds and entrained-flow gasifiers¹. The choice of gasifier is dependent on feedstock type and quality.

The ratio between H₂ and CO is adjusted in the sour shift by the water gas shift reaction. A sulphur resistant catalyst, such as Haldor Topsøe SSK-10 catalyst, is utilised for this.

The syngas coming from the sour shift is rich in sulphur (H₂S) and CO₂. As sulphur is a poison to the methanation catalyst and in any case unwanted in the product, it has to be removed.

In order to reach the right hydrogen to carbon ratio, as described later in this article, most of the CO₂ is to be removed. The removal of H₂S and CO₂ is done in the acid gas removal (AGR) unit. CO₂ from the AGR can be sequestered or used for other purposes.

The sulphur in the stream from the AGR can be recovered in a sulphur recovery unit. This could be a traditional Claus unit producing elemental sulphur or a Haldor

What is SNG?

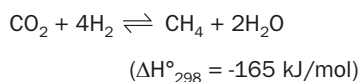
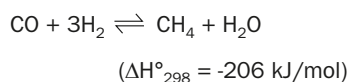
SNG or Substitute Natural Gas is a high-methane replacement for natural gas. Typically, the methane content of the gas is above 90%, with the rest being inerts nitrogen and argon, and limited levels of H₂, CO and CO₂. SNG can be used on-site (re-fuel), fed into a natural gas pipeline or be liquefied into LNG. It is a direct replacement for natural gas.

Topsøe WSA unit, where H_2S is converted into sulphuric acid, which is a high value product in many regions².

Methanation plant overview

Methanation has been used for years as the final purification step in ammonia plants (and formerly also in H_2 plants), but methanation for SNG production is at a different level due to the higher content of CO and CO_2 .

CO and CO_2 are hydrogenated according to the methanation reactions, both favoured by low water content and high pressure:



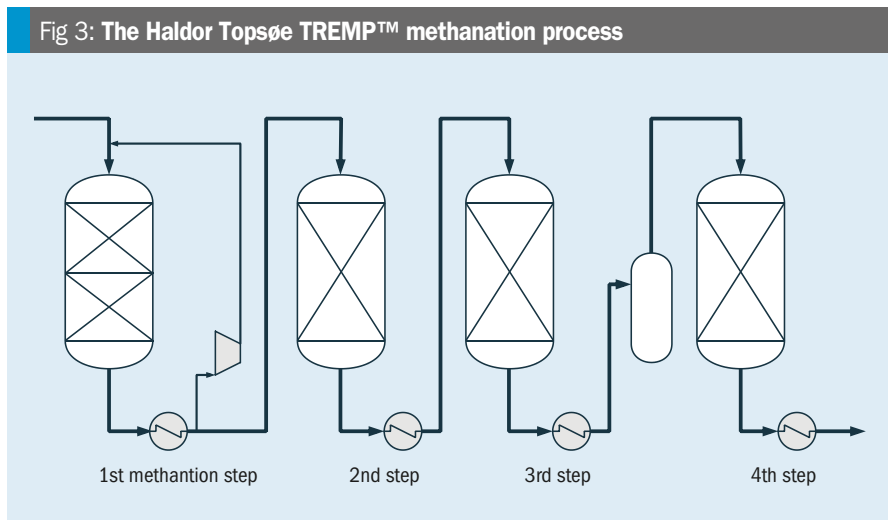
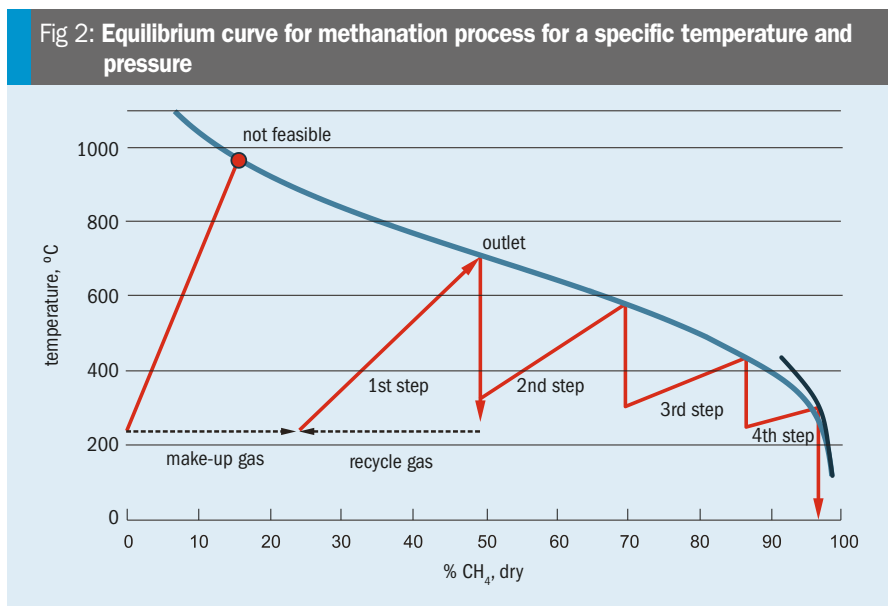
Since the methanation reactions are reverse reforming reactions, and as the reforming reactions are strongly endothermic, it follows that they are strongly exothermic.

There are many similarities between reforming and advanced methanation. Both utilise nickel catalyst and many of the same challenges are present in both processes. Knowledge of reforming is, however, just the starting point of advanced methanation.

Worldwide there are currently no industrial SNG plants that are operated at the high temperatures required by an energy efficient design (620-750°C).

The high potential adiabatic temperature increase is a challenge since it requires a high-temperature stable catalyst that also has a high activity at low temperatures. If syngas with a minimum methane level is introduced to an adiabatic methanation reactor at 300°C, the reaction may reach temperatures above 900°C. This could in principle be handled by using traditional reforming catalysts, but due to challenges with respect to material selection and insufficient catalyst activity³, this is not feasible. Instead, the strong exothermic reactions have traditionally been handled by having a high recycle and thus diluting the inlet gas in order to keep the temperature below 450°C.

The disadvantage of recycling effluent is the necessity of compression and increased volumetric flow in the first methanation step. Compressors are expensive items of equipment, require power, special housing, main-



tenance, etc. To minimise compression cost it is beneficial to minimise the recirculation flow and the compression ratio and, in order to minimise the recycle flow, a higher temperature increase must be accepted. This can be obtained by either reducing the inlet temperature or increasing the outlet temperature, or by applying both.

If the recycle of the methanation is controlled to limit the outlet temperature to 700°C, the conversion is still not enough to reach a sufficient product quality for an efficient process. As seen from the example equilibrium curve in Fig. 2, low temperatures favour high conversion of CO and CO_2 . Thus to reach CH_4 levels of 95-98%, it is therefore necessary to use several methanation steps in adiabatic reactors operating at decreasing temperature levels and split by intermediate cooling. Depending on required product quality, the final reactor

is operated at temperatures around 200-300°C. The number of reactors is a result of an optimisation based on requirements of product gas quality and heat recovery.

Besides reducing the recycle, a high methanation temperature also offers potential for high-pressure steam production and superheating. Complete excess heat utilisation can be achieved by DMW and BFW preheating at lower temperature methanation steps.

TREMP™ methanation technology

TREMP™ is the Haldor Topsøe proprietary methanation technology (see Fig. 3). The TREMP™ technology addresses the essential question of minimum recycle cost and heat recovery in the most efficient manner by recovering the heat as high-pressure superheated steam.

Based upon the limitations and opportunities mentioned, the TREMP™ was improved as illustrated. The feed is first passed through a sulphur guard bed for removal of traces of sulphur components that have not been picked up by the upstream acid gas removal unit. The desulphurised feed is then mixed with recycle gas to control the maximum temperature rise and passed to the first methanation reactor.

The exothermic methanation reaction results in a high outlet temperature, which allows the reaction heat to be recovered for generation of superheated high-pressure steam in the downstream heat exchangers. After cooling, the partly methanated syngas passes through two or three additional methanation reactors in series for complete conversion of the CO into methane. The number of methanation reactors will depend on the operating conditions, such as pressure, as well as the SNG product specification. Before the last methanation step, the water generated in upstream methanation steps is removed in order to push the equilibrium further towards methane production. The process stream leaving the last methanation reactor is cooled, dried and compressed to meet the pipeline specifications or LNG production requirements. The methanation reaction is favoured by high pressure, and works well with syngas from all types of coal or biomass gasifiers.

Operating parameters and catalyst aspects

As mentioned above, it is considered beneficial to operate the first methanation step with a maximum temperature increase in order to limit the recycle as much as possible. With a superior catalyst system, it will be possible to reduce or even eliminate the recycle. This can be a catalyst either allowing a lower inlet temperature or being stable at higher outlet temperatures.

Low temperature operation

At low inlet temperatures (200-300°C), the challenge with a Ni-based catalyst is that with the high CO content there is affinity towards nickel carbonyl formation⁴ and the poisoning becomes much more severe as the sulphur coverage of the catalyst increases with decreasing temperature⁵. In addition, the combination of low temperature and high CO partial pressure may cause relatively fast deactivation, also known as β -deactivation. Instead of being hydrogenated to methane, the adsorbed intermediate α -carbon reacts forming an inactive intermediate encapsulating the



MCR-2X Catalyst. The “heart” of the TREMP™

The research & development activities at Haldor Topsøe have led to the development of the proprietary MCR catalyst. The MCR catalyst is based on a ceramic support with a stabilised micropore system, which effectively prevents sintering of the nickel crystals. The resulting high nickel surface area results in the desired high methanation activity even at relatively low temperature. The MCR-2X catalyst has been thoroughly tested in several tests and large demonstration programmes with a total of more than 45,000 operating hours in the temperature range of 600-800°C.

Transmission electron microscopy is a powerful tool for understanding heterogeneous catalysis.



Demonstration plant in Jülich “ADAM” The MCR catalyst was already used in the plant of Jülich, in Germany in the 1970-80s, with a commercial use of the produced SNG. The plant had a capacity of 48,000 Nm³/d (as SNG) and it was operated stably with an exit temperature more than 700°C. The MCR catalyst was operated for more than 8,000 hrs until it was decided to cease operation as a consequence of the decreasing price of natural gas following the oil crisis in the 1980s.

Ni crystal, causing loss of the activity³. In summary, a Ni-based catalyst will have an unacceptable short lifetime at temperatures in the range of 200-300°C for the first methanation steps.

In order to maximise the temperature increase across the first methanation steps in the TREMP™ process, a combination of a non-Ni catalyst and an Ni catalyst is used allowing the inlet temperature to be as low as 220°C against 320°C traditionally used.

High temperature operation

At higher temperatures the sintering of the Ni crystals need to be restricted in order to ensure sufficient activity of the aged catalyst. This requires a stable support and restriction of nickel crystal growth. The sintering process follows two different paths at different temperature levels. At lower temperature, the sintering is following the particle migration mechanism (particles migrate over the carrier surface and coalesce) and at higher temperature atoms (or small agglomerates) migrate from one particle to another particle (atom migration mechanism). The type of migration mechanism affects the loss of activity, and the atom migration mechanism causes an activity loss which cannot be explained only by reduction of loss of surface area but may be related to a change in the structure of the surface. The cross-over temperature between the two mechanisms is typically in the temperature range of 500-600°C⁶. On this basis it is important to restrict the sintering – especially above the cross-over temperature.

At temperatures above 550-650°C thermodynamical potential for carbon formation (“whisker carbon”) exists but it is known from the reforming catalysts that the size of the Ni crystals affects the whisker carbon growth rate⁷. The extensive knowledge of the reforming catalysts and the means (including catalyst production methods) for eliminating whisker growth causing catalyst disintegration has been used in connection with the development of methanation catalysts and determination of optimum operating parameters.

The stoichiometric ratio – “feed gas module”

In order to achieve a product with as high methane content as possible it is important that the feed gas for the methanation section should have a composition with

the correct ratio between the reactants, i.e. CO, H₂ and CO₂

The predominant methanation reaction is normally the methanation from CO, and from the reaction equation it is seen that the stoichiometric ratio between H₂ and CO is 3. However, in order to take into account the content of CO₂ in the feed gas for the methanation, the “feed gas module” has been developed:

$$M = \frac{X_{H_2, \text{ feed}} - X_{CO_2, \text{ feed}}}{X_{CO, \text{ feed}} + X_{CO_2, \text{ feed}}} = 3$$

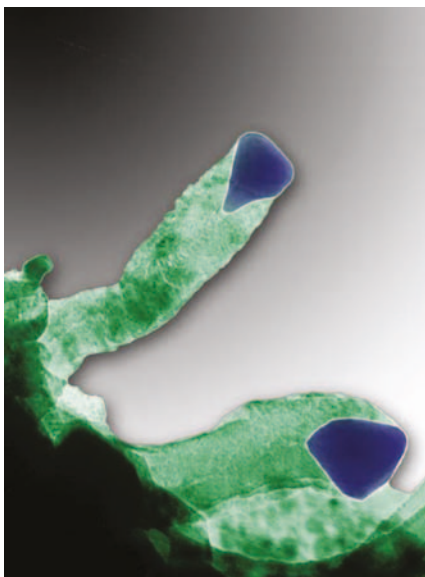
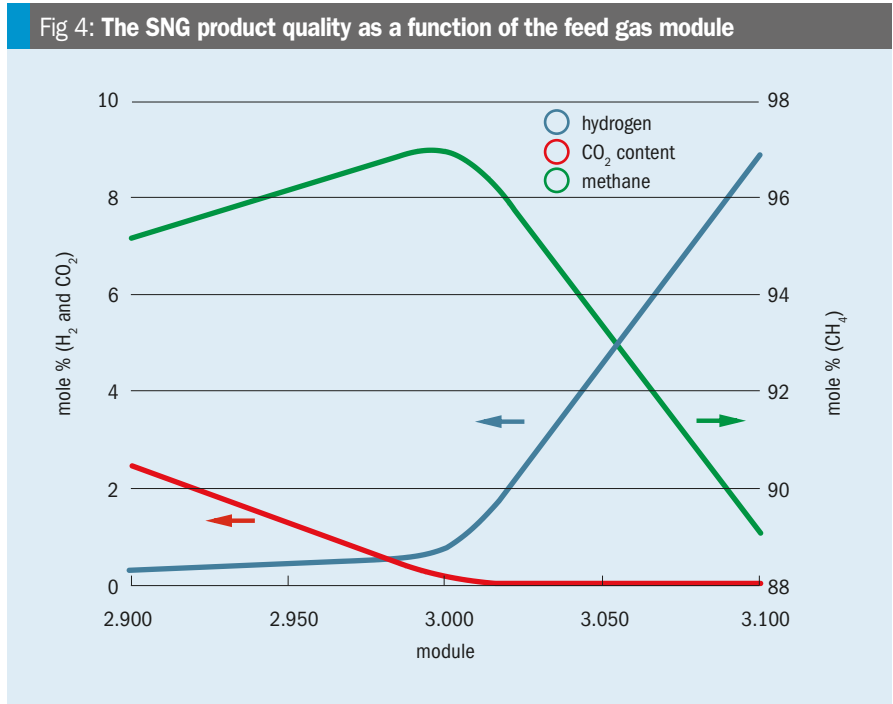
The basis for the module is to have a measurement for the most optimum feed gas composition. As the module is defined from a stoichiometric ratio for the methanation reactions, it will be unchanged throughout the methanation section. However, as the methanation section “amplifies” the offset in module, a small variation in the ratio of the reactants in the feed gas results in a large variation in the product SNG composition. In Fig. 4 the effect on CH₄, H₂, and CO₂ contents in the SNG product is seen. In Table 1, examples of feed gases with modules from 2.90 to 3.10 are shown.

Module control

The module of the gas to the methanation unit is controlled by adjusting the by-pass of the sour shift unit. By increasing the by-pass, less CO and water is converted into H₂ and

Table 1: Typical feed gas compositions for different modules

Module	2.900	2.980	3.000	3.020	3.100
H ₂ , mol-%	74.17	74.68	74.80	74.92	75.40
CO, mol-%	24.23	23.72	23.60	23.48	23.00
CO ₂ , mol-%	1.00	1.00	1.00	1.00	1.00
CH ₄ , mol-%	0.10	0.10	0.10	0.10	0.10
Ar + N ₂ , mol-%	0.50	0.50	0.50	0.50	0.50
Total	100.00	100.00	100.00	100.00	100.00



Whisker carbon formed on Ni crystal. In order to avoid detrimental growth of the whiskers, catalysts with high surface area and with low tendency to sintering are used to be able to operate deep into an area with thermodynamical potential for carbon formation

CO₂ through the water gas shift reaction. This does not affect the module but, as the CO₂ is removed downstream in the AGR to an almost constant level, the module will decrease when the sour shift by-pass is increased. As the content of CO, CO₂, and H₂ is consumed in the methanation unit and due to the fact that the gas volume reduces as the methanation reactions take place, even small variations in the feed gas composition during normal operation will disturb the SNG product quality. In some cases, it may be difficult to control the feed module within the limits required to obtain the quality of the SNG.

A solution to this can be to make the final module adjustment in the TREMP™ unit by adding a minor stream rich in one of the reactants (normally CO₂ or H₂) in the last methanation reactors and in this way fine-tune the module utilising the “amplification” of the module off-set in the methanation unit⁸. In this way, the quality of the SNG product gas can be kept within strict requirements, e.g. in connection with LNG production.

Heat integration

As discussed earlier, the methanation reactions are exothermic, i.e. heat evolves as the reactions take place. For a typical feed gas composition as given in Table 1, the heat evolved in the TREMP™ section corresponds to approximately 2,560 kcal/Nm³ SNG or, theoretically, 3.2 kg superheated high-pressure steam (10 MPa g, 540°C) per Nm³ SNG. In order to utilise the heat evolved in the optimum way, it is preferable to produce a “by-product” – superheated HP steam - with the highest potential. Having a high outlet temperature from the methanation reactors allows production and superheat of steam at high pressure and especially high temperature from a large fraction of the waste heat from the methanation reactions (typical split shown in Fig. 5) High pressure and high steam superheat temperature give the highest efficiency of the turbines utilising the steam.

Apart from the same issues with respect to high temperatures and high pressure on

Fig 5: Typical heat recovery in the TREMP™ unit

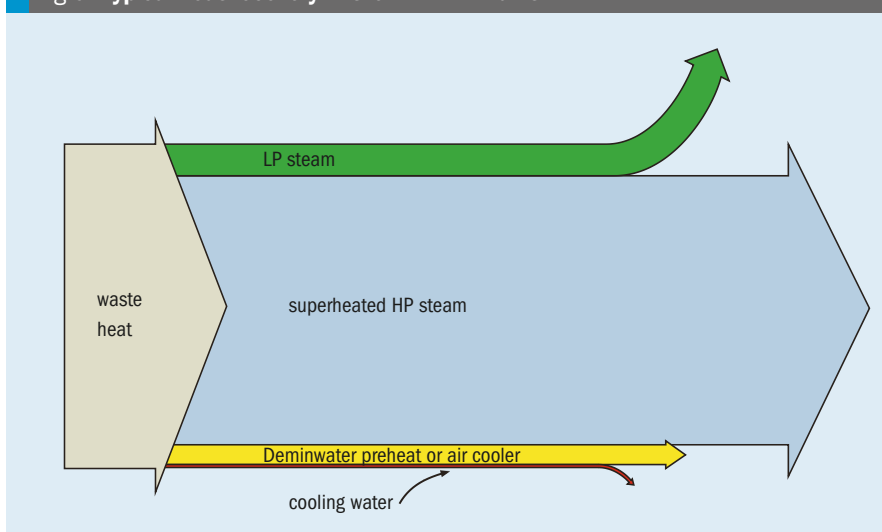


Table 2: Typical SNG product quality and ISO requirements¹⁰ to natural gas

	Typical composition	ISO 13686:1998
CH ₄ , mol-%	97.93	-
CO ₂ , mol-%	0.16	-
H ₂ , mol-%	1.36	-
CO, mole ppm	11	-
N ₂ + Ar, mol-%	0.53	-
Gross calorific value (HHV), MJ/m ³	39.0	30.2-47.2
Wobble index, MJ/m ³	51.6	46.1-56.5
Relative density	0.57	0.55-0.70

the steam side which are already known from the power plants, the heat exchangers used for steam production and steam superheat in the methanation section are also exposed to high pressure on the process side and a chemical composition giving challenges with respect to metal dusting. Metal dusting is a corrosion phenomena taking place in atmospheres with a significant CO partial pressure and metal temperatures typically in the range of 450-650°C (the range depends on the gas composition). In the waste heat boilers and in the steam superheaters, parts of the metal surfaces will pass through this temperature range, and it is important that the designers and manufacturers of this equipment have a thorough knowledge of the metal dusting. In the waste heat boilers, the metal areas exposed to temperatures in the critical range will be limited due to the fact that the boiling ensures a high heat transfer coefficient ensuring that most parts of the exchanger are operating close to the boiling point, i.e. typically below 350°C.

For the steam superheater, a significant part of the metal surface exposed to process gas will be in the critical range and

therefore in an area with potential for metal dusting. With respect to metal dusting, the steam superheater has many similarities with gas heated reformers, and utilising the long experience from gas heated reformers (e.g. HTCR, HTER and TBR)⁹ in connection with the critical design of steam superheaters for high superheat temperature, offers a significant advantage.

Product quality

Production and consumption figures will vary and are dependent on the type of coal, biomass and gasifier used as well as other design conditions of each specific plant. An example based on syngas with 15 mol-% methane is shown in Table 2. This is based on four methanation steps at a product pressure of 2.4 MPa g.

Nitrogen and argon in the oxygen from the air separation unit fed to the gasifier will pass through the process as inerts and end up in the SNG product. Due to the molar reduction by the methanation reaction, the concentration of the inerts in the feed will be quadrupled in the SNG product. Most of the carbon dioxide will be converted to methane.

Excess hydrogen in the feed will result in 0.5-2 mole-% hydrogen in the SNG product.

Plants under construction (coal based)

In 2010 Haldor Topsøe completed the design of the methanation section for the Qinghua, China, SNG project.

This is the largest single-train SNG plant ever designed with a production of 1.4 billion Nm³/year SNG. This is achievable by using the high-temperature resistant MCR catalyst and thereby reducing the recycle of the first methanation step. In turn this reduces the flow through the first reactor, whereby the reactor size can be reduced. Furthermore, the first methanation step is split into two in a split flow layout. In addition to the basic process design and catalyst supply, Haldor Topsøe's scope also included detailed pipe design and detailed steam superheater and WHB design.

Together with Linde Engineering, Haldor Topsøe is currently finalising the downstream of the gasifier part of an SNG plant for Posco, Korea.

Due to the close collaboration between Haldor Topsøe and Linde Engineering, the sour shift, sulphur recovery, acid gas removal and methanation sections are closely integrated and optimised. This means that the plant is optimised both from an operating flexibility and cost point of view.

However, as the product quality requirements are high for LNG production, the advanced module adjustment as described in this article is also employed and thus product fluctuations are avoided even when feed changes occur. ■

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