Coal to SNG – The Methanation Process
Christian Wix and Ib Dybkjær, Haldor Topsøe A/S, Lyngby Denmark,
and Niels R. Udengaard, Haldor Topsoe Inc., Houston TX

Presented at the

Twenty-forth Annual International Pittsburgh Coal Conference
September 10-14, 2007, Johannesburg, South Africa

Introduction

Conversion of coal or similar feedstock (petcoke, biomass, etc.) to Substitute Natural Gas (SNG) is becoming an attractive option in the energy landscape due to high and fluctuating natural gas prices as well as to political issues. In general, environmental concerns and security of energy supply are high on the political agenda. Alternative energy sources and flexibility in the conversion and distribution network are important to reduce the dependency on oil and natural gas.

Oil and natural gas reserves are limited and mainly concentrated at relatively few locations, often far from the main markets, and often ecologically or politically sensitive. In contrast, coal is abundantly available, also locally in important energy markets such as China, India, and the USA. Therefore, coal is now back as an important feedstock with gasification for production of synthesis gas (a mixture of mainly hydrogen and carbon monoxide) as a key technology.

Fig. 1 shows the main process steps in the conversion of coal or similar feedstock via gasification to products such as hydrogen, ammonia, methanol, di-methyl-ether (DME), liquid fuels (via Fischer-Tropsch technology or Topsøe's TIGAS technology), electric power with carbon dioxide sequestering, or SNG.
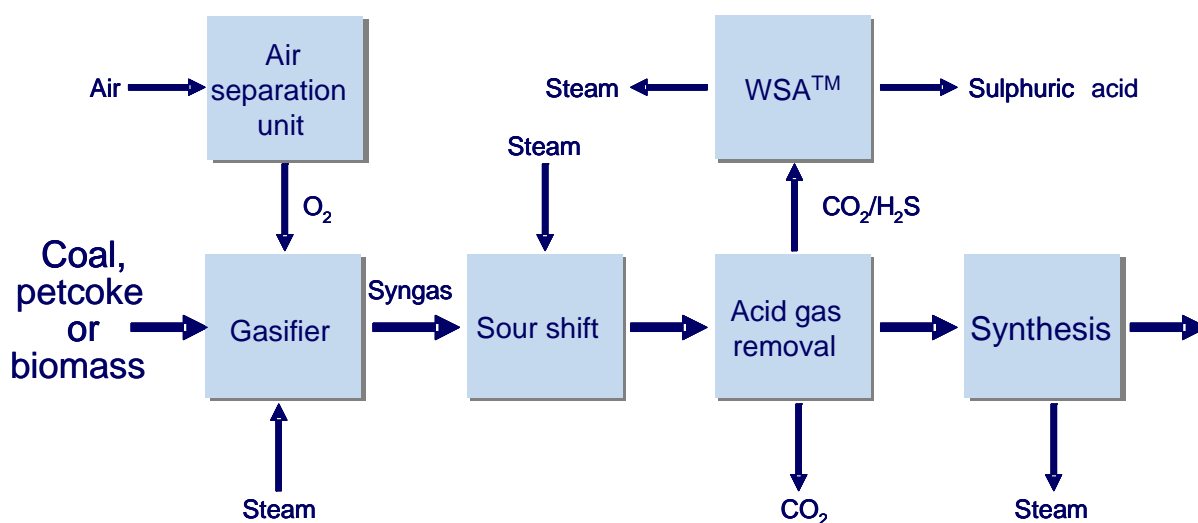

Fig. 1. Building Blocks in Coal Synthesis Plants

The main process steps are gasification of the feedstock with oxygen by one of several available technologies, adjustment of synthesis gas properties as required by the final synthesis process (mainly the H_2/CO ratio) by carbon monoxide conversion, e.g. using Topsøe's sour gas shift catalyst type SSK, acid gas removal by e.g. UOP's Selexol process, sulphur recovery by e.g. Topsøe's Wet Sulphuric Acid (WSA) process, and finally conversion of the synthesis gas to the desired product. When SNG is the product, only partial conversion of carbon monoxide and partial removal of carbon dioxide is required, since both are reactants in the methanation process. However, complete removal of sulphur is essential, since it is a poison to the methanation catalysts.

SNG will normally be exported as a product via a natural gas pipeline grid, and it must therefore comply with relevant gas specifications. A typical SNG specification is shown in Table 1.

Composition	Vol%
CH_4,	94 - 96
CO_2	0.5 - 1
H_2	0.5 - 1
CO	Nil
N_2 + Ar	2 - 3
HHV, Kcal/Nm^3	8900 - 9100

Table 1 Typical SNG Specification

However, there is no general pipeline gas or SNG specification available, and the conditions in the SNG production process must therefore be adjusted on a case to case basis to fit not only feedstock properties, but also the relevant product specification.
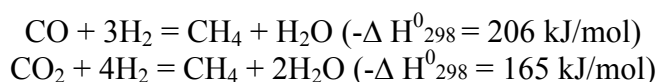
The Topsøe Recycle Methanation Process (TREMP^{TM}) as described in the following is a cost competitive process featuring the required flexibility to fit any realistic specification.

The TREMP^{TM} High Temperature Methanation Process

Chemistry and Catalysts
The TREMP^{TM} technology for manufacture of SNG by high temperature methanation was studied extensively in the 1970'ies (Ref. 1). The technology is today being further developed and optimized due to the present energy situation. Key challenges in this process are high temperatures and high concentrations of carbon monoxide in the feed (Ref. 2).

The hydrogenation of carbon oxides to methane takes place over nickel catalysts according to the following, exothermic reactions:

$$CO + 3H_2 = CH_4 + H_2O \ (-\Delta H^0_{298} = 206 \text{ kJ/mol})$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O \ (-\Delta H^0_{298} = 165 \text{ kJ/mol})$$

The high heat of reaction results in a large potential adiabatic temperature rise. A key challenge is therefore to manage the high heat of reaction by having a catalyst that has high activity at low temperature after long exposure to high temperatures.

Topsøe has developed the proprietary catalysts MCR-2X and PK-7. The MCR-2X catalyst, which is active at temperatures down to below 300 °C and stable at the very high temperature in the first methanation reactor, where the outlet temperature may be as high as 700 °C. The PK-7 catalyst is optimized for operation at low temperature and is always used in the last "clean-up" methanation reactor, which may operate at inlet temperatures as low as 200 °C. The type of catalyst installed in the intermediate reactor(s) is chosen on a case to case basis.

Process Layout
A typical process flow diagram for the Topsøe high temperature methanation process (TREMP^{TM}) is shown in Figure 2.
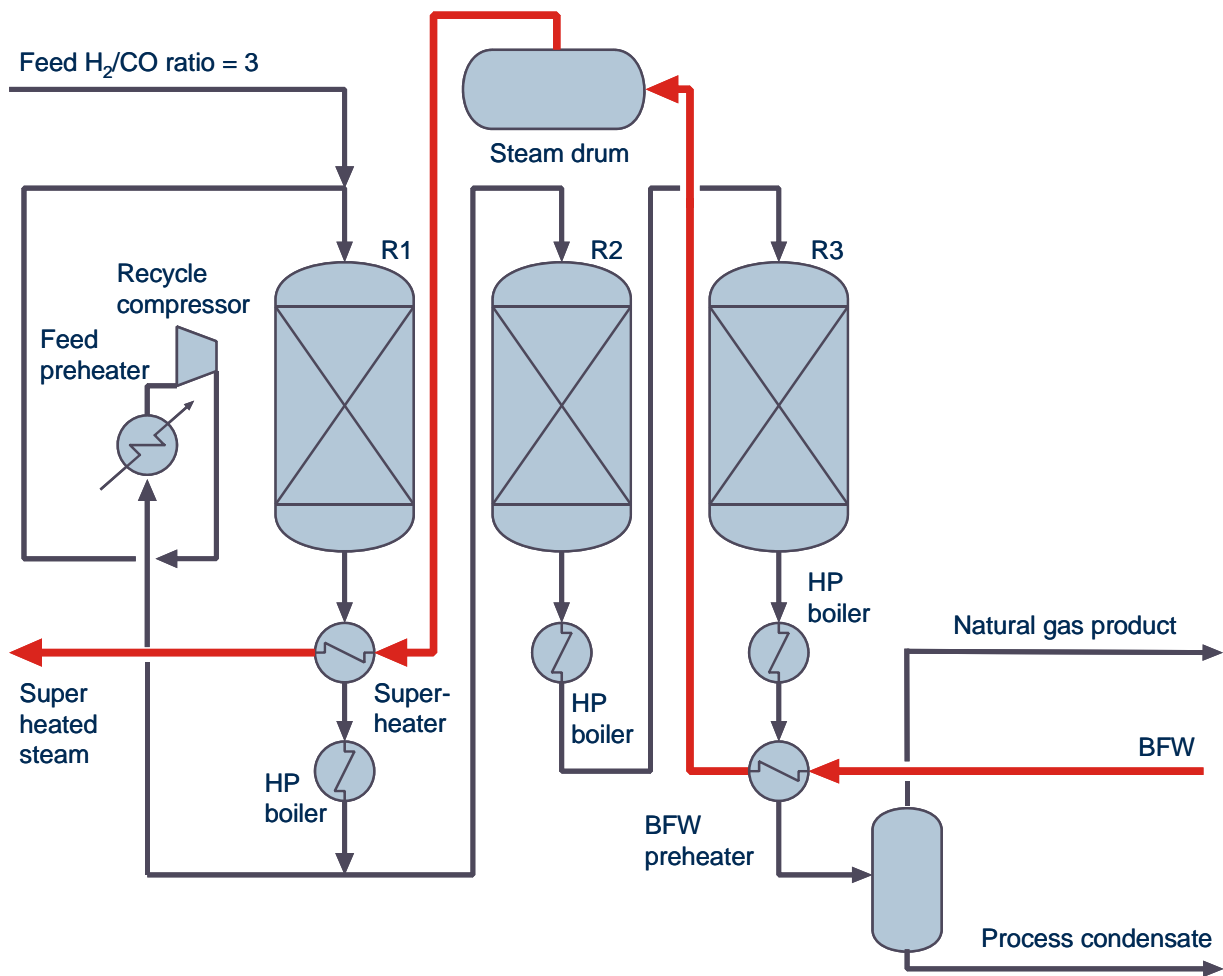

Figure 2 TREMP^{TM} High Temperature Methanation Process Flow Diagram

A case with only one reactor between the first high temperature reactor and the last "clean-up" reactor is shown. In some cases, depending on the operating conditions such as pressure as well as the SNG product specification, a second intermediate reactor is required to obtain sufficient conversion. The coal-based synthesis gas, which has been passed through a sour shift unit and an acid gas removal unit for removal of hydrogen sulphide and excess carbon as carbon dioxide, enters the TREMP^{TM} unit with a value of the stoichiometric ratio M = (H$_2$ − CO$_2$)/(CO + CO$_2$) of about 3.0. In order to protect the methanation catalyst from sulfur poisoning, the feed is first passed

through a sulfur guard bed for removal of traces of sulfur components that have not been picked up by the acid gas removal unit. The desulphurized feed is then mixed with recycle gas to control the maximum allowable temperature rise and passed to the first methanation reactor.

The exit gas from the first methanation reactor is cooled by generation of superheated high pressure steam. After cooling recycle gas is extracted, and the remaining, partly methanated synthesis gas passes through one or two intermediate methanation reactors in series, before it is passed to the "clean-up" reactor for complete conversion of the carbon oxides into methane. The process stream leaving the last methanation reactor is cooled, dried and compressed to meet the relevant pipeline specification.

The optimal recovery of the substantial heat of reaction from the methanation reactors is important for an optimized operating economy. The ability of the MCR-2X methanation catalyst to operate at high reactor exit temperatures makes the production of valuable, superheated high pressure steam possible. Such steam may be used in steam turbines for driving compressors and pumps or for production of electric power. It is worth noting that when the steam is produced at 120 Bar g and 520 °C, then it will produce an excess of power compared to the amount required for the production of oxygen for the gasifier.

The methanation reaction is favored by high pressure and works well with synthesis gas from all types of coal gasifiers. A typical product specification is given in Table 1. The HHV of the SNG is typically between 8900 – 9100 Kcal/Nm^3. For comparison it may be noted that the HHV of pure methane is 9494 Kcal/Nm^3. Nitrogen and argon in the oxygen from the air separation unit will pass through the process as inerts and end up in the SNG product. Due to the volume 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 0.5-1 vol% hydrogen in the SNG product.

Production & consumption figures will vary and depend on the type of coal gasifier used as well as other design conditions of each specific plant. An example based on synthesis gas from a GE coal gasifier is given in Table 2.

PRODUCTION:	
- SNG Product	
Flow, Nm^3/h	180,000
HHV, $kcal/Nm^3$	9,100
- Superheated HP Steam Export	
Flow, kg/h	600,000
Pressure, barg	85
Temperature, ^oC	485
CONSUMPTION:	
- Feed Gas	
Flow, Nm^3/h	720,000
HHV, $kcal/Nm^3$	2,950
- Power, MWh/h	2.3
- Boiler Feed Water Make-Up, kg/h	485,000
- Cooling Water, m^3/h ($\Delta T = 10^0C$)	310

Table 2 Typical Production & Consumption Figures

Process Economy
The production cost of SNG as is shown on the y-axis in Figure 3 has been calculated as the sum of the following three major components:

1. The production cost of the scrubbed synthesis gas leaving the gasifier including CAPEX and OPEX of the coal handling & preparation unit, the air separation unit and the gasifier & synthesis gas scrubbing unit. This cost portion is expressed as the "Synthesis gas Cost" on the x-axis in Figure 3.
2. The cost of the coal/petcoke feed shown as an indirect variable in Figure 3.
3. The CAPEX and OPEX cost of the sulfur-tolerant shift unit based on the Topsøe Sulfur Tolerant Shift and COS Hydrolysis technology, the acid gas removal unit, the sulfur recovery unit based on the Topsøe WSA sulfuric acid technology, and the methanation unit based on the Topsøe TREMP^{TM} high temperature methanation technology.

The basis for calculating the cost portion under point 3 above is as follows:

1. Capital Cost is based on early 2007 price level.
2. Utility costs:
   a. Power $0.05/kWh
   b. Cooling Water $0. 1/1000 gallons
   c. Boiler Feed Water $1/1000 lbs
   d. Export Steam Credit $9.3/1000 lbs
   e. Sulfuric Acid Export $40/ST
3. Operating Labor & Maintenance as 3% of Capital Cost.
4. Depreciation & Interest as 15% of Capital Cost.

A depreciation rate & interest of less than 15% will be applicable in countries like China and India and would result in lower production cost of the SNG product. A depreciation rate & interest of 10% would result in a 20% lower SNG production cost assuming that all other factors are kept the same.

Price of coal and cost of synthesis gas are the major contributors to the SNG production cost.
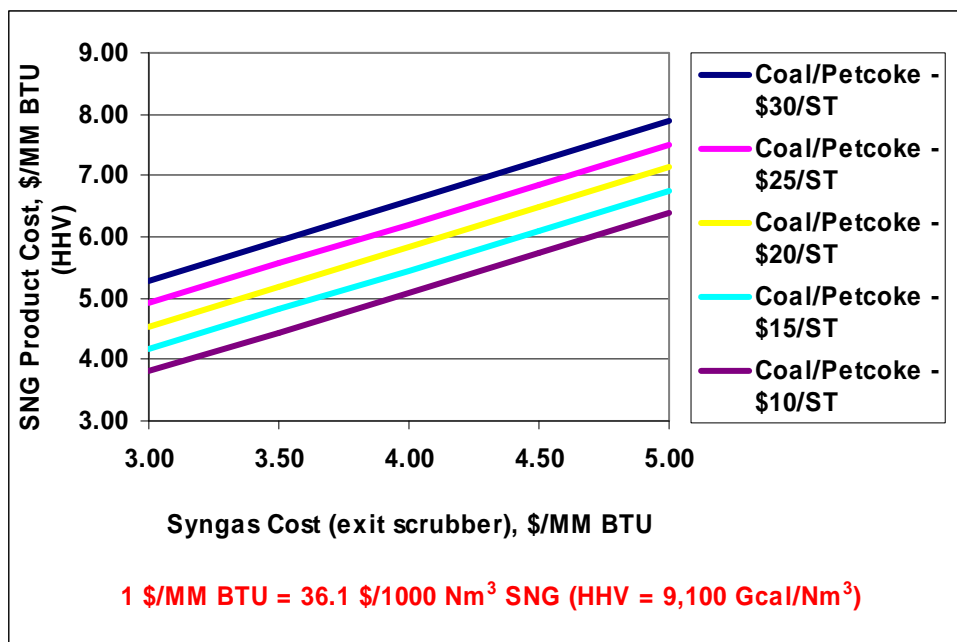

Figure 3 Production Cost of SNG Product

Influence on Performance of Feed Gas Composition and Operating Conditions
The layout of the TREMP^{TM} process is based on the outstanding capabilities of the MCR-2X catalyst, which were established in the late seventies. Recent research has confirmed that the traditional layout is close to the optimum but still may be optimized on a case to case basis depending on the synthesis gas composition and other parameters.

In order to illustrate the effect of parameter variations, a series of simulations were made. The simulations were carried out with a fixed number of reactors, with fixed inlet temperatures and fixed outlet temperatures of the first adiabatic reactor. The effects on recycle compressor power consumption, high pressure steam production and higher heating value were evaluated. The reference case in the evaluations is a raw gas with a stoichiometric ratio $M = (H_2 - CO_2)/(CO + CO_2)$ of 2.99, a carbon dioxide concentration of 1 vol%, and a methane concentration of 0.1 vol%.

Concentration of Carbon Dioxide in the Feed

Variations in carbon dioxide slip from the Acid Gas Removal Unit have been simulated, because this parameter has an impact on the overall cost of the plant. A higher carbon dioxide slip will require a lower equilibrium temperature in the Sour Shift Section, and this will require a larger catalyst volume and lead to a lower production of high pressure steam in this unit. In the Acid Gas Removal Unit, a requirement for very low carbon dioxide slip is expensive, and a higher slip of carbon dioxide leads to savings of both in investment and operating cost.

The effect of the carbon dioxide slip on the Methanation Section is shown in figure 4. The variations of the high pressure steam production and power consumption in the recycle compressor are shown relative to the base case with 1 vol% carbon dioxide in the feed.
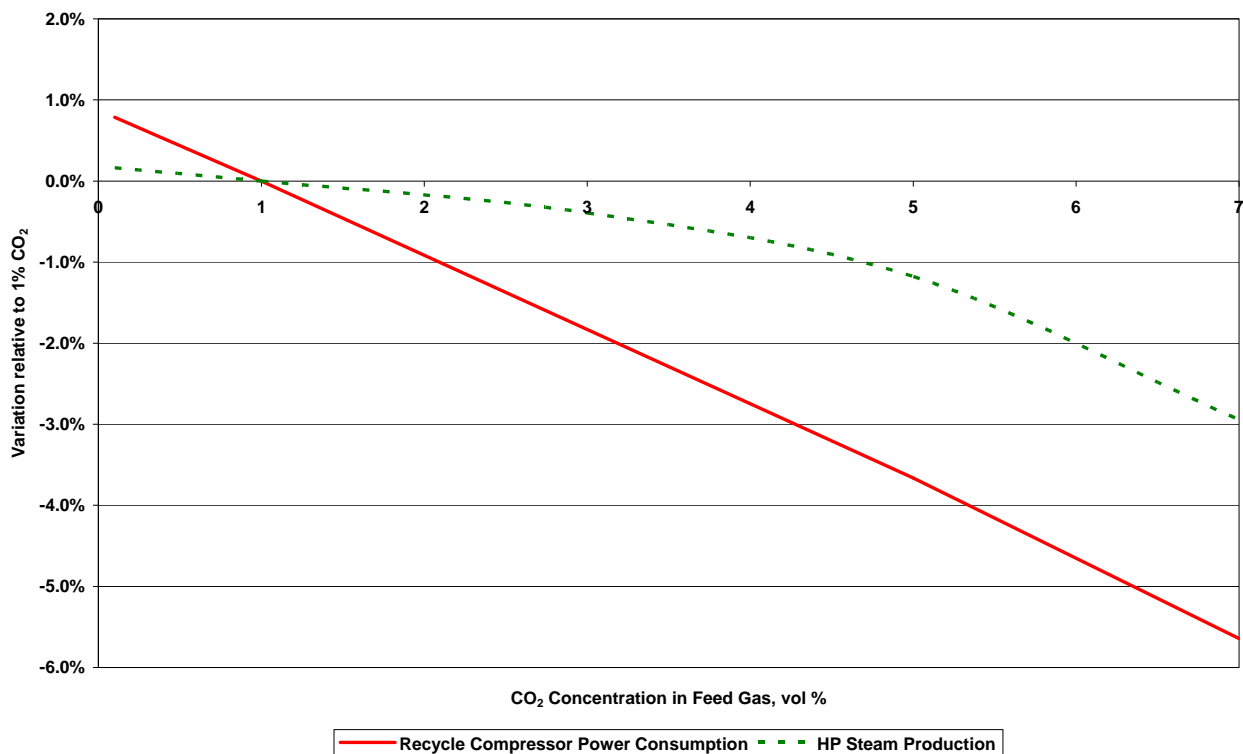

Figure 4 Effect of CO_2 Concentration in the Feed

It is clear that the optimum does not lie below 1 vol% carbon dioxide, and that the effect on the recycle compressor is almost linear. Thus an increased carbon dioxide concentration in the feed reduces the recycle flow. However, at carbon dioxide concentrations above 5 vol% in the feed, the

production of superheated high pressure steam starts to decrease significantly with a corresponding negative effect on the economics.

Concentration of Methane in the Feed

Some gasifiers are known to form methane (e.g. E-Gas, BGL and the HTW gasifier). This is a disadvantage when the final product is chemicals such as ammonia, methanol, or synthetic fuels. However, for SNG-production it would be surprising if the presence of methane is a disadvantage.
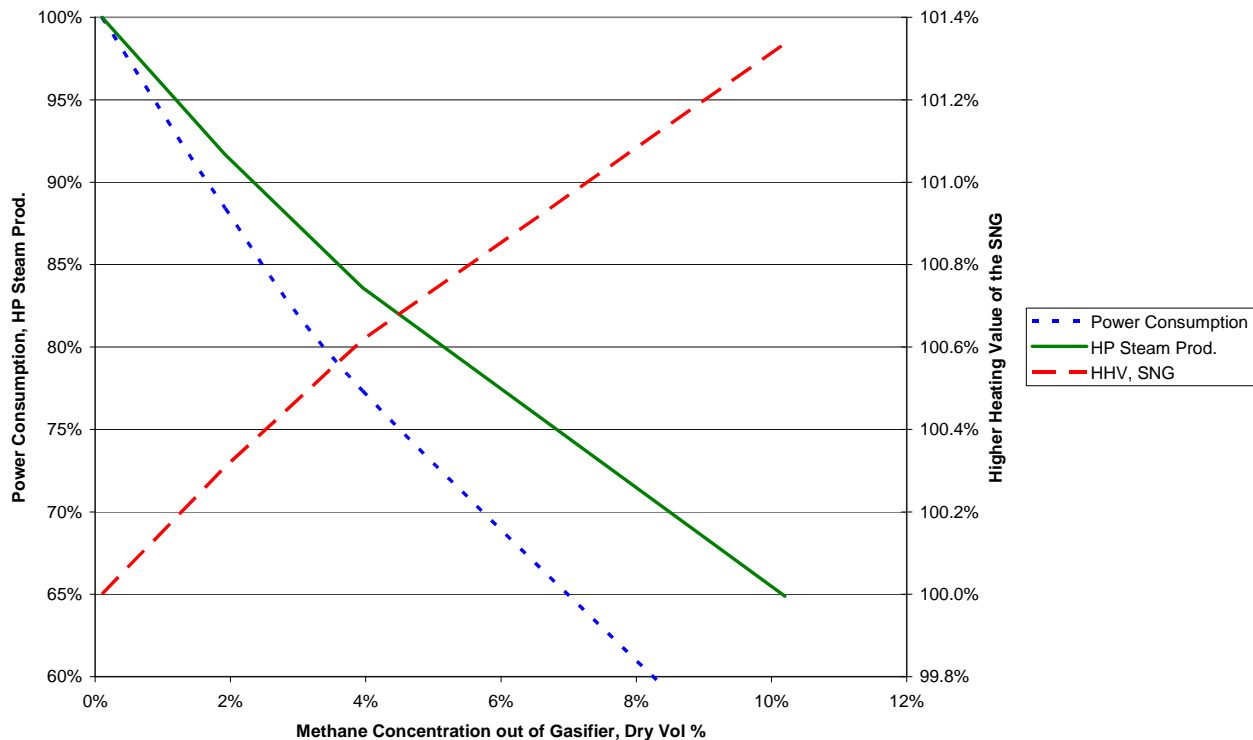

Figure 5 Effects of Methane Concentration, Relative to 0.1% Methane

Figure 5 shows that an increased methane concentration leads to reduced recycle ratio and reduced steam production, but that the product quality is improved.

Temperature Increase in the First Methanation Reactor

The MRC-2X catalyst allows a wide temperature range in the first adiabatic reactor. High outlet temperature facilitates the production of the superheated steam, which is generated in the TREMP^{TM} process. The standard temperature of the superheated steam is 520°C, and it is possible to superheat much more steam to this temperature than generated in the TREMP^{TM} section itself (e.g. steam from the gasifier cooling train and/or the shift section).

The temperature increase over the first reactor is proportional to the conversion of carbon monoxide and carbon dioxide to methane. It is known that low inlet temperatures may result in problems with nickel carbonyls. However, high outlet temperatures make the equipment more expensive.

A parameter variation has been made where the temperature increase over the first reactor has been increased by 4.3% by either increasing the outlet temperature or decreasing the inlet temperature. The effect on recycle compressor power requirement and steam production was studied.
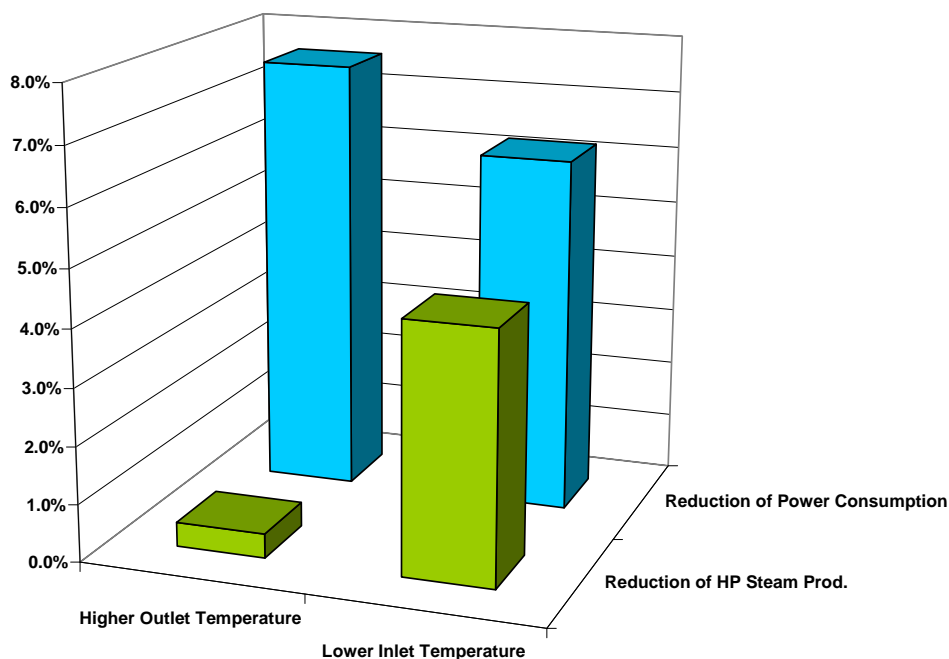

Figure 6 Effects of 4.3% Temperature Adjustments in the 1st Methanator

The results of the equal variations of inlet and outlet temperature are shown in figure 6, and it is clear that the low inlet temperature brings down the power consumption, but also the production of high pressure superheated steam. If the inlet temperature is kept constant and the outlet temperature is increased, then the same positive effect on the power consumption is seen with almost no impact on the steam production.

Conclusions

The TREMP^{TM} high temperature methanation process is a robust, simple, and economically competitive process allowing production of SNG meeting pipeline specifications from synthesis gas with varying composition. The process is based on the use of the catalyst MCR-2X, which allows a large temperature increase over the first methanation reactor. This minimizes equipment size and cost, reduces power consumption for recycle and facilitates production of superheated high pressure steam. The process is flexible, and layout and operating conditions may be adjusted on a case to case based to obtain the optimal result.

The optimization of the methanation section should be made together with the entire SNG plant, because the composition of the feed gas has a significant impact on the design of the methanation section. It is clear that a methane rich feed gas is an advantage for the methanation section, and the effect methane has on the Acid Gas Removal and the Shift Section should be examined.

The carbon dioxide slip of the Acid Gas Removal Section should be more that 1-3%, but less that 5% to reduce the power consumption in the recycle compressor. This concentration range does not have any significant effect on the steam production.

The high temperatures in a TREMP^{TM} plant ensure a high production of superheated high pressure steam, which potentially corresponds to a power production close to 1 kWh / Nm^3 SNG.

References

1. Udengaard, N.R., Olsen, A., Wix-Nielsen, C. "High Temperature Methanation Process – Revisited", Pittsburg Coal Conf. 2006

2. Rostrup-Nielsen J.R., Sehested. J. in Proc. 20 North Amer.Cat.Soc. Meeting, Houston, June 2007 , Paper O-S6-10.