Synthesis Gas Processes
for Synfuels Production

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Abstract

Synthetic fuels offer an extremely flexible means of marketing remote sources of natural gas. Different synthesis processes require different synthesis gas specifications. The paper highlights the importance of matching the synthesis gas production process to the needs of the individual synthesis process. Examples discussed cover single-stage and two-stage reforming as well as partial oxidation.

1 Introduction

It is a truism to observe that the world's hydrocarbon resources are not evenly distributed and in particular that a substantial proportion of known reserves are situated in locations remote from areas of high consumption. Transportation of liquid hydrocarbons from source to consumer is a task for which a large and flexible infrastructure exists. However, where natural gas deposits in remote locations are to be exploited, the transportation task becomes a major challenge - particularly if geography, economics or a combination of both preclude the possibility of a pipeline.

This challenge can be met by conversion of natural gas into a transportable and saleable form or product. Historically this has implied LNG, ammonia or methanol as the medium of bringing remote natural gas to the market place. Each of these has its limitations - the heavy investment and, relatively speaking, small number of receiving terminals limits the marketing flexibility for LNG. Neither the ammonia nor the methanol market is large enough to accept the potential volumes available from exploitable natural gas reserves. Current prices for both products would indicate that we are close to these marketing limits - unless of course legislation drives motor fuels in the direction of methanol.

An alternative which is gaining increasing attention is the conversion of natural gas to synfuels - ranging from gasoline to middle distillates. This approach avoids the infrastructural limitations of LNG and at the same time provides a market large enough to accept the potential volumes.

2 Synthesis Gas Specifications

There are two routes for the production of synthetic fuels,

a) the Fischer-Tropsch route and

b) the Methanol route.

The first step for both routes is the conversion of natural gas into synthesis gas - a mixture of hydrogen, carbon monoxide and carbon dioxide. The proportions of these components in the mixture vary according to the individual synthesis process selected and also according to the product slate desired. Typical values of the principle characteristic, the H2/CO ratio, for different processes are given in Table 1 (van der Burgt & Sie, 1984 and Supp, 1984). As can be seen, this covers a wide range from below 1 to nearly 3.

In addition varying amounts of pure hydrogen may be required for hydrogenation of the crude product from the synthesis.

The wide range of H2/CO ratios required for the different synthesis processes means that considerable effort is required to match the syngas generation and synthesis process so as to ensure the optimum overall conversion rate.

Synthesis	H2/CO	Remarks
Dow	0,85	
Union Carbide	1,	
ARGE	1,3 - 3	
Gulf-Badger	1,5 - 2	
SMDS	2	
Synthol	2,6	
Methanol	2,4 - 3	(H2-CO2)/(CO+CO2) = 2,05

* Process with commercial scale plant in operation or under

Table 1: Synthesis Gas Specifications

3 Synthesis Gas Production Processes

The number of chemical reactions involved in the manufacture of synthesis gas is very large. The most important of these (limited to methane for the sake of simplicity) are listed in Figure 1. Given the objective of producing CO and H2 from the methane, the most desirable reactions are those of reforming (reaction 1) and partial oxidation (reaction 3) producing H2/CO ratios of 3 and 2 respectively. If a source of CO2 is available (or for a CO2 rich natural gas) reforming with CO2 (reaction 2) provides an H2/CO ratio of 1. The figures for higher hydrocarbons in the natural gas are correspondingly lower. The final H2/CO ratio is influenced further by the CO shift reaction (5).

Reforming (strongly endothermic)

CH4 + H2O ↔ CO + 3 H2 (1)
CH4 + CO2 ↔ 2 CO + 2 H2 (2)

Combustion (strongly exothermic)

2 CH4 + O2 → 2 CO + 4 H2 (3)
CH4 + 2 O2 → CO2 + 2 H2O (4)

Shift conversion (mildly exothermic)

CO + H2O ↔ CO2 + H2 (5)

Carbon

CH4 → 2 H2 + C (6)
2 CO → CO2 + C (7)

Figure 1: Synthesis Gas Production – Principal Reactions

The reforming reactions (1 and 2) are strongly endothermic and must be supported by the strongly exothermic reactions of partial oxidation (3) and/or complete combustion (4). The latter reaction is, however, in principle less desirable since neither H2 nor CO is produced.

The three main industrially proven processes of tubular steam reforming, catalytic autothermal reforming and non-catalytic partial oxidation can be characterized as follows.

In **tubular steam reforming** reaction (1) takes place over a catalyst in a tube which is externally heated. A large steam surplus is required to suppress carbon formation in the catalyst. This tends to drive the shift reaction (5) to the right resulting in a hydrogen rich synthesis gas. The heat is supplied largely by the undesirable complete combustion reaction (4) outside the tubes.

In **catalytic autothermal reforming** oxygen is added to the feed. The heat requirement for reaction (1) is largely met by the partial oxidation reaction (3) thus producing a lower H2/CO ratio in the syngas product. As in tubular reforming considerable amounts of steam are required to suppress carbon formation. The absence of the metallurgical limitations of the catalyst tubes of a steam reformer allows higher operating temperatures thus reducing methane slip. At these higher temperatures the CO shift equilibrium is also more favourable to CO than in the case of the tubular steam reformer.

In **non-catalytic partial oxidation** reaction (3) is dominant. The absence of any catalyst means that the process is tolerant of a small degree of carbon formation and allows even higher operating temperatures. It is thus possible to operate partial oxidation without any steam addition. The resulting gas is the most CO rich of the three.

The art of selecting the right syngas generation process - or combination of processes - consists of ensuring the correct gas specification as required by the selected synthesis while simultaneously minimizing certain inherent inefficiencies of the individual processes. In the case of tubular reforming this inherent inefficiency lies in the use of external complete combustion requiring an expensive heat recovery train and still involving substantial losses in the stack gas. In the case of autothermal reforming and partial oxidation the inefficiency lies in the energy requirement and investment for the oxygen plant.

4 State of the Art Processes

LURGI GMBH is currently involved in the design and supply of synthesis gas production units for two major synfuel projects - one based on SASOL's Synthol process and the other using SHELL's SMDS synthesis. As can be seen from the published data in Table 1 there is a substantial difference in the H2/CO ratios required by the two processes and this has led to the selection of different syngas production routes. In the Synthol case LURGI's own Combined Reforming was selected. In the SMDS case SHELL's SGP partial oxidation route is being used.

The figures used in the following discussions to illustrate particular features of these two syngas production processes are based on a total hydrocarbon product capacity of 1,000,000 tons/year with a product slate typical for the synthesis process selected. In both cases the same natural gas quality has been assumed.

4.1 LURGI's Combined Reforming

LURGI's Combined Reforming process was originally developed for large-scale methanol production and it is with an example from this application that it is described here. In the synfuels context it is suitable as a building block for MOBIL's MTG or MOGD processes. For a Synthol flow sheet some CO2 would need to be purged from the system (Swanepoel, 1987). The conventional tubular steam reforming process as used for methanol syngas production produces an H2/CO ratio of over 4 and a stoichiometric ratio of 2.6 to 2.9 depending on the natural gas quality, i.e. a hydrogen-rich gas.

Autothermal reforming or partial oxidation produce carbon monoxide rich gases with an H2/CO ratio 1.8 to 3.5 and a stoichiometric number of around 1.8. The block flow diagram in Figure 2 shows how a tubular reformer (the primary) and an autothermal reformer (the secondary) are combined to produce an optimum methanol synthesis gas quality.

Approximately half the feed is processed in the tubular primary reformer. The other half, together with the primary reformer effluent, is autothermally reformed with pure oxygen in the secondary reformer. Besides matching hydrogen-rich and carbon monoxide-rich process steps to produce an optimum stoichiometric ratio, the Combined Reforming process has additional beneficial effects, which are illustrated with the data shown in Table 2.

- The methane slip of the overall reforming process is governed by the temperature of the secondary reformer which is not subject to the same limitations of tube metallurgy as the tubular reformer. The combined process can thus provide a lower methane slip.
- Less synthesis gas of the optimized quality is required per ton of methanol, reducing both the syngas compressor load and the capital cost of the synthesis unit.

- The operating temperature of the primary reformer need no longer be chosen to minimize methane slip. It can be operated under mild conditions. The higher operating pressure thus possible enables the syngas compressor load to be further reduced.

- The reduced throughput through the primary reformer together with the lower operating temperature combine to reduce the tubular reformer to about 25% of the size of that required for the single stage process. This reduces the stack gas losses referred to earlier by the same amount. Simultaneously a substantial saving in capital cost is achieved.

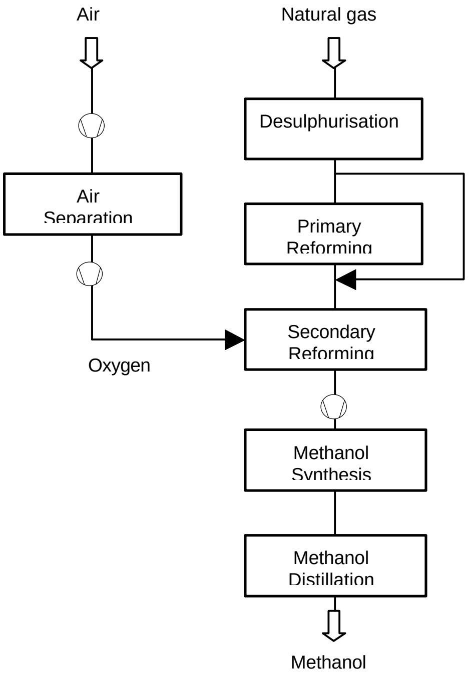

Figure 2: Lurgi Combined Reforming to Methanol

Looking at the 1 000 000 t/y gasoline plant, equivalent to about 7 000 t/d of methanol, two medium size reformers (400 tubes) would be required. Compare this with the conventional plant requiring three extremely large reformers with 896 tubes each.

Of course no one gets anything quite for nothing. Both energy and investment are required to generate the oxygen used in the secondary reformer. Nonetheless, the net energy saving for the combined process including oxygen production lies between 6.5% and 10% depending on the natural gas quality. The investment savings on the tubular reformer more than compensate for investment in the oxygen unit above a break-even size of 1 200 – 1 500 t/d methanol - certainly at the scale required for synfuels production.

		Conventional Reforming	**Lurgi Combined Reforming**
No. of trains		3	2
Methanol product per train	t/d	2 330	3 500
Natural gas feed per train	kmol/h	3 470	4 585
Natural gas fuel per train	kmol/h	180	335
Total natural gas	kmol/h	10 952	10 280
Synthesis gas			
H_2/CO		4.4	3.12
SN		2.92	2.05
CH_4	%	3.71	1.19
Flow/train	kmol/h	13 530	15 450
Primary reformer			
Operating temperature	°C	900	780
Operating pressure	bar	22	29
No. tubes per train		896	400
Secondary reformer			
Operating temperature	°C	-	980
Operating pressure	bar	-	27.50
Diameter	m	-	4.30

Table 2: Syngas Plants for MTG Route, 1 000 000 t/y Gasoline plus LPG

4.2 SHELL's SGP Process

SHELL's SGP process for which LURGI is the licensing agent is a much older process, the basic development having been made in the 1950's and some 150 units having been built in the meantime. With natural gas feed it produces a synthesis gas with an H_2/CO ratio of typically 1.7 - 1.8 and a CO_2 content of 1.7 - 3 depending on the steam addition rate.

A simplified flow diagram of a gas based SGP unit is shown in Figure 3. The gas feed is preheated with the raw gas to a temperature of about 380°C for desulphurization prior to being fed to the SGP reactor with the oxygen. The partial oxidation reaction takes place at about 1300 - 1400°C in the refractory lined reactor. The sensible heat of the hot gas is used to generate high-pressure steam, with or without superheat as required.

As mentioned previously the non-catalytic partial oxidation reactor produces small amounts of soot which are washed out in a scrubber. The carbon is concentrated in the reaction water which is discharged to the waste water treatment. The gas - now free of soot - is ready for use in the synthesis with an analysis as shown in table 3.

		SGP
No. of trains		8
Natural gas feed (total)	kmol/h	9 915
Oxygen (total)	kmol/h	5 785
Synthesis gas		
H2/CO		1.86
CH4		1.27
Flow (total)	kmol/h	27 861

Table 3: Syngas Plant for F-T Synthesis 1 000 000 t/y Middle Distillates

If we compare the synthesis gas quality with that produced by Combined Reforming we see a considerably lower H2/CO ratio of 1.86 compared with 3.14 for Combined Reforming making SGP a better match for, for instance, the SMDS process. The amount of natural gas required to produce the synthesis gas is some 3.5% lower than for the Combined Reforming case. These advantages are bought at the cost of higher oxygen consumption.

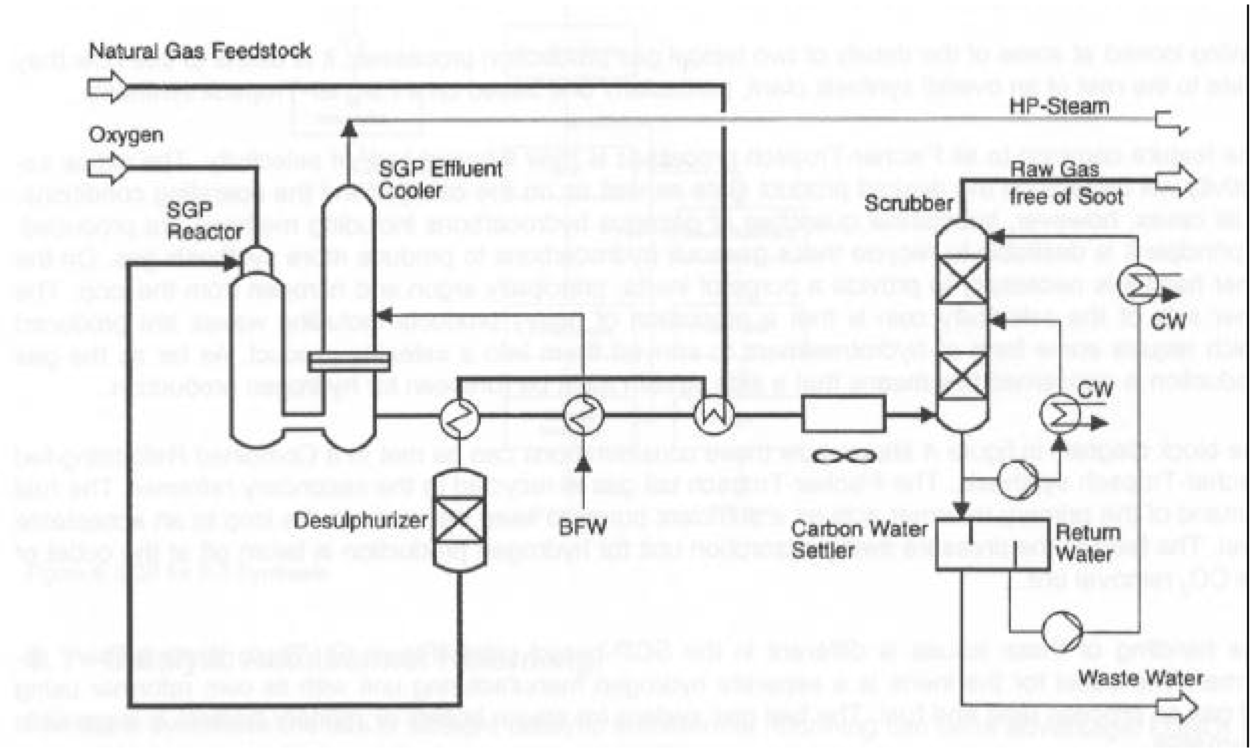

Figure 3: Shell Gasification Process ('SGP')

4.3 Process Integration

Having looked at some of the details of two typical gas production processes, it is useful to see how they relate to the rest of an overall synfuels plant, particularly one based on a Fischer-Tropsch synthesis.

One feature common to all Fischer-Tropsch processes is their inherent lack of selectivity. The actual selectivity will depend on the desired product slate as well as on the catalyst and the operating conditions. In all cases, however, substantial quantities of gaseous hydrocarbons including methane are produced. In principle it is desirable to recycle these gaseous hydrocarbons to produce more synthesis gas. On the other hand it is necessary to provide a purge of inerts, principally argon and nitrogen from the loop. The other side of the selectivity coin is that a proportion of heavy products including waxes are produced which require some form of hydrotreatment to convert them into a saleable product. As far as the gas production is concerned this means that a side stream must be foreseen for hydrogen production.

The block diagram in Figure 4 shows how these considerations can be met in a Combined Reforming-fed Fischer-Tropsch synthesis. The Fischer-Tropsch tail gas is recycled to the secondary reformer. The fuel demand of the primary reformer acts as a sufficient purge to keep the inerts in the loop to an acceptable level. The feed to the pressure swing adsorption unit for hydrogen production is taken off at the outlet of the CO2 removal unit.

The handling of these issues is different in the SGP-based plant (Figure 5). There is no primary reformer. The outlet for the inerts is a separate hydrogen manufacturing unit with its own reformer using tail gas as process feed and fuel. The fuel gas system for steam boilers or refinery heaters is a possible alternative.

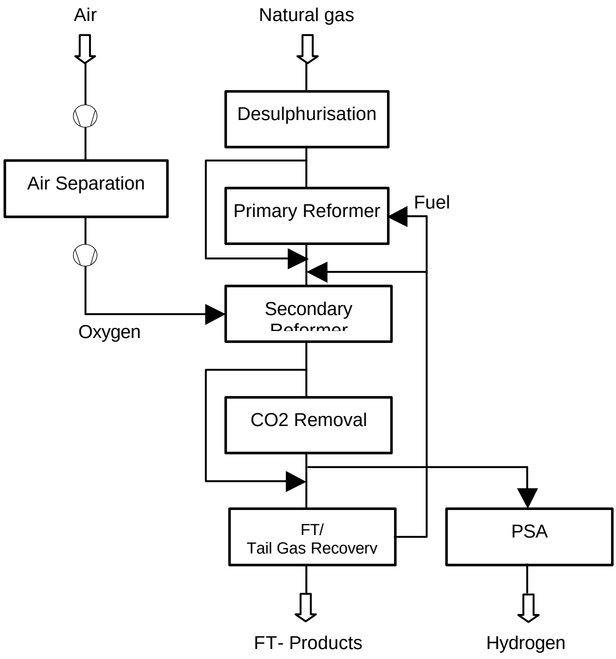

Figure 4: Lurgi Combined Reforming for F-T Synthesis

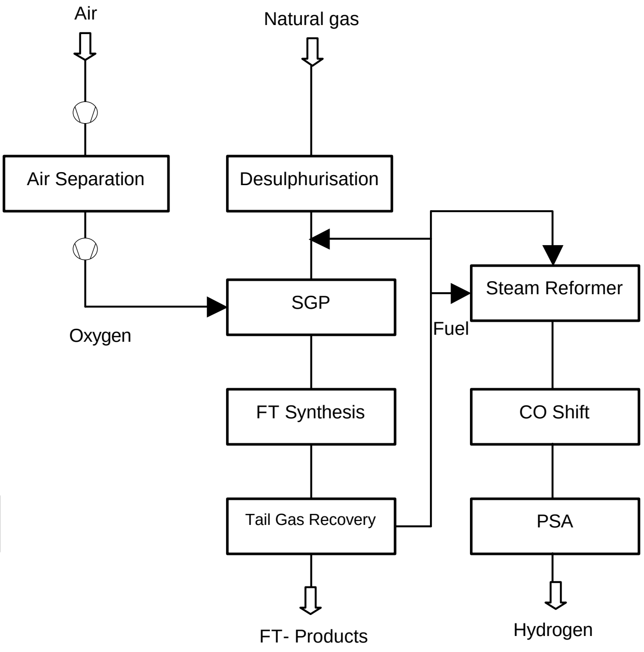

Figure 5: SGP for F-T Synthesis

5 Future Developments

The emphasis of this paper is on state of the art processes. The fact that both the syngas production routes described above are based on proven technologies provides us with reliable starting points for the development of processes which offer the potential for further reduction of both capital and operating costs. Two such developments are discussed below.

5.1 Catalytic Autothermal Reforming

For some syntheses the use of straight catalytic autothermal reforming can be of advantage. LURGI has used this process both for methanol production (1958) and treating Fischer-Tropsch tail gases (1977). Whereas in a secondary reformer configuration the hot hydrogen-rich primary reformer effluent is self-igniting, ignition of a straight autothermal reformer requires the use of a noble-metal-promoted ignition catalyst. Velocities in the ignition-catalyst area must be kept high to eliminate any possibility of back-burning. These high velocities lead over a period of time to mechanical attrition of the expensive ignition catalyst.

As part of the on-going development of its reforming processes, LURGI has modified the process arrangement to bring the operating conditions closer to that of a secondary reformer thus dispensing with the need for the ignition catalyst.

5.2 HCT Reforming

From the discussion of the Combined Reforming process it will be realized that considerable savings in investment and operating cost can be achieved if the reforming process is modified in a way, which reduces the size of the convection bank. This can be of particular importance in a synfuels plant where considerable steam surplus can be expected from the synthesis unit. Besides the Combined Reforming process LURGI has also developed a reforming technology with internal heat transfer, which offers savings without the use of oxygen.

This technology is based on the use of the so-called HCT reformer tube. In principle this is a normal centrifugally cast reformer tube, catalyst filled, heated from outside and normally designed for downflow of the process gas through the catalyst bed. But on the inside it encloses a double helix made of tubes of suitable material embedded in the catalyst (see Figure 6). The reformed process gas passes this double helix in counterflow to the process gas flow through the catalyst bed, thus transferring a part of its sensible heat to the reforming process. Calculations and practical experience have shown that based on an inlet temperature of 450°C and reaction end temperature of 860°C this internal heat transfer covers up to 20% of sensible and reaction heat of the process gas. In addition to the resultant saving of fuel, an investment saving of ca. 15% can be expected - the bulk of which is attributable to the smaller convection bank required.

Experience with HCT tubes has been made in LURGI's R & D centre with a single full scale commercial tube over ca. 7000 hrs under varied test conditions and also in a nuclear research centre in Germany for approx. 20 000 hrs. In the synfuels environment the application of such an HCT reformer would typically be the hydrogen plant in an SGP-based synfuels complex, thus providing an economical outlet for inerts without generating unnecessary quantities of steam.

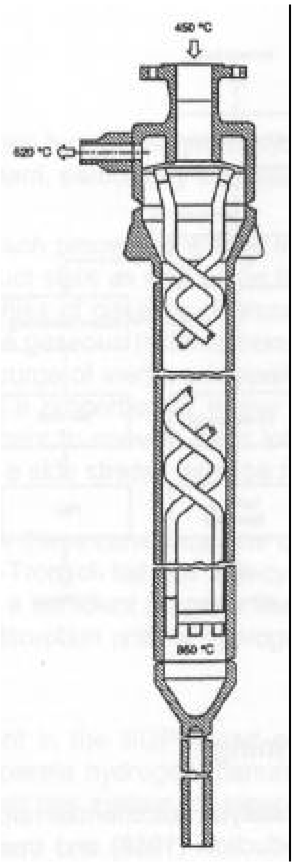

Figure 6: Principal arrangement, HCT Reformer Tube

6 Conclusions

The production of synfuels can provide a means of moving natural gas from remote locations with a maximum of marketing flexibility. A range of proven processes is available for both syngas production and synthesis. It is, however, of utmost importance for the economics of an individual project to tailor the syngas production process to that of the synthesis.

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