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Update on synthesis gas production for GTL

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1. Introduction

Gas-to-liquid (GTL) is the conversion of natural gas to liquid fuels, mainly diesel, but the aspects described in this paper are also valid for methanol, another GTL product. GTL is attracting attention as a promising area for future development in the energy sector. Proven technology is available, and several large projects are in advanced stages of development for diesel or methanol production.

The preparation of synthesis gas is the most capital-intensive part of a GTL-complex. It may account for in the order of 40% of the total investment (including air separation unit (ASU)) in a GTL-complex. Hence, there is a considerable incentive to optimise and further develop syngas production technologies for the purpose of cost reduction.

Available processes for the production of synthesis gas for GTL plants are based on steam reforming, partial oxidation or combinations hereof. The most attractive and economical technology today is considered to be oxygen-blown autothermal reforming (ATR), which has been commercialised by Haldor Topsøe A/S (Topsøe) at a steam to carbon (S/C) ratio of 0.6. A European plant has been in commercial operation for >3 years, and a plant corresponding to 2 × 8500 bbl/d GTL capacity was commissioned in July 2004 in South Africa with excellent operating records so far. Other plants are close to start-up or in advanced stages of engineering and/or construction in Qatar and Nigeria.

This paper focuses on potential, new or improved technologies for synthesis gas production in large GTL plants:

- Next generation of ATR.
- ATR in combination with gas-heated reforming.
- Catalytic partial oxidation (CPO).
- Ceramic membrane reforming (CMR).

2. Technology status

A typical process concept for the production of synthesis gas based on ATR is shown in Fig. 1. The key steps in the process scheme are desulphurisation, adiabatic pre-reforming, ATR and heat recovery.

The adiabatic pre-reformer converts the higher hydrocarbons by steam reforming into a mixture of methane, steam, hydrogen and carbon oxides.

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2 \tag{1}$$

$$CO + 3H_2 \rightleftarrows H_2O + CH_4 \tag{2}$$

$$CO + H_2O \rightleftarrows CO_2 + H_4 \tag{3}$$

The removal of higher hydrocarbons allows a higher pre-heat temperature to the ATR, thus saving oxygen. The pre-reformer is loaded with a highly active nickel catalyst with a ceramic support such as $MgAl_2O_4$.

The autothermal reformer is the key part of the synthesis gas unit in a GTL plant. The ATR reactor has a compact design consisting of burner, combustion chamber and catalyst bed placed in a refractory-lined steel vessel. The pre-reformed natural gas reacts with oxygen and steam in a sub-stoichiometric combustion. The burner provides proper mixing of the feed streams in a turbulent diffusion flame. All the oxygen is consumed to extinction.

In the catalyst bed, the gas is equilibrated with respect to the methane steam reforming (reverse of (2)) and shift reactions (3). The catalyst also ensures that soot precursors (e.g. ethylene and acetylene) known to be formed in the combustion chamber are destroyed. The produced synthesis gas is completely free of soot and oxygen.

The desired syngas composition for Fischer Tropsch (FT) based diesel production is often characterised by an H_2/CO-ratio of about 2.0. This ratio cannot be produced by the ATR-

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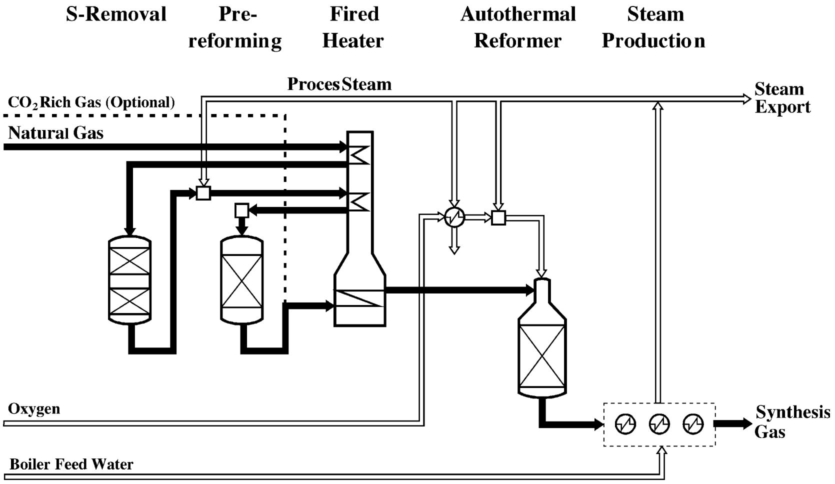

Fig. 1. Typical process flow diagram for synthesis gas production.

based process alone except at very low S/C-ratio and by adjusting the pre-heat temperatures and the ATR exit temperature. Instead CO_2 or other carbon-rich gases may be recycled, e.g. from the FT synthesis section of the plant to adjust the H_2/CO-ratio to the desired value.

3. ATR at lower S/C-ratio

The ATR technology has considerable potential for further optimisation, especially by reduction of the S/C-ratio. Lower S/C-ratio improves the syngas composition and reduces the CO_2 recycle. The result is reduced investment per barrel of product and the possibility for higher single-line capacity.

However, reducing the S/C-ratio also reduces the margin to carbon formation in the pre-reformer and to soot formation in the ATR. Operation for an extended period of time at $S/C < 0.40$ has been demonstrated in Topsøe's process demonstration unit in Houston, Texas, to ensure availability of necessary data for designing a plant with sufficient margins to the above mentioned parameters.

In Table 1, comparative indexed flows for various key parameters are shown to illustrate the impact on single-line capacity when reducing the S/C-ratio from 0.6 to 0.4.

Mechanical design optimisation of the ATR-reactor including burner, refractory and catalyst, and other main equipment has been carried out in parallel with the development towards lower S/C-ratio. The optimised design in combination with the reduction of the S/C-ratio will result in a major increase in the single-line capacity by >15% within the next few years.

Commercialisation of the ATR A/C = 0.4 technology is expected within the near future.

Table 1
Index flow as function of S/C-ratio

S/C	0.6	0.4
NG feed + fuel	100	101
O_2	100	98
CO_2 recycle	100	56
H_2 + CO syngas	100	100
Exit ATR	100	93

4. Combination of ATR and process gas-heated reforming

One of the main cost elements in the front-end of a GTL-complex is the air separation unit. The ASU has a high capital cost and the physical size of major rotating machinery sets the limits for the plant capacity. Reduction of the oxygen consumption will therefore have several effects.

High inlet temperatures and low outlet temperatures in ATR stand-alone units will reduce oxygen requirement. Low outlet temperature will increase the H_2/CO-ratio with the result that a higher recycle of CO_2 is required. Although this isolated may increase the process carbon efficiency, the drawback is a high content of CO_2 and CH_4 in the syngas, both of which are inert in the low-temperature FT synthesis.

By the Topsøe exchange reformer (HTER-p/s) part of the heat in the ATR effluent is used for steam reforming and feed pre-heat in a heat exchange type of reformer. The high level of steam reforming (as compared to adiabatic pre-reforming alone) and the lower oxygen consumption increases by itself the H_2/CO-ratio. Similar to the above, more CO_2 must be recycled to obtain the target H_2/CO-ratio. This increases the overall carbon efficiency of the plant.

There are two principally different layouts for incorporating gas heated reforming in combination with ATR: a parallel arrangement and a series arrangement, as is shown in Fig. 2.

In the parallel arrangement, the two reformers are fed independently, giving freedom to optimise the S/C-ratio

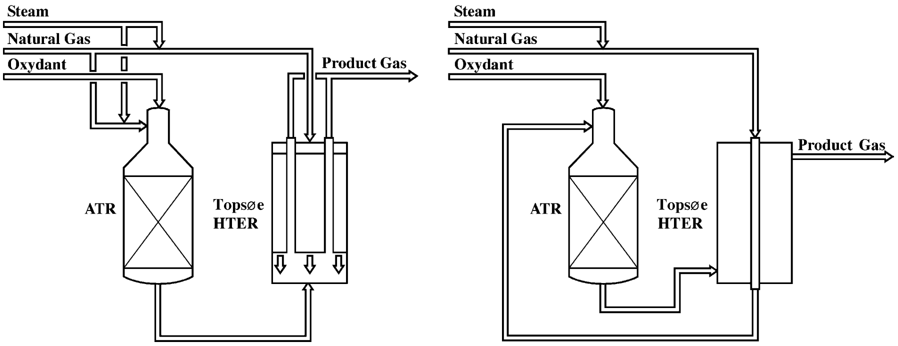

Fig. 2. Gas-heated reforming in combination with ATR.

Table 2
Results from a comparative study

Case	ATR (base)	ATR at lower S/C	ATR with parallel HTER	ATR with series HTER
S/C-ratio	0.6	0.4	0.4/1.1	0.4/0.55
O_2 consumption, tonnes per bbl produced index	100	92	82	81
Total LHV efficiency index	100	105	108	109
SGU investment per bbl/d index	100	69	81	76
ASU investment per bbl/d index	100	83	76	74
SGU + ASU investment per bbl/d index	100	76	79	75

individually. However, the HTER-p must operate at a higher temperature than in the series arrangement to obtain a low CH_4-leakage. In the series arrangement, all gas passes through the HTER-s unit and then the ATR. This will mean that the presently available steam reforming catalyst may set the lower limit for the S/C-ratio. The main problem in the series and the parallel arrangement is the risk of metal-dusting corrosion. Mechanical design, including choice of materials, is critical. An HTER-p designed by Topsøe, operating in a parallel arrangement with ATR at relatively low S/C-ratio, has been in operation at Sasol's facilities in Secunda, South Africa, since early 2003 with excellent operating records.

The results from the comparative study presented in Table 2 show that due to better understanding of the operating parameters and due to new technology, a significantly higher single train capacity is to be expected. The cost reduction compared to current state of the art technology is substantial. It is noteworthy that the low S/C ATR technology is still competitive with the new reforming technologies. Comparing the overall LHV efficiencies reveals that the HTER-p/s technology is especially attractive if the price of energy is high.

5. Catalytic partial oxidation and ceramic membrane reforming

The process concept in a flow sheet of a GTL-complex based on CPO or ATR is similar. The difference is that no burner is used in CPO and that all chemical reactions take place in a catalyst bed or monolith reactor.

It has been claimed that syngas can be produced in a CPO directly by the following exothermic reaction:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (4)$$

This reaction would result directly in the wanted stoichiometry of the product gas and could be performed at low temperature. However, even though fundamental studies indicate that reaction (4) may take place at high temperature, it will in practice always be accompanied by steam reforming and shift reaction, as well as combustion of the reactant and product gases.

The product gas composition can therefore be predicted from thermodynamics and assuming the same operating parameters, not to be different from ATR.

It is not possible to pre-heat the feed to the CPO to the same level as in an ATR due to the presence of a highly flammable mixture upstream the catalyst. The auto-ignition temperature of this mixture will typically be about 250 °C, depending on the gas properties. This is a severe drawback in

Table 3
Relative natural gas and oxygen consumption for CPO and ATR-based front-ends for GTL-plants at S/C = 0.30

Reactor	Feed temperature, reactor inlet	Oxygen consumption	Natural gas consumption
ATR	650	100	100
CPO	200	118	107

the potential of CPO for GTL plants. Table 3 illustrates the increased natural gas and oxygen consumption caused by the constraint in inlet temperature. Considering that the ASU-investment is a large fraction of the GTL-complex cost, CPO does not appear economical.

With CMR, the ASU is avoided. Air is introduced at one side of a membrane through which oxygen with 100% selectivity is transported to the other side, where it reacts with hydrocarbons to produce syngas.

The mechanical integrity and the stability of the membrane are severe challenges in the development of CMR. It may render CMR non-economical, if air must be compressed to process pressure. With ambient air pressure, the technological principle appears promising in small and possibly medium scale, but the feasibility remains to be proven. It is difficult to see that CMR is competitive for large-scale plants, because the membrane area scales directly with capacity, as opposed to an ASU, which has a better economy of scale.

6. Conclusion

This paper demonstrates that the ATR technology holds promises for significant, further improvements, both as a stand-alone technology and in combination with HTER in series arrangement. These technologies will be the dominant, at least for the next 5–10 years horizon. Of the new, more radical technologies emerging, CMR shows promising results. However, with substantial issues still to be solved, CMR is not considered as a real competitor to ATR or combinations of ATR/HTER within the next 10 years.