Figure 1. Transport of synthesis gas waste heat boiler for one of the ORYX units.

Synthesis gas technology

Ib Dybkjær, Haldor Topsøe A/S, Denmark, provides an update on state of the art synthesis gas technology and discusses possible future developments of the technology.

A breakthrough in the development of the emerging gas to liquids (GTL) industry is, at the time of writing, scheduled to happen on 6th June 2006, when the Oryx plant in Qatar will be officially inaugurated. Oryx is the first full scale, modern GTL production facility in the world. It is based on a global cooperation agreement between Sasol and Haldor Topsøe made in 1998, combining the Sasol Fischer-Tropsch and Haldor Topsøe synthesis gas technologies. Figure 1 shows one of the synthesis gas waste heat boilers during transport and may serve to illustrate the physical size of the equipment used in this plant.

Owned by Qatar Petroleum and Sasol, the Oryx plant has required an investment of close to US$ 1 billion. Its two identical lines will convert a total of 330 MMSCFD of natural gas to synthesis gas using technology licensed from Haldor Topsøe. The synthesis gas will be converted to an intermediate wax product by Sasol's slurry phase distillate (SPD) process and finally to synthetic fuels (24 000 bpd high quality diesel, 9000 bpd naphtha, and 1000 bpd LPG) using hydrocracking technology from Chevron. A similar plant, the Escravos project in Nigeria, is under construction, based on the Sasol/Haldor Topsøe cooperation, and other, even larger projects are planned. Background information concerning the emerging GTL industry and the chemistry of synthesis gas production may be found in reference 1. A comprehensive review of synthesis gas technologies is given in reference 2.

This article will celebrate the inauguration of the Oryx plant by reviewing the state of the art synthesis gas technology and by discussing possible further developments of the technology.

State of the art technology

A competitive technology commercially available today for production of synthesis gas for Fischer-Tropsch (FT) synthesis using C o-based catalysts is autothermal reforming (ATR) at a low steam to carbon of 0.6. It may be combined with prereforming and reheat of prereformed feed to the maximum allowable temperature. This technology was developed by Haldor Topsøe during the 1990s through extensive efforts involving pilot plant operation, CFD simulations, reactor modelling, catalyst development, and industrial scale demonstrations. Industrial plants using the technology are in operation in Europe (since early 2002) and in Sasolburg in South Africa (two lines, since

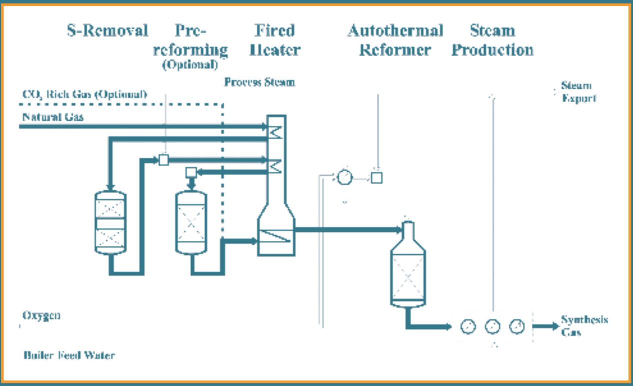

Figure 2. Typical process flow diagram for synthesis gas production.

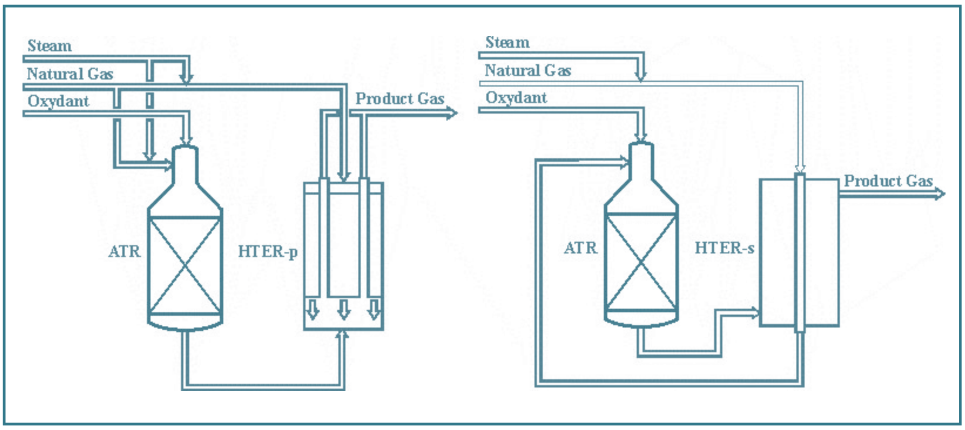

Figure 3. Combination of ATR and HTER.

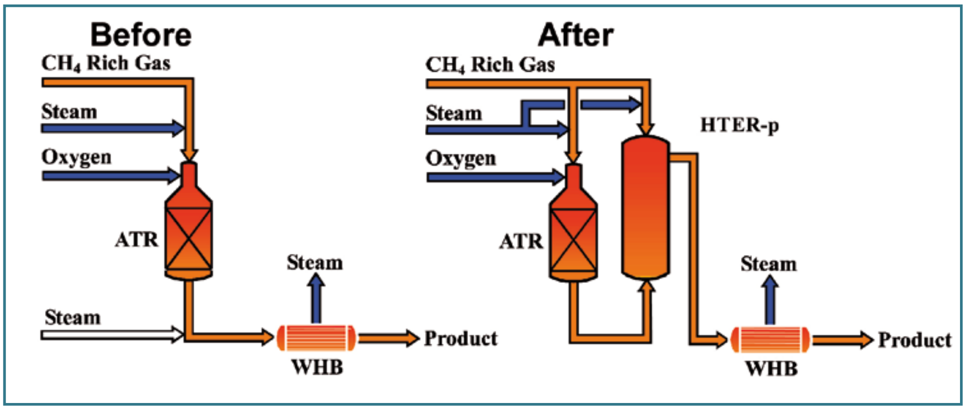

Figure 4. Gas heated reforming in South Africa.

late 2004). The technology has also been selected for the first of the new generation of large GTL plants, the Oryx plant and the Escravos GTL project in Nigeria. Furthermore, the technology has been chosen for the 7500 tpd VIVA methanol project in Nigeria and for several large GTL projects in various stages of planning.

A typical, simplified flow diagram for the preferred process for synthesis production is shown in Figure 2. Natural gas feed is mixed with a small amount of hydrogen and desulfurised over a hydrogenation catalyst followed by zinc oxide, which absorbs the hydrogen sulfide formed by the hydrogenation reaction. The desulfurised feed is mixed with process steam to an overall steam to carbon ratio of 0.6 and passed to the prereformer, where all higher hydrocarbons are converted adiabatically over a Ni catalyst. In addition, the methane reforming reaction and the shift reaction are equilibrated. The resulting mixture of methane, hydrogen, carbon monoxide, carbon dioxide and steam is heated to the highest possible temperature, mixed with external recycle gas in the amount required to ensure the correct hydrogen to carbon monoxide ratio in the final synthesis gas, and passed to the ATR reactor. Here, it is partially burned with oxygen in the mixer/burner and in the combustion chamber above the catalyst bed, and further reacted to equilibrium for the methane reforming reaction and the shift reaction in the catalyst bed. In addition, the catalyst converts any soot precursors formed in the combustion reaction to harmless substances so that the product gas is free of soot.

The product gas from the ATR is cooled by the production of saturated high pressure steam and further by air and/or water cooling, before condensate is separated, and the final synthesis gas is introduced into the FT synthesis section. The feedstock is preheated in a fired heater before the desulfurisation and before and after the prereformer using excess offgas from the FT synthesis and the hydrocracking unit as fuel. Oxygen is preheated by MP steam from the FT section and mixed with a small amount of saturated HP steam before it is introduced into the ATR. The main part of the high pressure steam is superheated in a fired heater and used in turbines driving the compressors in the air separation unit (ASU) producing oxygen for the ATR. Excess MP steam is used for various purposes.

Process condensate is stripped and reused as boiler feed water, making the synthesis gas unit a net water producer.

Next generation ATR

ATR holds promise for significant further improvement, both as a stand alone technology and as part of process concepts combining the ATR with other technologies, for example heat exchange reforming, as discussed below. Intensive development work is ongoing to further improve the technology, especially by reducing the steam to carbon ratio and increasing the unit capacity. The goal of these efforts is mainly to reduce investments and to allow construction of ever larger single line units. Energy efficiency per se is of secondary importance since feedstock for GTL is normally cheap. However, high energy efficiency means smaller feed pretreatment units and reduced requirements for utilities and is thus indirectly important for the economics also in cases, where feedstock cost is very low. Furthermore, high energy efficiency means low release of carbon dioxide, which is desirable for environmental reasons.

The potential for improvement of the ATR technology mainly lies in reduction of the steam to carbon ratio and in increased single line capacity. As mentioned above, the technology has today been commercialised at a steam to carbon ratio of 0.6. However, pilot plant operation has demonstrated steam to carbon ratios as low as 0.2[3].

Heat exchange reforming plus ATR

Heat exchange reforming is explored by several parties as a means of improving the processes for production of synthesis gas for GTL units and other purposes. The concepts use heat available in the process gas downstream an ATR for steam reforming in a heat exchanger type of reactor. The purpose is to increase the ratio between steam reforming and partial oxidation so that the recycle of tail gas can be optimised outside the range which is possible with ATR alone (leading to reduced oxygen consumption and higher overall carbon efficiency[4]), and to do this without additional firing, which would lead to an undesired excess of waste heat.

The principle of heat exchange reforming is not new. It has been practised in industrial units since the 1980s, albeit at conditions much less severe than those prevailing in GTL plants. Different arrangements are possible, as illustrated in Figure 3.

Table 1. Combination of ATR and HTER

Case	ATR (Base)	ATR low S/C	ATR with parallel HTER	ATR with series HTER
S/C-ratio	0.6	0.4	0.4/1.1	0.4
O_2 Cons. per bpd product - index	100	92	82	81
Total LHV efficiency - index	100	105	108	109
SGU investment per bpd - index	100	69	81	76
ASU investment per bpd - index	100	83	76	74
SGU + ASU investment per bpd - index	100	76	79	75

In the series arrangement, all gas passes through the steam reforming unit and then through the ATR. This will mean that the steam reforming catalyst may set the lower limit for the steam to carbon ratio. In the parallel arrangement the two reformers are fed independently, giving freedom to optimise the steam to carbon ratio individually. However, the heat exchange reformer must operate at a higher temperature than in the series arrangement in order to obtain a low methane concentration in the synthesis gas.

The main challenge in both the series and the parallel arrangement is the control of metal dusting corrosion in the heat exchange reformer. Mechanical design including choice of materials is very critical. Metal dusting is an attack on the metal surface resulting in pits or general loss of material. The mechanism is related to the destruction of the protective oxide layer on the surface followed by carbide formation in grain boundaries, causing disintegration of the material. The potential for metal dusting is highest in carbon monoxide rich gases at temperatures of 400 - 800 ˚C, i.e. at conditions which are likely to prevail for equipment during cooling of the synthesis gas downstream the ATR reactor. Very significant efforts are exerted to improve the understanding of the phenomena and to identify satisfactory materials and/or protection methods. However, metal dusting corrosion will remain a challenge in the design of processes and equipment until the ultimate materials or protection methods are developed, and a complete understanding of the phenomena is acquired.

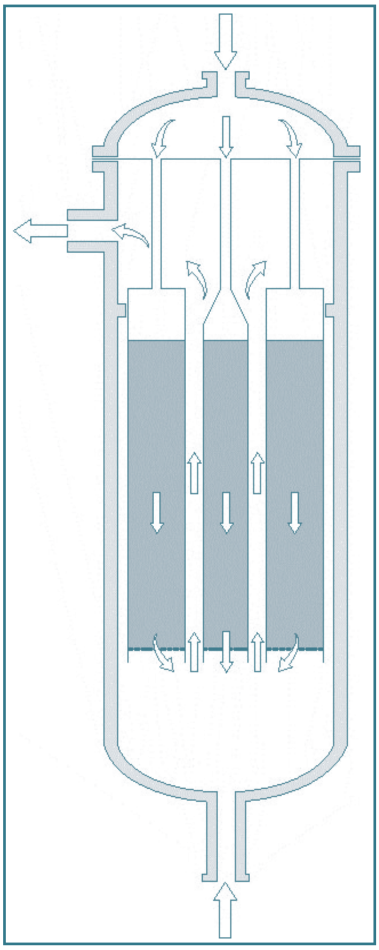

Figure 5. Gas heated reforming in South Africa.

A heat exchange reformer designed by Haldor Topsøe for operating in tandem with an ATR at low steam to carbon ratio was started up at Sasol´s facilities in Secunda, South Africa, in late 2002[5]. The heat exchange reformer was installed as a revamp of an existing installation to increase the capacity by approximately one third, and it is today an integrated part of the industrial operation. The process concepts before and after the revamp are shown in Figure 4. The feed is split into two streams: one to the original ATR, and the other to the new heat exchange reformer. After passing the two reformers, the converted gases are mixed, and the mixture serves as heat source for the steam reforming reaction in the heat exchange reformer. The heat exchange reformer is a proprietary Haldor Topsøe design denominated HTER-p (earlier the design was referred to as GHHER[5]), illustrated in Figure 5. The reformer contains two catalyst beds installed together with the required heat transfer surface inside one pressure shell. The heat transfer surface is inside double tubes, and one catalyst bed is inside the inner tube, while the other is in the space between the outer tubes.

Process studies

Comparative studies have been made to explore the effect of changing from the present ATR technology to future technologies presently under development. The goals of the studies were to obtain an increase in single line capacity of 15%, an increase in energy efficiency of at least 5%, and a reduction in investments of more than 20%. Some results are shown in Table 1. In the three last cases, advantage has been taken of optimised process conditions, new equipment designs, and increased unit capacity. It is seen that significant reductions in both investments and consumption figures are predicted.

Conclusion

GTL is attracting attention as a promising area for future developments in the energy sector. Proven technology is available, and several large projects are in advanced stages of development. The first project, the Oryx plant in Qatar, will start up in the very near future.

The most attractive technology today is oxygen blown ATR at low steam to carbon ratio, and this technology has been chosen for the projects which are closest to realisation. ATR holds potential for further optimisation and for adjustment to the requirements following from possible future developments in FT technology. It is also attractive for combinations with various forms of heat exchange reforming once these are developed for industrial use at the relevant conditions.

References

1. DYBKJÆR, I., 'Synthesis Gas Technology for GTL in: Fundamentals of Gas-to Liquids', *Petroleum Economist*, 2003.
2. AASBERG-PETERSEN, K., CHRISTENSEN, T.S., DYBKJÆR, I., SEHESTED, J., ØSTBERG, M., COERTZEN, R.M., KEYSER, M.J. and STEYNBERG, A.P., 'Synthesis Gas Production for FT Synthesis', *Stud. Surf. Sci. Cat. 152*, 258/405, 2004.
3. CHRISTENSEN, T.S., ØSTBERG, M. and BAK-HANSEN, J.-H., Process Demonstration of Autothermal Reforming at Low Steam-to-Carbon Ratios for Production of Synthesis Gas, AIChE Annual Meeting, Reno, Nevada, USA, 4-9 November 2001.
4. BAKKERUD, P.K., GØL, J.N., AASBERG-PETERSEN, K. and DYBKJÆR, I., 'Preferred synthesis gas production routes for GTL', *Stud. Surf. Sci. Cat. 147*, 13/18, 2004.
5. LOOCK, S., ERNST, W.S., THOMSEN, S.G. and JENSEN, M.F. Improving carbon efficiency in an auto-thermal methane reforming plant with Gas Heated Heat Exchange Reforming technology, Presented at the World Congress of Chemical Engineering 2005, Glasgow, UK, 2005.