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Syngas in perspective

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Abstract

Syngas manufacture is an important part of a Fischer–Tropsch (FT) plant as it is responsible for ca. 60% of the investments. The developments of syngas technologies are summarized in Section 1. The present choice for large-scale FT plants based on natural gas is autothermal reforming. The requirements to the syngas and the state of art are summarized. The main costs of an ATR unit are related to the manufacture of oxygen. Air-blown technologies are discussed and compared with ATR.

Keywords: Syngas; Fischer–Tropsch; Natural gas

1. Historical review

1.1. Steam reforming

Efficient syngas technology is a necessity for commercial Fischer–Tropsch (FT) synthesis [1]. Actually, one of the early studies of the reforming reactions was carried out by Fischer and Tropsch [2]. They reported nickel and cobalt to be active for CO_2 reforming of methane and that methane in coking gas was equally well converted by CO_2 or H_2O and endothermic reforming reactions:

$$CH_4 + H_2O = CO + 3H_2 \quad (1)$$

$$CH_4 + CO_2 = 2CO + 2H_2 \quad (2)$$

The first patent on supported nickel catalysts was used by Mittasch and coworkers [3,4] in 1912 for steam reforming. The first tubular reformer using natural gas or feedstock [5,6] was installed by Standard Oil in Baton Rouge in 1930 and later similar units were installed. The breakthrough of the steam reforming technology occurred in 1962 when ICI succeeded in starting two tubular reformers operating at pressure (15 bar) [6,7]. In addition, the plants were based on steam reforming of naphtha:

$$C_nH_m + nH_2O = nCO + (n + \tfrac{1}{2}m)H_2 \quad (3)$$

This is the reverse FT reaction.

Conversely, the diesel product from the FT synthesis can be reformed into hydrogen-rich gas as illustrated in Fig. 1. This may be a way of providing hydrogen for fuel cells in cars [8].

Low-temperature steam reforming of naphtha was used to produce methane-rich gas. This reaction was pioneered by British Gas [9], originally using methanol as fuel. During the energy crisis in the 1970s, this technology followed by methanation was used to convert naphtha into substitute natural gas [10]:

$$CO + 3H_2 = CH_4 + H_2O \quad (4)$$

Thereby, the syngas cycle is closed as illustrated in Fig. 2.

The first Topsoe reformer was started in 1956 and the further industrial milestones are summarized in Table 1.

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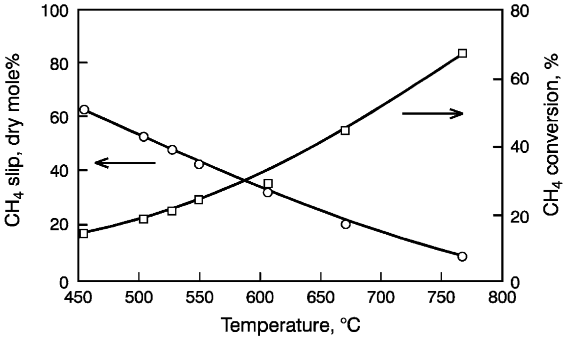

Fig. 1. FT diesel conversion over RKNGR ($H_2O/C = 3.7$, 25 bar).

1.2. Partial oxidation

A parallel development in syngas technology was based on conversion with steam and oxygen. In this way, there was no need for external heat

$$CH_4 + \tfrac{3}{2}O_2 = CO + 2H_2O \tag{5}$$

followed by reactions (1) and (2). The thermal processes at pressure were developed by Texaco [11] and Shell [12] during 1945, whereas the principle of a catalytic process was mentioned already by Mittasch and coworkers [3,4].

The hybride solution, autothermal reforming, using partial combustion in a flame followed by catalytic reaction was pioneered by SBA and BASF in the 1930s [4]. Topsoe and SBA in the 1950s [13] and later Topsoe alone [14] further developed the technology at first for ammonia plants and later for syngas for large-scale gas to liquid plants [15,16] as illustrated in Table 2.

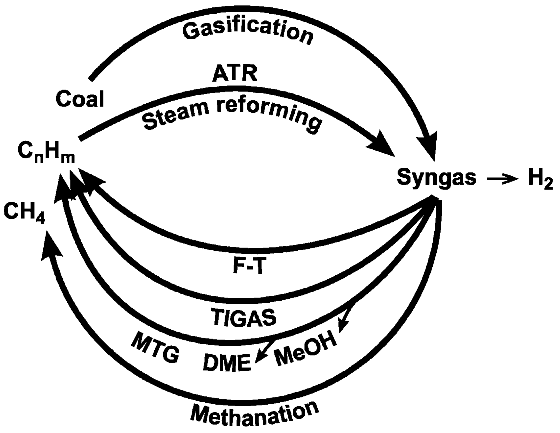

Fig. 2. The syngas cycle.

Table 1
Industrial milestones for Topsoe steam reforming (first start-ups of reformer)

Steam reformer	1957
Hydrogen plant	1962
Naphtha reformer	1965
42 bar reformer	1966
RKNR-based reformer	1968
Reformer with CO_2 recycle	1969
Heat exchange reformer (HER)	1984
Steam reformer based on advanced reforming ($H_2O/C = 1.5$, $T_{exit} = 950\,^{\circ}C$)	1985
Prereformer	1986
Steam reformer based on SPARG technology ($H_2O/CH_4 = 0.7$; $CO_2/CH_4 = 0.8$)	1987
Second generation heat exchange reformer (HTCR)	1995
CO plant based on noble metal catalyst	1997
Steam reformer with flux >100.000 kcal/m^2/h	2001

Catalytic partial oxidation with no flame was practised at low pressure in 1950s [12] and later by Lurgi at pressure [17]. The syngas manufacture by CPO millisecond reactors [18] has not yet been applied at industrial scale.

1.3. Research efforts

The development of Topsoe's technologies has been a multi-disciplinary effort over a number of decades. The catalyst development was a result of optimization of the magnesium alumina spinel system as well as stabilized magnesia supports. Earlier, the work was based on fundamental understanding of parameters

Table 2
Industrial milestones for Topsoe oxygen-blown autothermal reforming (first start-up)

Industrial autothermal reformer[a]	1958
Large-scale single line ATR (1000 MTPD NH_3)[a]	1978
Oxygen-blown ATR for syngas, $H_2O/C = 2.0$	1987
Modified to $H_2O/C = 1.3$	1989
CTS-burner in revamps	1992
Two-step reformer for MeOH plant	1997
Industrial demo of $H_2O/C = 0.6$	1999
Industrial syngas plant, $H_2O/C = 0.6$[b]	2000
Industrial GTL plants[b]	2001

[a] Enriched air.

[b] Contracts.

influencing the nickel surface area and the specific activity [19] as well as promoter effects for inhibition of carbon formation [20]. The initial vague ideas on the mechanism of the reforming reactions and the promoter effects have been clarified by recent ultra high vacuum studies at well-defined surfaces as well as by DFT-calculations [21]. The feedstocks ranged from natural gas to diesel [22] and with steam or carbon dioxide as reactants [23]. It was also shown that carbon limits could be broken on a sulphur passivated catalyst [24] and alloy catalysts [25].

In parallel to these developments, the steam and CO_2 reforming process was studied in full size monotube pilot plants at first at Frederikssund in Denmark in 1960s [26], and later from the 1980s at Houston, TX [27,28]. Apart from demonstration, the units were used to establish a design basis and explore the limits of the heat transfer reforming technology. The heat transfer parameters at the very high Reynolds numbers are not known from literature. Often, the reformer tube was equipped with so many thermocouples and gas sampling systems that one could fear they influenced the performance. The result was a pseudo-homogeneous two-dimensional reformer model which allowed better optimization and safe design [27].

The explorative studies indicated that catalyst activity would not be the limiting factor when boosting the capacity [29]. The pilot results, the feedback from industry as well as the availability of new tube materials led to the advanced reforming design with more economic operation at tube wall temperatures, higher heat flux and lower steam to carbon ratio with the use of a prereformer, the feedstock range could include naphtha and diesel [29].

The study of the autothermal reforming process was hardly possible at laboratory scale. Most of the pioneering work was done on some of the first industrial units. Further optimization was carried out at the Houston pilot during the 1990s [15]. This led to the development of the CTS burner and demonstration of soot-free operation at low steam to carbon ratio [15]. The pilot work was supplemented by cold flow simulations and CFD-calculations [30].

2. ATR for FT syngas

Oxygen-blown ATR is the preferred technology for large-scale FT plants [1]. It becomes cheaper than steam (and CO_2) reforming because of a more favourable economy of scale for oxygen plants than for the tubular reformer [1].

CO is the only reactant for the low-temperature FT synthesis for wax and diesel and the cobalt catalyst is not active for the shift reaction. The desirable composition of the syngas for the low-temperature FT corresponds to a ratio H_2/CO of ca. 2.

This is different from the high-temperature FT synthesis and the methanol synthesis for which the catalyst are active for the shift reaction. CO_2 is also the main reactant in the methanol synthesis. Hence, a different integration of synthesis and syngas plant is required. For the low-temperature FT synthesis, CO_2 remains inert and is lost or returned to syngas plant [1] as shown in Fig. 3.

Direct production of a gas with $H_2O/C = 2$ is achieved by ATR only at very low H_2O/C ratio and high exit temperature [1,15]. At higher H_2O/C ratio,

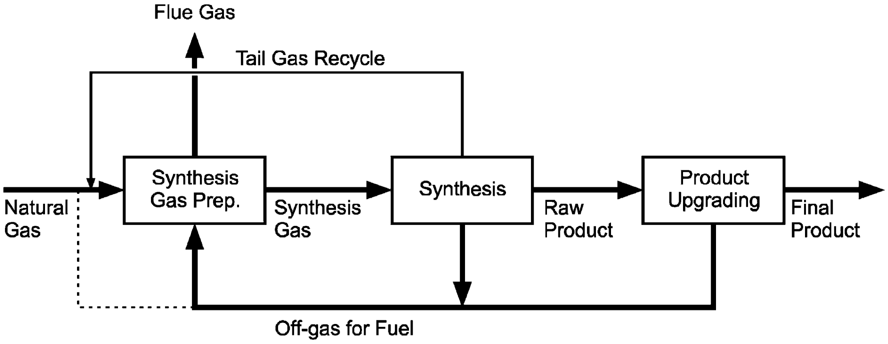

Fig. 3. Flow scheme for natural gas based low-temperature FT synthesis [1].

the value of 2 is best obtained by partial recycling of CO_2 or CO_2-rich tail gas [1] (Fig. 3). It may be combined with removal of H_2 from the syngas. This could be an attractive way of producing H_2 for the hydrocracking of FT wax to diesel.

In the ATR process as practised by Topsoe [15,16], the feedstock is reacted with a mixture of oxygen and steam by the use of a proprietary burner and a fixed catalyst bed for the equilibration of the gas and removal of soot precursors.

The autothermal reformer is a very simple piece of equipment with a proprietary burner and a catalyst bed in a brick-lined reactor. The most expensive part of the plant is the oxygen plant, typically amounting to 30–40% of the investments of the syngas unit.

At very low steam to carbon ratio, the ratio $H_2/CO = 2.0$ can be achieved almost without CO_2 recycle [15]. These conditions have been demonstrated for the ATR process [16].

For very large FT plants, it was found [15] that the ATR technology does not set the limit for the size of single stream units. Capacities of at least 35.000 bbl/day FT products can be accommodated in one ATR reactor (but not necessarily by other parts of the plant, e.g. boilers, compressors, etc.). The Topsoe ATR process has been selected for two F.T. Projects (Nigeria and Quatar). They each have a capacity of 35,000 bpd and are based on Sasol/cherron technology for synthesis and hydrocracking.

3. Alternative routes

Other reactor concepts for the ATR process introduce complexity. Irrespective of whether a thermal burner or a catalytic burner or fixed or fluidized catalyst bed is used, the composition of the product exit gas will be determined by the thermodynamic equilibrium at the exit temperature which is determined by the feed composition and the adiabatic temperature increase. However, catalytic partial oxidation [18] may appear as the ideal solution:

$$CH_4 + \tfrac{1}{2}O_2 = CO + H_2 \qquad (6)$$

if it was not accompanied by reactions (1) and (2).

This “dream reaction” has the right $H_2/CO = 2$ and a very low heat of reaction (9 kcal/mol) comparable to that of the CO-shift reaction. However, the ATR with the equilibration of reactions (1) and (2) has a high selectivity for reaction (6) as illustrated in Table 3 [1,15].

Table 3
ATR—selectivity for $CO + H_2$ (data from pilot test [1,15])[a]

Product gas analysis (vol.%)	
H_2	56.8
N_2	0.2
CO	29.0
CO_2	2.9
CH_4	1.0
H_2O	10.1
Total	100.0
CH_4 conversion (%)	96.9
Selectivity to CO (%)	90.8
Equilibrium temperatures	
Reforming (°C)	1063
Shift (°C)	1076

[a] $H_2O/C = 0.21, O_2/C = 0.59, P = 24.5\,\text{bar}, T_{\text{exit}} = 1057\,^{\circ}C$.

Studies of CPO have indicated that H_2/CO ratios lower than predicted at equilibrium can be achieved at partial conversion [18]. However, at full conversion, the gas most likely approaches thermodynamic equilibrium [31].

The main costs (up to 40%) of the costs of a syngas plant based on ATR (CPO or POX) are related to the oxygen plant [1]. As a result, routes based on air, eliminating the cryogenic air separation plant, have been suggested [32–34].

The use of air in the process stream is possible only in once-through synthesis schemes to avoid a huge accumulation of nitrogen (the syngas will contain about 50 vol.% N_2). Attempts to use air instead of oxygen result in big gas volumes and consequently big feed/effluent heat exchangers and compressors [1]. This is hardly feasible for large-scale plants. The scheme also results in big purge gas stream which can be utilized only for export of energy as steam or electricity. The additional energy consumption involved in compressing air is substantial. This was illustrated by a study [35] comparing FT plants based on air-blown ATR with oxygen-blown ATR. Results are summarized in Table 4.

The energy consumption is significantly higher for the air-blown scheme, whereas the investments of

Table 4
Comparison of air-blown and oxygen-blown ATR schemes [35]

Oxidant	Air	Oxygen
Feed + fuel (vol.%)	1.11	1.00
Syngas flow (vol.%)	1.93	1.00
Export steam	1.57	1.00
Power for oxidant	4.60	1.00
Net energy consumption	1.13	1.00

the two syngas plants are comparable. An air-blown process suggested in literature [33] results in an energy consumption more than twice that for an oxygen-blown scheme because of a low conversion in the once-through FT synthesis [35].

Cheaper technology for oxygen manufacture may be another route to reduce costs of syngas manufacture. One attempt is to eliminate the oxygen plant and to include a reactor concept with oxygen addition through a membrane [36].

With the high driving force across the membrane, there is no need for compression of air to the process pressure. However there is still a need for big feed/effluent heat exchanger in the process scheme for catalytic membrane reforming (CMR). The reported oxygen ion diffusion on fluxes [37] make a syngas unit possible, but still the feasibility has to be proven.

4. Conclusions

Large-scale conversion of natural gas into FT products may play an important role in the energy economy. A key parameter is the cost of the manufacture of syngas. Today ATR appears the cheapest solution fulfilling the optimum requirements of the FT synthesis. Future improvements may be related to reduction of the costs of manufacture of oxygen and a tight integration of the oxygen plant with the syngas unit.

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