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Production of synthesis gas

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Abstract

The state-of-the-art for the production of synthesis gas from the steam reforming of methane is reviewed and discussed. Particular attention is given to the design of the tubular reformer and carbon formation on the nickel catalyst. Improvements in syngas technology are discussed, including: CO_2 reforming, autothermal reforming and heat exchange reforming, and the energy efficiencies of direct and indirect methane conversion are compared and contrasted.

1. INTRODUCTION

Natural gas and light hydrocarbons will remain the major feedstock for the manufacture of syngas. Although coal reserves are large and coal remain available at lower prices than hydrocarbons, the investments in a coal-based syngas plant may amount to three times those required for a natural-gas-based plant.

Steam reforming is the established process for converting natural gas and other hydrocarbons into synthesis gas and important products [1–3]. Ammonia synthesis is still the largest single consumer of syngas, but the growing interest in C_1 chemistry and in large-scale conversion of natural gas into liquid products has created a need to explore the limits of the reforming technology to make more cost-effective syngas [3]. Steam reforming will also play an increasing role in providing the marginal hydrogen for refineries [4]. This demand results from increased hydrotreatment of diesel fractions, which is taking place simultaneously with a reduction in the usual hydrogen supply from catalytic reforming because of the demand for less aromatics in "reformulated" gasoline. Hydrogen-rich off-gas from methanol plants supplying feed to MTBE production may contribute to the "hydrogen pool" in refineries.

Hydrogen from gasification of heavy oil fractions may eventually supplement hydrogen from steam reforming.

The steam-reforming process converts two stable molecules into the more reactive syngas, and hence the overall reaction is strongly endothermic:

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$$CH_4 + H_2O = CO + 3H_2 \quad (-\Delta H^{\circ}_{298} = -206\ \text{kJ/mol}) \tag{1}$$

$$CO + H_2O = CO_2 + H_2 \quad (-\Delta H^{\circ}_{298} = 41\ \text{kJ/mol}) \tag{2}$$

Higher hydrocarbons in natural gas, LPG or liquid hydrocarbons will react in a similar way:

$$C_nH_m + nH_2O = nCO + \left(n + \frac{m}{2}\right)H_2 \quad \text{endothermic} \tag{3}$$

Steam may be replaced by CO_2, which gives a much more favourable H_2/CO ratio for many syntheses:

$$CH_4 + CO_2 = 2CO + 2H_2 \quad (-\Delta H^{\circ}_{298} = -247\ \text{kJ/mol}) \tag{4}$$

Reactions (1)–(4) require a catalyst typically supported on nickel.

Methane may also be converted by means of oxygen into synthesis gas through partial oxidation:

$$CH_4 + \tfrac{1}{2}O_2 = CO + 2H_2 \quad (-\Delta H^{\circ}_{298} = 38\ \text{kJ/mol}) \tag{5}$$

This reaction will be accompanied by complete gasification. The partial combustion may be non-catalytic or use a catalyst, typically supported nickel or platinum.

2. STATE OF THE ART

2.1 Tubular reformer

In order to supply the heat for the overall endothermic steam-reforming reaction, the catalyst is loaded into a number of high-alloy tubes placed inside a furnace equipped with burners as shown in Fig. 1. Typical inlet temperatures are 450–650°C, and the product gas leaves the reformer at 700–950°C depending on the applications.

In a typical tubular reformer furnace, about 50% of the heat produced by combustion in the burners is transferred through the reformer tube walls and absorbed by the process [1,3]. The other half of the fired duty is available in the hot flue gas and is recovered in the waste heat section of the reformer for preheat duties and for steam production. In this way, the overall thermal efficiency of the reformer approaches 95%.

The reformer tubes are subject to very large stresses since they operate at high temperatures with very large temperature gradients. The maximum allowable stress value in the tubes is strongly influenced by the maximum tube wall temperature and the maximum heat flux. Even a slight increase in the maximum tube wall temperature may result in a serious reduction of the expected life of the tube.

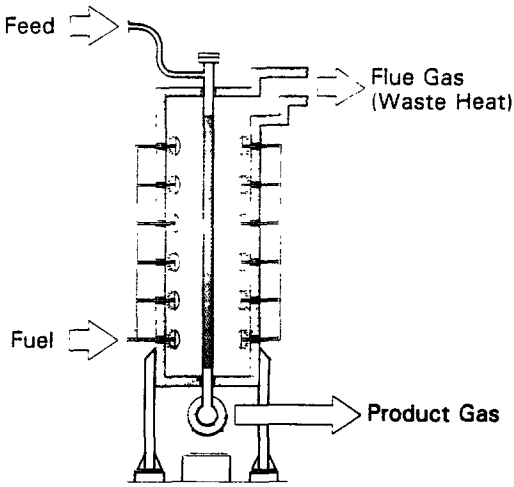

Fig. 1. Tubular reformer.

Reformer tubes are normally designed for an average expected lifetime of 100 000 hours, and much knowledge is required for the choice of heat flux, tube dimensions, design temperatures and tube materials. New materials having superior creep rupture characteristics allow a design [3] with a considerably reduced tube wall thickness and with exit temperatures exceeding 950°C, corresponding to tube wall temperatures of up to 1050°C.

The heat input through the reformer tube wall results in radial temperature and concentration gradients in addition to the axial gradients. The radial temperature gradients are significant, in particular at the tube wall, whereas radial concentration gradients are insignificant. Therefore, a two-dimensional model [1,3,5] is required for working out the details of the conversion and temperature profiles.

Fig. 2 shows typical conversion profiles in a tubular reformer. The gas rapidly approaches the equilibrium of eqn. (1) and (2) with the axial temperature gradient becoming the driving force for the further conversion of methane [1].

The effectiveness factor [1,6] of the reforming reactor, η, decreases away from the reactor inlet with typical values below 0.1. Mass transfer restrictions are caused by pore diffusion, whereas heat transfer restrictions are located in the gas film. The strong endothermic reaction results in a temperature drop

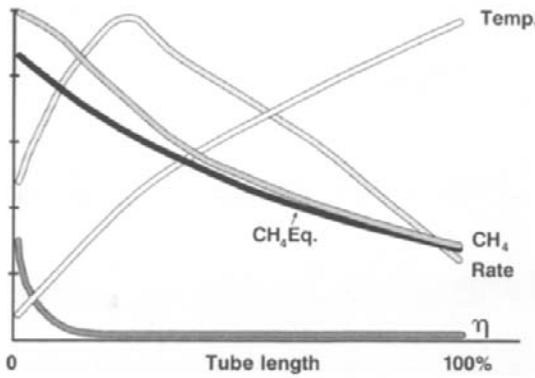

Fig. 2. Typical conversion profiles in a tubular reformer.

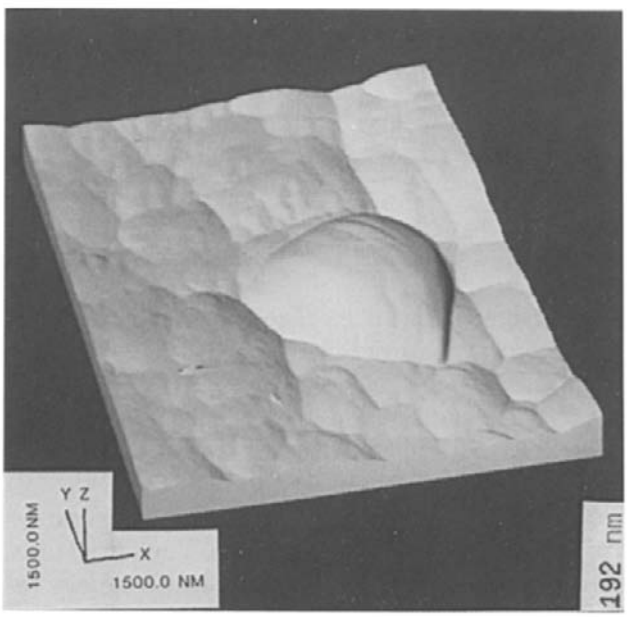

Fig. 3. Image of commercial steam reforming catalyst [7] (DME rasterscope 3000 atomic force microscope).

of 5–10°C over the gas film in spite of a high mass velocity, corresponding to Reynolds numbers of about 10 000.

The catalyst particle size and shape should be optimized to achieve maximum activity and maximum heat transfer while minimizing the pressure drop. The high mass velocities necessitate a relatively large catalyst particle size to obtain a low pressure drop across the catalyst bed. The steam reforming catalyst is normally based on nickel. Cobalt and noble metals are also active but

more expensive. The metal catalysts are susceptible to sulphur poisoning [1]. Attempts to use non-metallic or sulphur resistant catalysts have had no commercial success because of the low activity. The catalyst properties required are dictated by the severe operating conditions, i.e. temperatures at the inlet of app. 450–650°C, and at the exit of 700–950°C, plus steam partial pressures up to 30 bar. The activity depends on the nickel surface area with a typical dispersion of 1% (particle size 20–200 nm). The nickel crystals will sinter rapidly above the Tammann temperature, which is 590°C for nickel [1]. Fig. 3 shows an image of a very large (700 nm) nickel crystal on a sintered commercial steam reforming catalyst observed in an atomic force microscope [7]:

2.2 Mechanism and kinetics

The chemisorption of methane on nickel involves the direct breaking of a C–H bond with no adsorbed molecule as precursor [8,9]. This requires that the molecule has sufficient energy to overcome a barrier of about 52 kJ/mol and that it hits the free nickel site with free neighbouring sites. The adsorbed CH_3* species is converted into an adsorbed carbon atom through step-wise dehydrogenation [10].

$$CH_4 = CH_3* \rightarrow CH_2* \rightarrow CH* = C* \tag{6}$$

The rate of adsorption is an order of magnitude higher on the open (110) nickel surface plane than on the dense (111) surface plane [11]. Adsorbed oxygen atoms were found to have no impact the chemisorption of methane except for decreasing the number of sites available [12]. By micro-kinetic analysis [10] of the experiments done to study the formation of carbon on the nickel surface exposed to methane and hydrogen, it was found that the best fit was obtained when the first, second and third dehydrogenation steps were assumed to be irreversible.

Early work on the kinetics of the steam reforming of methane [13] assumed the methane adsorption to be rate determining, which is in agreement with the general assumption of a first order dependence on methane. Later work [14] avoided the discussion of a rate determining step (rds) by using a steady state approach, and the following rate expression was obtained for the temperature range of 470–700°C:

$$r = \frac{k \cdot p_{CH_4} \cdot p_{H_2O}(1 - Q_R/K_p)}{f(p_{H_2O}, p_{H_2})(1 + K_{H_2O} \cdot (p_{H_2O}/p_{H_2}))} \tag{7}$$

where Q_R and K_p are the reaction quotient and the equilibrium constant, respectively for reaction (1), and $f(p_{H_2}, p_{H_2O})$ is a polynomial in p_{H_2}, p_{H_2O}. Eqn. (7) contains five temperature dependent constants.

Recently, Froment and co-workers [15] established a complex Langmuir-

Hinshelwood expression, using a classic approach, on the basis of 280 measurements but for a narrow range of parameters, with temperatures of 500–575°C, pressures of 3–10 bar and H_2O/CH_4 of 3–5. A number of rate equations were established on the basis of a mechanism involving 13 steps, assuming one of the steps to be the single rds.

The rate of reaction (1) is represented by:

$$r=\frac{\frac{kp_{CH_4}\cdot p_{H_2O}}{p_{H_2}^{2.5}}(1-Q_R/K_p)}{1+K_{CO}\cdot p_{CO}+K_{H_2}\cdot p_{H_2}+K_{CH_4}\cdot p_{CH_4}+K_{H_2O}(p_{H_2O}/p_{H_2})} \quad (8)$$

Also eqn. (8) contains five temperature dependent equilibrium constants. The model implies an unlikely negative heat of adsorption of steam. This may be a result of the narrow range of H_2O/CH_4 and temperatures studied. As a consequence, eqn. (8) was not able to predict the decrease in rate when replacing steam by carbon dioxide [16] (eqn. (4)). Apparently, the mechanism of the steam reforming reactions cannot be represented by a single rds for a wide range of conditions. The retarding effect of steam reflected by K_{H_2O} in eqns. (7) and (8) and in other kinetic expressions [1] for reaction (1) may also explain that the negative reaction order with respect to steam varies from catalyst to catalyst. Thus, the addition of alkali or the use of magnesia as support results in enhanced steam adsorption which is useful in eliminating carbon formation [1].

2.3 Carbon formation

Steam reforming involves the risk of carbon formation by the Boudouard reaction and by the decomposition of methane and other hydrocarbons.

$$2CO=C+CO_2 \quad (-\Delta H^\circ_{298}=172\ \text{kJ/mol}) \quad (9)$$

$$CH_4=C+2H_2 \quad (-\Delta H^\circ_{298}=-75\ \text{kJ/mol}) \quad (10)$$

$$C_nH_m\rightarrow nC+\frac{m}{2}H_2 \quad (11)$$

At high temperatures (above about 650°C), higher hydrocarbons may react in parallel to reaction (11) by thermal cracking (pyrolysis or steam cracking) into olefins which may easily form coke:

$$C_nH_m\rightarrow\text{olefins}\rightarrow\text{polymers}\rightarrow\text{coke} \quad (12)$$

Eqs. (9)–(11) are catalysed by nickel. The carbon grows as a fibre (whisker) [1,17] with a nickel crystal at the top. Adsorbed carbon atoms that do not react with gaseous molecules are dissolved in the nickel crystal and solve as carbon nucleated from the unexposed side of the crystal. The carbon is not

ideal, and the deviation from graphite data increases with decreasing size of the nickel crystals [1]. The higher the temperature of carbon formation, the less pronounced the effect. As illustrated in Fig. 4, the graphite planes in the whisker are almost parallel with the nickel surface which is reconstructed into a disordered surface close to the (111) plane [18]. The formation of the whisker may result in a reconstruction of the nickel crystal into a pear-like shape, as illustrated in Fig. 4. The non-ideal whisker structure results in equilibrium constants which are smaller than those calculated on the basis of graphite data [1,16] as illustrated in Fig. 5.

Eqn. (12) results in pyrolytic carbon encapsulating the catalyst [1].

Carbon formation may lead to breakdown of the catalyst, and the build-up of carbon deposits and degraded catalyst may cause partial or total blockage of reformer tubes, resulting in the development of "hot spots" or hot tubes. The uneven flow distribution will cause a self-accelerating situation with further overheating of the hot tubes. Therefore, carbon formation cannot be tolerated in tubular reformers.

For steam reforming of methane, there are two different carbon limits to consider [1].

Limit A is dictated by kinetics. It corresponds to conditions in the reformer where the kinetics allow methane to decompose into carbon instead of reacting with steam, even if thermodynamics predict no carbon formation after equilibrium has been reached in reactions (1) and (2). Carbon is stable in a

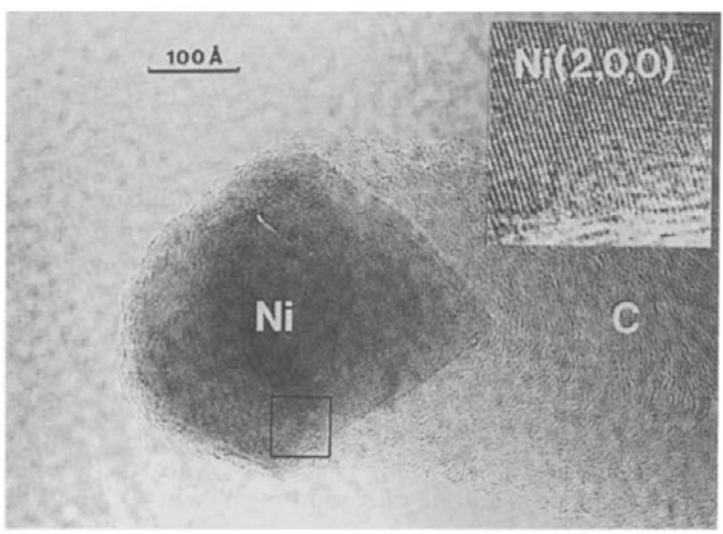

Fig. 4. High resolution electron microscopy of carbon whisker on commercial steam reforming catalyst [18]. Methane decomposition at 500°C. The graphite planes and nickel planes are apparent (JEM-4000 EX, electron microscope, Lund University, Sweden).

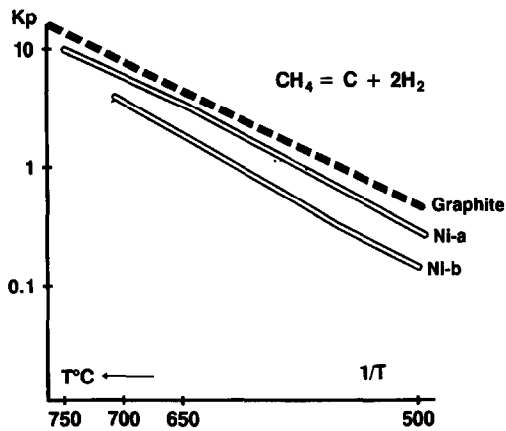

Fig. 5. Equilibrium constants for methane decomposition on nickel catalysts. Ni-a: commercial steam reforming catalyst, Ni-b: steam reforming catalyst (maximum Ni crystal size = 10 nm).

steady state. Carbon formation is then a question of kinetics, local process conditions and reformer design.

If the actual gas above the catalyst shows affinity for carbon formation according to reaction (10), there will be a tendency towards carbon formation. This can be expressed by the carbon activity [1] $a_c^{eq.}$ expressed by:

$$a_c^{eq.} = K_c \cdot \frac{p_{CH_4}}{p_{H_2}^2} \tag{13}$$

in which K_c is the equilibrium constant for the methane decomposition (eqn. 10), taking into consideration the deviation from graphite data caused by the whisker structure.

A safe, conservative design criterion [1] would be to require $a_c^{eq.} < 1$ at any position in the reformer tube.

However, at the inlet of the reformer with almost no hydrogen present, $a_c^{eq.}$ is much larger than one, which means that there is a possibility of carbon formation, but in practice no carbon is formed. Therefore, an important question for the industrial operation is: what is the maximum allowable inlet temperature before carbon will be formed? A similar situation may exist at other positions in the reformer close to the tube wall. Whether carbon-free operation is possible for $a_c^{eq.} > 1$ depends on whether the steady state activity [1] of carbon, $a_c^s < 1$.

a_c^s can be expressed by balancing the rate of carbon formation without the presence of steam with the rate of gasification of the adsorbed carbon atoms [1]. It can be shown [1] that $a_c^s \leqslant a_c^{eq.}$.

Limit B is dictated by thermodynamics. Carbon will be formed if the equilibrated gas shows affinity for carbon. This is called the "principle of equili-

brated gas" [1]. The equilibrated gas composition is achieved by calculating the gas composition with equilibration of eqns. (1) and (2). The principle is justified by the fact that the gas will be at equilibrium in most of the catalyst particle because of the low effectiveness factor. Normal reformers cannot operate if the principle of equilibrated gas is violated.

2.4 Higher hydrocarbons

Higher hydrocarbons give rise to carbon formation (reactions (11) and (12)) more easily than does methane, and special catalysts containing alkali [1,2] or based on active magnesia [1] are required. Using these special catalysts, tubular reformers can be operated with liquid hydrocarbons at $H_2O/C=2-3$, depending on feedstock characteristics, catalyst and reformer design. With a high-activity catalyst [1], the limit on the final boiling point is related mainly to the possibility of desulphurizing the feed to below 0.1 ppm, rather than to the reactivity of the hydrocarbons. With proper desulphurization, it has been possible to convert light gas oil into syngas with no trace of higher hydrocarbons in the product gas [1,19].

Olefins are the most critical higher hydrocarbons with respect to carbon formation [1]. The rate of carbon formation for olefins is several orders of magnitude higher than for other hydrocarbons. Olefins are normally not present in the feedstock, but they could easily be formed by thermal cracking of higher hydrocarbons in over-heated preheaters or even by oxidative coupling of methane in the presence of air in the feedstock. This problem can be eliminated with a pre-reformer [1,20,21], in which case, it is possible to use a high preheating temperature (650°C or above) without the risk of carbon formation [3,20].

Through adiabatic pre-reforming [3,22], all higher hydrocarbons are converted to methane and carbon oxides at conditions where carbon formation does not occur. The product stream can therefore be preheated with no risk of thermal cracking [20]. In this way, it is possible to replace part of the fired duty of the reformer furnace by external preheating and hence to reduce the costs [3]. In adiabatic pre-reformers, it is possible to process natural gas as well as full range naphtha. Typical operating temperatures [3,21,22] are in the range of 380–500°C.

2.5 Process schemes

The manufacture of syngas for ammonia synthesis has been described in detail elsewhere [3,23]. It is produced by a series of process steps comprising hydrodesulphurization, primary tubular steam reforming and secondary (air-fired) reforming, high and low temperature-shift conversion, carbon dioxide removal, and methanation. This results in a net energy consumption as low

as 27.2 GJ/t of ammonia for a stand-alone ammonia plant [23] at a cooling water temperature of 30°C.

For methanol synthesis, it is desirable to have a syngas with a module $(H_2-CO_2)/(CO+CO_2)$ slightly above 2 which corresponds to a value close to stoichiometry. If the module is larger than 2, surplus hydrogen is recycled to the reformer as fuel. If the module is below 2, the formation of by-products (higher alcohols, etc.) becomes excessive. For larger units (above 1000 t/d), it is economical to adjust the module to the optimum value by adding an oxygen plant and an oxygen fired secondary reformer downstream of the tubular steam reformer as shown in Fig. 6. A methanol plant based on this two-step [24] front-end has a total energy consumption of about 29.3 GJ/t corresponding to a thermal efficiency (LHV) of 68% with 80% being the theoretical maximum [3,25].

Fig. 7 shows an example of the state of the art for the manufacture of syngas with a high CO/H_2 ratio [26] through "advanced steam reforming technology". The naphtha feed is desulphurized and converted into C_1 components in the adiabatic pre-reformer operating at ca. 500°C. The effluent is pre-

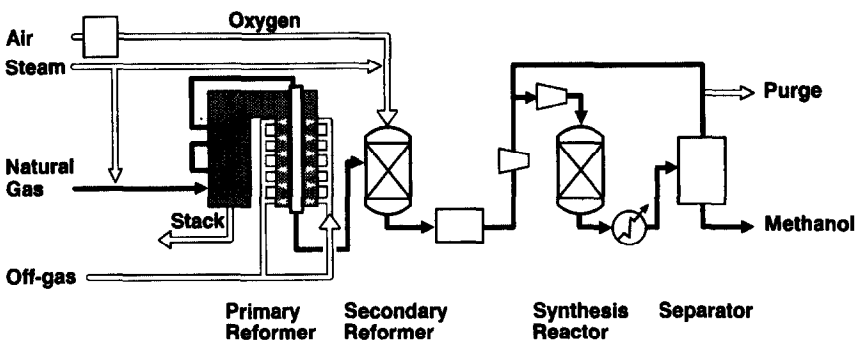

Fig. 6. Simplified process diagram of a methanol plant [25].

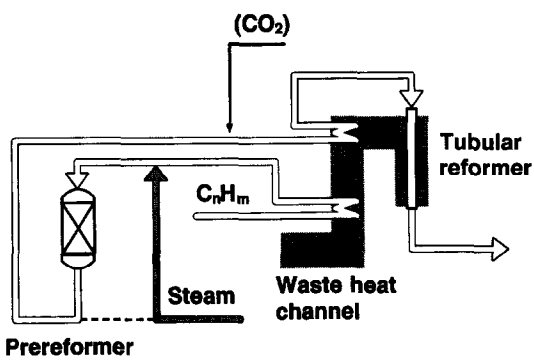

Fig. 7. State-of-the-art syngas plant for the manufacture of CO-rich gas.

heated to 635 °C before entering the tubular reformer, which operates with an exit temperature of 950 °C at an average heat flux of 82 kW/m^2. The overall H_2O/C ratio is 1.5 and CO_2 may be added to the effluent ($CO_2/C=0.4$) of the pre-reformer to reduce the H_2/CO ratio further.

3. IMPROVEMENTS IN SYNGAS TECHNOLOGY

3.1 CO_2 reforming

Steam may be replaced by carbon dioxide in the reforming reaction:

$$CH_4 + CO_2 = 2CO + 2H_2 \quad (4)$$

Eqn. (4) is of industrial interest because of the lower H_2/CO ratio in the product gas. CO_2 reforming is being practised in industry in various processes [27,28,29]. Recently, reaction (4) has attracted interest as a CO_2 consuming reaction [30,31].

Reaction (4) was studied over a number of base metal catalysts by Fischer and Tropsch [32] in 1928. A study of the kinetics of reaction (4) was published in 1967 by Bodrov and Apel'baum [33], who found that the data could be represented by a kinetic expression obtained for steam reforming under similar conditions on a nickel film [13]. A recent study [16] confirmed that replacing steam with carbon dioxide in the reforming reaction has no drastic effect on the mechanism. The activity trend for various groups of metals observed for steam reforming [1] with ruthenium and rhodium being the most active metals, is less pronounced for CO_2 reforming.

Thermodynamic calculations show that the carbon limits are approached when carbon dioxide is added to the reformer feed. With high CO_2 contents in the feed gas or when operating on carbon dioxide and methane alone, thermodynamics predict the formation of carbon [3].

The rate of carbon formation is known to be far lower on noble metals than on nickel, which is ascribed to a smaller dissolution of carbon into these metals [34]. Carbon-free CO_2 reforming has been reported on noble metal catalysts [16,31,35]. As with nickel, the noble metals show smaller equilibrium constants for methane decomposition [16] than those calculated on the basis of graphite, but the effect is even more pronounced and could probably be ascribed to the even smaller metal particles in these catalysts and the smaller dissolution of carbon.

Rhodium and ruthenium were found to have the highest selectivity for carbon-free operation [16], and this can be ascribed to the high reforming activity combined with low carbon growth rates. However, the availability of ruthenium and rhodium is too low to have a major impact on the total reforming catalyst market.

Similar results were achieved with a sulphur-passivated nickel catalyst,

however, high operating temperatures were required to achieve reasonable reforming rates [27,36]. Carbon-free CO_2 reforming could be achieved by "ensemble control" [37] on a partly sulphur-poisoned nickel catalyst. In this case, the sites for carbon formation are blocked, but sufficient sites are available for the reforming reactions. This effect is obtained by adding sulphur to the process feed. With sulphur coverage, the rate of carbon formation decreases more than does reforming showing that the ensemble for the reforming reaction is smaller than that required for the nucleation of the carbon whisker. Ensemble control allows operation at $(H_2O+CO_2)/CH_4$ ratios close to stoichiometry [27]. Operation on mixtures of CO_2 and methane without steam is also possible [27], except for the steam required for prereforming of the higher hydrocarbons in the feed.

3.2 Autothermal reforming

When using oxygen for the conversion of hydrocarbons, it is possible to achieve high equilibrium temperatures. This allows the use of high pressures (40–50 bar) while maintaining a low methane content in the product gas. Non-catalytic partial oxidation (Texaco, Shell) requires a very high temperature (ca. 1400°C) in order to cope with carbon formation. This requires a O_2/CH_4 ratio of about 0.7 [38].

Autothermal reforming as practised in the Topsoe process [39,40] solves the carbon formation problem by using of a proprietary burner and a fixed catalyst bed for equilibration of the gas. This results in a lower oxygen consumption ($O_2/CH_4=0.55$–0.6), however, with a certain amount of steam added to the feedstock to eliminate carbon formation. The burner design is critical. A typical reactor lay-out is shown in Fig. 8.

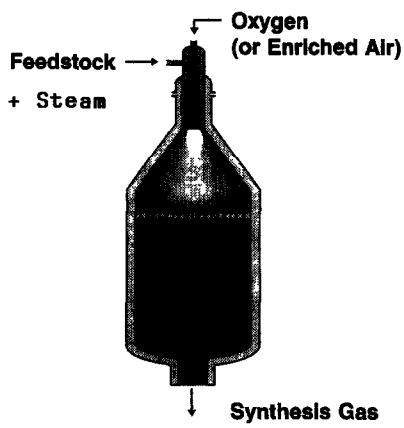

Fig. 8. Autothermal reformer.

The autothermal reformer was originally used for ammonia plants [39] to maximize hydrogen production, but it can be applied in the manufacture of CO-rich gases [40]. Recent tests [3,41] have shown that it is possible to operate at H_2O/C below 1.0, resulting in H_2/CO ratios of the product gas as illustrated in Fig. 9.

It was also shown that CO_2 could be added to the process and more CO could then be produced essentially by the reverse shift reaction (2) as illustrated in Fig. 10.

Hence, autothermal reforming offers an alternative to tubular reforming when cheap oxygen is available [3].

The autothermal reformer is an inexpensive piece of equipment with a spe-

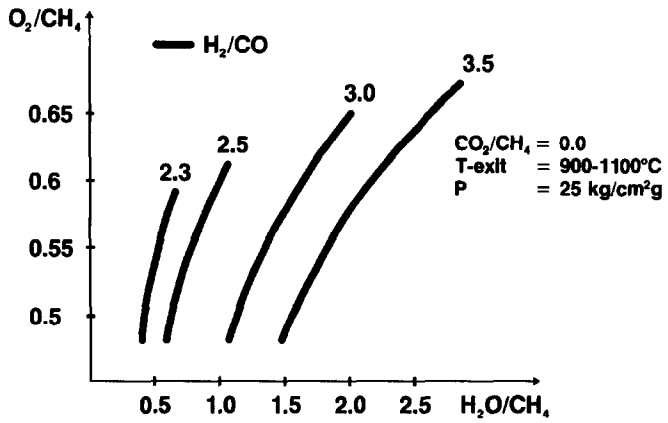

Fig. 9. Calculated gas compositions from autothermal reformer.

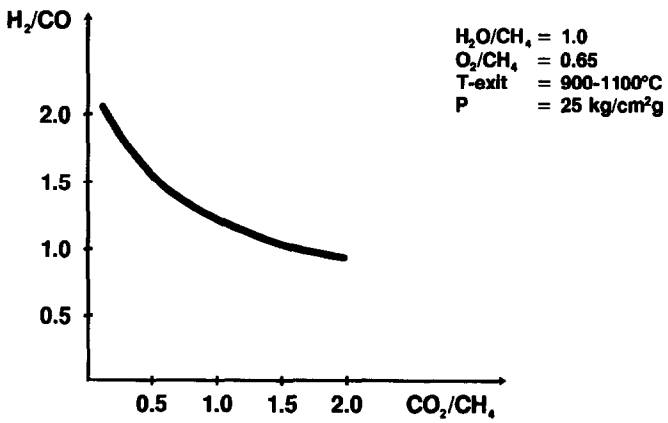

Fig. 10. Calculated gas compositions from autothermal reformer. Effect of adding CO_2 to the feed.

cial burner and a fixed catalyst bed placed in a lined reactor as shown in Fig. 8. Irrespective of whether a thermal burner or a catalytic burner, a fixed or a 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 itself determined by the adiabatic temperature increase.

Direct catalytic combustion over noble metals was studied by Hickmann and Schmidt [42]. It was shown that carbon monoxide and hydrogen are the primary products. At partial conversion, product gas was obtained with higher CO/H_2 ratios than predicted at equilibrium. However, at industrial conditions, no catalyst has, so far, yielded a CO_2 production less than that predicted by thermodynamics.

It would be tempting with a catalytic burner, provided the catalyst could promote selective oxidation while avoiding further oxidation of the products:

$$CH_4 + \tfrac{1}{2}O_2 = CO + 2H_2 \quad (-\Delta H^{\circ}_{298} = 38\ \text{kJ/mol}) \tag{14}$$

$$CO + \tfrac{1}{2}O_2 = CO_2 \quad (-\Delta H^{\circ}_{298} = 286\ \text{kJ/mol}) \tag{15}$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O \quad (-\Delta H^{\circ}_{298} = 244\ \text{kJ/mol}) \tag{16}$$

Eqn. (14) is only slightly exothermic with a heat of reaction comparable to that of the shift reaction (reaction (2)). With a catalyst selective for reaction (14), it would be possible to produce syngas suitable for e.g. methanol synthesis at a low temperature and without the large heat production. This could represent a challenge similar to that of direct conversion of methane into products.

However, attempts so far have been in vain, since it is extremely difficult to eliminate the oxidation of CO and H_2. One study [43] claimed high selectivity, but the data were shown to be close to thermodynamic equilibrium when taking reactions (1)–(3) into account.

A study by Choudhary et al. [44] showed oxidation of methane with high yields of carbon monoxide and hydrogen at reactor temperatures as low as 300°C. The product gas compositions corresponded to equilibrium of the steam reforming reaction at temperatures 600–700°C. However, it could be estimated [45] that the catalyst particles might have an over-temperature of 3–400°C (considering reaction (14)) because of strong film diffusion. Therefore, the product gas most likely reflects the gas equilibrium at the catalyst surface temperature.

3.3 Heat exchange reforming

The manufacture of syngas is expensive. For an example, the major part of the investment (ca. 70%) in a methanol plant is related to the manufacture of syngas [3,25] (including syngas compression). Therefore, it is essential that this part of the plant be optimized.

When the feedstock is natural gas, the heat available in the process gas leaving the oxygen-fired secondary reformer in a methanol plant (Fig. 6) matches

the heat required for primary reforming. It is therefore tempting to consider the use of a heat exchange reformer using the hot synthesis gas from the secondary reformer instead of an expensive fired reformer [3,46]. If so, however, only medium pressure steam could be recovered from the syngas manufacturing unit and it would be necessary to import electric power to the plant for the large synthesis compressor.

This problem might be solved in future by the use of high efficiency gas turbines or by a future low-pressure methanol synthesis process. In order to represent a major breakthrough, a future low-pressure synthesis should achieve full conversion in a one-pass operation, but it should also be able to accept the normal CO_2 content (ca. 5%) in the synthesis gas. Otherwise, the savings in the synthesis would be easily balanced out by a more expensive front-end. By using air instead of oxygen for the manufacture of synthesis gas, the oxygen plant could be eliminated. However, the additional costs involved in compressing air are substantial and very low synthesis pressure would be required to ensure that the use of air represented a saving in the overall production costs.

In the ammonia process, the amount of heat available downstream of the secondary reformer (at temperatures above 450°C) corresponds to about 60% of the duty required for primary reforming. Therefore, one could consider using this heat for the primary reformer in a heat exchange reformer [23,47]. However, the plant would be dependent on the import of energy, and hence process schemes based on heat exchange reforming are mainly of interest in special situations [3,23] where energy, especially process feed, is very expensive, or where cheap power — in the form of imported electric power or power generated from excess steam or from other installations — is available to supplement the insufficient amount of power gained from waste heat from the ammonia plant.

A conventional hydrogen plant for refineries operates at a steam-to-carbon-ratio of 5–6. Since, it is not possible to utilize part of the fired duty that could be recovered in the waste heat channel, a typical hydrogen plant will be a steam exporter. The energy balance may be satisfactory, but it results in a higher investment per hydrogen unit produced. With the development of technology for pressure swing adsorption, it has been possible to accept higher methane slippage from the reformer in a hydrogen plant and thereby operation at a lower steam-to-carbon ratio [3]. This reduces the fired duty in the reformer per hydrogen unit.

Further attempts to reduce the steam export have led to the development of heat exchange reformers [48,49] in which both the flue gas as well as the hot product gases are cooled by heat exchange with the process gas flowing through the catalyst bed. With this principle, the duty transferred to the catalyst bed can be increased from about 50% in a conventional reformer furnace to about 80%. Heat exchange reformers were first developed for use in

fuel cell power plants [48,50], but they may also be useful for providing refineries and other users with marginal hydrogen production, without any steam export.

3.4 New reforming equipment

A number of reactor systems have been proposed which would utilize the heat from secondary reforming for internal heat exchange with endothermic steam reforming [38]. These reactors would represent a saving in investments because far less waste heat would need to be recovered from steam production, preheating, etc. as discussed above. The thickness of the reformer tubes could be decreased because of the use of high pressure on both sides, but would be essential if savings were to be achieved in tube material that the heat exchange should take place at heat fluxes approaching those obtained in the fired reformer.

The design of the combined reformer should eliminate the risk of "metal dusting" corrosion [1,3,51] which may take place when the product gas from the secondary reformer is cooled to below the equilibrium temperature of the Boudouard reaction (eqn. (9)).

The design of a steam reformer is limited by the heat transfer coefficient at the tube wall being the rate determining step [1,3]. This determines the overall heat transfer surface required, and hence the associated catalyst volume which is dictated by the tubular geometry. With a given heat flux, the catalyst volume would increase linearly with the tube diameter, which is selected according to mechanical criteria [1]. The catalyst volume therefore ends up being larger than necessary and the catalyst pellet has to be large to reduce the pressure drop [3]. The surplus activity can be used in more advanced reformer designs by having only thin layers of active catalyst material, e.g. honeycomb catalysts having a low pressure drop, or even using metal-supported catalysts on heat transfer surfaces [52]. A special development has been catalysed hardware for internal reforming in high-temperature fuel cells [50].

TABLE 1

Reforming of CH_4 in the presence of a Pd membrane [54], $P=20$ bar abs, $T=500°C$, $H_2O/CH_4=3.0$. Conversion and gas composition (vol.-%)

	Conversion of CH_4 (%)	CH_4	H_2	CO	CO_2	H_2O	Secondary gas (%)
Membrane reactor	52.0	14.9	9.2	0.70	15.2	59.9	22% H_2 in N_2
Equilibrium (no membrane)	14.4	20.0	13.3	0.14	3.23	63.4	–

Coupling steam reforming with a hydrogen selective membrane (e.g. palladium [53,54] or ceramic membranes [55] may offer new opportunities. By extracting hydrogen from the reforming process, the equilibrium may be pushed towards full conversion at low temperatures as illustrated by the data in Table 1 [54]. This would allow the use of low temperature heat as input to the reforming reactions. So far, palladium membranes are not feasible and there are several material problems still to be solved [53].

4. INDIRECT OR DIRECT CONVERSION

The oxidative conversion of methane directly into methanol or ethylene has attracted much interest as an alternative route for converting natural gas into useful products [56,57].

Direct conversion to methanol

$$CH_4 + \tfrac{1}{2}O_2 = CH_3OH \quad (-\Delta H^\circ_{298} = 126\ \text{kJ/mol}) \tag{17}$$

has the added potential given by the theoretical ceiling of a thermal efficiency of 80% (LHV) and the demonstrated efficiency of the syngas route to methanol of 68% (LHV). The latter figure is linked to a formation of CO_2 amounting to 21% of the carbon atoms in the feed and the reformer fuel [3,25].

One argument in favour of the direct conversion of methane has been that steam reforming requires a large heat input which is only partly recovered in the synthesis and at lower temperatures. This argument is misleading. The indirect routes are selfsufficient in energy and have no steam export.

Fig. 11 illustrates the internal heat recovery for a methanol plant [3] using a two-step syngas manufacturing process as shown in Fig. 6. The excess heat available for steam and preheating shown in the diagram is used for product purification.

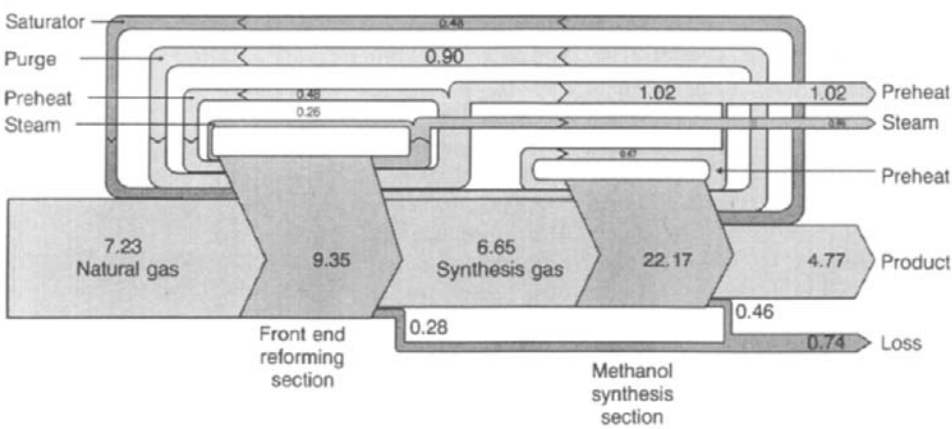

Fig. 11. Energy flow diagram for MeOH plant [3].

Most of the heat produced in the reforming route (88%) is recovered from the waste heat of the flue gas from the reformer furnace and from the hot effluent of the secondary reformer. In the synthesis loop, 60% of the heat of reaction is recovered, the rest being lost by condensation of methanol. Other heat losses include the heat from the reformer flue gas and from the cooling water. The total heat losses amounts to 15% of the heat added to the two-step reforming process, plus the heat of reaction in the synthesis.

5. CONCLUSIONS

Syngas manufacture by steam reforming will continue to play a major role in the chemical industry. The efficiency is high, but it is coupled to large investments. A better understanding of the limits of the process has resulted in more economical operation. Future developments will focus on designing new equipment to reduce investment costs.

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