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Methanol synthesis: a short review of technology improvements

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Abstract

Methanol synthesis has undergone continuous improvements for over nearly a century. Among others are the advent of low-pressure synthesis, once-through designs, and advanced reforming technologies. In reviewing some 25 technologies, we will not dwell in technical details but focus on one major goal, i.e. minimising the investment costs. Our pragmatic indicator for investment savings will be the minimisation of energy transfer duty and, particularly, the minimisation of gas recycle and fuel firing. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since its commercial implementation in 1923, methanol synthesis has undergone numerous improvements. These are mainly driven by reduction of investment costs which dominate in the production cost of methanol. Indeed, the conversion of remote gas to methanol offers a clear economic advantage on raw material costs compared to oil refining. However, this advantage is offset by larger investment costs. This trade-off (Fig. 1) is, in fact, a general characteristic of natural gas conversion processes [1].

In reviewing some 25 technologies, we will not dwell in technical details but focus on one major goal, i.e. minimising the investment costs. Our pragmatic indicator for savings will be the minimisation of energy transfer duty within the process segments. This transfer can take the form of heat transfer in heat exchangers, in heated and cooled reactors, or in condensers and reboilers in distillation trains. It can also be in the form of impulse, e.g. in gas compressors and pumps. The global transfer of energy within a process, indeed, shows a direct correlation with global investment costs [1,2]. Attempts to minimise investment costs should, therefore, focus on minimising the energy transfer duties. Obviously, additional factors should be considered when transfer duties are comparable.

The present paper will try to illustrate this point by reviewing several generations of methanol synthesis processes with particular attention to the improvements in energy transfer duty. The paper will focus on processes based on synthesis gas, although alternative routes will be briefly addressed at the end. This short review intends to be illustrative rather than exhaustive. Hence, the author apologises up-front for the possible omission of mentioning some interesting technologies.

2. Synthesis gas conversion

2.1. Overall chemical reaction

The conversion of synthesis gas to methanol (Eq. (1)) is strongly influenced by thermodynamic factors.

$$\mathrm{CO} + 2\mathrm{H}_2 \leftrightarrow \mathrm{CH}_3\mathrm{OH} \quad (\Delta H_{298\,\mathrm{K}} = -91\,\mathrm{kJ/mol}) \tag{1}$$

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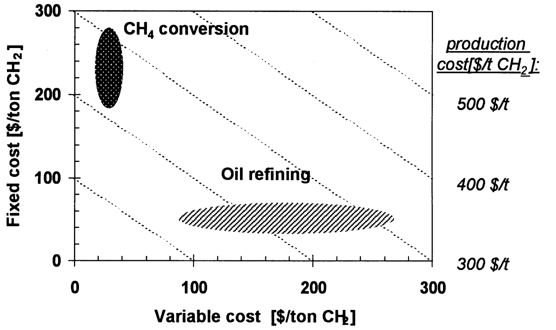

Fig. 1. The economics of oil refining is dominated by raw material costs whereas that of natural gas conversion is dominated by plant investment. The diagonal lines represent overall production costs. (The variable costs are based on a gas price of \$0.5/GJ and an oil price varying between \$10 and \$30/bbl; the annual fixed costs are assumed to amount to 35% of the total investment.)

It is subjected to a thermodynamic equilibrium that limits the process to low conversion per pass and, therefore, implies a large recycle of unconverted gas. The reaction is also strongly exothermic and, consequently, requires significant cooling duty. The resulting recycle and cooling duty are largely responsible for the investment cost of this process segment.

The reader should realise that the ideal synthesis gas stoichiometry is not the molar ratio $H_2/CO = 2$ as suggested by Eq. (1), but rather molar ratio $(H_2–CO_2)/(CO + CO_2) = 2$, also called the stoichiometric number. CO_2 appears in the stoichiometric number because it is present in the synthesis gas and consumes hydrogen through the reverse of the water-gas shift reaction (Eq. (2)) during the methanol synthesis.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (\Delta H_{298\,K} = +41\,\text{kJ/mol}) \tag{2}$$

The importance of the stoichiometric number will become clear later in the text.

2.2. From high- to low-pressure process

The first technology, commercialised by BASF in 1923, was based on a $ZnO–Cr_2O_3$ catalyst that could hydrogenate CO to methanol at 240–300 bar and 350–400°C [3]. This catalyst also produced methane and other light hydrocarbons with 2–5 wt.% selectivity.

A major improvement was achieved in the 1960s by producing a sulphur-free synthesis gas that enabled ICI to use the more active Cu/ZnO catalyst [3]. Thanks to its high activity, this catalyst could operate at much lower pressure and temperature, namely 60–80 bar and 250–280°C. These improvements resulted in a significant reduction of the compression and heat exchange duty in the recycle loop. The lower reaction temperature also improved the selectivity by virtually suppressing the co-production of light hydrocarbons. Besides reducing the consumption of synthesis gas by a few percent, it also saved 5–10% cooling duty by avoiding the heat released by the side reactions (e.g. $\Delta H_{298\,K} = -206$ kJ/mol for forming CH_4).

The methanol synthesis reactors seem to have been designed around three major aspirations, i.e. high cooling duty, low pressure drop, and favourable economy of scale. Cooling designs included internal cooling coils cooled by water or by cold feed (Fig. 2a–c) as well as the injections of cold synthesis gas (Fig. 2d) [4,5]. Notice that the designs (Fig. 2a and b) transfer the heat of reaction to a water loop and cool the hot reactor effluent with the cold feed in a feed–effluent heat exchanger. In contrast, the designs (Fig. 2c and d) transfer the heat of reaction to the cold feed and cool the hot effluent with water. The periodic reversal of

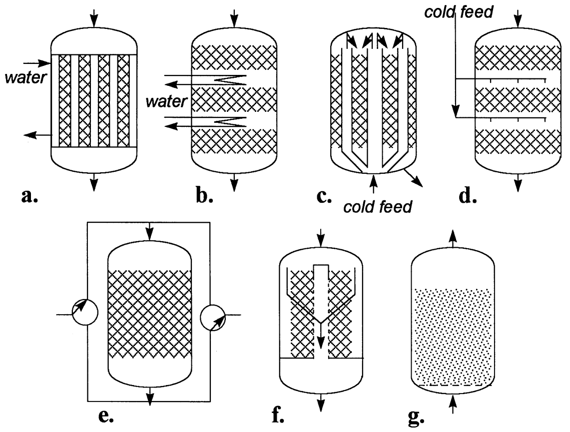

Fig. 2. Methanol synthesis reactors are designed for efficient cooling (a–d), optionally with feed pre-heating (c–e), as well as for low pressure drop (f and g). (a) Cooling with water bath; (b) cooling with water coils; (c) cooling with cold feed; (d) feed gas quench; (e) feed–effluent heat exchange by periodic flow reversal; (f) lateral flow; (g) fluidised bed.

flow direction (Fig. 2e) has also been proposed as an alternative for the feed–effluent heat exchanger [6,7]. However, a dedicated water cooling system is still required to remove the heat of reaction [6]. In fact, all these designs do not differ significantly in overall heat transfer duty, unless they do differ in conversion per pass and recycle ratio. This can be achieved, e.g. by applying a lower temperature at the reactor outlet [4]. The author is not aware of any paper that discusses the conversion that is achieved in a single pass for the various reactors.

Low pressure drop has been attempted by means of radial flow and fluidised bed reactors (Fig. 2f and g) [5]. The benefit of low pressure drop is obviously a savings in recycle gas compression. As for the economy of scale, an interesting discussion is available in [5], although it is limited to the reactor and neglects the rest of the conversion loop.

2.3. Once-through processes

More recently, various schemes for once-through operation have been conceived to avoid the large gas recycle. Some once-through schemes were based on multiple reactors placed in series with interstage removal of methanol, e.g. by means of condensation [8], by absorption in an liquid [9] or by reactive chromatography [10]. Other once-through schemes attempt to remove the methanol inside the synthesis reactor, e.g. by means of a methanol permeating membrane [11], by means of a trickling liquid absorbent or trickling solid adsorbent particles [12,13], or by means of methanol condensation [14].

One should realise that most of these once-through schemes substitute the large energy duty of the gas recycle loop by other large transfer duties. For example, the series scheme of van Dijk and Fraley [8] requires extensive interstage cooling. The use of solid adsorbent [9,12] and liquid absorbent [13] require regeneration of the adsorbent/absorbent. Reactive chromatography [10] requires important energy transfer duty in the sweep gas line. In a first approach, one could reasonably expect that such substitutions of energy transfer duties should have a limited economic potential.

The in situ removal of methanol by means of a selective membrane or by means of condensation does not imply large heat transfer duty. It still has its limitations, however. The membrane reactor is expected to be fairly expensive to construct at large scale. As for the condensation reactor, the low operation temperature implies low volumetric productivity and, therefore, large and costly reactors.

3. Synthesis gas manufacture

3.1. Basic processes: steam reforming and partial oxidation

Synthesis gas is commonly produced by steam reforming of methane (Eq. (3)) [15,16]:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (\Delta H_{298\,K} = +206\,kJ/mol) \tag{3}$$

The reaction proceeds on a Ni-based catalyst, though more expensive noble metals are also effective [15]. Being endothermic, steam reforming requires the firing of large amounts of fuel near the reactor tubes to supply the heat of reaction (Fig. 3a). High temperature (900°C) and excess of steam ($H_2O/C = 3$) are required for shifting the thermodynamic equilibrium to deep conversion. The excess of steam also leads to the subsequent steam reforming of large amounts of CO to CO_2. The resulting synthesis gas is rich in H_2 and is characterised by a high stoichiometric number of ∼3. The need for fuel firing together with the heating and cooling of the gas and excess steam imply large heat transfer duty and, consequently, large investment cost.

The other basic route to manufacture synthesis gas is the partial oxidation with oxygen (Eq. (4)) which

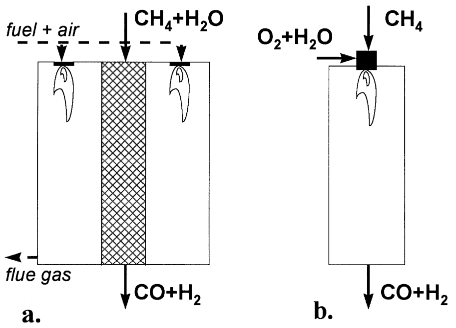

Fig. 3. Conventional for manufacturing synthesis gas: (a) steam reforming; (b) partial oxidation.

was developed by Shell in the 1950s for converting a variety of hydrocarbon sources [17].

$$CH_4 + \tfrac{1}{2}O_2 \leftrightarrow CO + 2H_2 \quad (\Delta H_{298\,K} = -35\,kJ/mol) \tag{4}$$

The partial oxidation is slightly exothermic and proceeds in the gas phase via radical reactions within the flame of a burner (Fig. 3b). A small excess of oxygen is required to achieve high conversion by favouring some deep oxidation to CO_2 and H_2O in order to bring the synthesis gas to the desired high temperature (1000–1200°C). Steam can be fed to protect the burner against excessive temperatures and to increase the H_2/CO ratio. It does not increase the stoichiometric number significantly, however.

The partial oxidation of methane produces a CO-rich synthesis gas with a stoichiometric number of ~1.6. Although below the ideal value of 2, this stoichiometric number represents a significant improvement over steam reforming. It represents, in fact, one of the major economic benefits of partial oxidation. It improves the conversion per pass in the methanol synthesis step, thereby reducing the recycle and purge of unconverted synthesis gas.

With its fairly low energy transfer duty, the partial oxidation process usually requires low investments. However, the installation of an expensive air separation unit that delivers the pure oxygen will compensate for this low investment. Indeed, the air separation also requires extensive heat exchange and compression duty.

3.2. Improvements in partial oxidation

Conventional partial oxidation proceeds in a flame through pure gas phase reactions. These reactions do not fully reach thermodynamic equilibrium. True equilibrium composition has been achieved in Topsoe's autothermal reforming [18] by incorporating a Ni-based steam reforming catalyst downstream of the burner flame (Fig. 4a). More drastically, however, Hickman and Schmidt [19] proposed to apply a catalytic burner to achieve equilibrium synthesis gas (Fig. 4b). The partial oxidation catalyst is then based on noble metal such as Rh. Other catalytic variations of the partial oxidation process include a fluidised bed reactor developed by Exxon [20] and a reactor with periodic flow reversal [6]. By improving the yield in synthesis gas by a few percent, these developments lead to a small reduction in oxygen consumption as well as some capital reduction in the methanol synthesis step. However, they do not result in major reduction in energy transfer duty. Scale-up potential then becomes a critical factor to differentiate these processes.

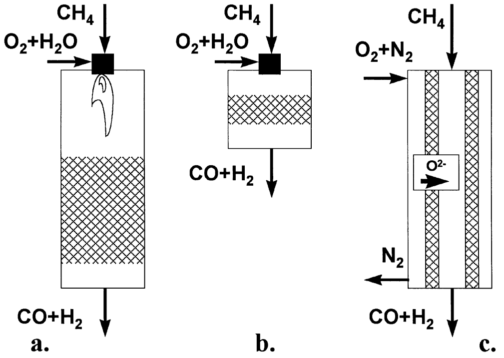

Fig. 4. Improved partial oxidation processes for manufacturing synthesis gas: (a) autothermal reformer; (b) catalytic partial oxidation; (c) oxygen-permeable catalytic membrane reformer.

Attempts for more drastic cost reductions have been sought for by substituting air or O_2-enriched air for the more expensive O_2 in partial oxidation. Obviously, the N_2 present in the synthesis gas will accumulate in the synthesis gas recycle loop and depress the conversion per pass by lowering the effective partial pressure of the synthesis gas. Hence, the cost of increased transfer duty rapidly offsets the savings made by omitting the O_2 manufacture unit [21].

Alternatively, a ceramic membrane reactor has been proposed for air-blown partial oxidation [22]. The high temperature, O^{2-}-conducting membrane lets oxygen permeate to the process stream and keep nitrogen outside (Fig. 4c). It avoids thereby most of the shortcomings mentioned above for air-blown partial oxidation, except for the need to heat and cool nitrogen to and from reforming temperature. Although at its infancy, this concept is quite promising for small-scale applications. It might not easily compete for large-scale applications, however.

3.3. Combining steam reforming and partial oxidation

Significant reduction in costs have been claimed for combinations of steam reforming and partial oxida-

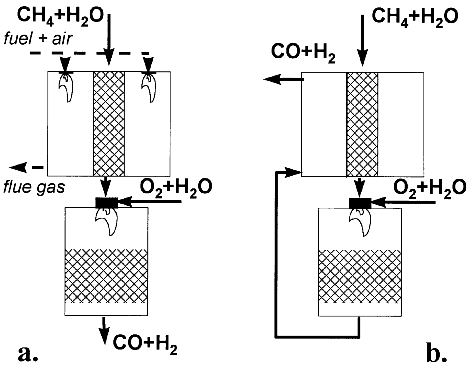

Fig. 5. Combination of steam reforming and partial oxidation can comprise (a) mass integration for: (i) improved synthesis gas quality as well as (ii) mass and heat integration; (b) for improved energy efficiency.

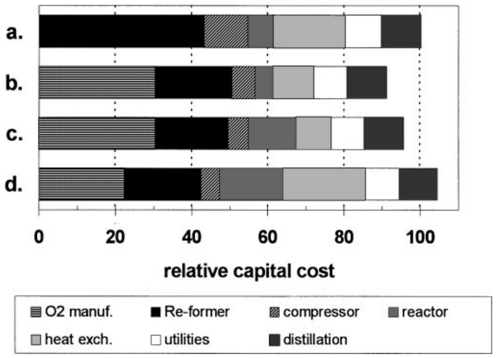

Fig. 6. Investment costs of process schemes for methanol synthesis: (a) steam reformer and conversion in recycle reactor; (b) partial oxidation and conversion in recycle reactor; (c) partial oxidation and conversion in reactor series; (d) air-blown partial oxidation (44% O_2) and conversion in reactor series.

tion [16,23,24]. A simple combination of the H_2-rich effluent of a steam reformer with the CO-rich effluent of partial oxidation provides the ideal stoichiometric number of 2. This is the basis of the 'combined' or 'two-step' reforming processes developed, e.g. by Lurgi and Haldor-Topsoe (Fig. 5a).

More sophisticated combinations are attempting to integrate the heat fluxes of the two processes. The heat of the hot effluent of the partial oxidation reactor is then utilised to drive the endothermic steam reforming reaction (Fig. 5b). This avoids the need for firing fuel and reduces the overall transfer of heat. Haldor-Topsoe, ICI and Kellogg developed processes based on two separate reforming vessels while Uhde proposed a single vessel design [16,23,24]. These technologies promise significant reductions in heat transfer duty and in investment cost.

4. Economics of methanol processes

The discussion made above was limited to qualitative arguments in order to underline key factors in the evolution of the methanol synthesis. These qualitative arguments can be easily applied to understand the numerous economic analyses reported in the literature [4,21,25]. I will illustrate this point by looking at the analysis reported in [21].

Lange [21] reported economic analysis of several process schemes for a methanol plant of 10 kt daily capacity. The breakdown costs of several process schemes are given in Fig. 6. Accordingly, the substitution of a partial oxidation process (autothermal reformer, Fig. 6b) for the conventional steam reformer (Fig. 6a) does not lead to significant savings in synthesis gas manufacture. The cost of the air separation unit clearly offsets the savings made by using a cheaper reformer. However, the improved stoichiometric number of the synthesis gas results in clear savings in the synthesis gas conversion step. Fig. 6 also shows that a series of four reactors with interstage condensation of methanol (Fig. 6c) does not offer any savings over the four reactors with conventional synthesis gas recycle. Furthermore, the combination of the reactor series with an autothermal reformer fed with air enriched to 40% O_2 (Fig. 6d) is more expensive than the combination of recycle scheme with O_2-blown reformer.

5. Processes not based on synthesis gas

So far, I have showed the usefulness of an energy transfer analysis for evaluating and ranking variations of basic process schemes. Although more tricky and less accurate, such an analysis is also informative when comparing processes of very different natures. It has been applied for ranking methanol synthesis processes that are not based on synthesis gas but proceed either via direct oxidation with oxygen or via intermediates such as methyl chloride and methyl bisulphate (Fig. 7). The reader is referred to [21] and the references therein

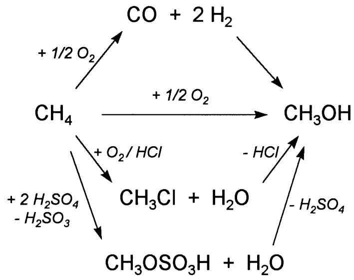

Fig. 7. Methane can be converted to methanol via numerous routes.

for further detail on these processes and on their capital requirements.

6. Conclusions

Methanol synthesis processes have been subjected to impressive improvements throughout nearly the whole 20th century. The energy analysis made here was an attempt to understand the core and the potential of these developments. It highlighted the importance of heat management, of fuel firing, of temperature and pressure changes, of synthesis gas stoichiometry, and the recycle of unconverted feed. Some 80 years of commercial practice do not seem to have exhausted the creativity of scientists and engineers in this field, as evidenced by the numerous improvements proposed during the past two decades. Indeed, there is still room for further reduction of energy transfer duty and increase in process scale. It is estimated that an ideal process needs less than 50% of the transfer duty required today [21].

Since the first oil crisis, methanol has been proclaimed to substitute crude oil as source for fuel and chemicals. This promise did not materialise as the oil prices dropped deeper than did the manufacturing cost of methanol. It still holds today, however, as one expects the oil reserves to decrease faster than the natural gas reserves. The promise is even stronger now that the mankind is attempting to forge a new and sustainable world economy in which biomass gasification and methanol might play an important role.

Of course, the present energy transfer analysis can be applied to other processes, e.g. for fuel or chemical manufacture [2]. It could help researchers and technologists to better understand the improvements that are required in that field.

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