Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Catalysis Today 106 (2005) 99–102
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Methanol synthesis at near-critical conditions combined zwith ATR synthesis gas technology
The technology choice for large-scale methanol production

Jens Perregaard

Haldor Topsøe A/S, DK-2800 Lyngby, Denmark

Abstract

New technical development primarily within the area of synthesis gas preparation based on autothermal reforming (ATR) has opened the door for considering considerably larger methanol plant capacities than normal in the industry today. This paper deals with taking advantage of this synthesis gas preparation capability in an optimal manner via applying a new methanol synthesis technology. The synthesis technology is operated at near-critical conditions. This makes it possible to design plants without recycle of unconverted gas in the synthesis section.

Keywords: Autothermal reforming; Methanol production; Near-critical conditions

1. Introduction

Over the last decade, one of the dominating trends in the design of methanol production plants has been that of ever increasing capacities. This trend is naturally strongly related to economy-of-scale, i.e. lower production costs for large-scale units than for corresponding small-scale plants. Large-scale plants are most applicable in areas with easy access to cheap natural gas and, consequently, the main focus is on the investment related to the plant.

The economy-of-scale effect is, however, subject to the constraints imposed by size limitations of process equipment. Therefore, the ability to process very large amounts of synthesis gas in comparatively small process equipment units is becoming increasingly important. It is the objective of this paper to demonstrate how a combination of two technologies, i.e. a methanol synthesis technology at near-critical conditions and a synthesis gas technology based on an autothermal reformer (ATR) operating at a very low steam-to-carbon ratio, constitutes the optimal choice for production of methanol in large-scale plants.

At the same time the presented technology has the potential to take advantage of the less severe requirements related to new methanol applications. Examples of such applications are olefin and DME production as well as application of methanol directly as a fuel. The applications have in common that the specifications of ketones and ethanol are far less severe than for Grade AA Methanol. The methanol synthesis unit can therefore be fed with a much more aggressive feed gas than traditional plants. Thus, the optimum feed gas for methanol synthesis can be used without any penalties in the downstream distillation – on the contrary – the presented design leads to extremely high synthesis efficiency, a compact distillation design and a very low loss of hydrogen in the form of water formation in the synthesis.

All commercially available methanol technologies consist of three process units and a utility section as listed below (Hansen [5,6]):

- synthesis gas preparation (reforming);
- methanol synthesis;
- methanol purification;
- utilities.

E-mail address: jep@topsoe.dk.

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.07.186

As mentioned above, this paper focuses on a new and optimal technology for synthesis gas preparation as well as a new technology for the methanol synthesis section. The methanol synthesis technology presented here can with advantage be applied not only for synthesis gas based on natural gas but also for synthesis gas from gasification or partial oxidation of residual oil fractions, coal or other carbon sources. However, only aspects related to natural gas as feed are presented in this paper.

2. Synthesis gas preparation

In the synthesis gas preparation section of a methanol plant, the natural gas feedstock is purified of for instance sulphur before being converted into synthesis gas at high temperature and subsequently compressed to the synthesis pressure. Several reforming technologies are available for the natural gas conversion, e.g.:

- one-step reforming with a tubular reformer;
- two-step reforming;
- autothermal reforming (ATR).

The merits of the processes are presented by Dybkjær et al. [1,4] concluding that tubular steam reforming based processes are most favourable for small-scale plants. For large-scale plants (capacities above 5000 MTD) ATR has the lowest investment, while the two-step reforming option is most economical at the intermediate capacities. Synthesis gas is characterised by the stoichiometric ratio $(H_2 - CO_2)/(CO + CO_2)$, often referred to as module M. A module of 2 defines a stoichiometric synthesis gas with respect to formation of methanol. In both one-step and two-step reforming, the synthesis gas prepared has a surplus of hydrogen ($M > 2$) whereas application of the ATR technology leads to an M between 1.7 and 1.8.

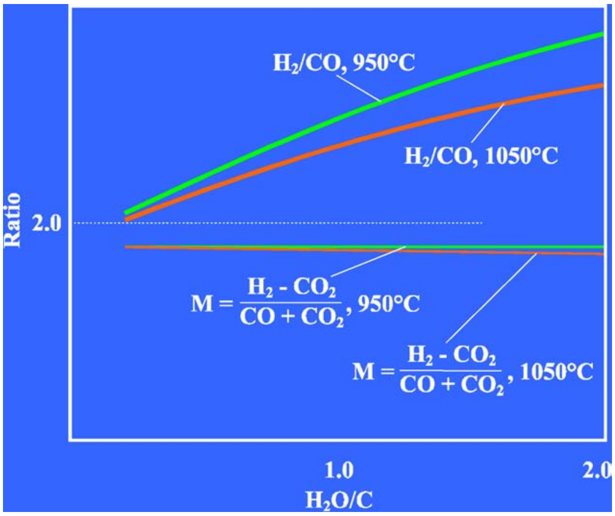

Fig. 1. ATR synthesis gas properties.

Table 1
Plant key figures for three technologies for synthesis gas generation, 10,000 MTPD methanol

Technology	One-step	Two-step	ATR
Steam-to-carbon ratio	2.5	1.9	0.6
Natural gas flow index	100	85	84
Oxygen consumption MTPD	0	4600	5800
Flow exit reformer section, index	100	88	59
CO/CO_2 ratio	2.5	2.6	5.1

Fig. 1 shows that the module only has a weak dependency on the steam-to-carbon ratio applied in the ATR synthesis gas preparation whereas the ratio of H_2-to-CO is strongly dependent on the steam-to-carbon ratio. At low steam-to-carbon ratios, the H_2-to-CO ratio is lower and thus the synthesis gas is much richer in CO than in CO_2. From Eqs. (1) to (3), it can be deduced that each CO_2 molecule fed to the methanol synthesis section of the plant results in formation of water (and thus H_2 consumption). Consequently, ATR technologies capable of operating at low steam-to-carbon ratios are more suitable for integration with methanol synthesis in general – and with the near-critical methanol synthesis technology in particular – compared to technologies using a higher steam-to-carbon ratio.

Table 1 compares the production and consumption figures for the three synthesis gas preparation technologies for a 10,000 MTPD methanol plant. The main advantage of the ATR process compared to tubular steam reforming is the lower flows resulting in smaller equipment and less compression power. An air separation unit (ASU) is required for both two-step reforming and for ATR, and it should be noted that at high capacity the ASU economy-of-scale is superior to that of the tubular reformer, which has a scale factor close to unity.

3. Methanol synthesis

The methanol synthesis can be described by the following reactions:

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \quad (-\Delta H_{298K,\,50bar} = 40.9\,\mathrm{kJ/mol}) \tag{1}$$

$$CO + 2H_2 \Leftrightarrow CH_3OH \, (-\Delta H_{298K,\,50bar} = 90.7\,\mathrm{kJ/mol}) \tag{2}$$

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \, (-\Delta H_{298K,\,50bar} = 49.8\,\mathrm{kJ/mol}) \tag{3}$$

A combination of either Eqs. (1) and (3) or Eqs. (2) and (3) completely describes the system from a thermodynamic point of view, whereas all three equations are generally considered when a kinetic description of the synthesis is required.

It can be seen from Eqs. (1) to (3) that the methanol synthesis is exothermic and decreases the number of molecules. Thus, according to Le Chatelier's principle, the maximum conversion is obtained at low temperature and high pressure. A challenge in the design of a methanol synthesis unit is to remove the heat of reaction efficiently and economically – i.e. at high temperature – but at the same time to equilibrate the synthesis reaction at low temperature, thereby ensuring a high conversion per pass. It should be noted that, even in a stoichiometric synthesis gas free from inerts, the maximum conversion will decrease with increasing CO_2 content. At typical synthesis conditions (7.5 MPa, 225 °C) the carbon conversion (conversion of carbon oxides to methanol) in traditional gas phase reactors cannot exceed the thermodynamic limit of around 60%. As a consequence, recycle of unconverted gas is needed in traditional methanol synthesis sections.

A way of overcoming the gas-phase thermodynamic limitation is by condensing the methanol product in situ in the reactor. The possibility of operating a methanol synthesis reactor using this principle was demonstrated by Hansen and Joensen [2,3] nearly 20 years ago. However, the synthesis gas preparation was at the time not ready for supplying a suitable synthesis gas making the overall plant economical. This has changed. Hansen and Joensen [2] also demonstrated experimentally that operation of the methanol reactor at two-phase conditions actually makes it possible to achieve a once-through carbon efficiency in the synthesis section above 92%, thus opening the door for considering process layouts without recycle of unconverted gas.

Fig. 2 illustrates the advantage of this novel approach, i.e. using a condensing methanol synthesis reactor and process layout without recycle. In the figure, the once-through carbon efficiency of the synthesis section as a function of the reaction temperature is plotted. As can be seen, the carbon efficiency increases quite rapidly as the reaction temperature is lowered. Computer simulation of the concept reveals that when the temperature reaches the dew point, condensation starts, and the achievable carbon efficiency increases even faster as the temperature decreases. For the sake of illustration, the carbon efficiency without condensation is also plotted (dotted curve). At 200 °C, the attainable once-through conversion increases from 89 to 94% due to condensation.

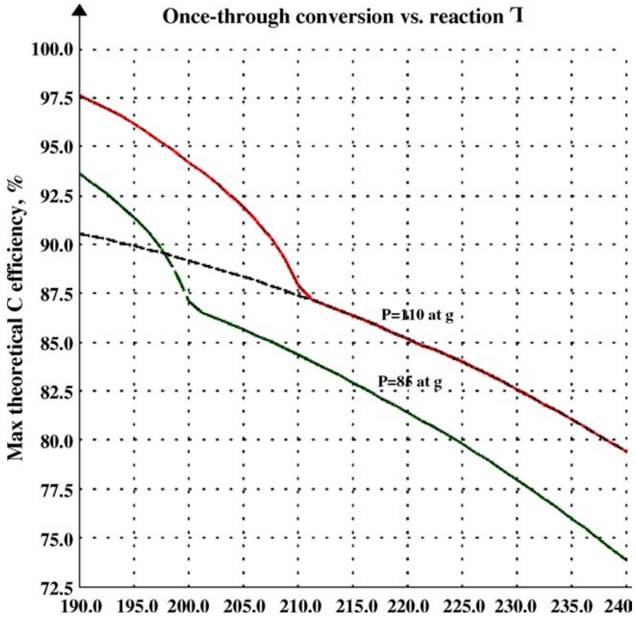

Fig. 2. Once-through conversion of synthesis gas to methanol.

Table 2
10,000 MTPD methanol plant, key-figures for selection of synthesis configuration

Process description	Loop		Condensing
Synthesis pressure, at *g*	85	110	110
Converter flow, MTPD	22,200	18,300	11,900
Temperature outlet methanol reactor	255	236	244/201
Water/methanol ratio (mol/mol) outlet methanol reactor × 100	2.7	2.4	0.9
Methanol concentration (mol %) exit methanol reactor	21	27	66

The rate of reaction is highly influenced by the approach to chemical equilibrium. Hence, the condensation enhances not only the carbon efficiency but also the rate of reaction at a given temperature.

Nonetheless, the fresh synthesis gas is far from the dew point, and the initial conversion is therefore carried out at approximately the same reaction temperatures as in traditional processes. Upon formation of methanol, the dew point increases, and the temperature can be decreased to take advantage of the condensation. In the condensing methanol process, the catalyst is therefore installed in two reactors operating at different temperature levels.

Table 2 summarises the main process data for two traditional processes and the novel approach. In all three cases, the process conditions were set so as to obtain 90% carbon efficiency in the synthesis section. For the condensing methanol process, the desired carbon efficiency was obtained by lowering the outlet temperature from the methanol reactor. For the conventional processes, the amount of recycle gas was adjusted to match the specified conversion.

4. Discussion and evaluation

New achievements, resulting from the development in the gas-to-liquid technologies (Bakkerud et al. [7]), have made it possible with the ATR technology to operate at a low steam-to-carbon ratio in an efficient and economical manner and to produce a synthesis gas with a high CO/CO_2 ratio. This is durable in a single-line unit (single reactor) and corresponds to more than double the capacity of today's normal industrial methanol unit, i.e. an amount corresponding to 10,000 MTPD of methanol. The synthesis gas produced has a lower module than traditional processes. As a

Table 3
Cost breakdown for a 9000 MTPD fuel grade methanol plant

Cost	Traditional gas phase process	Combination of ATR and near-critical methanol synthesis
Synthesis gas preparation (%)	60	<60
Methanol synthesis (%)	10	7
Methanol purification (%)	10	3
Utilities, etc. (%)	20	20
Total (%)	100	<90

consequence, the carbon efficiency is less important and the hydrogen efficiency is more important.

The new standard for large-scale synthesis gas production poses challenges to the methanol synthesis section of a methanol plant on different levels, such as:

- by-product formation as a consequence of the new synthesis gas;
- single-line capacity.

The presented layout of the methanol synthesis unit operating at near-critical conditions is capable of taking advantage of the new synthesis gas properties without being severely penalised on by-product formation. In the first reactor in the methanol synthesis section, the temperature is close to normal temperatures for methanol synthesis reactors. Thus, the formation of by-products is potentially high with the aggressive synthesis gas. However, a more detailed analysis reveals that the hot-spot in the reactor is significantly below what would be observed with a traditional layout. This is a consequence of the high linear velocity used in the reactor. Traditional reactors would not be able to operate efficiently under these conditions due to the much larger gas flow (pressure drop) and the demand for a high conversion in the loop. In the second reactor, the temperature is much lower and condensation takes place. The effect is that a very high once-through conversion is achieved and the by-products are equilibrated at a relatively low temperature.

The effect of the low amount of CO_2 can be directly deduced from the equations governing the methanol formation (Eqs. (1)–(3)). It is seen from these reactions that each molecule of CO_2 entering into the methanol synthesis results in the formation of one molecule of water. In traditional processes, where there is a surplus of hydrogen, this has a limited effect. However, in the case of the ATR technology, it is essential that the hydrogen efficiency is high. It should be noted that with the new technology, the raw methanol produced contains a very limited amount of water. Thus, the raw methanol is directly applicable for downstream methanol applications such as DME formation, MTP/MTO as well as for fuel applications.

It should also be noted that the single-line capacity of the presented methanol synthesis technology is roughly the double of that of conventional technologies, and the process can efficiently be operated in a once-through mode.

A cost estimate of the process indicates that the cost of the synthesis section – including compression of the synthesis gas – for a 10,000 MTPD methanol plant can be reduced by more than 15%. Table 3 gives a breakdown of the overall investment for a 9000 MTPD fuel grade methanol plant comparing a traditional technology with the near-critical technology. The table shows that a significant saving in investment can be achieved.

5. Conclusion

For maximum single-line capacity, a combination of ATR at low steam-to-carbon ratio with condensing methanol synthesis technology is the best choice. This combination eliminates recycle in the methanol synthesis section and reduces the water content in the raw methanol. Hence, combining ATR and condensing methanol synthesis may in many cases completely eliminate the requirement for a distillation unit, which makes this technology the preferred choice for large-scale methanol plants.

References

[1] I. Dybkjær, J.N. Gøl, Alternate Use of Natural Gas, Aust. GTL Forum, 2002.

[2] J.B. Hansen, J. Joensen, High conversion of synthesis gas into oxygenates, in: Proceeding of the NGCS, Oslo, August 12–17, 1990, pp. 457–467.

[3] US Patent 5262,443, November 16 (1993).

[4] I. Dybkjær, T.S. Christensen, Large-scale Conversion of Natural Gas to Liquid Fuels, NGCS, Alaska, 2001.

[5] J.B. Hansen, Methanol synthesis, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 4, VCH Verlagsgesellschaft mbH, D69451, Weinheim, 1997, p. 1856.

[6] J.B. Hansen, Operating experience with a commercial low temperature ethanol synthesis catalyst in different industrial and pilot converter types, in: AIChE Spring Meeting 1990, Paper No. 109 c., FL, USA, 1990.

[7] P.K. Bakkerud, J.N. Gøl, J. Nergaard, K. Aasberg-Petersen, I. Dybkjær, Preferred synthesis gas production routes for GTL, Stud. Surf. Sci. Catal. 147 (2004) 13–18.