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Methanol synthesis at near-critical conditions combined zwith ATR synthesis gas technology

The technology choice for large-scale methanol production

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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.
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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.

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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.

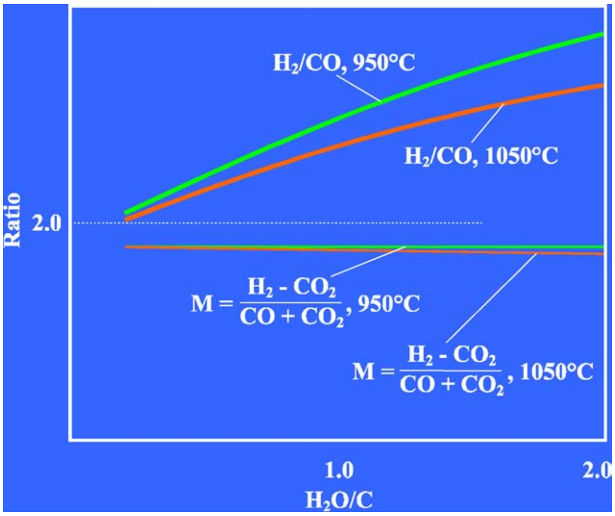

Fig. 1. ATR synthesis gas properties.

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.