Introduction

Due to the high cost of natural gas and oil, the more abundant coal is gaining relative importance as a chemical raw material. One step on the road from coal to chemicals (and liquid fuels) is methanol, for decades one of the most important bulk chemicals.

In order to exploit the economics of scale, gasification plants are often built as large complexes producing more than one final product, see Fig 1. As shown on the diagram (with blue colour), Topsøe is one of a very few companies who can offer several of the technologies used in such a complex.

This presentation focuses on Topsøe’s methanol technology and its adaptability to the special requirements of coal gasification plants.

Topsøe’s experience as a Licensor of Methanol Technology:

- More than 40 charges of Topsøe methanol catalyst, MK-101/MK-121/MK-151, are currently in operation
- 35 complete methanol synthesis units, out of which 15 units based on oil or coal gasification
- 15 complete methanol distillation units
- 10 ammonia/methanol co-production units
- 7 CMD quench converter revamps
Topsøe’s standing in the market today is based on in-house development work carried out in close collaboration between R&D, Catalyst and Technology Departments. This work has produced a row of unique methanol catalysts, the latest being MK-151 FENCE™ characterized by having the highest activity and durability available in the market.

The outstanding properties of MK-151 FENCE™ lead to very attractive features of the Topsøe methanol synthesis loop: Low consumption figures and a compact, and thus competitive, reactor design.

**Process Layout**

The H₂-CO rich synthesis gas coming from the sour gas removed system is almost sulphur free ie. the total sulphur content in the feed gas to the methanol synthesis loop is less than 0.1 vol ppm (100 vol ppb). However, even a sulphur concentration as low as 100 ppb would have a significant impact on the lifetime of the methanol synthesis catalyst. Therefore it is recommended to install a sulphur guard upstream the methanol reactor. The sulphur guard is designed to reduce the sulphur concentration in the make-up gas to a few ppb by absorbing the sulphur on promoted zinc oxide, type HTZ-51.
After having passed the sulphur guard the make-up gas is mixed with preheated recycle gas and the combined gas is sent to the methanol reactor, where hydrogen and carbon oxide react to form methanol, as shown in Fig. 2

In the design of a methanol synthesis loop it is important to consider the following:

- **Catalyst Properties**
  Desirable properties are high and stable activity, high selectivity for methanol production, high mechanical strength and a wide range of operating temperatures.

- **Heat Recovery and Temperature Control**
  The heat of reaction should be recovered at the highest possible temperature, e.g., by generating the steam at high pressure. Heat recovery should be designed to allow simple and reliable control of the catalyst bed temperatures.

- **Investment Cost**
  A low investment cost is obtained when the recycle ratio is low – a low gas flow means equipment of a smaller size. Single-stream operation in the loop allows economy of scale to be realised in large units.

- **Power Consumption for Recycle Compression**
  Low power consumption is obtained at a low recycle ratio (high conversion per pass) and a low pressure drop in reactors and other equipment.

- **Flexibility with respect to Operating Conditions**
  Available make-up gas should be utilised efficiently at all times. The loop design should allow adjustment of the operating conditions to compensate for decreasing catalyst activity and for changes in the amount or composition of the make-up gas.

**Reactor Design**

The design of the Topsøe methanol synthesis loop is based on the use of boiling water reactors (BWR), i.e., tubular reactors with catalyst loaded into several tubes surrounded by boiling water on the shell side. The boiling water efficiently removes the heat liberated by the methanol synthesis reaction and thus ensures an almost isothermal reaction path at conditions close to the maximum rate of reaction. This not only ensures a high conversion per pass and thus high catalyst utilisation as well as low recirculation, but also low by-product formation.

In order to compensate for loss of activity through the life of a catalyst charge, the operating pressure and the catalyst temperatures will be increased, ensuring a constant high efficiency of the synthesis loop.

As an alternative to a boiling water reactor in its pure form it is possible to use a combination of an adiabatic and a tubular reactor. The adiabatic reaction step may be placed before or after the BWR. For a given capacity the combination results in a smaller reactor diameter compared to the case of a pure BWR. Especially for large plants this can be a decisive factor because transport restrictions may set a limit on the reactor diameter.
Catalyst

Topsøe’s methanol synthesis catalyst MK-151 FENCE™ matches the requirements of today’s methanol plants with regard to high and lasting activity, high selectivity and operational flexibility.

The MK-151 FENCE™ offers:

- Longer useful catalyst lifetime
- Higher conversion and carbon efficiency during its lifetime
- Lower by-product level in the crude methanol
- Operational flexibility at the entire range of synthesis gas compositions

Thorough knowledge of the reaction kinetics is of course needed when designing methanol synthesis reactors. It is, however, equally important to have a detailed knowledge of the formation of by-products as this is required in order to make an optimum design of the distillation section. In general, it can be stated that the selectivity of the methanol synthesis catalyst decreases when operating at:

- Higher pressures
- Higher temperatures
- Higher CO/H₂ ratios
- Higher CO/CO₂ ratios
- Lower space velocities

It is thus seen that production of methanol from coal or heavy oil by partial oxidation is more challenging with regard to selectivity compared to a natural gas case since the coal based synthesis gas normally has a higher CO/H₂ as well as a high CO/CO₂ ratio.

Since its introduction in 2009 MK-151 FENCE™ has fulfilled all expectation by its successful industrial operation.
Distillation

Over the years Topsøe has designed a number of methanol distillation units, all tailor-made, to meet each customer’s individual requirements.

Normally these requirements are easily met with a three-column system and a total heat input of approximately 0.6 Gcal/MT of methanol, ensuring a sound ration between investment and energy consumption.

The three-column layout consists of a stabiliser column where low-boiling compounds and dissolved gases are stripped off, and two concentration columns yielding the final methanol product and an almost pure water stream, which is exported, see Fig 3. The energy efficiency is high due to the fact that the reboiler heat for the 2nd column is obtained by cooling of the top gas from the 3rd column.
DME Synthesis

DME has been found to be a competitive fuel for markets that cannot be directly reached by low-cost natural gas and is a valuable option by major gas producing countries. Market application can be as fuel for power generation and as alternative to LPG.

The Topsøe process for production of DME, as shown in Fig. 4 is based on dehydration of methanol. The main features are the following:

- Feed stock flexibility: Both crude methanol and fine methanol can be used as feed
- Simple adiabatic reactor
- Catalyst with high selectivity over a wide temperature range
- Product quality from fuel to propellant grade

Product purification system lay-out will depend upon the product requirement. Normally a two column system is applied where the first column serves to up-concentrate the DME and the second column separates water and methanol.