

# **Proven autothermal reforming technology for modern large- scale methanol plants**

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*With global demand for methanol continuing its steady rise, improvements in methanol plant capacity is becoming increasingly urgent in order to remain competitive in today's market. Capacity expansion takes advantage of economy of scale, leading to significant reductions in costs. The modern-day large-scale methanol plant produces twice as much as the typical capacity at the beginning of the millennium. Specialized technology, both for syngas generation and for methanol synthesis, is essential in order to achieve world-class production capacities. Topsøe has invested significant efforts in developing such technologies, from which one of the results is the implementation of stand-alone autothermal reforming (ATR) for syngas generation. With its low steam-to-carbon ratio, the unique stand-alone ATR technology can lower costs considerably. A combination of ATR technology with an optimized Topsøe methanol reactor layout and high-performance Topsøe methanol synthesis catalyst leads to optimal feedstock utilization and maximum operation efficiency. This paper describes Topsøe's industrial operating experiences within autothermal reforming, as well as process conditions, catalysts, and design requirements to ensure high availability and reliability in large-scale methanol plants.*

## INTRODUCTION

Today, the dominant feedstock for methanol production is natural gas, and this will likely continue to be the case for many years, especially due to the large strides recently made in shale gas production. The current trend of increasing production and decreasing price of natural gas is expected to drive up the demand for new methanol plants based on natural gas.

The current capacity of a world-scale methanol plant is 5,000 MTPD, and plans are already underway for plants with twice that capacity at 10,000 MTPD. Such large plants require a significant amount of investment, which presents the incentive to maximize single-line capacity and benefit from economy of scale.

The costs associated with large-scale methanol plants are largely due to the energy- and capital-intensive processes involved in manufacturing the syngas necessary for methanol production. Estimates suggest that syngas production, including compression and oxygen supply, may account for as much as 60% or more of the investment. One process that greatly benefits from energy and cost optimization is the reforming process.

Stand-alone autothermal reforming (ATR) is advantageous because it does not require the supply or dissipation of thermal energy to or from the reaction. This feature makes ATR useful for many applications, and it has been proven industrially to provide quality syngas for large-scale plants. Together with the right selection of process conditions and catalysts, ATR technology can offer methanol producers high availability factors and reliability of operation.

This paper describes the benefits of using ATR technology together with Topsøe's efficient methanol synthesis technology and catalysts. Full integration and overall optimization are key factors in the design of a methanol plant.

## CONVENTIONAL TWO-STEP REFORMING

Topsøe's conventional technology for producing syngas in methanol plants involves the so-called "two-step reforming" concept [1] (Fig.1). The process layout includes adiabatic prereforming [2], tubular reforming, and oxygen-blown secondary reforming. The oxygen acts as a source for internal combustion of hydrocarbons.

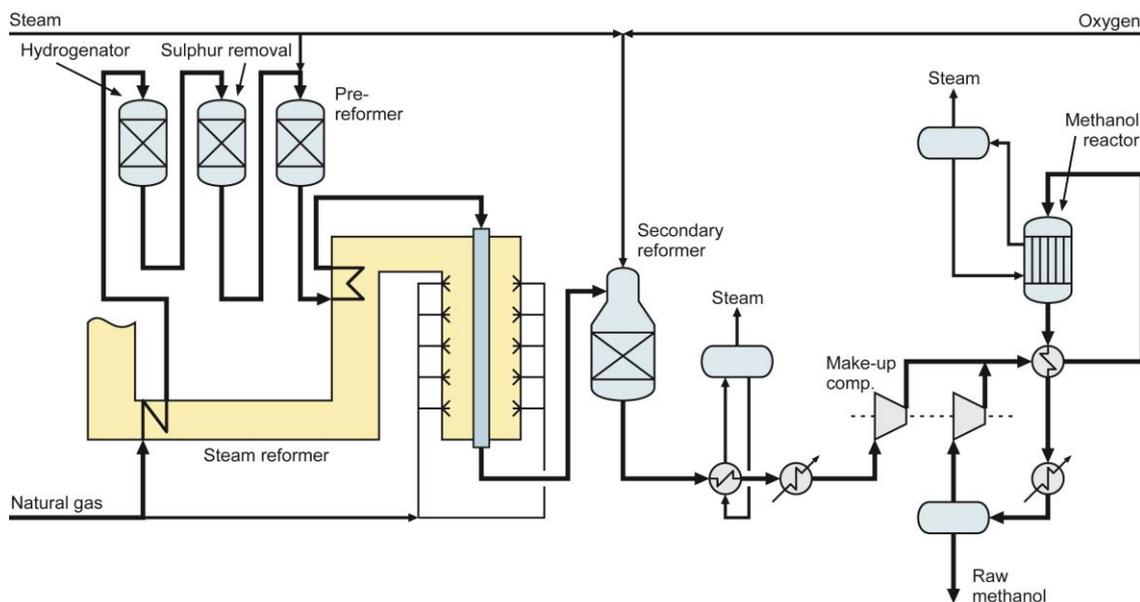


Fig. 1: Methanol plant process layout with Topsøe two-step reforming [14].

## AUTOTHERMAL REFORMING

The use of autothermal reformers in syngas manufacture for ammonia and methanol production began in the middle of the last century [3, 4]. Today, ATR technology replaces two-step reforming technology in Topsøe's optimized solution for large-scale methanol plants [1]. ATR is also the preferred technology for syngas manufacture in gas-to-liquid (GTL) plants, in which diesel is produced via Fischer-Tropsch (FT) synthesis [5], due to its feature of directly producing syngas with a  $H_2/CO$  ratio of 2.0. In fact, many of the developments in ATR technology were the result of renewed interest in GTL processes, which in 2006 resulted in the successful start-up of the first large-scale GTL plant in the world by Oryx GTL [6].

The technology based on stand-alone ATR is a process that does not require a tubular reformer. Instead, prereformed natural gas is sent directly to an ATR reformer, where hydrocarbons undergo combustion in the presence of oxygen (Fig. 2). By eliminating the need for a tubular reformer, the steam addition to the feedstreams can be reduced significantly.

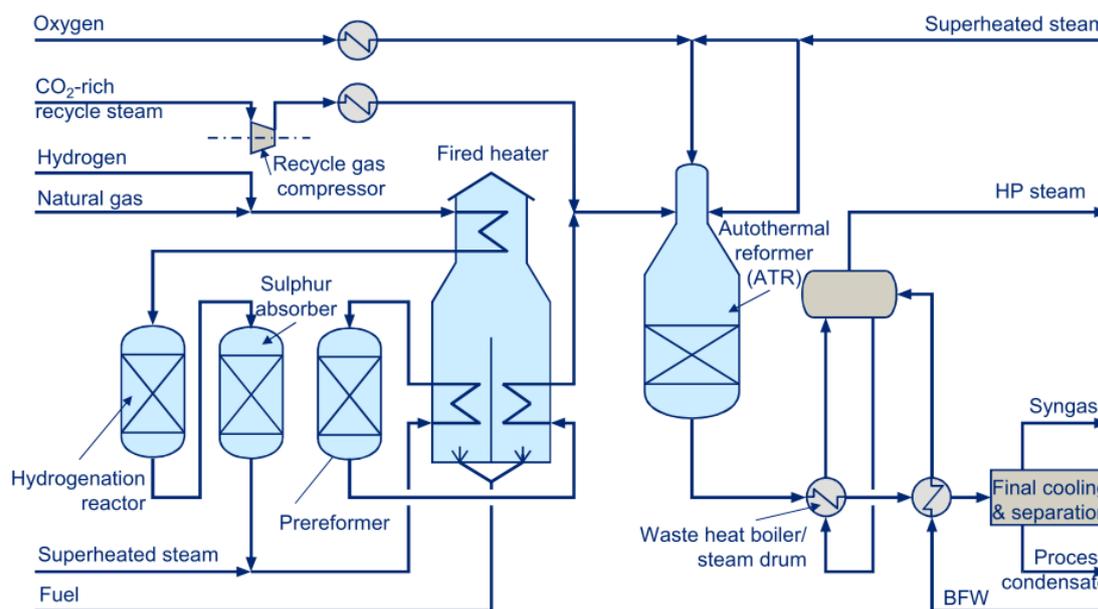


Fig. 2: Syngas production equipped with Topsøe ATR stand-alone reforming [14].

### Low steam-to-carbon ratio

There are a number of advantages of a low steam-to-carbon (S/C) ratio. A lower steam requirement implies that the syngas unit can be reduced in size, thus saving on capital expenditures (CAPEX). Low S/C also enables larger single-train capacity as discussed in [7]. Furthermore, the water-gas shift equilibrium dictates that under low S/C conditions, the syngas is characterized by low  $H_2/CO$  ratios and high  $CO/CO_2$  ratios. An advantage of high  $CO/CO_2$  ratios is reduction in size of the methanol synthesis section. Syngas properties, including  $CO/CO_2$  ratios, are further discussed in a later section entitled "Syngas properties for methanol production".

The drawbacks of low S/C ratios are higher methane slip and higher risk of by-product formation in methanol synthesis. Methane is an inert in the methanol synthesis process and must be purged. However, the impact of the higher methane content is limited because additional purge is already required due to the excess amount of carbon oxides in the syngas. The higher risk of by-product formation requires that the methanol synthesis process is operated at lower temperatures, which results in a larger methanol reactor and a reduction in energy efficiency. However, the net result still shows a savings in CAPEX and similar overall energy consumption when compared to higher S/C conditions. Furthermore, by-product formation is not a relevant issue if the final methanol product is not grade AA or similar.

## Integrated solution for large-scale methanol production

Syngas generation in a stand-alone ATR unit consists of a fired heater for preheating of feed gases and an oxygen-blown ATR reformer. A two-step reforming unit consists of a steam reformer, which includes a waste heat section for preheating of feed gases, followed by an oxygen-blown secondary reformer. The oxygen consumption is considerably higher in the ATR unit. However, in large plants, this extra cost in ASU (air separation unit) is offset by the absence of an expensive steam reformer. For unit capacities lower than approximately 2,500 MTPD, oxygen supply is typically more expensive than steam reforming.

In general, ATR technology is favored over conventional reforming options under the same conditions that favor the use of oxygen-blown secondary reforming. Savings in CAPEX as well as operational expenses (OPEX) strongly recommend ATR technology as the optimal solution for large-scale methanol plants. Very recent studies suggest that CAPEX and OPEX are also lower when ATR technology is applied to medium- to large-scale methanol plants (e.g., larger than ~2,500 MTPD) that commonly operate with two-step reforming.

Table 1 shows a comparison of typical operating parameters at a 5,000-MTPD grade-AA methanol plant, where the syngas is produced with either ATR or two-step reforming technology. In both cases, the feedstock is natural gas having the same composition and plant inlet pressure. The methanol synthesis process occurs at 90 bar in a standard loop with parallel boiling water reactors (BWR).

<b>Operating parameter</b>	<b>ATR</b>	<b>Two-step</b>
S/C	<b>0.6</b>	<b>1.8</b>
Specific O <sub>2</sub> consumption per unit MeOH, index	<b>100</b>	<b>69</b>
Reforming and preheating duty, index *	<b>100</b>	<b>297</b>
CO/CO <sub>2</sub> ratio in syngas	<b>5.4</b>	<b>3.0</b>
H <sub>2</sub> O in raw product, wt %	<b>7</b>	<b>12</b>
MU gas compressor size, index	<b>100</b>	<b>132</b>
Recycle gas compressor size, index	<b>100</b>	<b>96</b>
Carbon dioxide release, index	<b>100</b>	<b>143</b>
Energy consumption, index	<b>100</b>	<b>101</b>
ISBL cost index, incl. ASU, index	<b>100</b>	<b>110</b>
<i>* Transferred duty per unit methanol product including all preheat duties and heat transferred through the tubes in the steam reformer (in the case of two-step reforming).</i>		

As illustrated in Table 1, the net result of the comparison is a savings in CAPEX of 10% with similar or better total energy consumption. Other major process differences include that of S/C ratio and of oxygen consumption.

CO<sub>2</sub> release via flue gas from ATR operation is less than that from two-step reforming. This comparison does not consider the factors associated with production of oxygen and power. The total energy consumption indicates that the environmental impacts are similar for ATR and two-step reforming, although the impacts can differ in how and where the CO<sub>2</sub> is released.

It should be noted that there is currently a shift towards reduced S/C in two-step reforming. S/C ratios as low as 1.4 are possible today, which reduce the disparity between ATR and two-step reforming technologies.

## ATR design

Operating conditions for the ATR are more severe than they are for an oxygen-blown secondary reformer, which therefore necessitates a very robust process burner. In addition, with the lower S/C feed ratio, combustion intensity and flame temperature are higher in ATR reformers. Many improvements addressing these challenges were made in the 1990s, and by 2002, Topsøe ATR technology was capable of industrial operation at S/C ratios as low as 0.6 [6, 8].

The reactor design of the ATR, as well as oxygen-blown secondary reformers, consists of a burner, a combustion chamber, a fixed catalyst bed, a refractory lining and a reactor pressure shell as illustrated in Fig. 3. The key elements are the burner and the catalyst:

- The *burner* provides proper mixing of the oxidant and hydrocarbon feeds, and the fuel-rich combustion takes place in a turbulent diffusion flame. Intensive mixing is essential to avoid soot formation. The flame core may exceed 3,000°C. It is essential to minimize heat transfer by thermal radiation from the flame and hot gas recirculation to the burner parts.
- The *catalyst* equilibrates the syngas and converts soot precursors. The catalyst particle size and shape are optimized to achieve high activity and low pressure drop in order to obtain a compact reactor design.

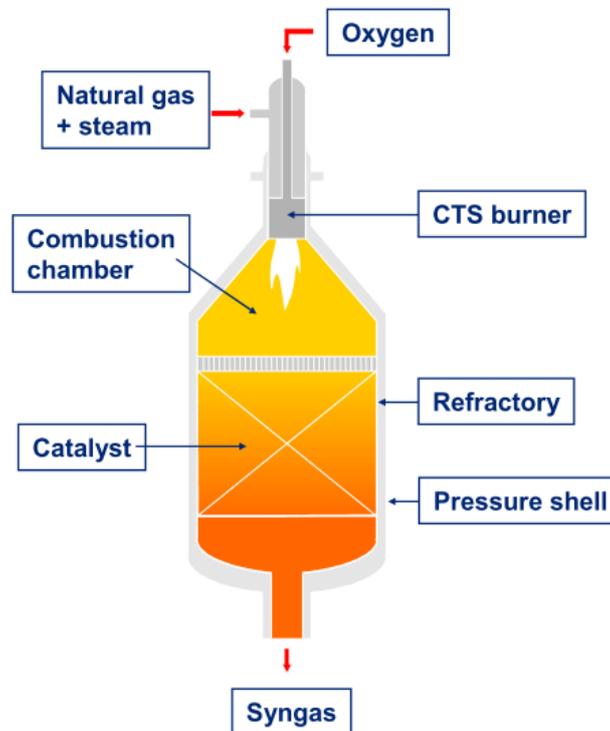


Fig. 3: Schematic of the Topsøe ATR reformer [6].

## Topsøe process burner

In the design of the burner and the combustion chamber, it must be ensured that safe operation and satisfactory equipment lifetime are obtained. A good burner is characterized by:

- Centered flame
- Protection of refractory from the hot flame core
- Efficient mixing at the burner nozzles

- Low metal temperatures of the burner nozzles
- Soot-free combustion
- Homogeneous gas and temperature distribution from combustion chamber to top of catalyst bed

The first Topsøe CTS burner [9] was developed in 1991. CTS burners have been in successful operation since 1992 in ATR reactors and in oxygen-blown secondary reformers that were used for the production of a variety of products from methanol, hydrogen, and ammonia to pure CO and Fischer-Tropsch products.

A new and optimized version of the CTS burner was developed in 1999 with special focus on operation at low S/C ratios with high flame temperatures in ATR reformers. The flow pattern and mechanical design of the burner nozzles have been optimized by use of tools like CFD, stress analysis with Finite Element Analysis (FEA), and real-time environment testing in pilot-scale and in full-size demonstrations.



Fig. 4: Topsøe CTS burner.

### **Topsøe reforming catalysts**

The very high temperatures in the ATR require that the installed catalyst has excellent thermal stability. Topsøe offers two types of catalysts for ATR purposes: RKA-02 and the RKS-2 series. RKA-02, a nickel-based catalyst on a stabilized alumina carrier, is used as the top layer. The stabilization of the carrier material makes RKA-02 well suited for operation at the extreme conditions in the very top of the catalyst bed. The RKS-2 catalyst series is also a nickel-based catalyst, but has a carrier composed of Mg-Al spinel. The unique Mg-Al carrier has an even higher melting point and thermal stability than alpha-alumina.

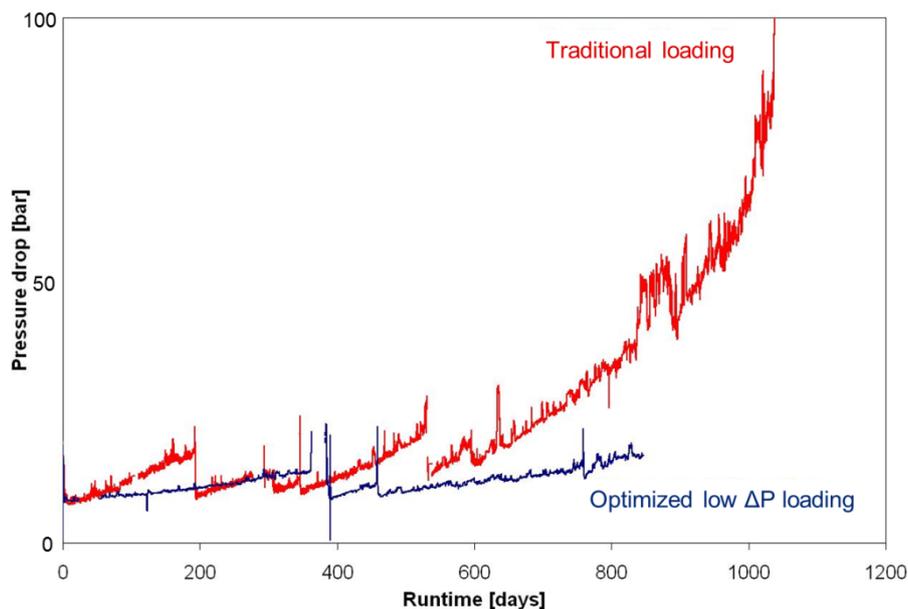
RKA-02 is a ring-shaped catalyst, while the RKS-2 series consists of two shapes: ring and 7-hole (Fig. 5). A combination of these catalysts is used to design the optimal ATR catalyst loading.



**Fig. 5: Topsøe reforming catalysts.**

One of the challenges facing ATR catalysts is the development of high pressure drops across the catalyst bed. This could lead to hot spots on the reactor shell as a consequence of gas bypass into the refractory lining (Fig. 3). Increases in pressure drop are caused by alumina deposits on the catalyst pellets, which fill the void space between the pellets and occur when alumina from the refractory material evaporate at the high temperatures of the combustion chamber and come into contact with the catalyst. The conditions are favorable for alumina vapor deposition because the catalyst is kept relatively cool by the endothermic reforming reaction.

The effect of alumina deposition can be minimized by catalyst loading optimization. The result of such an optimization in an industrial ATR operating at a S/C ratio of 0.6 is shown in Fig. 6, which illustrates a considerable reduction in pressure drop development. These observations are particularly significant given that the operating conditions of this ATR are exceptionally demanding, i.e., the low S/C ratio implies higher temperatures in the combustion chamber.



**Fig. 6: Pressure drop profiles in an industrial ATR unit.**

Optimized operation of ATR technology also depends on the performance of the prereforming catalyst. Higher hydrocarbons are converted in the prereformer, and the preheat temperature to the ATR unit can be increased to enable reduced oxygen consumption. Additional benefits of the prereformer include an increased margin to soot formation in the ATR and faster start-up.

Topsøe's prereforming catalyst, AR-401, offers operational flexibility in feedstocks ranging from natural gas to naphtha. It also operates at a wide range of temperatures and S/C ratios. AR-401 has a very high and stable reforming activity as well as excellent resistance against carbon formation.

## SYNGAS PROPERTIES FOR METHANOL PRODUCTION

The hydrogen and carbon oxides in syngas react via the following equilibrium reactions to produce methanol:



The thermodynamic equilibrium limits the process flow to low conversion per pass and implies a large recycle of unconverted gas. The reaction is strongly exothermic, and maximum conversion is obtained at low temperatures and high pressures. Details on thermodynamics, reaction mechanism, kinetics, and catalyst properties are further discussed in [10].

In methanol synthesis, the ideal syngas stoichiometry is the molar ratio  $M = 2$ , where  $M$  is defined as:

$$(\text{H}_2 - \text{CO}_2) / (\text{CO} + \text{CO}_2)$$

If purging is required, e.g., when inerts are present in the gas, then  $M$  is ideally slightly higher than 2. The inerts usually found in methanol syngas are methane, argon, and nitrogen, and a high concentration of inerts lowers the partial pressure of the active reactants.

The differences between syngas produced from ATR versus two-step reforming are shown in Table 2. In the case of two-step reforming, the ratio  $M$  of the produced syngas is close to 2, whereas the ATR unit produces syngas with  $M < 2$ .

	<b>ATR</b>	<b>Two-step reforming</b>
H <sub>2</sub>	<b>64.1</b>	<b>68.1</b>
N <sub>2</sub>	<b>1.6</b>	<b>1.3</b>
Ar	<b>0.</b>	<b>0.</b>
CO	<b>27.0</b>	<b>22.2</b>
CO <sub>2</sub>	<b>5.0</b>	<b>7.4</b>
CH <sub>4</sub>	<b>1.8</b>	<b>0.4</b>
H <sub>2</sub> O	<b>0.5</b>	<b>0.6</b>
<b><u>M</u></b>	<b><u>1.84</u></b>	<b><u>2.05</u></b>

If  $M$  in the make-up syngas deviates from the stoichiometric requirement of 2, then either surplus hydrogen or surplus carbon oxides has to be removed from the synthesis loop. In both cases, the purge is used to remove the excess components. The excess purge is typically used as fuel or as a hydrogen source. For  $M$  less than 2, the majority of the hydrogen is usually recovered from the purge gas and recycled to the make-up gas. The reaction efficiency of the limiting components is normally 94-96%, assuming an inert concentration of 1% in the make-up gas.

$M$  is, however, independent of the shift equilibrium equation (Eq. (3)) and should therefore not be used to describe the reactivity of syngas. Instead, it is suggested to use the CO/CO<sub>2</sub> ratio for this purpose. More specifically, a high CO/CO<sub>2</sub> ratio will increase the reaction rate and the achievable per-pass conversion because CO is preferred over CO<sub>2</sub> as a reactant by copper catalysts. In addition, the formation of water will decrease, reducing both the catalyst deactivation rate and the water content in the methanol product.

The CO/CO<sub>2</sub> ratio is determined by the method of syngas generation. In general, oxygen-blown reforming, e.g., ATR, leads to the highest CO/CO<sub>2</sub> ratios in syngas. With an efficient hydrogen recovery unit, the additional purge required to remove excess carbon is achieved without extra loss of hydrogen. Reaction efficiency remains unchanged at approximately 94-96%.

The above discussion and that of low S/C ratios highlight the three key features of ATR technology that establish it as the optimal choice for syngas production in large-scale methanol plants. These features are:

- High CO/CO<sub>2</sub> ratios in the syngas, which result in higher methanol reaction rates
- Low steam requirements, which lead to lower CAPEX and OPEX in methanol plants with capacities above ~2,500 MTPD
- Low steam throughput, which enables larger single-line capacity

## **METHANOL SYNTHESIS TECHNOLOGY**

Stand-alone ATR-produced syngas is a more reactive gas compared to syngas from two-step reforming, but compared to syngas from gasification processes, it is less reactive. Numerous methanol plants based on syngas from gasification are in operation today. The challenge for syngas produced from stand-alone ATR is thus not the reactivity, but the optimal integration between the reforming section and methanol synthesis.

In order to design an efficient methanol synthesis process, the following conditions must be taken into consideration:

- Syngas with a high CO/CO<sub>2</sub> ratio
- Handling of a highly exothermic process at low temperature
- Minimization of by-product formation
- Efficient use of released reaction energy
- Efficient disposal of surplus reactants and inerts

## **Boiling water reactor**

Figure 7 shows a typical methanol synthesis loop, including optional units. The heart of the process is the boiling water reactor (BWR). This type of reactor provides very efficient and easy control of the reaction temperature and simultaneously ensures that the released reaction heat can be used efficiently. Figure 8 shows a typical temperature profile in a BWR. By controlling the steam pressure and thus fixing the steam-side temperature in the full length of the reactor, the reaction temperature is controlled throughout the reactor. The isothermal nature of the BWR gives a high conversion compared to the amount of catalyst installed. The average reaction temperature is usually between 250 and 260°C. The BWR is a prerequisite for optimal design of a methanol synthesis loop fed with very active make-up syngas, e.g., syngas generated by autothermal reforming of natural gas or coal gasification.

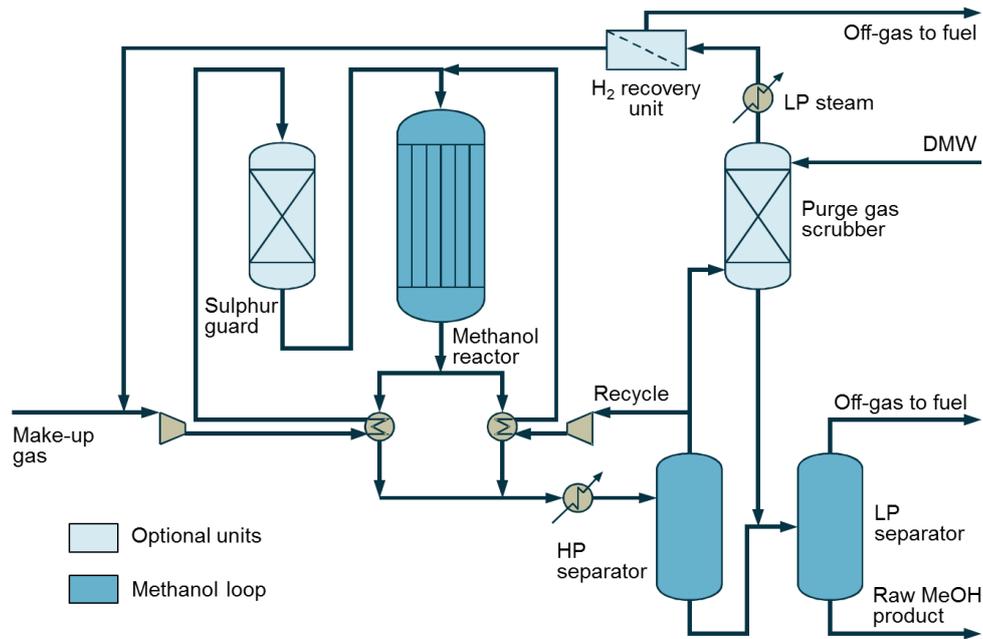


Fig. 7: Typical methanol synthesis loop, including optional units.

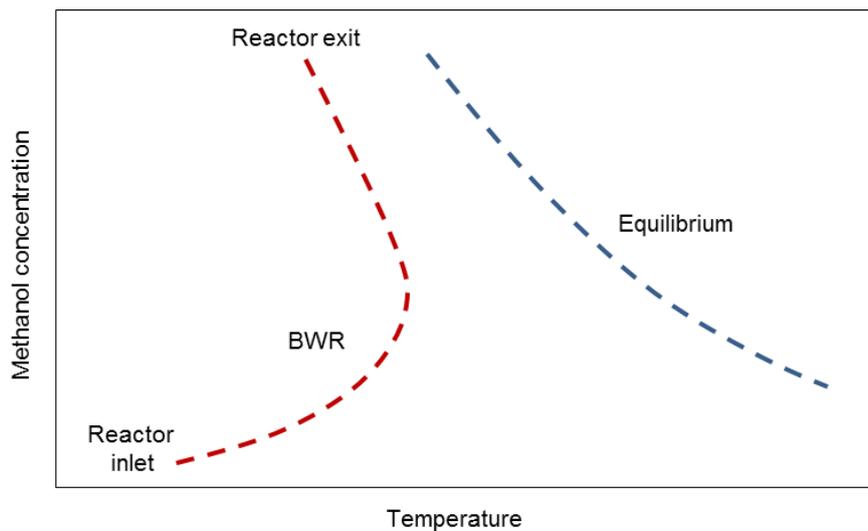


Fig. 8: Catalyst bed temperature and methanol concentration profiles in BWR reactors.

There are a number of different BWR designs available on the market. The Topsøe BWR is a shell-and-tube type with catalyst in the tubes and boiling water on the shell side. The catalyst bed temperature is limited by the diameter of the tube and the boiling water temperature. The steam side is designed to allow natural circulation of the boiling water with less than 10% evaporation per pass, which results in a uniform steam side temperature. The produced steam is easily separated in an external steam drum and utilized in steam turbines and/or as process steam.

### Reactor temperature control and by-product formation

Topsøe's methanol synthesis catalyst is highly selective. A selectivity of 99.9% is not uncommon. This is remarkable considering that the formation of by-product is thermodynamically favored over methanol. Typical by-products include DME, higher alcohols, other oxygenates, and minor amounts of acids and aldehydes. By-product formation is mainly related to the maximum reaction temperature and is more likely to occur at hot zones in a methanol synthesis catalyst bed. For this reason, the temperature control in a

methanol synthesis reactor is of particular importance, especially in the presence of very active feed gas and catalyst.

The level of by-product is most relevant when the end product is grade-AA methanol or similar. For other applications, such as MTO (methanol to olefins) or gasoline, a higher level of by-products is acceptable but still needs to be controlled. Full control of the reaction temperature, such as is available with the Topsøe BWR, allows a methanol synthesis plant to be optimized to meet a specific product requirement.

For practical reasons, one BWR is limited in size to produce 1,500 to 2,200 MTPD, the range mainly depending on the syngas activity. For larger capacities, a parallel reactor design is used. Such parallel reactors will operate with common steam pressure and are controlled as a single system.

## INDUSTRIAL EXPERIENCE

Topsøe has designed several methanol synthesis loops operating with feedgas from coal gasification units. A coal gasification syngas typically has a very high CO/CO<sub>2</sub> ratio, often 10 or higher. For example, one reference plant, Xianyang China, is producing 2,000 MTPD grade-AA methanol using one BWR with a syngas having a CO/CO<sub>2</sub> ratio of 10.5.

An example of multiple BWRs in operation is the Fanavaran plant with its 3 BWRs. Fanavaran can produce 3,000 MTPD from syngas generated by steam reforming with a very low CO/CO<sub>2</sub> ratio of 2.0.

The above two examples illustrate the effect of CO/CO<sub>2</sub> ratio on the size of a methanol synthesis unit. Overall, Topsøe has several years of successful experience with designing and operating methanol synthesis units using very active syngas.

The Topsøe CTS burner [9] was first introduced in a number of revamp projects during the 1990s, in both stand-alone ATR reformers and in oxygen-blown secondary reformers. In the Statoil methanol plant in Tjeldbergodden, a CTS burner has been in operation as part of a two-step reforming process for 15 years. The PetroSA GTL plant in Mosselbay, South Africa, has operated 3 syngas trains with CTS burners for approximately the same amount of time. The CTS burner has been proven industrially to provide long service lifetimes at severe conditions with pure oxygen as oxidant.

Industrial plants using Topsøe ATR technology at low S/C ratios have been in operation in European chemical plants since 2002 and at Sasol in their chemical complex in Sasolburg, South Africa, since 2004.

The first fully integrated GTL facility with ATR reforming was started in Qatar by Oryx GTL in 2006. A new-generation CTS burner was implemented in the ATR reformers and has been in satisfactory operation for several years, supporting maintenance periods of 2-3 years. Oryx GTL has recently reported excellent productivity, on-stream factors, and reliability [11].

Recently, Uzbekneftegaz, Sasol, and Petronas have formed a partnership in OLTIN YO'L GTL [12] and are in the engineering phase of a 38,000 BPD plant in Uzbekistan with scheduled completion in 2017 [13]. The plant will use the same technology as was pioneered in Oryx GTL with Sasol FT technology and with Topsøe ATR syngas technology. The process burner to be used will be the newest generation of the CTS burner from Topsøe.

Topsøe ATR syngas technology, which has proven to be reliable and efficient for large-scale GTL plants, can be applied in a similar layout for large-scale methanol production. ATR reformers in large-scale GTL operation currently cover an operating range equivalent to 7,000 MTPD methanol.

## SUMMARY

Methanol is one of the top chemical commodities in the world, and as a liquid, it is relatively easy to store and transport, which makes it attractive for new fuel and energy applications. With this potential for future expansion, along with the current trends in natural gas production and prices, it is expected that the methanol production industry will continue to grow. To meet the demands and to take advantage of the economy of scale, methanol plants exceeding 5,000 MTPD are being designed and constructed. Topsøe has made significant contributions towards the development and optimization of the technology used in large-scale methanol plants in order to maximize cost-effectiveness. Among these contributions is the implementation of autothermal reforming at low S/C ratios for syngas production in the front-end. The

autothermal reforming technology is already a well-proven solution for large syngas units in GTL plants and is recognized in the industry for its performance and reliability.

The most significant benefits of combining ATR technology with large-scale methanol synthesis are: (1) production of syngas with high CO/CO<sub>2</sub> ratios, which results in higher methanol reaction rates, (2) low steam requirements, which lead to lower CAPEX and OPEX in large methanol plants, and (3) low steam throughput, which enables larger single-line capacity. Autothermal reforming for syngas production in large-scale methanol plants with capacities exceeding ~2,500 MTPD will be the preferred solution for future plants, and further developments are anticipated as Topsøe continues its efforts to obtain higher efficiencies and longer runtimes by improving process concepts, catalysts and proprietary equipment.

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