

Large Scale Methanol Production from Natural Gas

RESEARCH | TECHNOLOGY | CATALYSTS



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Abstract

The capacity of methanol plants is increasing to reduce investments, taking advantage of the economy of scale. The capacity of a world scale plant has increased from 2500 MTPD a decade ago to about 5000 MTPD today. Even larger plants up to 10,000 MTPD or above are considered to further improve economics and to provide the feedstock for the Methanol-to-Olefin (MTO) process.

A methanol plant with natural gas feed can be divided into three main sections. In the first part of the plant natural gas is converted into synthesis gas. The synthesis gas reacts to produce methanol in the second section, and methanol is purified to the desired purity in the tail-end of the plant.

The capital cost of large scale methanol plants is substantial. The synthesis gas production including compression and oxygen production when required may account for 60% or more of the investment. In many plants today either tubular steam reforming or two-step reforming (tubular steam reforming followed by autothermal or oxygen blown secondary reforming) is used for the production of synthesis gas. However, stand-alone Autothermal Reforming (ATR) at low steam to carbon (S/C) ratio is the preferred technology for large scale plants by maximising the single line capacity and minimising the investment.

ATR combines substoichiometric combustion and catalytic steam reforming in one compact refractory lined reactor to produce synthesis gas for production of more than 10,000 MTPD of methanol. The ATR operates at low S/C ratio, thus reducing the flow through the plant and minimising the investment. The ATR produces a synthesis gas well suited for production of both fuel grade and high purity methanol.

The design of the methanol synthesis section is essential to ensure low investment. The optimal design and the choice of operating parameters depend on the desired product specification. In many plants Boiling Water Reactors (BWR) are used. The use or incorporation of adiabatic reactors may be advantageous.

The present paper describes the preferred technology for large scale production of methanol. The benefits of using ATR for synthesis gas production will be highlighted with emphasis on single line capacity. A process economic evaluation will be outlined illustrating the advantages of ATR technology compared to two-step reforming at large plant capacities. The use of an adiabatic top layer in the BWR and the impact on reactor size and investment will be described. The paper also covers ongoing developments of synthesis gas and synthesis technology including reduction of the S/C-ratio in the ATR to further increase single line capacity and reduce capital cost.

Introduction

The annual production of methanol exceeds 40 million tons and continues to grow by 4% per year. Methanol has traditionally been used as feed for production of a range of chemicals including acetic acid and formaldehyde. In recent years methanol has also been used for other markets such as production of DME (Di-methyl-ether) and olefins by the so-called methanol-to-olefins process (MTO) or as blendstock for motor fuels.

The production of methanol from coal is increasing in locations where natural gas is not available or expensive such as in China. However, most methanol is produced from natural gas. Several new plants have been constructed in areas where natural gas is available and cheap such as in the Middle East. There is little doubt that (cheap) natural gas will remain the predominant feed for methanol production for many years to come.

The capacity of methanol plants has increased significantly only during the last decade. In 1996 a world scale methanol plant with a capacity of 2500 MTPD was started up in Tjeldbergodden, Norway [1]. Today several plants are in operation with the double of this capacity e.g. [2].

Plants with capacities of 10,000 MTPD or more are considered and planned for example for the production of methanol for the MTO process [3]. Given the substantial investment in such large scale plants there is considerable incentive to maximise single line capacity to take advantage of economy of scale. This paper describes the state of the art methanol synthesis technology with focus on very large plants with a capacity of 10,000 MTPD or more. Technology developments that increase the single line capacity and further reduce the investment are outlined in the final part of the paper.

Methanol Production Technology

All commercial methanol technologies feature three process sections and a utility section as listed below:

- Synthesis gas preparation (reforming)
- Methanol synthesis
- Methanol purification
- Utilities

In the design of a methanol plant the three process sections may be considered independently, and the technology may be selected and optimised separately for each section. The normal criteria for the selection of technology are capital cost and plant efficiency. The synthesis gas preparation and compression typically accounts for about 60% of the investment, and almost all energy is consumed in this process section. Therefore, the selection of reforming technology is of paramount importance, regardless of the site.

Methanol synthesis gas is characterised by the stoichiometric ratio $(H_2 - CO_2) / (CO + CO_2)$, often referred to as the module M. A module of 2 defines a stoichiometric synthesis gas for formation of methanol. Other important properties of the synthesis gas are the CO to CO₂ ratio and the concentration of inerts. A high CO to CO₂ ratio will increase the reaction rate and the achievable per pass conversion. In addition, the formation of water will decrease, reducing the catalyst deactivation rate. High concentration of inerts will lower the partial pressure of the active reactants. Inerts in the methanol synthesis are typically methane, argon and nitrogen.

A comprehensive survey of methanol production technology is given in [4]. In the following a brief description is given covering technologies available for the three process sections.

Synthesis Gas Preparation

Several reforming technologies are available for producing synthesis gas:

- One-step reforming with fired tubular reforming
- Two-step reforming
- Autothermal reforming (ATR)

In one-step reforming, the synthesis gas is produced by tubular steam reforming alone (without the use of oxygen). This concept was traditionally dominating. Today it is mainly considered for up to 2,500 MTPD plants and for cases where CO₂ is contained in the natural gas or available at low cost from other sources.

The synthesis gas produced by one-step reforming will typically contain a surplus of hydrogen of about 40%. This hydrogen is carried unreacted through the synthesis section only to be purged and used as reformer fuel.

The addition of CO₂ permits optimization of the synthesis gas composition for methanol production. CO₂ constitutes a less expensive feedstock, and CO₂ emission to the environment is reduced. The application of CO₂ reforming results in a very energy efficient plant. The energy consumption is 5–10% less than that of a conventional plant [5]. A 3,030 MTPD methanol plant based on CO₂ reforming was started up in Iran in 2004.

The two-step reforming process features a combination of fired tubular reforming (primary reforming) followed by oxygen-fired adiabatic reforming (secondary reforming). A process flow diagram for a plant based on two-step reforming is shown in Figure 1.

By combining the two reforming technologies, it is possible to adjust the synthesis gas to obtain the most suitable composition (M close to 2).

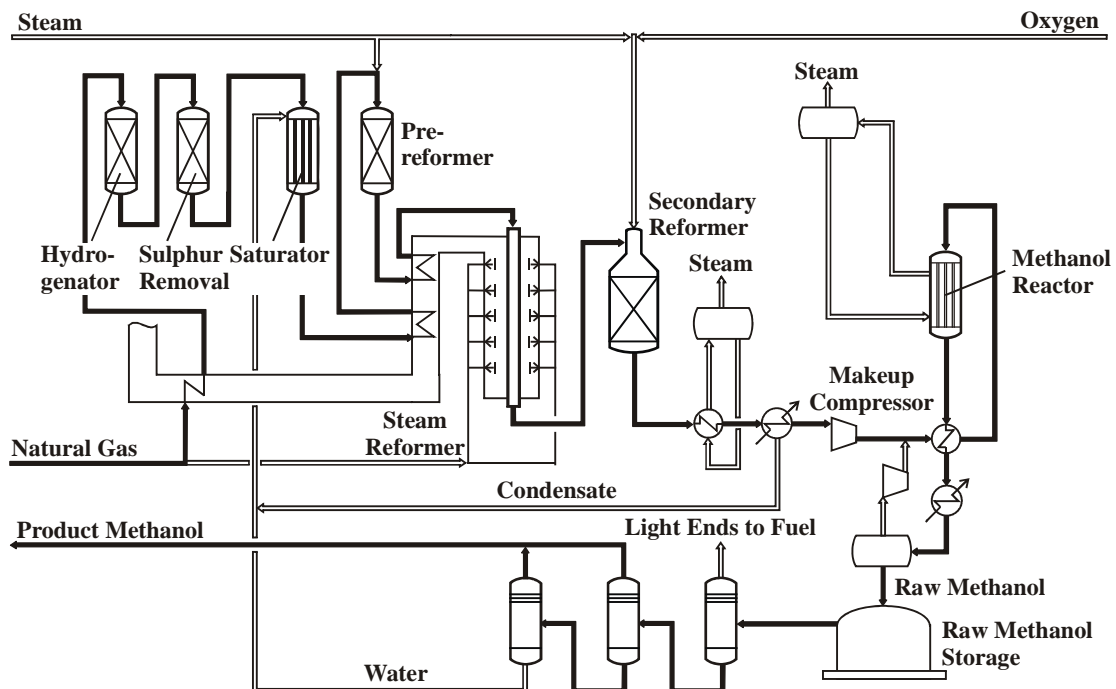


Figure 1: Methanol production by two-step reforming. Simplified process flow diagram

The balance required to obtain a desired value of M depends on the natural gas composition. This is shown in Figure 2 for two feed gas compositions: Pure methane (full lines) and a relatively heavy natural gas with the overall composition CH_{3.6} (broken lines). The heavy gas requires more steam reforming and less oxygen compared to the requirements for lean gas. The same is true for gas containing CO₂. Curves for a feed containing 95 mol% CH₄ and 5 mol% CO₂ are almost identical to the curves for the heavy natural gas in Figure 2.

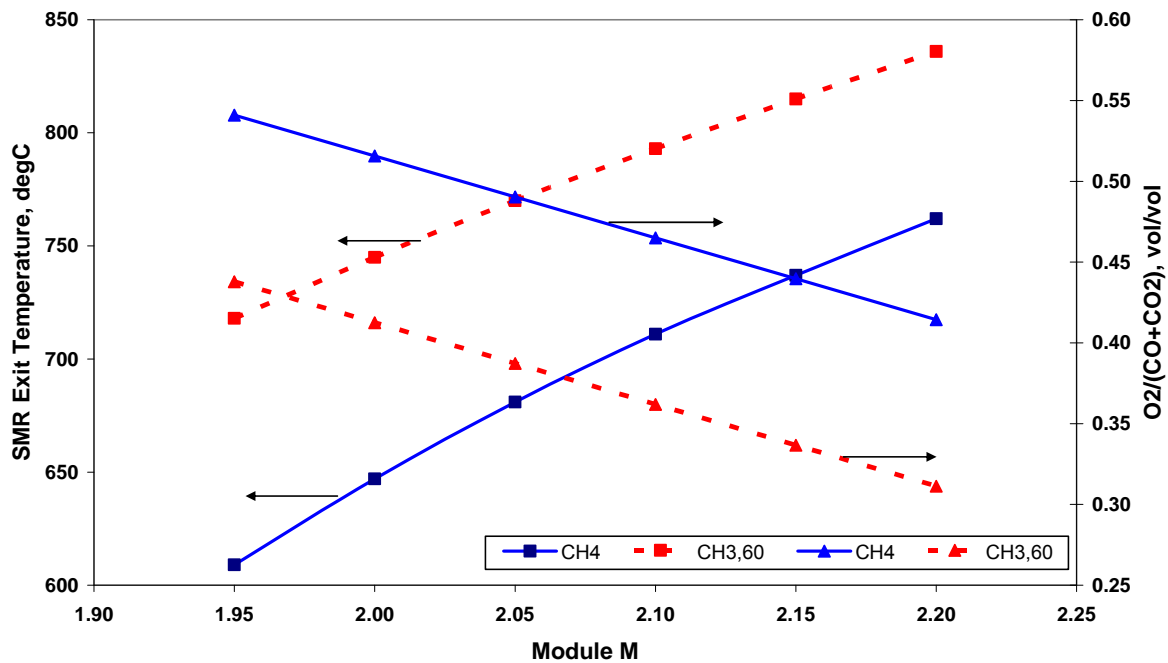


Figure 2: Correlation between steam reformer exit temperature, oxygen consumption and methanol module in two-step reforming

The secondary reformer requires that the primary reformer is operated with a significant leakage of unconverted methane (methane slip). Typically 35 to 45% of the reforming reaction occurs in the tubular reformer, the rest in the oxygen-fired reformer. As a consequence the tubular reformer is operated at low S/C ratio, low temperature and high pressure. These conditions lead to a reduction in the transferred duty by about 60% and in the reformer tube weight by 75 to 80% compared to one-step reforming.

The two-step reforming lay-out was first used in a 2400 MTPD methanol plant in Norway [1]. This plant was started up in 1997. A 5000 MTPD plant based on similar technology was started up in Saudi Arabia in 2008 [2].

Autothermal reforming (ATR) features a stand-alone, oxygen-fired reformer. The autothermal reformer design features a burner, a combustion zone, and a catalyst bed in a refractory lined pressure vessel as shown in Figure 3.

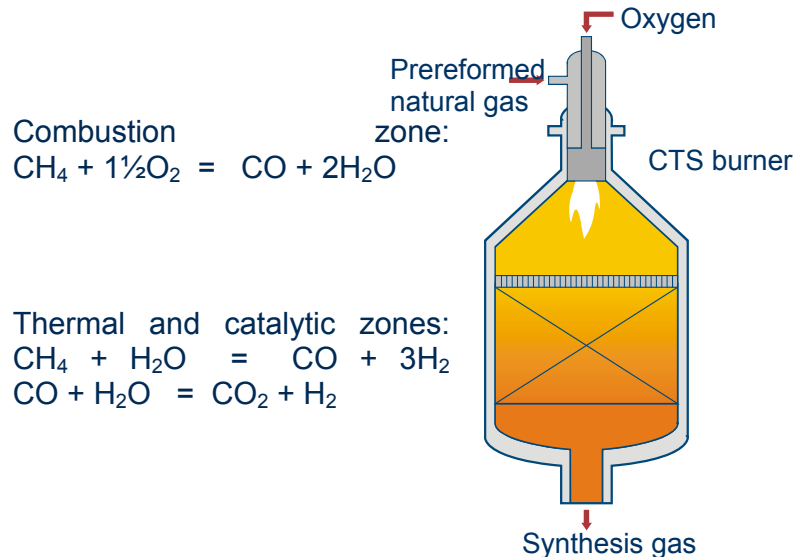


Figure 3. Autothermal Reformer

The burner provides mixing of the feed and the oxidant. In the combustion zone, the feed and oxygen react by sub-stoichiometric combustion in a turbulent diffusion flame. The catalyst bed brings the steam reforming and shift conversion reactions to equilibrium in the synthesis gas and destroys soot precursors, so that the operation of the ATR is soot-free. The catalyst loading is optimized with respect to activity and particle shape and size to ensure low pressure drop and compact reactor design.

The synthesis gas produced by autothermal reforming is rich in carbon monoxide, resulting in high reactivity of the gas. The synthesis gas has a module of 1.7 to 1.8 and is thus deficient in hydrogen. The module must be adjusted to a value of about 2 before the synthesis gas is suitable for methanol production. The adjustment can be done either by removing carbon dioxide from the synthesis gas or by recovering hydrogen from the synthesis loop purge gas and recycling the recovered hydrogen to the synthesis gas [6]. When the adjustment is done by CO_2 removal, a synthesis gas with very high CO/CO_2 ratio is produced. This gas resembles the synthesis gas in methanol plants based on coal gasification. Several synthesis units based on gas produced from coal are in operation, this proves the feasibility of methanol synthesis from very aggressive synthesis gas. Adjustment by hydrogen recovery can be done either by a membrane or a PSA unit. Both concepts are well proven in the industry. The synthesis gas produced by this type of module adjustment is less aggressive and may be preferred for production of high purity methanol.

Figure 4 shows a process flow diagram for a plant based on ATR with adjustment of the synthesis gas composition by hydrogen recovery in a membrane unit.

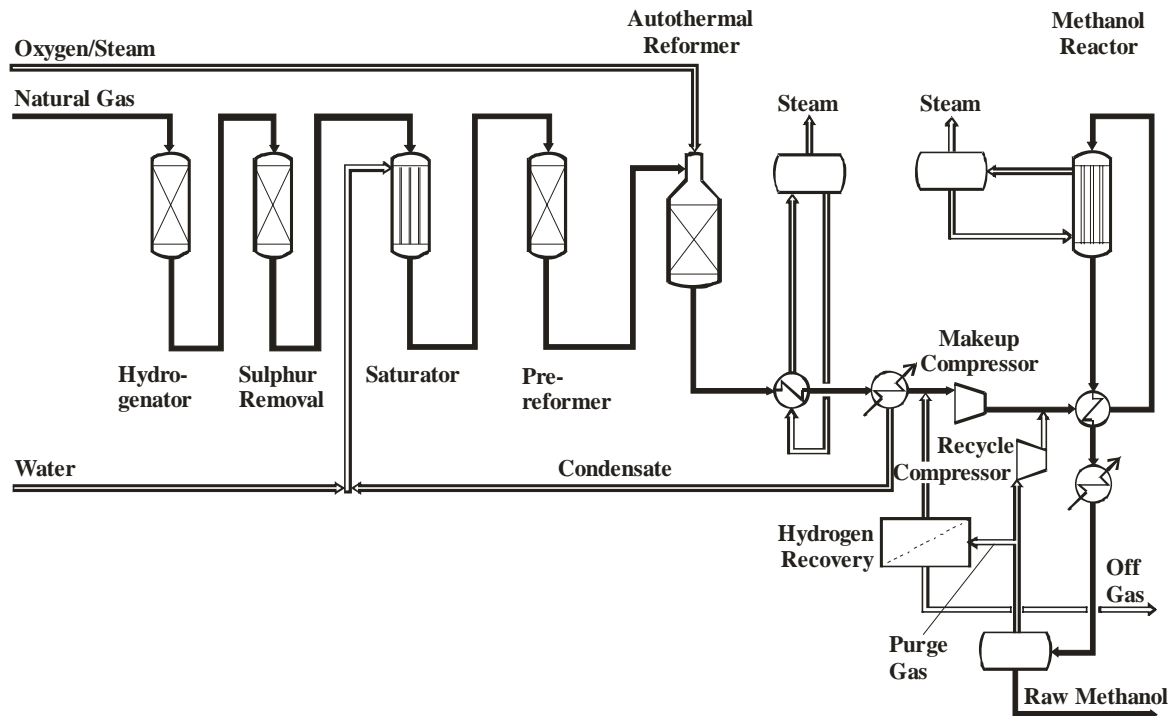


Figure 4: Methanol production by ATR at low S/C ratio. Adjustment of synthesis gas composition by hydrogen recovery and recycle. Simplified flow diagram.

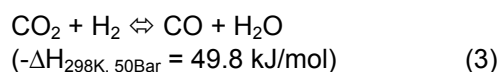
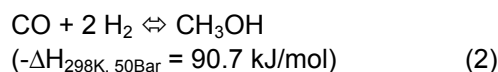
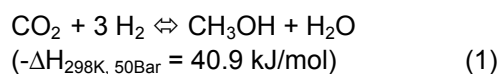
The first ATR in operation in commercial scale at H_2O/C ratio of 0.6 was an industrial demonstration in South Africa in 1999. The first commercial plant was started in Europe in 2002. Very large units were started in South Africa in 2004 and in Qatar in 2006 [7,8]. A methanol plant with a single line capacity of 10.000 MTPD is in the engineering phase for start-up in Nigeria in 2012 [3].

Methanol Synthesis and Purification

In the methanol synthesis conversion of synthesis gas into raw methanol takes place. Raw methanol is a mixture of methanol, a small amount of water, dissolved gases, and traces of by-products.

The methanol synthesis catalyst and process are highly selective. A selectivity of 99.9% is not uncommon. This is remarkable when it is considered that the by-products are thermodynamically more favoured than methanol. Typical byproducts include DME, higher alcohols, other oxygenates and minor amounts of acids and aldehydes.

The conversion of hydrogen and carbon oxides to methanol is described by the following reactions:



The methanol synthesis is exothermic and the maximum conversion is obtained at low temperature and high pressure. Thermodynamics, reaction mechanism, kinetics, and catalyst properties are discussed in [9].

A challenge in the design of a methanol synthesis is to remove the heat of reaction efficiently and economically - i.e. at high temperature - and at the same time to equilibrate the synthesis reaction at low temperature, ensuring high conversion per pass.

Different designs of methanol synthesis reactors have been used:

- Quench reactor
- Adiabatic reactors in series
- Boiling water reactors (BWR)

A **quench reactor** consists of a number of adiabatic catalyst beds installed in series in one pressure shell. In practice, up to five catalyst beds have been used. The reactor feed is split into several fractions and distributed to the synthesis reactor between the individual catalyst beds. The quench reactor design is today considered obsolete and not suitable for large capacity plants.

A synthesis loop with **adiabatic reactors** normally comprises a number (2-4) of fixed bed reactors placed in series with cooling between the reactors. The cooling may be by preheat of high pressure boiler feed water, generation of medium pressure steam, and/or by preheat of feed to the first reactor.

The adiabatic reactor system features good economy of scale. Mechanical simplicity contributes to low investment cost. The design can be scaled up to single-line capacities of 10,000 MTPD or more.

The **BWR** is in principle a shell and tube heat exchanger with catalyst on the tube side. Cooling of the reactor is provided by circulating boiling water on the shell side. By controlling the pressure of the circulating boiling water the reaction temperature is controlled and optimised. The steam produced may be used as process steam, either direct or via a falling film saturator.

The isothermal nature of the BWR gives a high conversion compared to the amount of catalyst installed. However, to ensure a proper reaction rate the reactor will operate at intermediate temperatures - say between 240°C and 260°C - and consequently the recycle ratio may still be significant.

Complex mechanical design of the BWR results in relatively high investment cost and limits the maximum size of the reactors. Thus, for very large scale plants several boiling water reactors must be installed in parallel.

An adiabatic catalyst bed may be installed before the cooled part of the BWR either in a separate vessel or preferably on top of the upper tube sheet. One effect of the adiabatic catalyst bed is to rapidly increase the inlet temperature to the boiling water part. This ensures optimum use of this relatively expensive unit, as the tubes are now used only for removal of reaction heat, not for preheat of the feed gas. This is illustrated in Figure 5, which compares the operating lines in identical service for BWRs with and without adiabatic top layer.

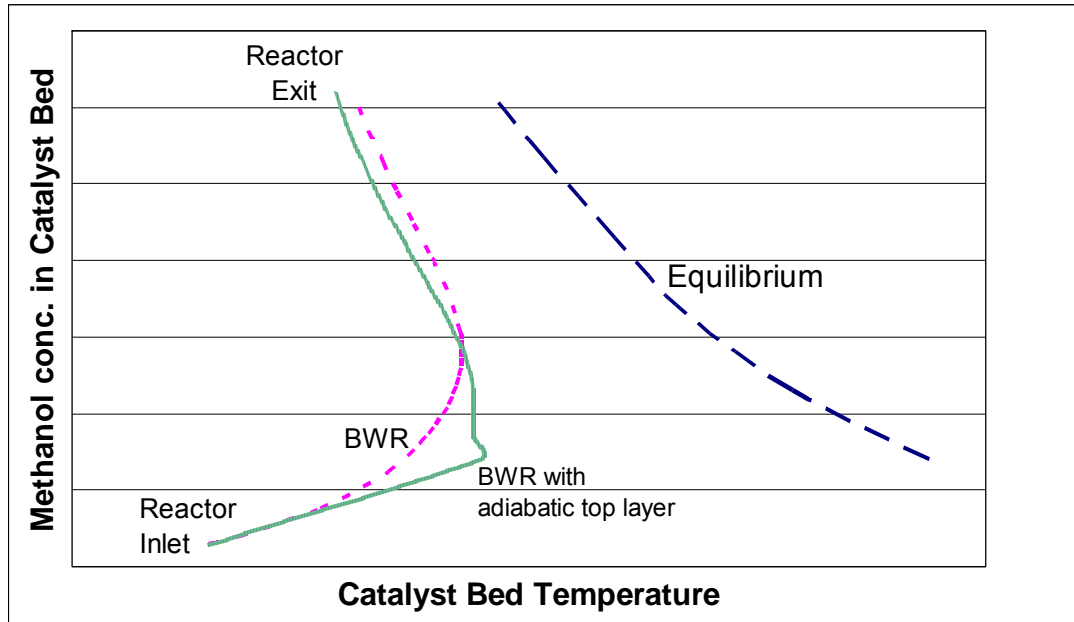


Figure 5: Temperature and methanol concentration profiles in BWR reactors with and without adiabatic top layer

The installation of the adiabatic top layer in the BWR reduces the total catalyst volume and the cost of the synthesis reactor by about 15-25%. The maximum capacity of one reactor may increase by about 20%.

A boiling water reactor with adiabatic top layer will be installed in a 1000 MTPD methanol plant in China.

The last section of the plant is purification of the raw methanol. The design of this unit depends on the desired end product. Grade AA methanol requires removal of essentially all water and byproducts while the requirements for fuel grade methanol are more relaxed. In all cases the purification can be handled by 1-3 columns, where the first is a stabiliser for removal of dissolved gases.

Optimal Technology for 10,000 MTPD

In the following, state-of-the-art ATR and two-step reforming for syngas production are compared for large scale (10,000 MTPD) fuel grade methanol plants. The same natural gas composition and plant inlet pressure has been used for all calculations. The methanol synthesis takes place at 100 bar in a standard loop with parallel BWR installed with adiabatic top layers. The plant lay-outs are illustrated by the simplified flow diagrams in Figures 1 and 4. Typical operating parameters for large scale plants in commercial operation have been selected. The module of the synthesis gas to the loop has in both cases been adjusted to 2.05. In the two-step reforming case this is done by adjusting the exit temperature of the primary reformer. For the ATR case hydrogen recovered from the loop purge gas is recycled to the synthesis gas. The two-step case has been designed with a loop carbon efficiency of 95% by setting the loop purge. Table 1 summarizes key parameters for the two cases.

Syngas generation process	ATR	Two-step
S/C	0.6	1.8
Single line MeOH capacity, index	100	75
Specific O ₂ consump. per unit MeOH, index	100	76
Reforming and preheating duty, index *	100	264
CO/CO ₂ ratio in syngas	6.3	2.7
H ₂ O in raw product, wt %	5	13
MU gas compressor size, index **	100	118
Recycle gas compressor size, index **	100	169
Loop carbon efficiency, %	90.5	95
Loop hydrogen efficiency, % ***	92.2	81.7

Table 1

Key parameters for synthesis gas generation technology for 10,000 MTPD MeOH plant.

* Transferred duty per unit MeOH product including all preheat duties and heat transferred through the tubes in the steam reformer (in the two-step case)

** Size based on specific power consumption per unit MeOH product

*** H in MeOH product divided by H in H₂ in MU gas

The single line capacity is defined by the maximum volumetric flow exit an ATR or secondary reformer. The higher S/C ratio in the two-step case results in a much larger reformer exit flow per unit of converted natural gas. Therefore, in spite of a slightly lower conversion of the feed, the low S/C ATR allows a remarkable 1/3 higher single line methanol capacity compared to two-step reforming.

Two-step reforming reduces the specific oxygen consumption by approximately 25%. In addition, the inlet temperature to the secondary reformer is higher than in ATR. This saves oxygen for heating up the feed gas. However, the required specific transferred duty (and thereby heat transfer area) for preheating the feed including heat for the endothermic methane conversion reaction in the primary reformer is almost three times larger in the two-step case than in the ATR-case. About half of this duty relates to the tubular reformer.

Two-step reforming imposes a larger pressure drop over the synthesis gas generation section than ATR. Therefore, the synthesis gas enters the MU gas compressor at a lower pressure. Also, the slightly higher conversion of methane in the two-step case increases the gas flow to the compressor. Even with credit for the higher loop carbon efficiency the two-step reforming imposes about 18% more compression work and larger gas volumes handled by the synthesis gas compressor.

Mainly due to the low S/C ratio, the synthesis gas in the ATR-based case has a high CO/CO₂ ratio and is lean in hydrogen. This makes the gas more reactive for MeOH synthesis and requires less recycling in the loop than with two-step reforming. The high loop carbon efficiency (95%) in the two-step reforming case requires a relatively high recycle ratio. However, decreasing the loop efficiency would further reduce the single line capacity, and is not seen as an attractive choice. The factors listed above have significant impact on the equipment size in the loop. For the recycle compressor the power (or size) increases by about 70% for the two-step case compared to the ATR case. Likewise, the size of other equipment in the loop (reactors, feed/effluent heat exchanger, piping, etc.) increases considerably with the two-step synthesis gas generation system.

The carbon efficiency is higher for the two-step reforming scheme. The carbon conversion in a loop fed by ATR is limited due to the lack of hydrogen in the sub-stoichiometric MU gas. However, the hydrogen efficiency is much higher in a synthesis loop after the ATR. This is mainly explained by the higher content of CO₂ in the synthesis gas produced by two-step reforming. The CO₂ reacts with hydrogen to produce water in the synthesis loop by the reverse shift reaction [3]. The net result is a lower hydrogen loop efficiency and a higher water content in the final product for the two-step reforming scheme.

The above considerations on equipment sizes are reflected in the investment cost indexes listed in Table 2.

Synthesis gas technology	ATR	Two-step
Capacity, MTPD MeOH	10,000	2 × 5,000
Investment cost index	100	118

Table 2: Investment cost index for 10,000 MTPD fuel grade MeOH plants

For medium plant capacities the cost advantage relating to the ATR technology is reduced and plants based on two-step reforming may be favoured. This is mainly due to high initial costs for establishing oxygen plants.

In analogy with the discussions above, the S/C ratio is a key parameter with respect to maximizing the single line capacity for an ATR-based methanol plant. Figure 6 (full line) shows how the maximum capacity decreases with increasing S/C ratio. In spite of a slightly higher (~1.5%) process C-efficiency with e.g. S/C=1.3 only about 88% of the capacity using S/C=0.6 is obtained.

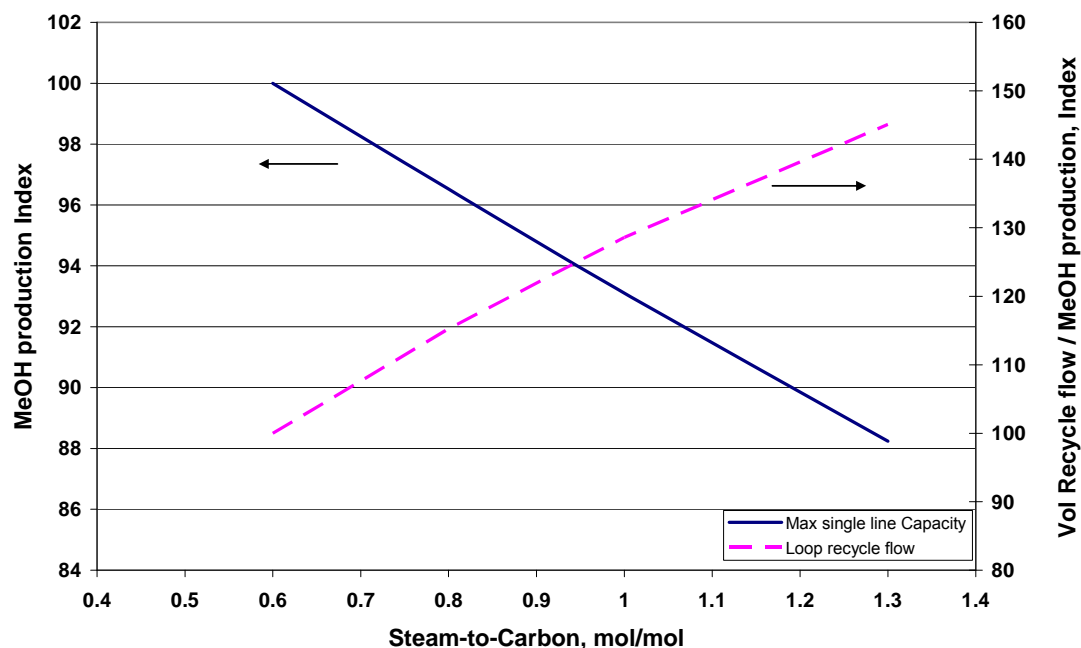


Figure 6: The influence of S/C ratio on single line MeOH capacity and synthesis loop size for ATR-based plants.

Figure 6 also indicates (broken line) how the methanol synthesis loop increases in size at increased S/C ratio. The more reactive synthesis gas with high CO/CO₂ ratio requires less recycling and therefore a smaller loop. Decreasing S/C from 1.3 to 0.6 reduces the loop flow per unit produced MeOH by about 45% point.

In summary; higher MeOH production is obtained with fixed equipment sizes at low S/C ratio. Therefore, the specific investment (EUR/ton MeOH capacity) is lower with low S/C ratio. This is in line with previous findings [6].

In this study the module is adjusted to 2.05 by recycling hydrogen recovered from the purge gas by a membrane. If the module were adjusted by removing CO₂ from the synthesis gas, the maximum single line capacity would be reduced by 3-5%. The loop C-efficiency would increase, because removing CO₂ will result in a stoichiometric gas being fed to the loop. However, the plant carbon efficiency will decrease due to the removed carbon. Still, it may in some cases be preferred to adjust the module by CO₂ removal. The optimal module adjustment must be considered on a case-to-case basis.

Further Developments

ATR at low S/C-ratio is the preferred technology for large scale methanol production at low cost as illustrated above. Several plants for production of synthesis gas for various applications operate today at S/C=0.6. Further reduction to S/C=0.4 would increase the single line capacity. Data for 10,000 MTPD methanol plants at S/C=0.4 and S/C=0.6 are compared in Table 3. This illustrates a higher single line capacity and a reduction of cost for the case with S/C = 0.4.

S/C-ratio	0.6	0.4
Single line capacity index	100	104
Capital cost index	100	96

Table 3: Single line capacity and investment for 10,000 MTPD methanol plant at S/C=0.6 and S/C=0.4.

The introduction of heat exchange reforming (HTER) either upstream (HTER-s) or in parallel with the ATR (HTER-p) has the potential to further reduce the costs. In both cases, the methanol module increases and the specific oxygen consumption is reduced. In the series scheme, all the feed gas passes through the HTER-s and the ATR. This results in a high feed conversion even at a low S/C ratio. In the parallel scheme, part of the feed gas is routed to the heat exchange reformer as illustrated in Figure 7. The required heat for the endothermic reaction is provided by the combined stream of the ATR effluent and the stream leaving the catalyst bed of the HTER-p. This scheme has a higher single line capacity than stand alone ATR and the series scheme. However, a higher S/C ratio in the HTER-p is required than in the ATR to obtain the same feed conversion. The effect of using an HTER-p and ATR is indicated in Table 4.

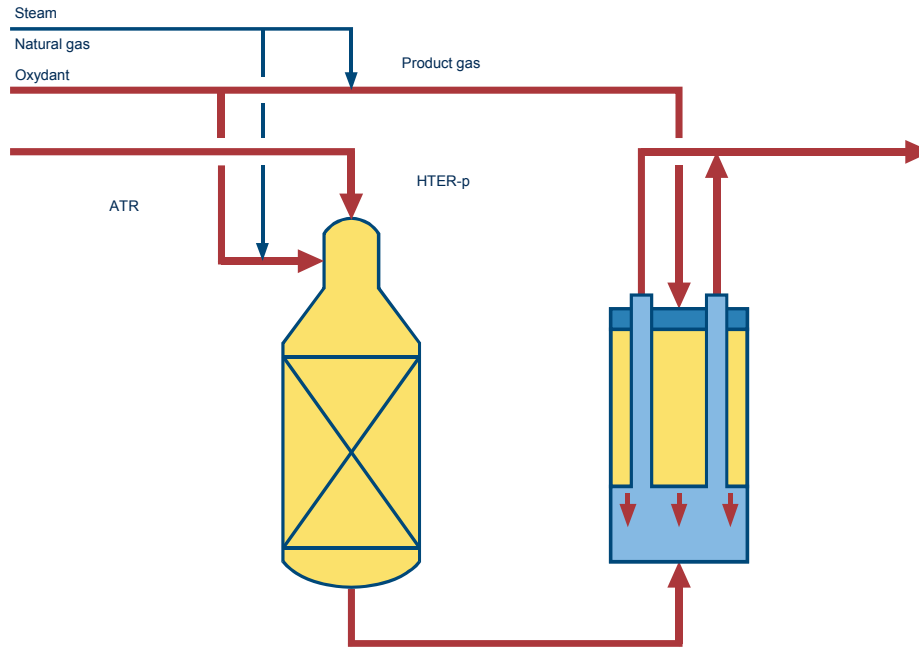


Figure 7: Production of synthesis gas by ATR and HTER-p

Process	ATR	ATR and HTER-p
Fraction of feed to HTER-p (%)	0	16
Module M	1.85	2.00
Oxygen consumption (index)	100	86

Table 4: Effect of using parallel heat exchange reforming (HTER-p) in production of synthesis gas for methanol [10].

The HTER-p may be used both in a grassroot design or as a capacity booster in a revamp of an existing plant. An example of the latter is the ATR/HTER-p reactors that have been in operation since early 2003 in Secunda, South Africa [11]. The introduction of the HTER-p increased the capacity in this unit by more than 30% along with a reduction of the oxygen consumption per unit of synthesis gas produced by 20% [11].

Further development of the methanol synthesis technology has the potential for reducing the overall plant cost. A large part of the cost arises from the reactor itself and from the recycle loop including the reactor feed/effluent heat exchanger typically used. It has been demonstrated [12, 13] that a higher conversion can be obtained by adjusting the operating conditions to condense the methanol in the reactor itself. Methanol is removed from the gas phase allowing a higher conversion of the reactants according to reactions 1-3. The once-through conversion can be increased to above 90%, thus avoiding the need for reactant recycle. Process economic evaluations indicate that the condensing methanol technology may reduce the overall investment by 10% or more for a 10,000 MTPD fuel grade methanol plant [13].

Conclusions

It is expected that most of the methanol needed in an expanding world market will be produced from natural gas in the future. Several technologies are available for methanol production, and the optimal choice depends mainly on scale. For large scale plants Autothermal Reforming (ATR) at a steam-to-carbon (S/C) ratio of 0.6 combined with boiling water reactors optionally with an adiabatic top layer for the synthesis represents the superior choice for low investment. A case study has shown that a plant with this technology will have a higher single line capacity and a 15-20% lower cost compared to plants based on combinations of steam reforming and Autothermal (or secondary) Reforming. The ATR based plants at low S/C-ratio may be designed to produce either fuel grade or high purity methanol.

Further development of the synthesis gas and methanol synthesis technology can further improve economics. The reduction of the S/C-ratio and the introduction of a parallel heat exchange reformer both increase the single line capacity. Both options and the use of a heat exchange reformer upstream and in series with the ATR may result in considerable cost savings. In the synthesis loop cost savings can be obtained by operating the reactor below the methanol dew point. This removes methanol from the gas phase and allows a higher reactant conversion. The result is a once through process with substantial cost reductions.

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