

Methanol Production

Feedstock:

Natural Gas

1- Methanol Basic Properties and Applications

Methanol is an alcoholic chemical compound that is considered to be the simplest alcohol. It is a light, colorless, flammable liquid at room temperature, and contains less carbon and more hydrogen than any other liquid fuel. The chemical formula for methanol is CH_3OH (often abbreviated as MeOH). Methanol appears naturally in the environment, and quickly breaks down in both aerobic and anaerobic conditions. Methanol is often called *wood alcohol* because it was once produced chiefly as a byproduct of the destructive distillation of wood. Today, the most common feedstocks for its production are natural gas and coal. This simple alcohol can be made from virtually anything that is, or ever was, a plant. This includes common fossil fuels – like natural gas and coal – and renewable resources like biomass, landfill gas, and even power plant emissions and CO_2 from the atmosphere [1].

To produce methanol, synthesis gas needs to be created from the feedstock first. Through gasification, synthesis gas can be produced from anything that is or ever was a plant, which includes biomass, agricultural and timber waste, solid municipal waste, recycled carbon dioxide and a number of other feedstocks in addition to natural gas and coal. In a typical facility, methanol production is carried out in two steps. The first step is to convert the feedstock into a synthesis gas consisting of CO , CO_2 , H_2O and H_2 . This is usually accomplished by the catalytic reforming of feed such as SMR^1 , POX^2 , ATR^3 and Combined Reforming. The second step is the catalytic synthesis of methanol from the synthesis gas [1].

Since the 1800s, methanol has been widely used as an industrial chemical compound to produce a variety of traditional chemical derivatives, including formaldehyde, acetic acid, dimethyl terephthalate, methyl methacrylate, and methyl chloride to manufacture a wide range of end products. With its diversity of feedstocks and array of applications, methanol is one of the world's most widely used industrial chemical. Currently, approximately 60% of the global demand for methanol comes from the industrial chemical market demand and 40% comes from fuels applications demand [1].

¹ Steam methane reforming

² Partial oxidation

³ Autothermal reforming

The major methanol end-uses in fuels applications include (Figure 1) [2]:

- 1) *Gasoline Blendstock*: In some countries, methanol is blended directly with gasoline. Methanol has attractive properties as a fuel blending component; it has a high octane number, combusts efficiently, emits fewer harmful by-products than gasoline, and is relatively low-cost.
- 2) *Dimethyl Ether (DME)*: DME can be used to blend into LPG⁴, as a replacement for LPG fuel in heating and cooking applications, as a transportation fuel in modified diesel engines, and for power generation.
- 3) *Methyl Tert-Butyl Ether (MTBE)*: MTBE (an oxygenate) is added to gasoline to increase its octane number. Use of MTBE in a gasoline blend also allows for a cleaner combustion process, emitting less pollution.
- 4) *Biodiesel*: Biodiesel is the product obtained when vegetable oil or animal fat is chemically reacted with an alcohol - methanol, for example - to produce a compound known as a fatty acid alkyl ester. When methanol is used, the product is fatty acid methyl ester (FAME).
- 5) *Methanol-to-Gasoline (MTG)*: MTG refers to the process of making gasoline via a methanol route. In some ways, MTG is a misnomer, because methanol is often an intermediate in the process, and units are back-integrated to coal or natural gas. Some MTG units in China may run on merchant methanol.
- 6) *Others*: Methanol can also be used as a fuel in power generation plants and in methanol fuel cells.

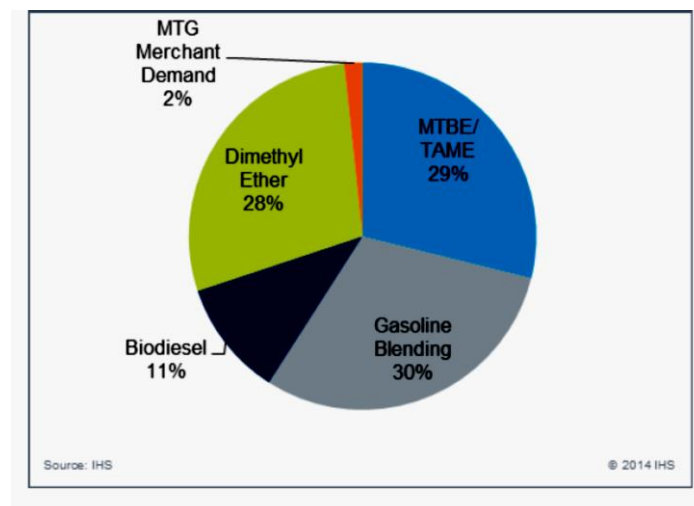


Figure 1: Global Methanol Fuel Demand [2].

⁴ Liquid petroleum gas

2- Production Processes

Today, methanol is manufactured using a proven technology based predominantly on natural gas, with a small portion of the world capacity being based on petroleum fractions and process off-gases. The basic concept (Figure 2), when using natural gas as the feedstock, comprises the following process steps [3]:

- 1) desulphurization of natural gas
- 2) synthesis gas generation
- 3) synthesis gas compression
- 4) methanol synthesis
- 5) methanol distillation

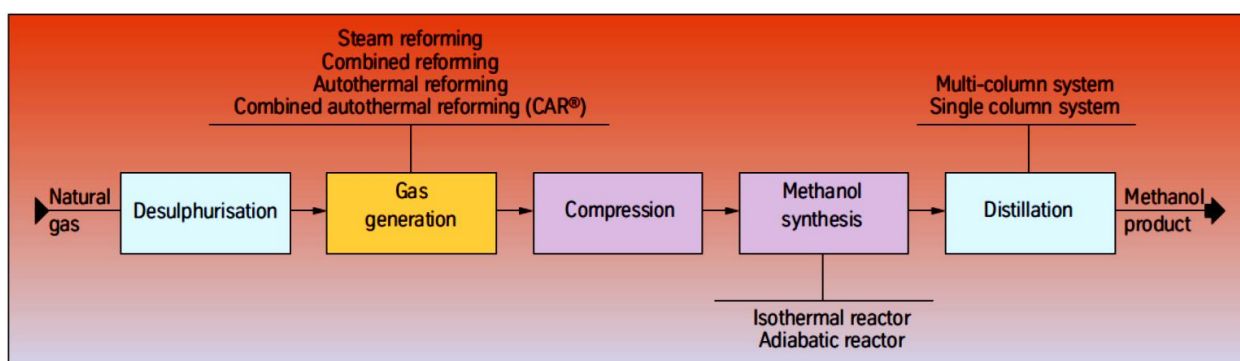
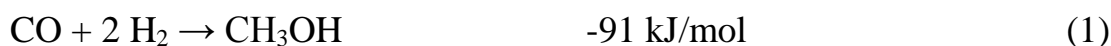


Figure 2: Basic steps of methanol production [3].

Figure 2 shows the various options available for the individual process steps. The option selected as the most suitable and, consequently, the plant configuration depends on the customer's requirements and local conditions. In addition, high pressure steam (HPS) and medium pressure steam (MPS) are usually produced by cooling the high temperature synthesis gas and methanol synthesis reactor, respectively [3].

The main reactions for methanol production are:



Therefore, the following ratio is ideal for methanol production [4]:

$$(\text{H}_2 - \text{CO}_2) / (\text{CO} + \text{CO}_2) = 2 \quad (3)$$

The synthesis of carbon oxides to methanol is based on a CuO/ZnO based catalysts, e.g. Syntex catalysts. This catalyst type has proved its performance in adiabatic as well as in isothermal reactors. The conversion of carbon oxides to methanol is an exothermic process which takes place at high pressures and low temperatures. The synthesis unit operates at 40 - 110 bar and around 200 to 300 °C. The aim is to achieve a relatively high carbon efficiency so as to minimize the amount of synthesis gas to be processed [3].

$$\text{Carbon eff.} = [\text{moles methanol produced} / \text{moles (CO + CO}_2\text{) in syngas}] \times 100\% \quad (4)$$

Many different Methanol production technologies are offered by licensors (Lurgi, Haldor Topsoe, Davy, Uhde) [5]. In the following sections, these technologies are described briefly.

2-1- Methanol production based on one step reforming

Steam methane reforming

A majority of the methanol plants operating today are based on steam reforming of natural gas, as shown in Figure 3. This technology is attractive at capacities greater than 2500-3000 mtpd methanol and the main licensor is Haldor Topsøe [5].

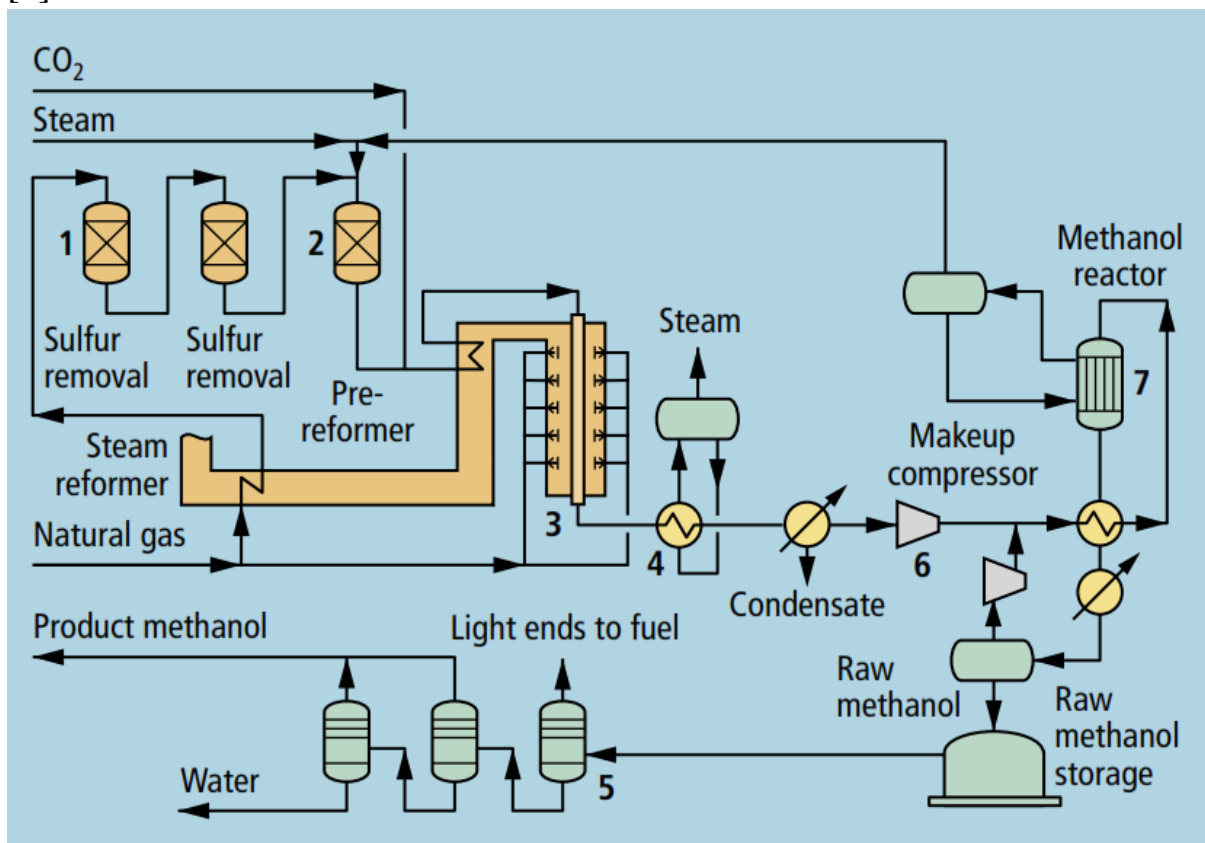


Figure 3: Methanol production based on steam reforming of natural gas [5].

The SMR reactions are:



These equations show that there is an excess of hydrogen, i.e. more hydrogen is obtained than is required to convert the carbon oxides to methanol.

One of the options is the addition of CO_2 to match the excess hydrogen. This obviously reduces the feed and fuel requirement per ton of methanol.

CO_2 can be admitted to the reformer with feed and steam, thereby increasing the CO to CO_2 ratio in the syngas, which in turn increases the carbon efficiency in the synthesis process. Alternatively it can be admitted directly into the methanol loop [3].

The total energy consumption for this process scheme per metric ton of grade AA methanol is about 32.4 GJ without CO_2 addition and about 29.5 GJ with CO_2 addition [3].

Autothermal reforming

Another technology with one step reforming, autothermal reforming (ATR), is shown in Figure 4. This technology is well suited for very large-scale plants as well as for the production of methanol to olefins or fuel-grade methanol and the main licensor is Haldor Topsøe [5].

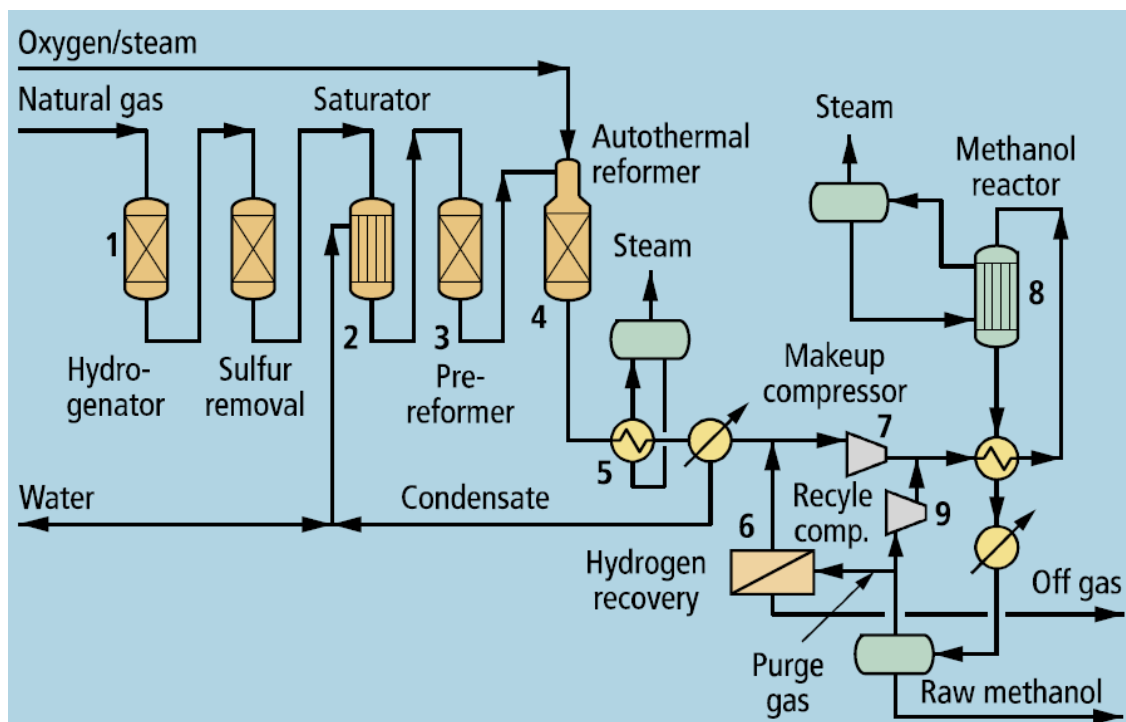


Figure 4: Methanol production based on ATR of natural gas [5].

Another difference between SMR and ATR technologies is that the technology based on ATR has deficient of hydrogen. Therefore a hydrogen recovery unit is added to the purge gas.

For large-scale plants, the total investment, including an oxygen plant, is approximately 10% lower than a conventional plant based on tubular steam reforming [5].

2-2- Methanol production based on two step reforming

The overall configuration of this technology which contain SMR as primary reformer and ATR as secondary reformer is shown in Figure 5. The main licensior of this technology is Haldor Topsøse [5].

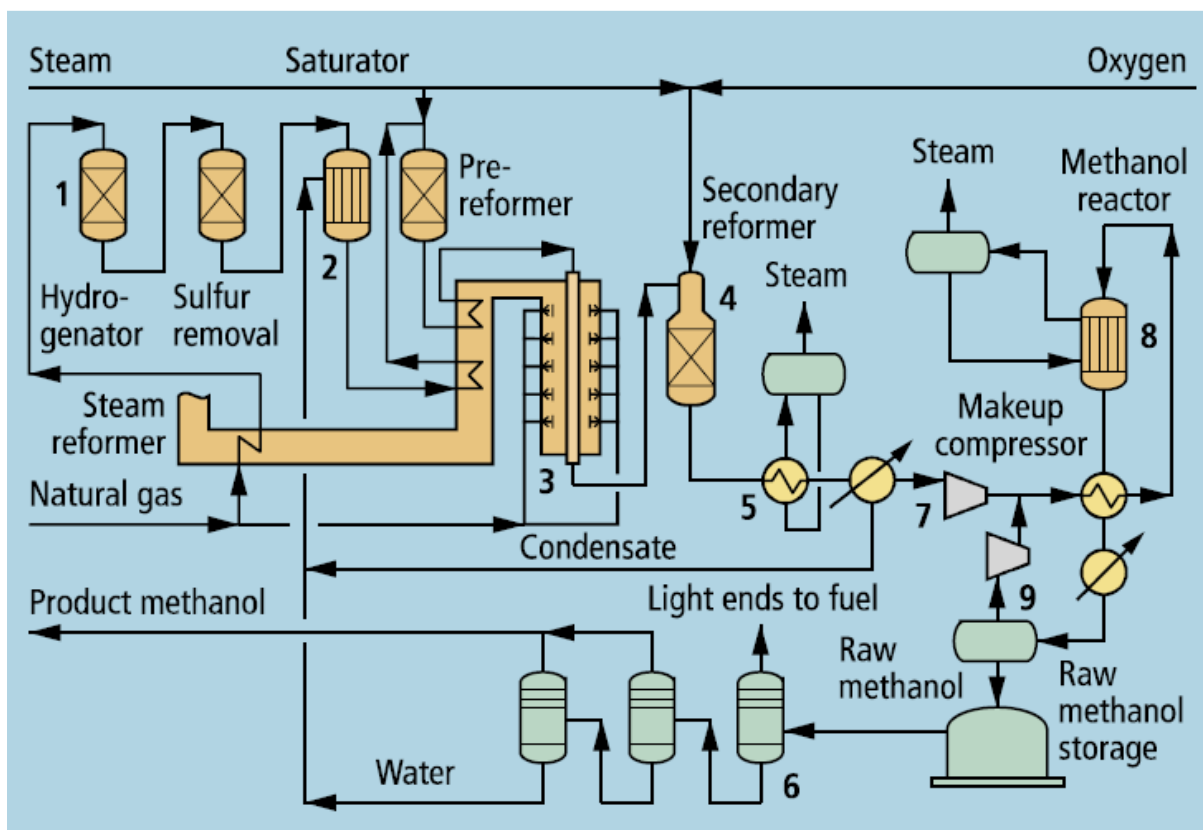


Figure 5: Methanol production based on two step reforming of natural gas [5].

This technology can be used for large and small-scale plants and offers a number of advantages compared to conventional steam reforming [3]:

- The CO, CO₂ and H₂ produced are in a stoichiometric ratio, thus minimizing feed consumption.

- The syngas generation pressure is higher (about 40 bar), thereby reducing the energy requirement for make-up gas compression (single stage compressor).
 - In spite of the higher pressure, the methane slip remains at a permissibly low level.
 - The steam reformer load is substantially reduced (down to 70%).
- Consequently, a smaller reformer and less fuel are required. This, in turn, reduces the required size of the related equipment in the flue gas duct area.

2-3- Methanol synthesis loop [3]

Synthesis loop for isothermal and adiabatic operations are shown in Figures 6 and 7, respectively.

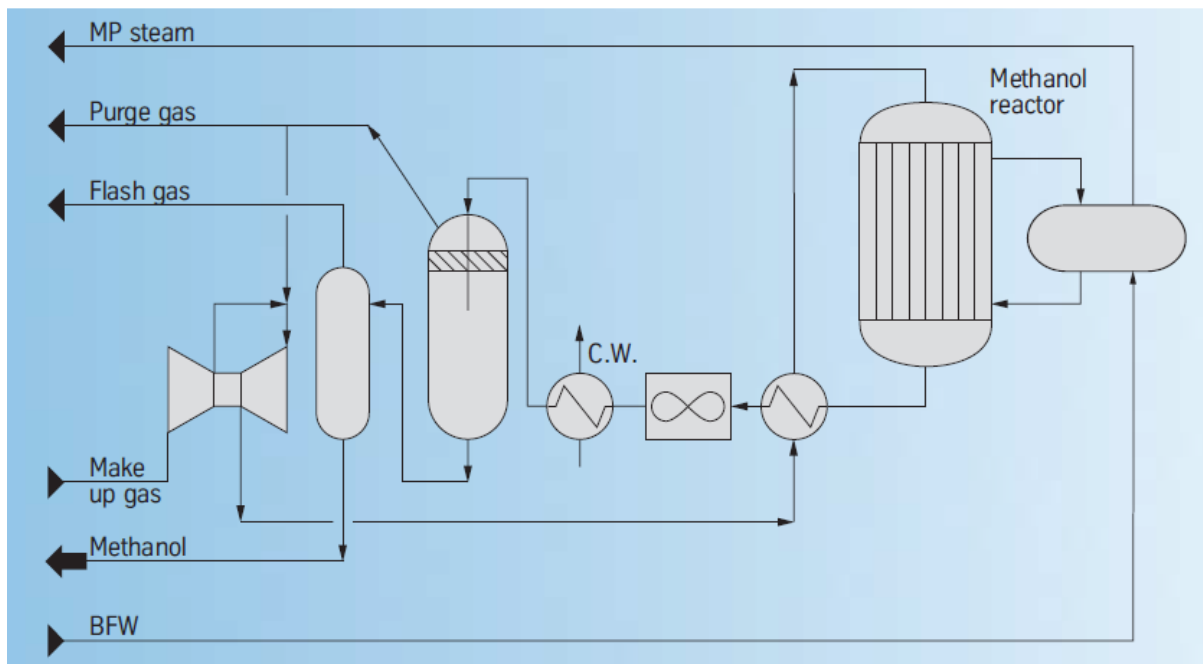


Figure 6: Methanol synthesis loop – isothermal reactor [3].

Vendors offer different reactor types (Figure 8). The isothermal reactor is the most efficient system, as the heat of reaction is directly utilized at reaction temperature level to generate medium-pressure steam. It should be mentioned, however, that the ARC (Axial Radial Concept) multi-bed quench is a low-cost reactor (Figure 8). It is normally used for plants which require no steam in synthesis units, due to the fact that surplus steam is produced during syngas generation (for instance steam reforming).

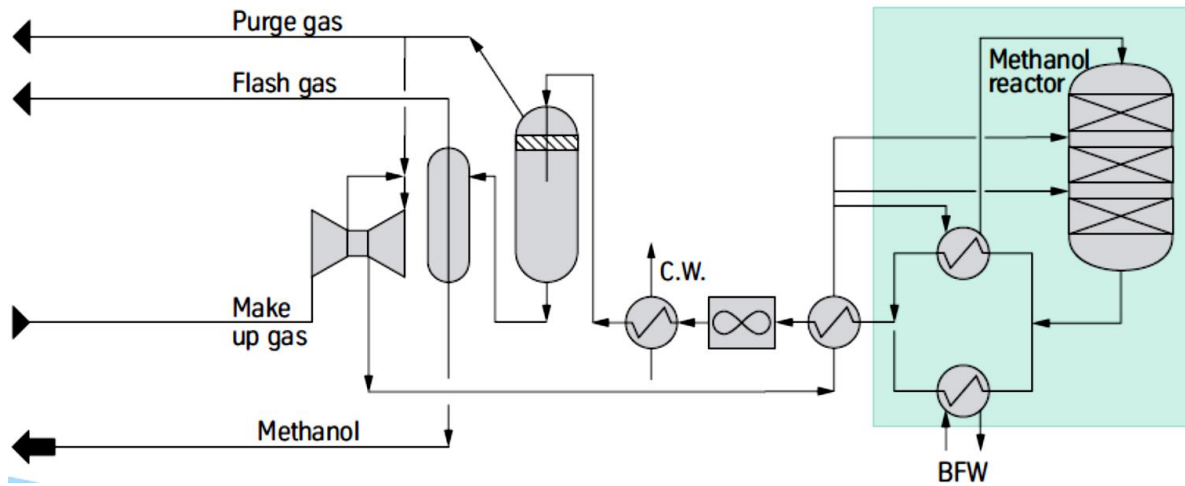


Figure 7: Methanol synthesis loop – adiabatic reactor [3].

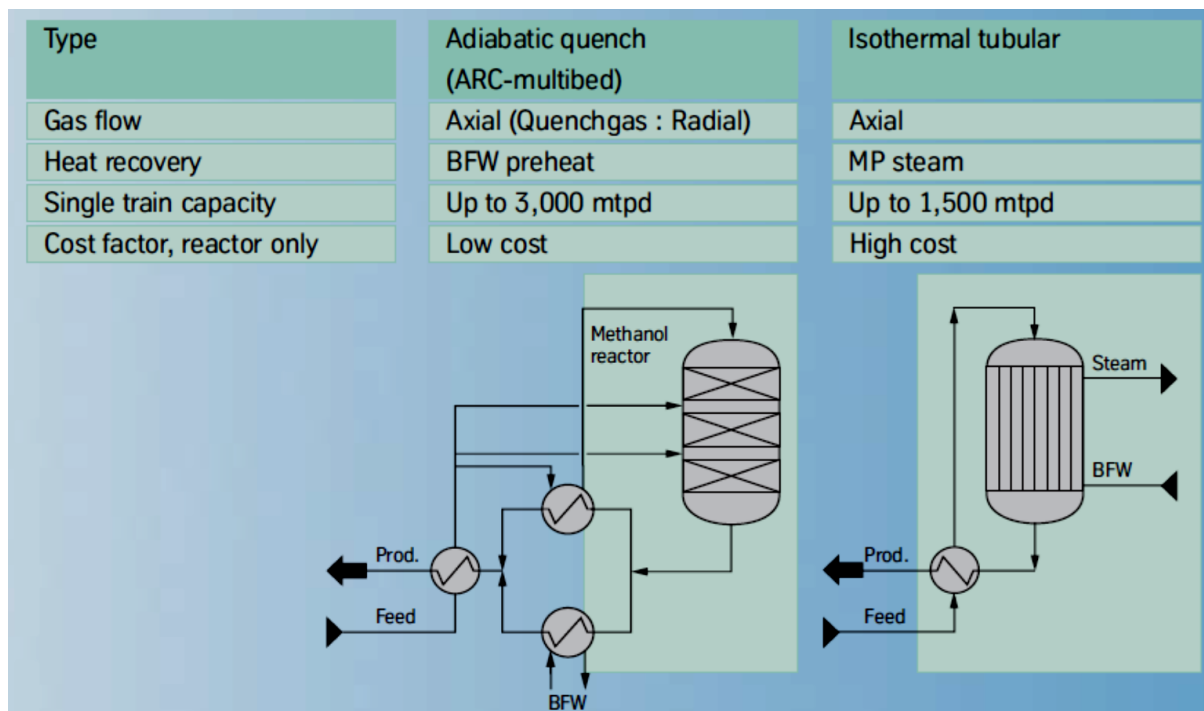


Figure 8: Methanol synthesis loop – different reactor types [3].

2-4- Methanol distillation [3]

The concepts presented here relate to the production of

- Grade AA methanol (typical chemical grade) and
- Fuel-grade methanol (blending component for gasoline).

The different qualities required are shown in Table 1. Components in the raw methanol are shown in Figure 9.

Table 1: Fuel and AA grade methanol [3].

	Grade AA	Fuel-grade
Dissolved gases	none	none
Acetone and aldehyde	max. 30 wt-ppm	not specified
Acetone	max. 10 wt-ppm	not specified
Ethanol	max. 10 wt-ppm	not limited
Higher alcohols	none	not limited
Hydrocarbons	clear product	not limited
Water	max. 1,000 wt-ppm	max. 500 ppm

The design of the methanol distillation unit primarily depends on the energy situation in the front end. The two-column distillation unit represents the low-cost unit and the three column distillation unit is the low-energy system.

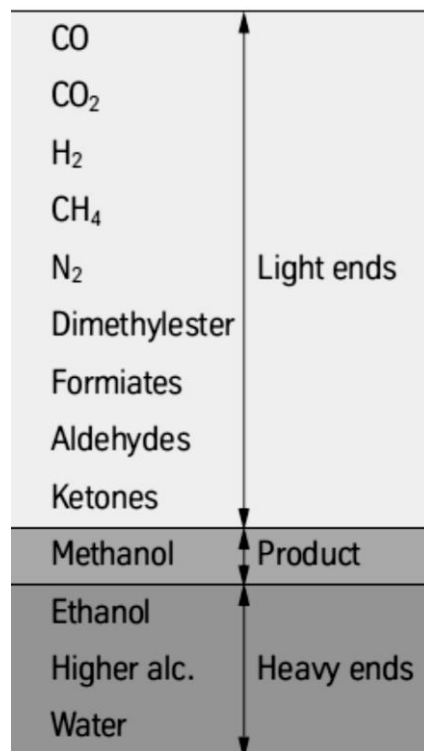


Figure 9: Components in raw methanol [3].

Grade AA methanol

The two-column distillation unit consists of a topping and a refining section. The light ends are removed in the topping column. The stabilized raw methanol, consisting of methanol, water and minor amounts of higher alcohols, is fractionated in the refining section to produce grade AA methanol.

The three-column distillation unit consists of a topping column and two refining columns (Figure 10). Refining column II operates at normal pressure. Refining column I operates at a higher pressure, thus utilizing the condensation duty of this column as the reboiler duty of refining column II. This substantially reduces the LP steam consumption of the distillation section.

The four-column design includes the three columns described above as well as an additional recovery column. The fusel oil purge from refining column II is processed in the recovery column to minimize methanol losses even further.

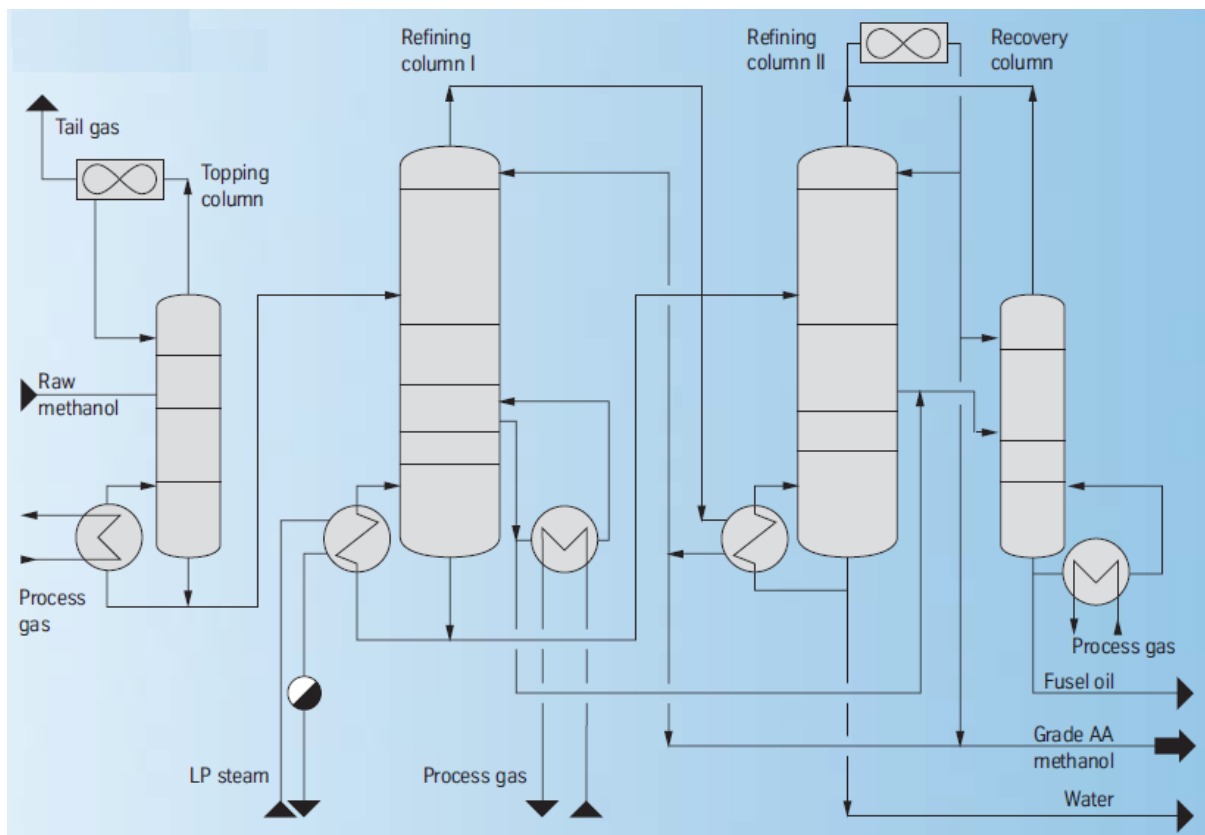


Figure 10: Three and four column distillation [3].

Typical yield and steam consumption data for the various designs are shown in Table 2.

Table 2: Yield and steam consumption for various design [3].

	Methanol yield (%)	LP steam consumed (t/t of methanol)
2-column design	98.5	1.2
3-column design	99.0	0.47
4-column design	99.5	0.45

The distillation design will depend primarily on the plant capacity, the heat available in the process plant and the energy export requirements. For instance, the four-column distillation unit is economically justified only at large capacities such as 5000 mtpd of methanol, whereas the choice of a two- or three-column distillation unit very much depends on the customer's requirements.

Fuel-grade methanol

For fuel-grade methanol as a blending component (for gasoline), a single column distillation with side-stream product can be used (Figure 11). Fuel-grade methanol should be free of dissolved gases and preferably should not contain more than 500 wt-ppm of water. The limitation of the water content is on account of its immiscibility with gasoline.

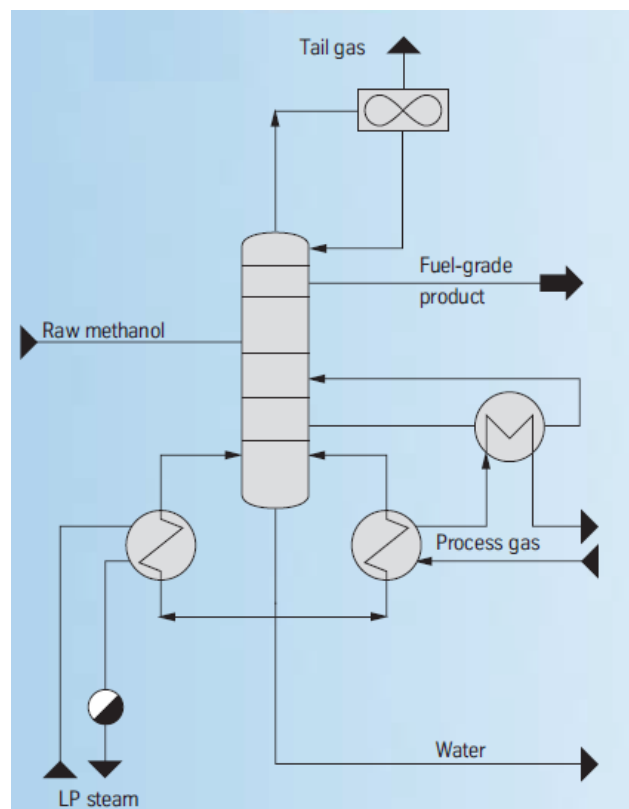


Figure 11: Fuel-grade distillation column [3].

3- References

- [1] Huang, P., Ju, H., Tan, S., Wang, H., and Zhao, T., The Future of Methanol Fuel, *Project Report*, 2015.
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