Methanol Plant Process Description

The Uhde low-pressure synthesis loop consists of a recycle compressor, feed/effluent exchanger, methanol reactor, final cooler, and crude methanol separator. The crude methanol, which is condensed downstream of the methanol reactor, is separated from unreacted gas in the separator and routed via an expansion drum to the crude methanol distillation. Water and minor quantities of by-products formed in the synthesis are removed by an energy saving Uhde-designed three-column distillation system.

Typical consumption figures (feed plus fuel) range from 29 to 33 GJ per metric ton of methanol produced. Waste heat from the syngas unit that fed this facility was being used in the Methanol Plant. Additional steam for heating will need to be made available if the plant is not linked to a syngas unit as before.

Uhde claims that the simple addition of a pre-reactor will increase this unit’s capacity by 20%.

**Input:**
- 50,000 m$^3$ Fresh synthesis gas
- 18 t/h Low-pressure steam
- 12 t/h 35 bar saturated steam
- 2,000 m$^3$/h Cooling water
- 4.5 MW Electricity

**Output:**
- 18,000 m$^3$/h Purge gas
- 14.5 t/h Pure methanol
Detailed Process Description

The plant consists of the following sections:

1. **Fresh gas compressor** that supplies the synthesis gas.
2. **Gas-cleaning section** with three catalyst bed reactors to remove impurities from the feed gas.
3. **Synthesis section** for the production of crude methanol.
4. **Distillation section** for the production of grade AA methanol.

**1. Synthesis Gas Compression:**
The fresh gas compressor boosts the synthesis gas from 20 bar to about 43 bar with the discharge temperature kept less than 130°C. The fresh gas compressor and the recirculation compressor are driven by a common electric motor. The fresh gas compressor has a suction throttle valve feature that adjusts over a wide flow range with a constant outlet pressure so that large pressure fluctuations are minimal.

The compressor is a 1995 Babcock-Borsig model JHXA-710LB-42. This centrifugal compressor operates with make-up gas (MUG) on one side and recycle (REC) gas on the other side. It compresses 50,000 Nm³/hr of make-up gas from 19 bar at 44°C to 44 bar at 117°C. It compresses 285,000 Nm³/hr of recycle gas from 37 bar at 37°C to 42 bar at 49°C. It has a 4,000 kW drive motor.
2. **Gas Cleaning Section:**

The first cleaning stage consists of the activated carbon reactor, which has a fixed bed with 5 m$^3$ of activated carbon and 19 m$^3$ of Al$_2$O catalyst type R 10/20. The activated carbon decomposes any carbonyls present in the gas, and the aluminum oxide absorbs the resulting compounds. The first reactor operates at 20 bar and 20°C and is constructed of carbon steel.

![Activated Carbon Reactor](image)

Prior to entering the second purification step, the gas is heated in a gas/gas exchanger to 125 - 150°C, depending on the catalyst activity. In the second cleaning stage, the deoxo reactor uses BASF Puristar palladium-based catalyst type RO-20/47 (catalyst has been removed and reclaimed). The palladium hydrogenates any oxygen, unsaturated hydrocarbons, and methylene chloride that might be present in the feed gas. The second reactor operates at 45 bar and 160°C and is constructed of carbon steel with a stainless steel liner.

The outlet of the DeOxo Reactor is cooled in a gas/gas exchanger to 115 - 125°C, depending on the catalyst activity. The third purification step takes place in the guard bed reactor, which utilizes a zinc oxide-based catalyst on top of 22 m$^3$ of a BASF Puristar copper-based catalyst type R3-15. This reactor removes the resulting products from the second purification step (hydrogenation of any oxygen, unsaturated hydrocarbons, and methylene chloride) and prevents any break-through of impurities from the second reactor. The third reactor operates at 45 bar and 210°C and is constructed of carbon steel.

A “slop system” is available for draining equipment in the distillation section due to maintenance or other reasons. This material is eventually re-worked through the plant as capacity is available.
3. Methanol Synthesis:

The gas leaving the deoxo reactor is combined with the recycle gas and heated to 235°C by cross-exchange with the hot gases exiting the methanol reactor. The heated feed gas then enters the tube side of the methanol reactor, which is a shell and tube exchanger. The tubes are packed with a copper-based BASF catalyst type S 3-86. The temperature in the catalyst tubes is monitored at the top and bottom by 12 thermocouples. The tube side operates at 45 bar and 250°C. The methanol reactor is constructed similar to a shell and tube exchanger with stainless steel tubes and a carbon steel shell. The reactor is 4 m in diameter by 12.5 m tall.

The exothermic reaction proceeds as follows:

\[ \text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \quad (-90.8 \text{ kJ/mol}) \]

\[ \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (-49.2 \text{ kJ/mol}) \]

Possible side reactions result the formation of dimethyl ethers, methyl formate, ethanol, isobutanol, etc. The proportion of these side reaction byproducts is related to the ratio of CO\(_2\) to CO in the feed gas, the feed gas purity, and the catalyst age.

This isothermal reactor design is the most efficient type. The advantages of this reactor are low by-product formation due to almost isothermal reaction conditions, high reaction heat recovery, and easy temperature control by regulating steam pressure. The methanol reaction heat is removed by partial evaporation of the boiler feed water, thus generating 1 metric ton of high-pressure steam per 1.4 metric tons of methanol. Boiler feed water is pumped to the shell side, where it is heated and fed to the steam separator. The resulting steam pressure can be controlled from 36 – 43 bar.
The partially reacted synthesis gas leaving the reactor is now about 4% methanol by volume and is approximately 260°C. As mentioned earlier, this stream is cross-exchanged with the cooler gas feed to the reactor. The crude methanol is then condensed and separated in a vertical separator vessel running at 45 bar and 217°C. The separator is 1.7 m in diameter and 4.1 m tall. It is constructed of carbon steel with a stainless steel liner.

The product then proceeds to the crude methanol intermediate storage tank, which holds about 12 hours of product at full capacity or 250 m³. This carbon steel tank is kept under a nitrogen pad.

The gas stream leaving the top of the vertical separator proceeds to the suction side of the recirculation compressor where it is compressed and added to the fresh gas stream prior to entering the methanol reactor. The quality of fresh and recycle gas is analyzed in multiple locations by infrared analyzers looking for CO, CO₂, H₂, N₂, and CH₄.

A weak solution of sodium hydroxide (1-2%) is added to the crude methanol prior to distillation to neutralize any trace of acids which are formed as byproducts in the methanol synthesis reaction. About 20 kg/hr is added, which maintains the pH of the wastewater from Refining Column-2 at about 9 to 11.
This plant uses BASF catalysts but they are interchangeable with Johnson Matthey Catalysts (JMC) catalyst products. JMC has over 50 years of experience in manufacturing methanol synthesis catalysts, design of related processes, and operation of methanol plants. They have developed a special composition and crystal structure that make for the higher activity of its new methanol synthesis catalyst Katalco™ 51-8. This catalyst for methanol synthesis has a high activity, particularly at lower temperatures, with very low by-product formation.

4. Distillation:
Uhde has developed various concepts to match the energy requirements of the distillation section with energy available from the synthesis reaction section of the plant. The distillation section uses 5 bar steam for heating.

The conventional distillation unit consists of a topping and a refining section. The light compounds present in the raw methanol are removed in the topping column. These would be dissolved gases such as CO, CO₂, H₂, N₂, and CH₄ in addition to some aldehydes, ketones, and dimethyl ether. The raw methanol, which consists of methanol, water, and minor amounts of higher alcohols, is then fractionated in the refining section to produce grade AA methanol.