Methanol Synthesis from Syngas

Methanol synthesis has played a crucial role in the search for an alternative liquid fuel and in reusing carbon dioxide which enhances the carbon neutrality political strategies. Methanol also served as an important chemical feedstock, extractant, and solvent for the chemical industry. In this project, synthesis gas (Syngas), a mixture of hydrogen (H2), carbon monoxide (CO), carbon dioxide (CO2), methane (CH4), etc., is used to produce methanol. Methanol synthesis itself has established numerous fields of research. The use of biomass to produce methanol is currently under a thorough investigation. Another aspect is Power-to-X technologies which convert both carbon dioxide and hydrogen to methanol. This technology is still currently being investigated, where carbon dioxide could be retained through direct air carbon capture (DAC) or available carbon storage and hydrogen through electrolysis. The scope of this project focuses on synthesizing methanol from syngas, improving energy integration within the process, and running a techno-economic analysis for feasibility and viability studies.

## Gas Compression

The process begins with compressing the synthesis gas to around 75 bar. This is done by multi-stage compression with intermediate cooling. Syngas is compressed from 29 bar to 75 bar. Multi-stage compression with intermediate cooling requires only 39.7 MWH of power, whereas compression without intermediate cooling requires 43 MWH of power. The multi-stage compression saves around 8% of the power. The only setback for multi-stage compression is the amount of cooling water needed to cool off the pressurized gas from the compressors. The heat produced through cooling can also be integrated into other operation units within the flowsheet where it is required. The pressure ratio for every compressor is around 1.3 which suits best for an axial compressor. Axial compressors have been known to be more effective than radial compressors for large-volume intake.

## Heat Exchanger

The pressurized gas is then mixed with the recycle stream and heated up to around 250 degrees Celsius. The mixed stream is heated through a counter-current heat exchanger. The hot stream required to heat the gas before being fed into the reactor came through the heat exchanger within the reactor itself. This heat integration saves around 23% of the required heat. Around 77% of the heat required should then be provided through external hot steams. This is done heuristically through sensitivity analysis which explores feasible heat transfer within the exchanger. The heat integration within the synthesis has room for improvement. The cold stream from the heat exchanger before the reactor is then used to cool off the stream behind the reactor before it enters the first flash. The heated cold stream is then used to heat off the stream before entering the second flash for off-gas removal. This stream which contains pure water is then cooled off to 20 degrees Celsius before it is then disposed to the water storage/ pond. The heat integration within the process is far from optimized. A further field of exploration includes improving the energy integration within the process through pinch analysis for a better conceptual heat integration or optimizing the integration through numerical optimization as an MINLP (mixed-integer nonlinear program) reformulation.

## Reactor and Separation Units

The reaction took place within a fixed-bed catalytic reactor. It comprises two main reactions: methanol synthesis from carbon dioxide (CO2) and hydrogen (H2) and reverse water gas shift reaction (RWGS). The kinetic model is based on Langmuir-Hinshelwood kinetics which enhances the gas-solid adsorption mechanism for the catalyzed reaction. Cu/ZnO/Al2O3 is a well-known commercial catalyst for methanol synthesis. The reactor is equipped with around 1200 tubes and a height of 15m with an integrated heat exchanger within the reactor. Water is used as a cooling fluid for this reaction. 120 tons/hour of water are used to maintain the reaction. The reaction within the reactor is highly exothermic. Excess heat produced could damage the catalyst if the reactor exceeds a certain temperature. This can be prevented through the counter-current flow of cooling fluid which maintains and control the temperature within the reactor. A yield of around 30% could be attained through the reaction with an integrated recycle stream.

Behind the reactors are two flashes. The first flash serves to separate the stream to be recycled. 94 % of the stream is being recycled back to the reactor. The second flash separates the remaining impurities to gain better purification at the end. The distillation column in this process does not require much heat duty because the dimethyl-ether (DME) synthesis does not require a methanol purity of 99.9%. The separation within the column should focus on reducing all the unused/inert gas to almost none. This results in a separation where the liquid phase is composed of 80% methanol and 20 % of water. This eases up the energy consumption within the whole process because separation processes are known to require a lot of heat either the reboiler- or the condenser duty to reach a higher purity.

## Integration of Off-Gas Flaming with combined heat and power plant (CHP)

Off-gas is removed through the purge stream, the second flash, and from the distillation column. The off-gas stream is heated to around 650 degrees Celsius before it is then flamed together within the combustion chamber/reactor with 1000 tons/hour of air intake, where the heat required is integrated through the cooling off of the cooling water. The flaming results in no trace of toxic gas such as methane (CH4), methanol (CH3OH), and carbon monoxide (CO) in the output stream. The combustion was modeled with an adiabatic reactor. The output temperature from the reactor reached around 1530 degrees Celsius. Excess energy through heat could be extracted from this output stream. The output stream should not be disposed directly to the environment, as this would cause big environmental issues to the surrounding ecology. Cooling the stream would require a huge amount of cooling fluids and thus increase the amount of utility cost at the end.

The idea is to integrate a Rankine cycle for combined heat and power plants (CHP). This would be a good idea for a cogeneration plant. Within the cycle, water will primarily be used to cool off the flamed output stream to around 85 degrees Celsius which is then disposed into the atmosphere. Through a recuperation unit, which consists of a heat exchanger, pressurized water is then heated up to 1124 degrees Celsius with a pressure of 170 bar. A Turbine is then modeled to replace a generator. The hot steam from the recuperation unit is then decompressed through the turbine to produce 257 MW (925 MWh). The decompressed steam needs to be cooled off through a heat exchanger to achieve the input stream conditions. A tremendous amount of heat is produced or required to cool off the stream. A fraction of heat is integrated into the heat exchanger in the dimethyl-ether (DME) process, and the excess heat would then serve to provide heat for district heating. This concept of the cogeneration process would then increase the efficiency of the Rankine by utilizing the heat and decreasing the amount of cooling fluid required to cool off the stream. Thermal energy storage could also be considered to store up the excess heat, which then could be used to generate electricity and provide heating utilities when needed.