Methane to Ethylene, the Holy Grail?

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Ethylene, the main building block of plastics, is currently produced via a steam cracking process that uses liquid fossil fuel products such as naphtha. Methane is an abundant hydrocarbon that can be used as an alternative raw material for the production of ethylene, especially since large quantities of shale-gas have been introduced in the market. This study uses Douglas' hierarchical design methodology, to make a feasibility study for an industrial production plant of 100 kta ethylene from methane at 99.9% purity. The aim of this study is to find the reaction pathway with the most potential, identifying the major bottlenecks for industrial application and to give specific recommendations for future research.

Methods for converting methane to ethylene directly require a pyrolysis reactor that works at highly elevated temperatures, which is not preferred in large scale operation. The focus of this study is on a two-step process where the intermediate chloromethane is utilized. The first reactor for producing chloromethane has several options in literature, while the second reactor has only one option for converting the chloromethane into ethylene. Two pathways for the first reactor are investigated, namely halogenation and oxychlorination, utilizing chlorine and hydrogen chloride respectively to form the intermediate chloromethane. Thereafter, a black box analysis was conducted resulting in several conceptual designs. The results were used to select the oxychlorination pathway, mainly due to the use of fewer unit operations, as the produced hydrogen chloride from the second reactor can directly be used in the first reactor, while the halogenation pathway needs to convert it to chlorine in a Deacon or electrolysis reactor first.

Chemistry

The first reactor has a conversion/selectivity challenge, see Figure 1. At higher conversion, the selectivity will move towards the combustion reaction of methane. For this study, a conversion of 10% is chosen with a selectivity of 80% towards chloromethane at 400°C and 2.5 bar in a multistage adiabatic reactor, while the second reactor works at 450°C and 40 bar in a pyrolysis reactor.

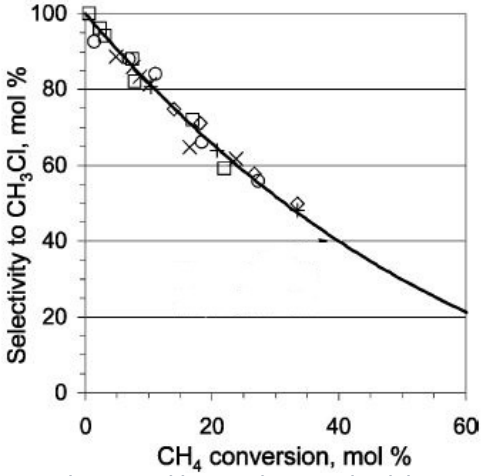

Figure 1:Chloromethane Selectivity as a function of methane conversion

Flowsheet

AspenPlus software is used to evaluate the process quantitatively for different set-ups. Figure 2 shows the final flowsheet. The main problems encountered are the large recycle stream after the first reactor giving high energy demands, the two absorber columns after the first and second reactor also giving high energy demands due to the large water streams and finally the distillation sequence before the second reactor which needs to separate dichloromethane and water, where an azeotrope is present.

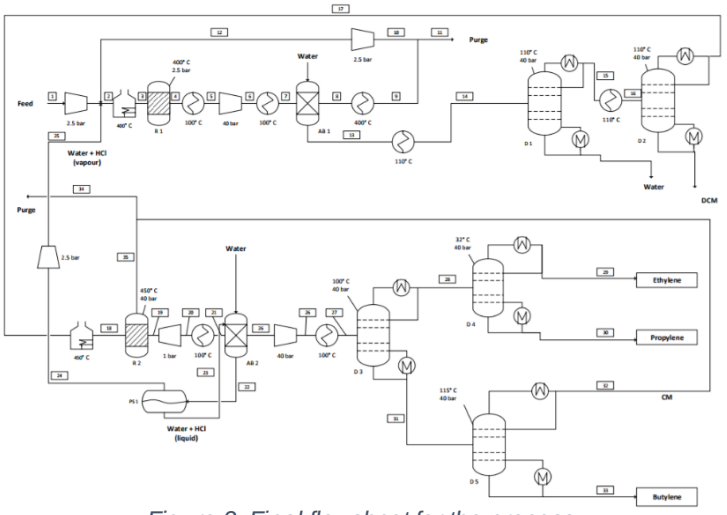

Figure 2: Final flowsheet for the process

Economic analysis

Also a first economical estimation has been made. This design results in a CAPEX of €375 million, an OPEX of €64 million, giving a break-even point of 7 years.

Recommendations & Conclusion

The process has high potential due to the high price of ethylene, while natural gas is relatively cheap. In the current state however, this process is not yet feasible. More research should be conducted towards the yield in the first reactor, the separation of the

chloromethane and the hydrogen chloride after the first and second reactor respectively and the possibility to convert dichloromethane to ethylene.