Abstract

The rising level of atmospheric CO_2 and its impact on our planet is driving a global call for collaborative actions to combat climate change. This PhD thesis was performed in this context and focused on the conversion of CO_2 captured from cement plants flue gases, in particular its catalytic hydrogenation into methanol.

The initial phase of this research introduces the low-carbon transition roadmap for cement technology. In this context, carbon capture and utilization technologies are summarized. To simulate the CO_2 conversion into methanol unit, an overview covering various catalysts, reaction mechanisms and kinetics, processes, reactor designs, and operating conditions, is provided.

In the experimental part, a home-made and shaped catalyst ($Cu/ZnO/ZrO_2$) is studied, highlighting the temperature's impact and the significance of the catalyst reduction step. The primary objective is to investigate the effects of scaling up by testing this shaped catalyst in a micro-pilot installation. The results are compared to those obtained using the powder form tested in smaller scale (micro-reactor). The same operating conditions in terms of temperature, pressure, and weight hourly space velocity are maintained. The comparison between large- and small-scale catalytic tests reveals a catalyst activity loss of up to 60%, attributed to the shaped catalyst explained by different reasons (e.g., the diffusional limitations and shaping effect).

The simulation of the conversion unit is carried out using the Graaf's model (developed on $Cu/ZnO/Al_2O_3$ catalyst) implemented in Aspen Plus software. The unit optimization is explored by minimizing its heat requirements. A two-section reactor design is adopted, with the first section being adiabatic for reactant preheating, and the second one being isothermal for enhanced CO_2 conversion and methanol selectivity. Distillation for methanol purification is also optimized to minimize the energy consumption of this step. The pinch analysis method is applied, and a heat exchanger network is designed, achieving complete internal heat integration within the conversion unit, bringing the energy demand to zero. An energy excess is allocated to the absorption-based capture unit, which treats 10% of a best available techniques cement plant flue gas, for solvent regeneration. This excess energy represents 5% of capture unit’s heat requirement.

Furthermore, a techno-economic assessment of the global CO_2 conversion process into methanol is conducted. The costs associated with this case are compared to the conversion of CO_2 into synthetic natural gas (SNG) route, revealing that the plant's cost is heavily influenced by the final product application. It was shown that while the CO_2-to-SNG route is cheaper than the methanol when considered as energy vector (€ per GJ), the CO_2-to-methanol one is more economical when it is considered as a chemical building block (€ per ton of product).

This study serves as a methodological framework for process simulation, optimization, and heat integration of the CO_2 to methanol process. It offers a comprehensive overview of the various steps involved, starting from selecting the kinetic model and optimizing the process, to conducting pinch analysis and designing the heat network for complete heat integration of the conversion unit. All these developments help to propose an environmentally friendly CO_2 to methanol process.