Conversion of industrial CO2 to value-added fuels and chemicals via Fischer-Tropsch upgrade

Summary

Different solutions can be implemented to reduce the impact of human activities on the environment and target the carbon transition towards a fossil-free society. Carbon capture and utilization (CCU) represents a way to reduce the concentration of CO_2 in the atmosphere, promote a circular economy production scheme, and avoid the extraction of fossil hydrocarbons. As such, mixing anthropogenic CO_2 with hydrogen obtained through electrolysis can generate synthetic carbon compounds that offset their fossil counterparts. In this framework, this doctoral dissertation explores the possibility of converting non-fossil carbon feedstocks (e.g., waste CO_2 and organic digestate) into marketable Fischer-Tropsch (FT) products. It combines Fischer-Tropsch (FT) kinetic model information with process modelling to derive techno-economic considerations on the most effective process route to produce Fischer-Tropsch waxes.

Chapter 1 presents the context and boundaries of this work, with reference to the concept of *circular economy* applied to carbon molecules/sources. An overview of the non-fossil carbon feedstock selected for this analysis, which are biogas, air, and digestate biomass, is provided. Concerning biogas and air, these can be regarded as flows having mildly concentrated CO_2 that can be captured and fed to downstream conversion processes. Digestate can be considered as a feedstock of carbon material coming from the process of anaerobic digestion. Finally, the market potential of Fischer-Tropsch waxes is covered.

Chapter 2 describes the FT technology. Different reactor designs and catalysts information are provided with reference to their *state-of-the-art.* Moreover, the chapter describes the activities carried out within this investigation on Fischer-Tropsch kinetic modeling. A Co-Pt/γ-Al_2O_3 catalyst was tested under several industrial-like conditions. Experimental data were collected using the online gas chromatography technique on the Fischer-Tropsch gas fraction and offline gas chromatography on the liquid and wax fractions. The experimental data were used to feed global and local optimization routines with non-linear least-squared fitting procedures to derive different kinetic models. The final kinetic model represented a detailed mechanistic one, capable of describing the FT product distribution of n-paraffins up to carbon number C_{80} and α-olefins up to carbon number C_{40}. Kinetic information was included in process modeling to find the most suitable plant designs to convert non-fossil compounds into Fischer-Tropsch liquids and waxes.

Chapter 3 and Chapter 4 provide the process modelling methodology and results, respectively. 11 process designs were investigated: 4 for the conversion of biogas, 2 for the conversion of digestate, and 5 for converting direct air CO_2. For biogas, the chemical scrubbing technology fed with MEA solvent was utilized for capturing CO_2. Moreover, the syngas required by the FT reactor was produced

inside a reverse water-gas shift reactor coupled with an alkaline electrolyser for green hydrogen generation or in a solid oxide electrolyser working at thermoneutral conditions. Both options operated at either ambient pressure or 25 bar. Additionally, digestate was gasified inside a dual fluidized bed reactor for syngas generation. Afterward, a solution utilizing the Fischer-Tropsch off-gas as fuel for electric generation was compared against recycling the off-gas into the gasifier for higher throughput of synthetic hydrocarbons. Lastly, CO_2 was extracted from the air with the direct air capture (DAC) technology operating at high temperature, coupled with H_2 production via alkaline electrolysers. Within this process route, it was assessed the substitution of fossil hydrocarbon with Fischer-Tropsch off-gas to sustain the capture process. Lastly, an electrified DAC option was investigated. All the process models were evaluated from both a technical and economic point of view. Key performance indicators were assessed to account for the system effectiveness in converting carbon material to FT compounds. Moreover, the cost of FT wax production was determined and compared. The outcomes of the techno-economic analysis show that using digestate as the carbon feedstock provides the least energy-intensive processes to generate FT material. From an economic point of view, biogas as carbon feedstock provides the most economically ready routes to generate FT waxes. On the contrary, using CO_2 from the air is the most expensive solution. Finally, the processes converting CO_2 from biogas and air present a higher variation of the wax production cost depending on the electricity cost than the routes utilizing digestate, given the presence of the electrolysers for H_2/syngas production.

Furthermore, the results of the techno-economic investigation of the biogas-to-FT and digestate-to-FT were engaged to account for the potential production of FT wax at the European level (Chapter 5). Specifically, it was assessed the potential outtake of carbon dioxide and digestate material coming from both biogas and biomethane plants currently operating in Europe. Biomethane plants are the ones with a *ready-to-use* stream of CO_2 derived from the installation of biogas upgrading units. Consequently, the amount of FT wax generated was evaluated. Lastly, it is possible to identify 17 plants with feasible market entry characteristics to produce the FT waxes throughout Europe.

Conclusions and outlooks of this investigation are provided in Chapter 6.