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Reactor and process modelling of CO2 hydrogenation reaction towards liquid and gaseous hydrocarbons production

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PURPOSE OF THE ABSTRACT

The raising efforts and objectives to mitigate global CO2 emissions[1] encourage to limit fossil resources use and thus result in a deployment of renewable energy production. Therefore, storage solution for the intermittent renewable power are increasing the interest in CO2 utilisation as feedstock for the synthesis of valuable products. This work focuses on one of these technologies aiming the direct synthesis of gaseous and liquid hydrocarbons (HCs) from a one step CO2 hydrogenation. The application of products are as wide as in the transport sector (e-fuels) and the petrochemical industry (CO2 neutral intermediates).[2]

Research in the field is mostly concentrated on the improvement of activity and selectivity of the reaction catalyst, while further investigation is needed about detailed kinetics, modelling of the reaction and global process design in order to evaluate the energy and environmental impact of such a process.[3]

In our work, CO2 hydrogenation process through a coupled Reverse Water Gas Shift (RWGS) and Fischer-Tropsch route is studied with the aim to develop detailed kinetics, model the reactor behaviour and estimate the global efficiency of the process.

A macro-kinetic model has been developed based on lab-scale tests of a 7K-10Fe/Al2O3 catalyst, synthetized by impregnation. They have been validated in an upscaled reactor within a wide range of operating conditions (T=250-350°C, Ptot=10-20 bar, H2/CO2 ratio=2-24, GHSV=500-3600 NmL/gcat/h).[4]

Based on this kinetic model, different reactor configurations (see figure 1) have been modelled and simulated (see figure 2). Finally, they have been integrated into a global process scheme using ProSim software in order to evaluate such a technology compared to a more conventional indirect approach which consists in performing RWGS and FT reactions in two successive units.

Both a ideal plug-flow and a 1D-heterogeneous reactor model, integrating the detailed macro-kinetic model able to describe the behaviour of the reaction in the range of operating values aforementioned, have been validated against experimental tests performed in a cooled fixed-bed reactor. The simulations of hydrogenation reaction on both models have shown slight differences showing that no limitations of heat and mass transfer occur in the reactor. Then, the simple plug-flow model was integrated the plug-flow model in an overall process simulation made by using ProSim software.

Then, the simulation of a direct CO2 hydrogenation process, with two reactors ? flash separation units, and a

recirculation of unreacted reactant after a membrane separation of flue gases. In this process configuration, a competitive energy efficiency of 66% was obtained while carbon utilization was maintained at 95%, which is a really high value in such processes.

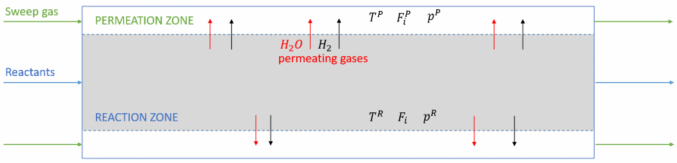
Anyway, in order to go further, a membrane reactor configuration was proposed (see figure 1) in order to :

- Limit the catalyst deactivation due to high water partial pressure
- Potentially increase the selectivity towards higher hydrocarbons which are easily separated and more valuable
- Increase CO2 conversion by displacing RWGS and FT equilibria

This higher performance reactor was able to increase the CO2 conversion rate up to 50% while the sweep gas was used for a direct cooling of the reaction.

Despite the lower maturity of direct CO2 hydrogenation towards hydrocarbons, promising results have been obtained by simulating the energy efficiency and carbon balance of the overall process. Moreover, the modelling of a membrane reactor showed that there are still ways to improve both durability and efficiency of such a process. Our next studies will be focused on the study of the impact of water on both reaction selectivity and catalyst lifetime, the experimental validation of the membrane reactor and its impact on the overall process performances.

FIGURES



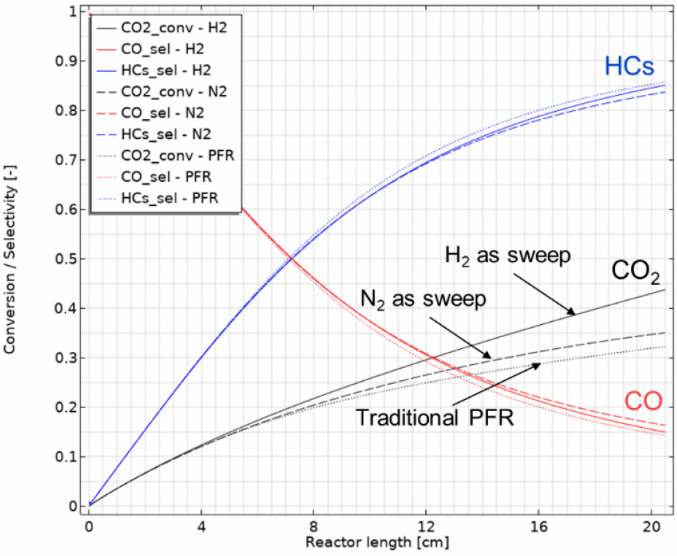


FIGURE 1

Figure 1

Configuration of the fixed-bed reactor with water removal via perm-selective membrane.

FIGURE 2

Figure 2

Evolution of CO2 conversion, CO selectivity and HCs selectivity along the reactor.

Simulations performed for a membrane reactor with H2 or N2 as sweep gas and for a traditional PFR without membrane.

KEYWORDS

Power-to-X | CO2 hydrogenation | Membrane reactor | Process simulation

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BIBLIOGRAPHY