

Direct hydrogenation of CO₂ into liquid hydrocarbons: kinetics and reactor design

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Significance and Relevance

This study aims to develop a new reactor technology for the direct CO_2 hydrogenation into sustainable aviation fuels. At first, a kinetic study is conducted by testing an iron-based catalyst under various conditions. The obtained " α " values are within the range of values generally obtained for traditional CO-FT processes. Then, the analysis of extensive experimental results has led to the development of a kinetic model, which is integrated in a reactor model. Based on these findings, a novel millistructured reactor design is proposed, with promising 3D simulation results.

Preferred and 2nd *choice for the topic:* CO₂ utilization and recycling, Sustainable and clean energy production and transport *Preferred presentation*: Oral preferred.

Introduction and Motivations

The direct hydrogenation of CO₂ to hydrocarbons (HC) via the Fischer-Tropsch (FT) process is a versatile method for producing various gaseous and liquid hydrocarbons. This approach combines the reverse water-gas shift (RWGS) reaction and FT synthesis in a single reactor, commonly using ironbased catalysts due to their dual activity. While advancements in catalyst development exist, reaction kinetics are often overlooked. Our group recently published data on a Fe-K/Al₂O₃ catalyst and developed a macro-kinetic model for producing linear alkanes, 1-alkenes and alcohols with up to 20 carbon atoms¹. This study seeks to test Fe-K supported catalyst, refine the kinetic model and examine reactor design impacts.

Materials and Methods

Our experimental work consists on testing a Fe-K supported iron catalyst in a fixed-bed tubular reactor (10.2 mm inner diameter, 210 mm total length) under different conditions in order to develop reaction kinetics model (using Matlab). Prior to each test, the catalyst undergoes in-situ reduction at 310°C for 24 hours under H_2/N_2 flow. Non-condensed gases and liquid products are analyzed using an online μ -GC system and an offline GC-MS system, respectively. The effects of several operating parameters are investigated: temperature (250 – 300°C), total pressure (10 – 20 bars), H_2/CO_2 ratio (3 – 12) and τ_{mod} defined as the catalyst mass divided by the total inlet gas volume flow (0.36 – 1.33 g·s·Nml⁻¹). Two- and three-dimensional (2D/3D) fixed-bed reactor models that incorporate the kinetic model of the FT-CO₂ reaction are developed using COMSOL Multiphysics.

Results and Discussion

For all the tests, the calculated total mass and carbon balances are very satisfactory (<15% error), confirming the high accuracy of the analyses of the gaseous, aqueous and organic phases resulting from the reaction. The results in figure 1 show that increasing the contact time of the gases with the catalyst, increases CO_2 conversion (X_ CO_2) from 25% to 35%, decreases CO selectivity (S_CO) from 32% to 10% and enhances the production of C_{5+} hydrocarbons by 7 to 10%. This means that the FT reaction is limiting and the conversion of CO to HC is favored. In addition, we found that HC are secondary products of the reaction and CO is formed first. The results also showed that increasing temperature favors X_ CO_2 , since the equilibrium of the RWGS reaction is shifted towards CO formation. Temperature favors dissociation of the CO formed, which decreases S_CO. Olefin production is enhanced (olefin/paraffin ratio increases); however, very little effect of temperature is observed on C_{5+} selectivity. Increasing H₂/ CO_2 ratio results in an increase of CH₄ production and a decrease in C_{2+}



hydrocarbon production due to excess of H_2 which promotes the hydrogenation of CO to CH₄. When increasing the total pressure from 10 to 20 bars, X_CO_2 is increased by 10% and S_CO selectiviy decreases by 50%. Above 15 bars, CH₄ production is stable but an increase in C₂₊ hydrocarbons is observed, which encourages to operate the reaction at at least 15 bars. On the other hand, the results showed an effect of adding CO at the inlet of the reactor on the HC distribution, due to competitive adsorption between CO and CO₂ where CO wins (X_CO₂ decreases and X_CO increases when increasing the molar fraction of CO at the reactor inlet).



Figure 1: a) CO₂ conversion and CO selectivity b) mole fraction of hydrocarbons vs contact time.

To describe the distribution of hydrocarbons obtained as products during FT synthesis, an important parameter is the probability α of chain growth of the hydrocarbon formed. By correlating the experimental data, an α between 0.70 - 0.73 is obtained. This is a very interesting result, since these α values are within the range of values generally obtained for traditional CO-FT processes ($\alpha = 0.7 - 0.8$ for CO-FT processes between 250-350°C for iron-based catalysts²).

Based on these obtained data, the kinetic model proposed in our previous work¹ is adjusted and integrated in the reactor model. This latter is able to describe with good accuracy the CO₂ conversion and CO selectivity, as well as hydrocarbons distribution according to their C number and their chemical nature. In the simulations as in the experiments, thermal profiles show a temperature rise (Δ T) of up to 15°C in the catalytic bed in the tubular reactor, potentially influencing selectivity for long-chain hydrocarbons³. To mitigate this, a structured reactor is designed and assessed via 3D simulations, showing a reduced Δ T of under 1°C while maintaining comparable performances to the tubular reactor. An optimized reactor design is proposed which allows sustaining performance with doubled production (g/h) and an acceptable Δ T (3°C). Although promising, further investigations are necessary. Sensitivity analyses are conducted by varying geometric parameters of the reactor to enhance efficiency in FT-CO₂ synthesis.

In conclusion, while significant progress has been made in developing catalysts for direct CO_2 hydrogenation, the influence of reactor design on performance has yet to be explored. This study aims to bridge this gap by presenting an innovative reactor technology specifically adapted for enhancing CO_2 valorization and process intensification.

References

- 1. C. Panzone, R. Philippe, C. Nikitine, L. Vanoye, A. Bengaouer, A. Chappaz, P. Fongarland, *Ind. Eng. Chem. Res.* **2021**, *60*, 16635–16652.
- 2. Chai et al., Catalysts 2023, 13, 1052.
- 3. R. Philippe, M. Lacroix, L. Dreibine, C. Pham-Huu, D. Edouard, S. Savin, F. Luck, D. Schweich, *Catal. Today.* **2009**, *147S*, S305-S312