Modeling, design and assessment of a milli structured reactor for Fischer Tropsch reaction

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1. Introduction and Short Description

Heat to Fuel (HtF) aims at delivering the next generation of biofuel production technologies towards the decarbonisation of the transportation sector. Fischer Tropsch (FT) is a promising technology for the efficient production of 2nd generation fuels. Among all the existing reactor technologies, the milli structured one has been selected to be investigated and implemented in the HtF system process.

This paper discusses:

- The state of the art of the FT reactors technology and R&D on intensified reactors
- The design process of an optimized FT milli structured reactor for HtF.
- Simulation and experimental results obtained at CEA

2. State of the art of FT reactors

Various FT technologies are already available and industrially operational at large scale (production capacity from 10000 to 100000bbl/day) for Coal to Liquid (CtL) or Gas to Liquid (GtL) applications. According to the level of operating temperature, the technologies differ. High Temperature Fischer Tropsch (HTFT) reactors (300-350°C) are mainly Circulating Fluidized Bed reactors (CFB) and Fixed Fluidized Bed reactors (FFB). Low Temperature FT (LTFT) reactors (200-240°C) are of two kinds, Multi Tubular Fixed Bed reactors and Slurry reactors. In the 2000s, small scale (about 1000bbl/day) intensified reactors have been developed for GtL and Biomass to Liquid (BtL) applications. Beginning of 2017, Velocys built a GtL unit for ENVIA.

3. R&D on intensified reactors

Research studies are mainly on long chain hydrocarbons production with low temperature reactions (<240°C) in catalytic (Co or Fe) fixed bed reactors. Most of the studies are performed on milli structured or micro structured fixed bed reactors and on monolith reactors and aim at enhancing the catalyst efficiency by reducing diffusion lengths and increasing mass and heat transfers.

4. Design process of an optimized millistructured fixed bed reactor for HtF

Here, the final objective is to provide an optimized large scale millistructured fixed bed reactor (~ 1.5Nm^3/h) filled with an innovative catalyst for a system integration.

Starting from a mini scale FT reactor (millistructured reactor prototype of 0.1Nm^3/h) and from a reference catalyst (Co on alumina), the upscaling of the reactor is proceeded step by step, based on experimental tests and on simulation results and in parallel to the improvement of the catalyst. Two reference catalysts, 16% Co/α alumina and 18% Co/γ alumina, are considered.

Manufactured millistructured reactor (mini scale)

5. Millistructured FT reactor modeling and simulations

A large bibliographic survey has been performed providing a state-of-the art on FT modeling.

Several kinetic models have been implemented and compared against existing conversion data. The kinetic model of Ma et al, 2011 [1], gives

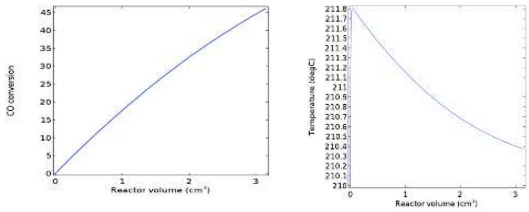
[1] Mal et al, 'Fischer Tropsch synthesis : support and cobalt cluster size effects on kinetics over Co/Al_2O_3 and Co/SiO_2 catalysts', Fuel n°90,2011, pp756-765

accurate results and has been selected and adjusted.

A heat transfer model has been developed (based on a literature review) taking into account the radial dispersion in the bed and the convection between the wall and the bed.

Those correlations have been implemented in different models; a 1D plug flow model, with a simplified heat balance and no mass diffusion, and a 2D model, with heat and mass diffusion.

The preliminary simulation results show that 1 pass conversion of 50% seems achievable for lab scale reactor at high Space Velocity (SV). The temperature rise along the bed is in the range of 2-5K. The pressure drop along the bed is low.

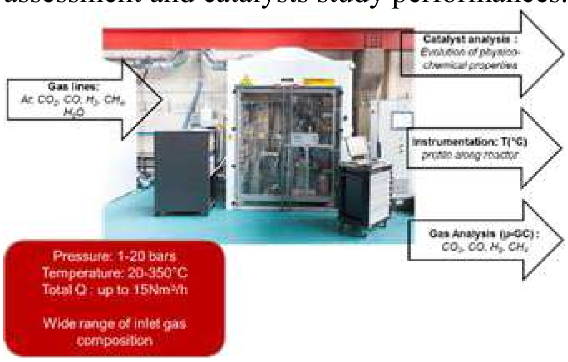


*Plug Flow simulation. Evolution of the CO conversion and temperature along the bed for SV 4.3 Nm3/kg*h, 210°C, 20 bar, diameter of particle=0.5 mm*

A more accurate model is being developed and will be assessed on the experimental data obtained on CEA bench tests. This accurate model will allow to design the large scale reactor to be implemented in the HtF system with confidence.

6. Experimentation characterization and first results

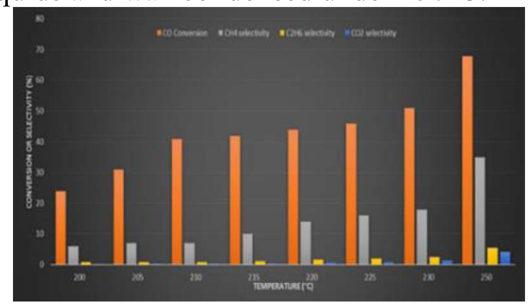
CEA has an experimental platform devoted to the study of FT synthesis, used for both, reactor assessment and catalysts study performances.



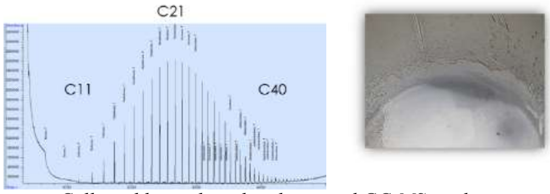
The available gases are H_2, CO, CO_2, CH_4 through gas lines and possibly other gases through bottles, which allow a wide range of gas composition. The inlet total flowrate may reach up to 3.6Nm^3/min. The working pressure range is 1-70 bars. Gases can be heated up to 350°C. Analysis of the resulting products are realized on site: outlet gases analysis with a µ-GS, Liquid Hydrocarbons analysis with a GC-MS, possible catalyst post analysis (evolution of physico-chemical properties).

A large series of tests has been performed on the mini scale reactor for both reference catalysts, with sensitivity tests to several parameters: inlet temperature from 200 to 250°C; SV from 3.5 to 15Nm3/kg*h, gas compositions at the inlet (presence of CH_4 and CO_2 additionally to H_2 and CO)

As examples of the obtained results, figures below show the sensitivity of the performances to the temperature for the CO/α alumina catalyst, and the GC-MS analysis the heavy liquids and wax condensed under 150°C.



Sensitivity to the temperature:
CO Conversion, CH4, C2H6 and CO2 selectivities for CO/α catalyst



Collected heavy liquid and wax and GC-MS analysis

The CO conversion decreases with the SV increase and increases with inlet gases temperature. Also, the maximum temperature increases. For T=250°C, the observed gradient is about 5°C, which is still acceptable. But the CH_4 selectivity increases which is not favorable. The recommended temperature is 210°C with an observed increase temperature of 2°C. There is a large impact of the composition on XCO and SCH_4. Comparing both reference catalysts, CO/α alumina catalyst seems more stable and performant compared to CO/γ alumina catalyst. IREC proposed CO/γ alumina catalyst improvement.

7. Conclusion

To provide an optimized FT millistructured reactor to be implemented in the HtF system an iterative and interactive process is underway. It is based on simulations results assessed on experimental data. Results obtained show that 50% CO conversion can be obtained at 210°C with low temperature increase and low CH4 selectivity. Those conditions are proposed as FT reactor optimal operational conditions in the HtF system.