

## Kinetic modeling of the Fischer-Tropsch synthesis.

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The Fischer-Tropsch synthesis (FTS) is based on the catalytic conversion of synthesis gas to a mixture of liquid hydrocarbons and oxygenates, mainly water. In principle the FTS process allows to obtain from natural gas products like fuels (mainly gasoline and diesel) and chemicals that usually derive from crude oil. Moreover the FTS process can be the solution to exploit in a profitable way the huge natural gas reserves present in different parts of the world. For these reasons it is becoming a strategically relevant technology.

High value added products are usually obtained by upgrading of the FT products with well established refinery processes, such as hydrocracking, hydrotreating, reforming and isomerization. The FT products distribution is strongly affected by the operating conditions of the process and the nature of the catalyst. For example, the synthesis of heavy hydrocarbons, i.e. waxes, which can be converted into fuels, is favored at low temperature (220-240°C) on supported cobalt catalysts. This represents the so called LTFT process, which is usually carried out on slurry bubble columns or fixed bed reactors.

The scale up of the process requires the implementation of the reactor model with the kinetic model of the synthesis. The aim of this work is the development of a CO conversion kinetic model of the FT process: data were produced testing a Co-based catalyst on two lab units, equipped with a slurry autoclave and a micro fixed bed reactor respectively. Accordingly information on the catalytic performances of the same catalyst in two reactor configurations could also be obtained.

Preliminary investigations of the experimental apparatus demonstrated that both the reactors can be considered as ideal systems (CSTR and PFR, respectively).

Kinetic data were obtained testing the catalyst under different conditions: pressure, temperature, feed gas composition (as H<sub>2</sub>/CO inlet ratio and inert content) and syngas space velocity were changed into within industrially relevant ranges. The experiments allowed the investigation of the effect of operating conditions on CO conversion, that was observed to increase upon increasing the pressure, temperature, residence time and H<sub>2</sub> content in the syngas.

Notably, very similar results in terms of CO conversion have been obtained with both reactors systems. The experimental data were then analyzed with different kinetic models, available in the literature; two mechanistic models derived by Sarup-Wojciechowski and Yates-Satterfield, respectively [referenze1, 2], and a simple power law rate expression were compared. The parameters of the different rate expressions were estimated by non-linear regression of the kinetic data collected on the two lab units. Notably, similar kinetic parameter estimates were obtained from the two reactor systems. For both reactor configurations the analysis of the model fittings showed that the power law rate expression and the Sarup-Wojciechowski model offer the best agreement with the experimental results, being able to adequately describe the effect of pressure, temperature, space velocity and H<sub>2</sub>/CO ratio on the CO conversion.

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1 B. Sarup, B.W. Wojciechowski, Can. J. Chem. Eng. 67 (1989) 62

2 I.C. Yates, C.N. Satterfield, Energy and Fuels 5 (1991) 168