

Influence of an Alternating Fischer-Tropsch/Hydrogenolysis Process on the Product Selectivity and Activity

A. Duerksen, C. Kern, A. Jess

Chair of Chemical Engineering, Faculty of Engineering Science, University of Bayreuth, Germany

Abstract

The Fischer-Tropsch (FT) process is the catalytic hydrogenation of carbon monoxide, which yields a wide range of hydrocarbons (HC) [1]. In combination with the concept of Power-to-Liquid (PtL) the process offers the possibility to produce sustainable synthetic fuel [2].

One of the established reactor designs for the FT-process is a multitubular, wall-cooled fixed-bed-reactor. The typical reaction conditions for the cobalt-based low-temperature FT process are temperatures between 200°C and 250°C and a pressure range of 10 to 40 bar. [1]

The main products are alkanes, alkenes and oxygenated organic compounds with varying chain length. The chain length distribution of the products normally can be described by the (Anderson-) Schulz-Flory distribution for polymerisation reactions.

Due to the different volatilities depending on the chain length, high-molecular hydrocarbons (wax) accumulate in the catalyst pores while the short-chained ones evaporate. The initial filling of the catalyst pores with liquid hydrocarbons leads to a decrease in activity due to diffusion limitations. Also, due to the higher diffusivity of H₂ than CO in wax an increase of the H₂:CO-ratio and thus a lower chain growth probability can occur. Only after reaching a completely filled pore system a significant amount of non-volatile compounds leaves the pores through overspill. [3]

Hence, to enhance the overall activity and to shift the product distribution towards a high liquid fuel amount, an alternating Fischer-Tropsch/Hydrogenolysis process was investigated.

Hydrogenolysis is the metal catalysed cracking by action of hydrogen to empty the catalyst pores from accumulated wax. By alternating the FTS with hydrogenolysis pore diffusion effects can be reduced and thus the effective catalyst productivity can be increased.

For potential estimation of the FTS pore filling time, H₂-partial pressure during hydrogenolysis and cycle times were varied in the alternating process with a Pt promoted Co/Al₂O₃-catalyst. Moreover parameter studies concerning the hydrogenolysis with model-substance-filled catalyst particles were carried out.

It could be shown that the main reaction during hydrogenolysis is a hydrogenolytic demethylation, which means that the terminal C-C bond of the adsorbed hydrocarbon radical cleaves with preference. The reaction rate strongly depends on the H₂-pressure with a negative order.

In the alternating process overall, a reduction of the C₁ and C₂₁₊-selectivity was found, while the FT-reaction rate increased. The distribution differs from a normal change of the chain growth probability. The improvement of these parameters depends on the ratio of filling-time and draining-time.

Sources:

[1] Jess, A. a. W. P., 2013. Chemical Technology. s.l.:Wiley-VCH.

[2] German Environment Agency, 2016. *Power-to-Liquids - Potentials and Perspectives for the Future Supply of Renewable Aviation Fuel*

[3] Raak, H. a. H. K., 1998. A pressurized reactor with Integrated load cell for measuring the activities of Fischer-Tropschtatalysts and their loadings with liquid reaction products (wax). Erdoel, Erdgas, Kohle.