

## **Accumulation of Higher Liquid Hydrocarbons in the Pores of a Cobalt Catalyst during the Initial Non-stationary Phase of Fixed-bed Fischer-Tropsch Synthesis**

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### **Abstract**

The production of synthetic fuel via Fischer-Tropsch synthesis (FTS) could play an important role in the energy transition to more environment friendly alternatives as part of the power to liquid concept if the feedstock consisting of hydrogen and carbon monoxide is produced carbon neutral. Even though FTS has an industrial history of over 80 years, there is still potential for optimization of the process to further enhance the effectiveness.

During low temperature FTS in a fixed-bed reactor higher liquid hydrocarbons (waxes) unavoidably accumulate in the pores of the heterogeneous catalyst. The resulting mass transport limitations may lead to a decrease in reaction rate and effectiveness factor of the catalyst. Additionally the formation of methane increases. These unwanted effects are amplified by larger catalyst pellet sizes which have to be used in industrial fixed-beds. A promising concept addressing this challenge is to switch alternately between filling (FTS) and emptying (hydrogenolysis of the accumulated wax) the catalyst pores in order to increase the overall product yield of the process. Therefore a detailed understanding of the filling process is crucial to achieve desirable process control.

The aim of this work is to gain knowledge about the filling time and composition of liquid hydrocarbons inside the catalyst pores along the fixed-bed under industrially relevant conditions at the non-stationary startup of the FT-reaction in order to derive a numerical model to describe the filling process properly and to verify it experimentally.

Therefore an already published model of a single catalyst pellet [1], which focuses on the fundamental behavior of evaporation of hydrocarbons in pores and the kinetics of the reaction, is extended by arranging a string of multiple pellets behind each other to approximate fixed-bed behavior and enable the investigation of the additional influence of axial gradients, mainly the partial pressure of hydrocarbons in the gas phase. The reactor setup ensures the assignment of particles to their original axial position after removing them from the reactor in order to analyze the filling degree and composition. Higher levels of CO conversion are attainable with this arrangement and during the investigation of reaction products some controversial observations could be made. Firstly, the product distribution (chain growth probability) changes with liquid pore filling and secondly, the reaction rate is significantly higher than the intrinsic reaction rate at the startup, only dropping below the intrinsic rate for a nearly fully liquid filled catalyst. These observations and others are implemented into the model to describe the pore filling at various reaction conditions.

[1] S. Rößler, C. Kern, A. Jess, *Catal. Sci. Technol.* 2019, 9, 4047.