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Kinetics, selectivity and scale up of the Fischer-Tropsch synthesis

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Conclusions and Epilogue

The major objective of this thesis is to develop a kinetic model that can predict Fischer-Tropsch conversion and product selectivities over a commercial precipitated iron catalyst with improved accuracy relative to existing models. A detailed multicomponent reaction engineering model for a commercial scale slurry bubble column reactor with use of these new kinetic and selectivity models is the final aim of this thesis. The work reported in this thesis consisted of: a) critical literature review on the kinetics and selectivity of the Fischer-Tropsch synthesis (Chapter 2), b) kinetic and selectivity modeling of experimental data obtained over a commercial precipitated Fe/Cu/K/SiO₂ catalyst both in a spinning basket reactor and a slurry reactor (Chapters 3-6) and c) reactor modeling of a large scale Fischer-Tropsch slurry bubble column reactor (Chapter 7). Data on the hydrodynamic behavior and mass transfer characteristics of the bubble column under the operating conditions applied were selected from literature. The major conclusions and suggestions for further research are summarized below.

Product Selectivity

The product selectivity to linear olefins and paraffins was studied both in a gas-solid spinning basket reactor (Chapter 4) and in a gas-slurry reactor (Chapter 6.3.1) over a wide range of industrially relevant process conditions on a precipitated iron catalyst. A new product selectivity model for linear hydrocarbons, the α -Olefin Readsorption Product Distribution Model (ORPDM), was developed. This model combines readsorption of α -olefins and chain growth on the same catalytic site. ORPDM predicts the selectivity to olefins and paraffins accurately at a constant temperature of 523 K. The ORPDM parameters (chain growth parameter p , olefin termination parameter t_O and readsorption parameter k_R) were described successfully by equations depending on the operating conditions only. In contrast to most literature models, the experimentally observed relatively high yield of methane, relatively low yield of ethene and the changing olefin to paraffin ratio and chain growth factor with chain length can all be

predicted from this model.

The current model is a basis for more advanced kinetic models which do take into account the effect of temperature. Ultimately, a small set of kinetic parameters must be obtained which are able to describe the synthesis gas consumption as well as the product selectivity over a wide range of feed component pressures, residence time and temperature. The main problem is to obtain the experimental kinetic data without severe catalyst deactivation. If necessary, the new model can be extended to describe the selectivity to minor amounts of oxygenated products (1-alcohols) or isomers (β -olefins, branched hydrocarbons) on iron catalysts. On cobalt catalysts, product selectivity models should include secondary hydrogenation of α -olefins to paraffins [1].

Reaction Kinetics

The reaction kinetics of both the Fischer-Tropsch and the water gas shift reactions over a precipitated iron catalyst were measured and modeled for both gas-solid and gas-slurry systems. A number of rate equations were derived on the basis of a detailed set of realistic reaction mechanisms. It was assumed that the formation of methylene, originating from the carbide mechanism, is the rate determining step in the Fischer-Tropsch reaction. 14 models for the FT reaction rate and 2 WGS reaction rate equations were fitted to the experimental data. Bartlett's test was applied to reduce the set of possible Fischer-Tropsch rate equations to 3 models for the gas-solid system (Chapter 5) and to 2 models for the gas-slurry system (Chapter 6.3.2), which were statistically indistinguishable. The rate equations for the water gas shift reaction are all based on the formate mechanism. Simulations using the optimal kinetic models derived showed good agreement both with experimental data and with some literature models. The slurry liquid appeared to affect the kinetic parameters and the adsorption constants. At low H_2/CO ratios, both the Fischer-Tropsch and the water gas shift reaction appeared to be lower than for the gas-solid kinetics.

The reaction kinetics were determined at a constant temperature of 523 K only. Further research should investigate the influence of the temperature and test the validity of the activation and adsorption energies according to the guidelines of Boudart [2].

The preferred way to present catalytic rate data is in the form of specific activity, such as turnover rates (TOR) or turnover frequencies (TOF) [3]. This way, different catalysts can be compared appropriately. Measurements of the surface area and the

metal dispersion are complicated on precipitated iron catalyst operating under industrial conditions in the slurry-phase due to wax-filled pores and changing composition of the iron phases. In this thesis, the reaction rates are given per mass unit of catalyst. These reaction rates can directly be applied in reaction engineering models, such as presented in Chapter 7.

Reaction Engineering Model for an FT Slurry Bubble Column Reactor

A reaction engineering model was developed for a commercial scale Fischer-Tropsch slurry bubble column reactor (Chapter 7). The model incorporates new hydrodynamic insights with respect to gas holdup and mass transfer in the heterogeneous flow regime [4] and improved kinetic models for the selectivity and the reaction rates based on own measurements (Chapter 6). The reactor model assumes plug flow for the large gas bubbles and ideal mixing for both the liquid, the small bubbles and the catalyst phase. The assumption of complete mixing of the small bubbles (dense phase) is conservative, because these bubbles can also be entrained by the large bubbles. The assumption on ideal mixing results in a conservative reactor design with respect to conversions and hydrocarbon production. However, the overall contribution of the dense phase is small in comparison to the large bubbles, especially at high gas velocities. The main novel aspect of this model is the prediction of the composition of both the gaseous and the liquid product streams of a slurry reactor operating in the heterogeneous flow regime as a function of process conditions. It provides information for reliable scale up, design and prediction of the performance of an industrial scale FT slurry reactor.

A number of patents deal with modifications of Fischer-Tropsch slurry bubble column reactors to reduce the back-mixing of both the liquid and the gas phase [5–7]. Arcuri [5] described the influence of various degrees of back-mixing on the selectivity and the productivity based on kinetic data obtained over a Co/TiO₂ catalyst, both in plug flow (fixed bed), bubble column and completely mixed reactors (CSTR). Arcuri [5] claimed that the productivity in a slurry bubble column is equal to or greater than for plug flow, and that the same selectivity is obtained for the completely mixed system. Koros [6] (Exxon Research) reported the invention of a slurry bubble column with plug flow in either the gas phase and the liquid phase. The patent describes a multi-tubular slurry bubble column reactor with cooling medium around the tubes. The presented example shows a reaction tube of 0.15 m mounted inside a 0.30 m pipe that served as a cooling jacket. According to our opinion, this reactor configuration has several disadvantages: 1) possibility of slug flow conditions, 2) large gas holdup

due to the influence of the column diameter on the large gas bubble holdup [8], 3) possibility of maldistribution of the gas, the liquid and the catalyst phases, and 4) low specific cooling area relative to, for example, 1.5 inch cooling tubes. A better option is staging the slurry bubble column horizontally as proposed earlier by Graaf [9] for slurry phase methanol synthesis. Maretto and Piccolo [7] reported the effect of staging a slurry bubble column. The temperature in each stage could be controlled separately. Their model assumed plug flow of the gas phase and complete mixing of the slurry in each stage. Maretto and Piccolo [7] claimed that the liquid phase in the multistage reactor may approach plug flow behavior, resulting in an increase of the synthesis gas conversion with increasing the number of stages. Our model can easily be extended to incorporate the effect of staging of a slurry bubble column. In addition to the study of Maretto and Piccolo [7], extension of the model presented will also predict the effect of staging on the product selectivity. Maretto and Piccolo [7] did not report on the engineering details of staging bubble columns. One of the possibilities would be the application of horizontal gauzes or perforated plates [10, 11]. These plates decrease the bubble size of large gas bubbles and slugs which results in a higher gas holdup and improvement of the plug flow characteristics of the gas and liquid phase.

Epilogue

With the current, extremely low, oil prices, the process economy of Fischer-Tropsch is unfavorable. Under certain conditions and in specific situations, FT processes are interesting: 1) availability of cheap natural gas (for example, Malaysia, Alaska, Qatar) or coal (South Africa); 2) production of chemicals or high-value clean diesel and gas oil; 3) governmental regulations on flaring of natural gas or on emissions in the transport sector.

The main barrier for Fischer-Tropsch technology is in the high costs of producing synthesis gas. A challenging development in this area is the ceramic membrane technology, which allows oxygen to transport from air to the natural gas, where it produces synthesis gas via partial oxidation. However, after a successful research stadium, commercial application is still more than 10 years away.

The optimal Fischer-Tropsch reactor for high molecular weight products is the slurry bubble column reactor. Good temperature control due to the excellent heat transfer allows the use of highly active catalysts. Major problem is the necessary catalyst-wax separation step. Cost reduction may be accomplished by increase of the reactor size to 10,000 - 20,000 bbl/day.

Parallel to the process development, catalytic design of Fischer-Tropsch catalysts remains important. Special aspects are the improvement of activity, selectivity, and resistance to attrition and deactivation. Most recent research deals with cobalt-based catalysts. Under certain conditions, the activity of iron catalysts is equal to or greater than that of cobalt catalysts [12, 13]. Cobalt catalysts are preferred at high CO conversions with a synthesis gas feed from natural gas ($H_2/CO=2$). Synthesis gas from coal or other carbon resources is preferably converted with iron catalysts because of their high water gas shift activities.

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