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

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**Kinetics, Selectivity
and Scale Up of the
Fischer-Tropsch Synthesis**

Gerard P. van der Laan

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and Scale Up of the
Fischer-Tropsch Synthesis**

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Summary

In the Fischer-Tropsch (FT) process, synthesis gas, a mixture of predominantly CO and H₂, obtained from either coal, peat, biomass or natural gas is converted to a multicomponent mixture of hydrocarbons. Currently, a promising topic in the energy industry is the conversion of remote natural gas to environmentally clean fuels, specialty chemicals and waxes. Fuels produced with the FT process are of high quality due to a very low aromaticity and absence of sulfur. These fuels can be used as blending stocks for transportation fuels derived from crude oil. Other valuable products besides fuels can be tailor-made with the FT in combination with upgrade processes: for example, ethene, propene, α -olefins, ketones, solvents, alcohols, and waxes.

The FT process is catalyzed by both iron and cobalt at pressures from 10 to 60 bar and temperatures from 200 to 300 °C. The FT synthesis is a surface polymerization reaction. The reactants, CO and H₂, adsorb and dissociate at the surface of the catalyst and react to form chain initiator (CH₃), methylene (CH₂) monomer and water. The hydrocarbons are formed by CH₂ insertion into metal-alkyl bonds and subsequent dehydrogenation or hydrogenation to an α -olefin or paraffin, respectively. Iron catalysts can also use synthesis gas with a H₂/CO ratio below 2, because excess of CO is converted with water to carbon dioxide and hydrogen in the water gas shift (WGS) reaction. The most important aspects for FT reactor development are the high reaction heats and the large number of products (gas, liquid and waxy hydrocarbons). The favorite reactor system for the Fischer-Tropsch synthesis of high molecular weight products is the slurry bubble column reactor. Excellent heat transfer characteristics of this reactor result in isothermal conditions.

An optimal design of a commercial scale reactor requires detailed information of the hydrodynamics, reaction kinetics, catalytic system and FT chemistry. Kinetic information is crucial for reliable design and scale up of commercial Fischer-Tropsch processes. The major aim of this thesis is to study the kinetics and selectivity over a commercial precipitated iron catalyst in laboratory reactors. A detailed multicomponent reaction engineering model for a slurry bubble column reactor on commercial scale with use of these detailed kinetic models is the final aim of this thesis.

A critical literature review on the kinetics and selectivity of the Fischer-Tropsch synthesis is given in Chapter 2. The kinetic equations for CO consumption to FT products do not present a uniform picture. Most studies aim at catalyst improvement and

postulate empirical power law kinetics, both for the carbon monoxide conversion rate and the water gas shift reaction. Relatively few studies aim at understanding the reaction mechanisms. Some authors derived Langmuir-Hinshelwood- Hougen-Watson (LHHW) or Eley-Rideal type of rate expressions for the reactant consumption. In most cases the rate determining step is assumed to be the formation of the building block or monomer, methylene. Simultaneous modeling of the WGS and FT reactions on iron catalysts with WGS activity has hardly been reported. The total product yield decreases exponentially with increasing chain length. Most studies assume the so-called Anderson-Schulz-Flory (ASF) distribution to model the product selectivity. The ASF model describes the entire product range by a single parameter, α , the probability of the addition of a carbon intermediate to a chain. However, significant deviations are reported in literature. It is concluded that the reinsertion or readsorption of α -olefins is the most important secondary reaction and that secondary hydrogenation of α -olefins may occur, depending on the catalytic system and process conditions. Accurate product distribution models must also include the change of the solubility and physisorption energy with carbon number. Until now, none of the available literature models obtains enough details to describe the complete FT product spectrum as a function of operating conditions.

The kinetics and selectivity of the Fischer-Tropsch synthesis over a commercial Fe-Cu-K-SiO₂ catalyst was studied in a gas-solid spinning basket reactor and in a gas-slurry laboratory reactor. For the gas-solid system, a new product distribution model for linear hydrocarbons, based on experiments in the spinning basket reactor, is proposed in Chapter 4 (see Figure 1). The α -Olefin Readsorption Product Distribution Model (ORPDM) can quantitatively describe the deviations from conventional Anderson-Schulz-Flory distributions. The model combines olefin readsorption with chain growth and termination on the same catalytic site. The olefin readsorption rate

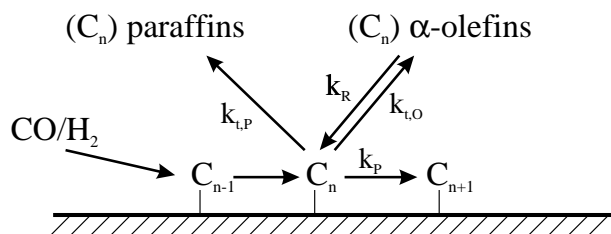


Figure 1 Scheme of the reaction network of the Olefin Readsorption Product Distribution Model.

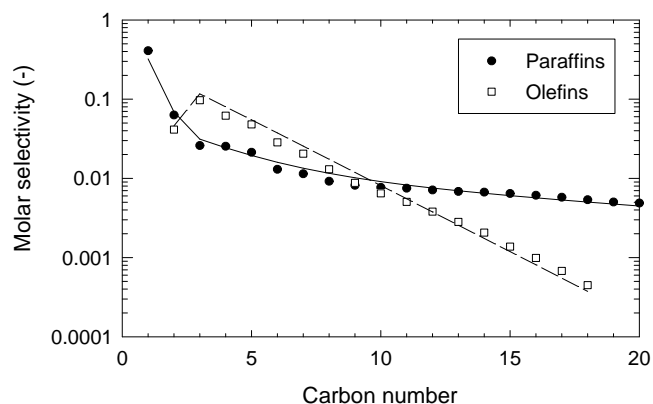


Figure 2 Product distribution for a typical gas-solid experiment (A1) in the spinning basket reactor. Symbols are experimental selectivities. Lines are model predictions.

depends on the chain length due to increasing physisorption strength and increasing solubility in FT-wax with increasing chain length. ORPDM predicts selectivities of linear paraffins and olefins over a wide range of industrially relevant process conditions. For each experimental product distribution three parameters were optimized. An example of a modeled product distribution is shown in Figure 2. The ORPDM parameters could be described successfully with semi-empirical equations containing operating variables only. The novel model, ORPDM, can also predict the selectivity obtained in a gas-slurry reactor accurately (Chapter 6). However, the presence of the slurry liquid appeared to affect both the values of the model parameters and the product selectivity relative to the gas-solid system. The slurry-phase system gives a higher olefin yield at comparable reaction conditions due to a decrease of both the readsorption rate and the termination rate to olefins.

The kinetics of both the Fischer-Tropsch and the water gas shift reactions were modeled simultaneously to experimental data (Chapters 5 and 6). It is generally accepted that the FT and WGS reaction proceed on different active sites on precipitated iron catalysts. A number of Langmuir-Hinshelwood-Hougen-Watson and Eley-Rideal type of rate equations were derived on the basis of a detailed set of possible reaction mechanisms based on the carbide mechanism for the hydrocarbon formation and the formate mechanism for the WGS reaction. Simulations using the optimal kinetic equations derived, showed good agreement both with experimental data and with some

kinetic models from literature. The presence of the slurry liquid appeared to affect the reaction kinetics. The reaction rates are comparable in the gas-solid and the gas-slurry systems at high H_2/CO ratios. However, at low H_2/CO ratios, the reaction rate of the FT reaction appeared to be lower in the slurry system due to CO_2 inhibition. The water gas shift reaction rate is also slower at these reaction conditions.

In Chapter 7, a multicomponent reaction engineering model is presented for a large scale slurry bubble column reactor (SBCR) operating in the heterogeneous or churn-turbulent regime (see Figure 3). Literature data on hydrodynamics and mass transfer are used to describe the performance of the SBCR. The model combines the FT reaction as well as the WGS reaction and the individual paraffin and olefin formation rates (based on original experimental work) with multicomponent vapor-liquid equilibria. Under the operating conditions investigated the SBCR is mainly reaction controlled. This is caused by the limited activity of iron catalysts on the one hand and the large value of the volumetric mass transfer coefficient of the large bubbles due to frequent bubble coalescence and breakup on the other hand. The model predicts the composition of the gaseous and the liquid product streams and the performance of a large scale SBCR. It provides all the data for a reliable design of these FT slurry reactors and for predicting their performance as a function of operating conditions, such as inlet gas velocity, catalyst concentration, and feed composition.

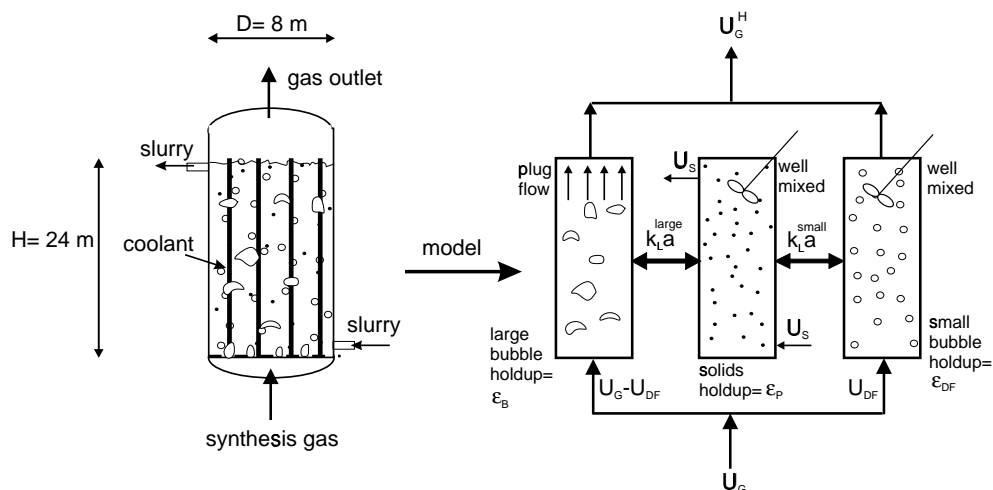


Figure 3 Model for Fischer-Tropsch slurry bubble column reactor in the heterogeneous flow regime.

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