

Modeling of Fischer-Tropsch Product Distribution over Fe-based Catalyst

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The kinetic models of Fischer-Tropsch synthesis (FTS) product distribution can be classified into two major groups: hydrocarbon selectivity models and detailed Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic models. In this study the two approaches to FTS product distribution modeling are presented and compared using the experimental data obtained in a stirred tank slurry reactor with promoted iron catalyst over a wide range of process conditions. Positive deviations from the classical Anderson-Schulz-Flory distribution and an exponential decrease in olefin-to-paraffin ratio with carbon number are predicted by the inclusion of solubility-enhanced 1-olefin readsorption and/or chain length dependent 1-olefin desorption concepts. In general the agreement between the model predictions and experimental data was very good, and modeling approaches are discussed in terms of fit quality, physical meaningfulness and practical utility.

1. Introduction

The main products of the FTS reaction are n-paraffins and 1- and 2-olefins. These products are obtained from a mixture of CO and H₂ over a heterogeneous catalyst (Bhatelia et al., 2011). FTS product distribution was initially described with the so called Anderson-Schulz-Flory (ASF) distribution characterized by the chain growth probability factor (α), independent of the number of carbon atoms in the product molecule. Later a change in growth probability with carbon number was observed over the Fe-based catalysts and today it is well known that deviations from the ASF distribution over all FTS catalyst types (Fe, Co, Ru etc.) include: high yield of methane, low yield of ethene and increasing chain growth probabilities with increasing carbon number (van der Laan and Beenackers, 1999a). Another important feature of the experimental product distribution is the exponential decrease in olefin-to-paraffin ratio (OPR) with carbon number (for C₃₊ hydrocarbons). In order to account for the behavior of the FTS product distribution many different models have been proposed in the literature. They can be classified into two major groups: hydrocarbon selectivity models and detailed Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic models.

The selectivity models are based on FTS reaction networks (simplified reaction mechanisms) and most can be grouped either as the double-alpha models or the olefin readsorption models. Latter are more frequently used because they calculate selectivity for various product species (paraffin and olefin), while the double-alpha models predict only the total hydrocarbon formation (lumped paraffin and olefin). Recently Botes (2007) proposed a third type of selectivity model for the Fe catalyst, based on the new hypothesis of chain length dependent olefin desorption, where the activation energy for olefin desorption increases with carbon number due to the effect of weak interactions between desorbing chain and the catalyst surface. Similar to the readsorption models, this model was also capable of predicting the deviations from ASF and the change of OPR with carbon number.

Contrary to these, the detailed LHHW kinetic models consider the entire FTS mechanism: adsorption of reactants, formation of monomer, chain initiation, propagation and termination. It is important to note that

these models also include concepts such as 1-olefin readsorption and/or chain length dependent olefin desorption in order to explain the product distribution variations with carbon number.

In this study we compare the two approaches to FTS product distribution modeling. The selectivity model was developed based on the FTS reaction network proposed by van der Laan and Beenackers (1999b), with the additions of 2-olefin formation. The detailed LHHW model was derived based on the carbide FTS mechanism and the chain length dependent 1-olefin desorption concept. The two models were used to analyze data obtained with a Fe-based catalyst in a stirred tank slurry reactor. Advantages and shortcomings of these approaches are discussed in terms of the quality of prediction, physical meaningfulness of parameter values and overall simplicity and practical applicability of the models.

2. Experimental

Experimental data were obtained from Bukur et al. (2007) study over an industrial precipitated iron catalyst (synthesized by Ruhrchemie AG), with a nominal composition of 100 % Fe / 4.3 % Cu / 4.1 % K / 25 % SiO₂ (mass basis). The size of the catalyst particles was 140 - 325 mesh. The catalyst was pretreated in CO at 280 °C, 0.8 MPa and 3 NL/g-cat/h for 12 h in a stirred tank slurry reactor (STSR). After the pretreatment, the catalyst was tested initially at 260 °C, 1.5 MPa, 4 NL/g-Fe/h and H₂/CO = 0.67 (referred to as the baseline condition). After reaching a stable steady-state value (~60 h on stream), the catalyst was tested at different process conditions. Kinetic experiments conducted in a STSR covered a wide range of process conditions. Temperatures used were 220, 240 and 260 °C, pressures 8, 15, 22.5 and 25 bar, H₂/CO ratios 0.67 and 2 and gas space velocities between 0.5 and 23.5 NL/g-Fe/h. The minimal time between changes in process conditions (mass balance period) was about 24 h. In total 27 mass balances were achieved with 3 baseline replicates and good reproducibility of data was observed.

3. Kinetic modeling

3.1 Hydrocarbon selectivity model

A selectivity model provides a prediction of the product formation rates (or product selectivity). One of the first attempts to explain the positive deviations from the ASF was the inclusion of the second chain growth probability by Huff and Satterfield (1984). They proposed that FTS reaction occurs on two separate sites that have different growth probability α_1 and α_2 ; and curvature in the product distribution was explained by the superposition of the two chain growth probabilities. Similar explanations were proposed by Dictor and Bell (1986) and Sarup and Wojciechowski (1988). However a deficiency of the double-alpha models is that they do not consider formation of different product species (paraffins and olefins) separately. These models are therefore unable to explain the experimentally observed changes in the OPR with carbon number. Another class of models considers the effect of secondary reactions of 1-olefins (readsorption, hydrogenation and isomerization). Readsorption models are based on a hypothesis that 1-olefin molecules readsorb onto the active sites and can initiate the chain growth. In order for readsorption to cause the observed increase in alpha and a decrease in OPR with carbon number, it was argued that the residence time of 1-olefin increases with the carbon number. This is a result of increased solubility (Zimmerman et al., 1992), physisorption (Kuipers et al., 1995) and/or decreasing diffusivity with carbon number (Iglesia et al., 1991). Models based on this approach (e.g. Nowicki et al., 2001) have been shown to accurately describe the formation of all main product species, predicting both the non-ASF distribution and the change in OPR with carbon number.

As stated above, the selectivity models are derived using a simplified mechanism for formation of hydrocarbons (reaction network), without considering steps that preceded to monomer formation or water gas shift reaction. This way the disappearance of reactants (CO and H₂) and the formation of inorganic products (H₂O, CO₂) are neglected. An assumption was made that the water gas shift (WGS) reaction takes place on a different type of active sites than the FTS reaction, allowing for a separate treatment of hydrocarbon formation. The parameters of a selectivity model are pseudo-kinetic constants, which include intrinsic kinetic constants and surface concentrations of reaction intermediates. Therefore the parameters will be dependent on reaction conditions (temperature, partial pressures and gas flow rate) and need to be estimated for each reaction condition separately.

In this study we present a selectivity model (model A) based on the reaction network proposed by van der Laan and Beenackers (1999b) which was expanded in order to include 2-olefin formation (Olewski, 2008). This model is therefore an extension of van der Laan and Beenackers (1999b) olefin readsorption product distribution model (ORPDM). Figure 1 depicts the FTS reaction network used in the model. Chain growth is initiated by hydrogenation of adsorbed monomer (CH₂-S₁) to adsorbed methyl group (CH₃-S₁). Chain propagation occurs via insertion of the adsorbed monomer into the adsorbed alkyl species (C_nH_{2n+1}-S₁),

which can terminate to n-paraffin by hydrogenation or to 1- or 2-olefin by dehydrogenation. According to the reaction network, 1-olefin can readsorb on the FTS active sites S_1 , which leads to adsorbed alkyl species, and the latter can either propagate or terminate.

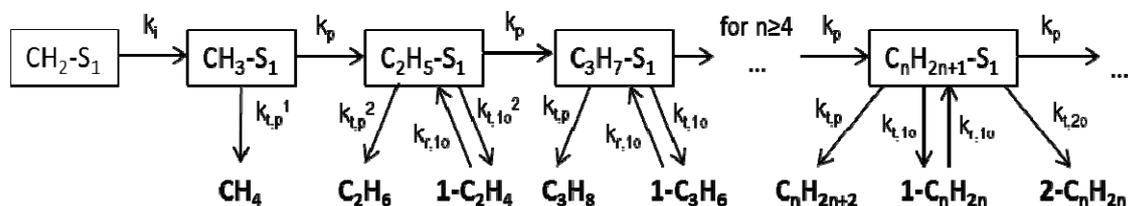


Figure 1: Reaction network for selectivity model A

Liquid phase concentration of 1-olefins, appearing in the model A, was calculated (as in Nowicki et al., 2001) by assuming that: 1) reaction rate of 1-olefin is proportional to its partial pressure in a CSTR; 2) gas and liquid phase are in equilibrium, and thus the liquid phase concentration of 1-olefins can be related to 1-olefin partial pressures by Henry's law constant; 3) 1-olefin Henry's constant (H_e) is changing with carbon number following an exponential dependency $H_{e,n} = a * e^{c*n}$, where a and c are constants. In order to account for the deviations in the C_1 and C_2 species, they are given separate parameters. A reparameterization with reference to the termination of n-paraffins was performed and the number of parameters for model A was reduced to nine (pseudo-kinetic constants).

3.2 Detailed LHHW kinetic model of product formation

The detailed kinetic model presented here is derived based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) methodology and predicts the product formation rates. Even though parts of this approach can be found in the selectivity model of Zimmerman et al. (1992), the first fully LHHW model was proposed by Lox and Froment (1993). This model did not consider secondary reactions of 1-olefins and effect of transport and/or thermodynamic properties and the model predictions were consistent with the classical ASF distribution. Wang et al. (2003) expanded this approach by adding different rate constant for methane formation and, more importantly, the 1-olefin readsorption step. These models offered some improvement compared to Lox and Froment (1993), but still failed to predict the extent of α and OPR changes with carbon number. A much better prediction of these deviations was obtained by Teng et al. (2007), who introduced an exponential dependency of olefin formation rates with carbon number. This type of dependency, as we will show below, can be directly derived using the chain length dependent 1-olefin desorption concept (Botes, 2007; Todić et al. 2013).

The detailed LHHW kinetic model (model B) was derived using a form of the carbide FTS mechanism (Table 1), here expanded to include 2-olefin formation elementary step. The main difference from the reaction network used in selectivity model A derivation is that in a detailed mechanism all elementary steps (including reactant adsorption and water formation) are considered. Applying the LHHW methodology allows us to obtain a detailed model in which all parameters are intrinsic kinetic constants. Several assumptions are made in derivation of rate equations: 1) only one type of FTS active site is present on the Fe-based catalyst surface and their number is constant; 2) methane, ethane and ethylene have different formation rate constants than other n-paraffins and 1-olefins; 3) following the chain-length-dependent 1-olefin desorption concept the rate constant of 1-olefin formation is exponentially dependent of carbon number (adding parameter c' , related to increase with carbon number in the activation energy of 1-olefin desorption step, results in $k_{\theta n} = k_{\theta,0} * e^{-c'*n}$); 4) elementary steps for the chain propagation, as well as the termination to n-paraffin, 1-olefin and 2-olefin are considered to be rate determining, while all others are considered to be quasi-equilibrated; 5) WGS reaction happens on a different type of site and is neglected. Model B has 13 intrinsic kinetic parameters (7 rate constants, 5 equilibrium constants and parameter c'), which are only dependent on reaction temperature and do not vary with pressure, reactant feed ratios or flow rates.

3.3 Estimation of model parameters

The optimal values of different model parameters were estimated by minimizing a multi-response objective function:

$$F_{obj} = \sum_{i=1}^{N_{resp}} \sum_{j=1}^{N_{exp}} w_{i,j} \times \left(\frac{R_{i,j}^{exp} - R_{i,j}^{cal}}{R_{i,j}^{exp}} \right)^2 \quad (1)$$

where N_{resp} is the number of responses (n-paraffin, 1-olefin and 2-olefin), N_{exp} is the number of experimental balances, $w_{i,j}$ is the weighting factor and $R_{i,j}$ is the formation rate of species i in a balance j . In

the case of selectivity model A, the parameters were estimated for each of the balances separately for C₁₋₂₀ hydrocarbons, while the parameter estimation for the LHHW model (model B) utilized all of the data points simultaneously. In order to speed up convergence and obtain meaningful values of model B parameters initial estimates of activation energies were constrained to a range of literature values and the parameter estimation is done using experimental hydrocarbon rates up to C₁₅.

Table 1: FTS reaction mechanism used in the derivation of model B

No.	Elementary reaction	Kinetic constant
1	CO + S ↔ CO-S	K ₁
2	H ₂ + 2S ↔ 2H-S	K ₂
3	CO-S + S ↔ C-S + O-S	K ₃
4	C-S + 2H-S ↔ CH ₂ -S + 2S	K ₄
5	O-S + 2H-S ↔ H ₂ O + 3S	K ₅
6 ^{RDS}	CH ₂ -S + H-S → CH ₃ -S + S	k ₆
	CH ₂ -S + CH ₃ -S → CH ₃ CH ₂ -S + S	
	CH ₂ -S + C _n H _{2n+1} -S → C _n H _{2n+1} CH ₂ -S + S	
7 ^{RDS}	CH ₃ -S + H-S → CH ₄ + 2S	k _{7M}
	C ₂ H ₅ -S + H-S → C ₂ H ₆ + 2S	k _{7E}
	C _n H _{2n+1} -S + H-S → C _n H _{2n+2} + 2S	k ₇
8 ^{RDS}	C ₂ H ₅ -S → C ₂ H ₄ + H-S	k _{8E}
	C _n H _{2n+1} -S → 1-C _n H _{2n} + H-S	k _{8n}
9 ^{RDS}	C _n H _{2n+1} -S → 2-C _n H _{2n} + H-S	k ₉

*Note: RDS – Rate determining step

4. Results and discussion

The accuracy of model predictions compared to the experimental data was obtained by statistical analysis with the mean absolute relative residual (MARR):

$$MARR = \sum_{i=1}^{N_{resp}} \sum_{j=1}^{N_{exp}} \left| \frac{R_{i,j}^{exp} - R_{i,j}^{cal}}{R_{i,j}^{exp}} \right| \times \frac{1}{N_{resp} \cdot N_{exp}} \times 100\% \quad (2)$$

The selectivity model A provided an excellent fit of the C₁-C₁₅ data with MARR of 23.6%. It showed the best fit at 260°C with MARR=18.7%, while MARR at 220 and 240°C were 33.8 and 29%, respectively. Illustration of model A results is given in Figure 2a. General trend is that the C₁₋₁₅ 1-olefins and n-paraffins are predicted very well (MARR_{n-par} = 20.6%, MARR_{1-ole} = 14.6%), while 2-olefins show a slightly worse fit (MARR_{2-ole} = 41.1%). This is because 2-olefins are present in small amounts and their experimental quantification is less accurate than that of 1-olefins and n-paraffins. Again, it should be pointed out that this model is an extension of Van der Laan and Beenackers' ORPDM (1999b) and the equations of model A for 1-olefin and n-paraffin formation are equivalent to those of the ORPDM. Parameter *c*, in the exponential dependency term, is estimated to be in the range 0.16-0.30 depending on process conditions and is consistent with previously reported values (Van der Laan and Beenackers, 1999a).

We also considered more complex reaction networks, involving a second type of active sites, with the possibility of hydrogenation and even reincorporation into the chain growth (similar to Nowicki and Bukur, 2001). However this approach only led to an increase in number of parameters without significant improvements in the quality of model predictions (Olewski, 2008).

The LHHW kinetic model B gives worse quantitative fit compared to model A with MARR_{n-par} = 33.8%, MARR_{1-ole} = 29.9% and MARR_{2-ole} = 56.3%. In general C₂-C₆ n-paraffins were under predicted. An F-test shows that model B gave a statistically meaningful fit of the data. Fit quality at one set of conditions is shown in Figure 2b. In addition model parameter values were tested and found to be consistent with all physicochemical tests. Estimated activation energy for n-paraffin is 91 kJ/mol and for 1-olefin increases linearly from 92 to 109 kJ/mol. These values are consistent with the previously reported values for Fe-based catalyst (Dictor and Bell, 1986). Lower formation rates of 2-olefins can be explained with high activation energy of 154 kJ/mol. Parameter *c'* for this model is in the 0.31-0.34 range, due to its temperature dependence (Todic et al. 2013).

The total hydrocarbon formation rates are obtained by summing up the rates of n-paraffins, 1-olefins and 2-olefins of the same carbon number. Figure 3 shows the comparison of model A and model B predictions of hydrocarbon product distribution, with the experimental data. Model A performed significantly better in the lower hydrocarbon range, while C₅₊ hydrocarbons (liquid products) were predicted well by both models.

Increasing growth probability with carbon number (changing slope in the ASF plot) was predicted by both models.

The 1-olefins are the dominant products in the C_2 - C_{10} range, but their formation decreases exponentially with carbon number. The formation of n-paraffins decreases much more gradually with carbon number than the 1-olefin formation and therefore they become the dominant product in the range above C_{10} . This causes for the so called “double alpha” to be observed in the ASF plot. Considering the shape of 1-olefin and n-paraffin product distribution it can be concluded that the apparent change of slope in the product distribution plot with carbon number, also known as the non-ASF behavior, is caused by the exponential decrease in the 1-olefin formation rate with carbon number. Therefore, the exponential dependency of carbon number in the 1-olefin formation rate equation is an essential part of any product distribution model. The reasons for this dependency are fundamental in nature and possible explanations are the chain length dependent 1-olefin desorption and the solubility, physisorption and/or diffusion enhanced 1-olefin readsorption. Both models provide a reasonable prediction of the non-ASF product distribution and the exponential decrease of OPR with increasing carbon number. However, additional theoretical and experimental studies are needed in order to discriminate between these effects.

The detailed LHHW models generally give an inferior fit of the data compared to selectivity models. However, considering that model B includes parameters, which were estimated over the entire data set (not for each balance individually as in the case of model A), the model fit can be considered as very good. In addition, it is worth emphasizing that model B can provide predictions for any of the conditions within the tested range. This is something that selectivity models are unable to do and this significantly limits practical applicability of selectivity models.

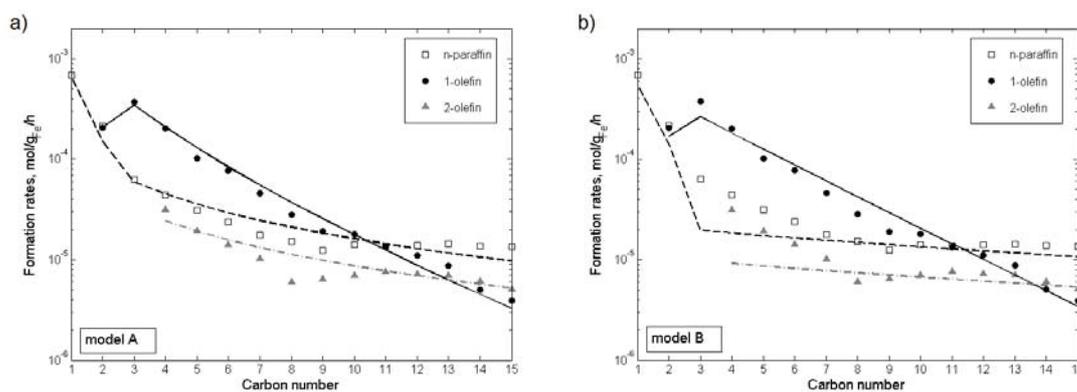


Figure 2: Comparison of experimental product formation rates (points) and model predictions (lines) at 533 K, 1.5 MPa, $H_2/CO = 0.67$, $SV = 4.0 \text{ NL/g}_{Fe}/h$ for: a) selectivity model A; b) LHHW kinetic model B

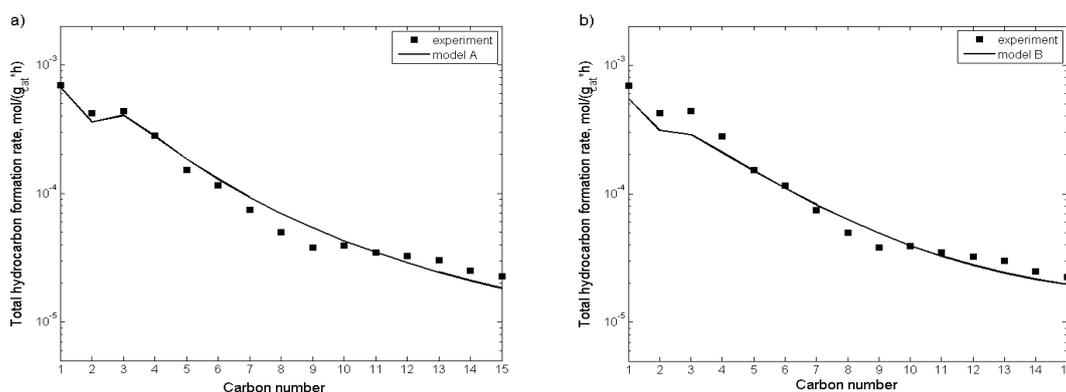


Figure 3: Comparison of experimental hydrocarbon product distributions (ASF plot) and model predictions at 533 K, 1.5 MPa, $H_2/CO = 0.67$, $SV = 4.0 \text{ NL/g}_{Fe}/h$ for: a) selectivity model A; b) LHHW kinetic model B

5. Conclusions

We compared different approaches to the Fischer-Tropsch Synthesis (FTS) product distribution modeling: the hydrocarbon selectivity model and the detailed LHHW kinetic model of hydrocarbon formation. Both

models showed a good ability to predict deviations from the ASF distribution and the changes in OPR with carbon number. Naturally, in addition to being relatively easy to use, the hydrocarbon selectivity model offered better precision for a given set of process conditions since the model parameters were optimized using experimental data for this particular set of conditions only. The model A (an extended ORPDM of Van der Laan and Beenackers, 1999b) prediction of n-paraffin and 1-olefin formation rates is very good, but is less accurate for 2-olefins (in part due to difficulties in their quantification). Our detailed kinetic model B, based on the carbide FTS mechanism, showed a good fit of all products, which is only slightly less accurate than that obtained with model A. Considering that the parameters of model B were estimated from all available data points, these parameters are likely to be more reliable for a broad range of industrially relevant conditions. The parameters of the detailed LHHW kinetic models are intrinsic kinetic constants and their physicochemical meaningfulness can be tested, giving them a distinct advantage over the pseudo-kinetic parameters of hydrocarbon selectivity models.

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