

Article

A Comprehensive Kinetic Model of Fischer-Tropsch Synthesis over Supported Cobalt Catalyst

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Abstract: A comprehensive kinetic model of the Fischer-Tropsch synthesis (FTS) is developed in a fixed bed reactor under operating conditions (temperature, 230–235°C, pressure, 20–25 bar, gas hourly space velocity, 4000–5000 cm³(STP)/h/g_{catalyst}, H₂/CO feed molar ratio, 2.1) over a Co based catalyst. Reaction rate equations based on Eley-Rideal (ER) type model for initiation step and Langmuir-Hinshelwood-Hougen-Watson (LHHW) type model for propagation and termination steps of the FTS reactions have been considered and the readsorption of olefins were taken into account. The model that was reported in the literature was modified in order to explain many significant deviations from the ASF distribution. Optimum parameters have been obtained by Genetic Algorithms (GA). The calculated activation energies to produce n-paraffins and 1-olefins were in the range of 82.24 to 90.68 kJ/mol and 100.66 to 105.24 kJ/mol, respectively. The hydrocarbon distribution in FTS reactions was satisfactorily predicted particularly for paraffins.

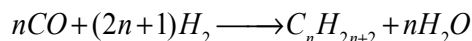
Keywords: Fischer-Tropsch synthesis; kinetics model; cobalt based catalyst

1. Introduction

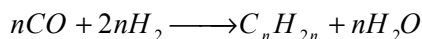
The Fischer-Tropsch synthesis reaction has seen a revival of interest due to the recent volatile price of oil recently. The result of the complex reactions of FTS is a wide distribution of products, namely straight chain hydrocarbons, which can be upgraded to produce gasoline, synthetic diesel, jet fuels, lubricants, and waxes. The FT synthesis is a surface polymerization reaction catalyzed commercially by both iron and cobalt catalyst at pressures from 10 to 60 bar and temperatures from 200 to 300°C [1]. The process includes a lot of desirable chemical reactions which produce paraffins, olefins and alcohols and some unfavorable and unwanted reactions result in aldehydes, ketones, acids, esters, carbon, etc. [2]. The hydrocarbons formation might be written as the stoichiometric equations.

Main reactions:

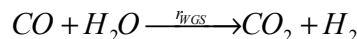
Formation of paraffins



Formation of olefins

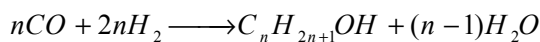


Water-gas shift reaction

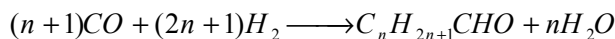


Side reactions:

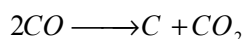
Formation of alcohols



Formation of aldehydes



Boudouard reaction



In order to achieve the required products, many factors influence the transition process, including operating conditions (reactor temperature and pressure, gas hourly space velocity, H₂/CO

feed molar ratio), type of reactor and catalyst and its support. Depending on these factors desirable product could be attained.

Numerous studies on the FTS reaction mechanism and kinetics have been conducted to date. Many attempts have been done for the rate equations describing the overall FT reaction rate [3-10]. In spite of these efforts there is a lack of comprehensive kinetic models which could be used for process simulation and optimization studies. Great efforts have been done to elucidate the FTS reaction mechanism by Yang et al. [9] over Fe catalyst. However, only few comprehensive models on the polymerization mechanism of the cobalt based Fischer-Tropsch reaction are described in literature [11-13]. The most important works on comprehensive kinetic model over cobalt catalyst have been done by Visconti [14], Fontenelle and Fernandes [11] and Kwack [15]. In these works, a single reaction rate has been assumed for initiation step and its entire reactions, which can be one of the weaknesses of these complete kinetic models.

Achieving desirable product distribution is one of the challenging and serious problems for FT synthesis. The first attempt to describe the FT product distribution has been done by Anderson known as the Anderson-Schulz-Flory (ASF) distribution [16]. In the ASF model, since polymerization mechanism dominates the process [17], products of FT synthesis approximately conform to a statistical hydrocarbon distribution. However, significant deviations from the ASF distribution are reported in the literature such as higher than expected yield of methane, lower selectivity of two carbon atoms C₂ (particularly ethylene) and decreasing slopes in the ASF diagram. Several reasons have been reported for these deviations such as the existence of different chain termination reactions and secondary reactions namely incorporation into growing chains, rapid readsorption, hydrogenation to ethylene or hydrogenolysis and the existence of two or multiple catalytic active sites particularly for Fe catalyst [9,18-20].

In this study, some modifications have been made to the kinetic model proposed by Yang et al. [9] in order to improve the performance of the kinetics model over Co catalyst. First, due to significant deviations from the ASF distribution for C₁ (methane) and C₂ (ethane and ethylene), separate reactions for each component was assumed. Secondly the water gas shift reaction was supposed to be negligible. Then, a comprehensive mathematical model was developed for the Fischer-Tropsch synthesis considering the olefin readsorption mechanisms and the ER type model for initiation step and LHHW type model propagation and termination steps.

2. Materials and Methods

2.1. Experimental

An excellent set of data for the Fischer-Tropsch reaction over a cobalt catalyst has been used for the calculation that is reported by Visconti et al. [14]. The reactions were performed in a fixed bed microreactor loaded with 2 gr of a Co/Al₂O₃ state-of-art catalyst in powder form (diameter 75 μ m) at temperature, 230–235°C; pressure, 20–25 bar; space velocity of, 4000–5000 cm³(STP)/h/g_{catalyst} and H₂/CO feed molar ratio, 2.1. The operating conditions for each run are presented in Table 1.

Table 1 - Operating conditions

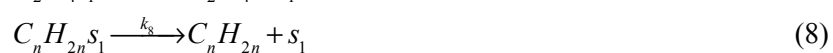
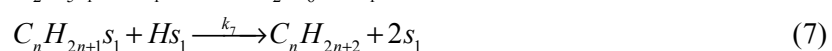
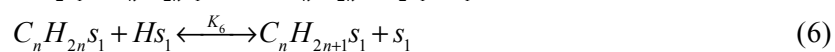
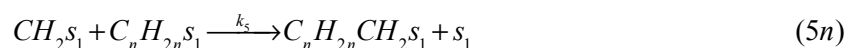
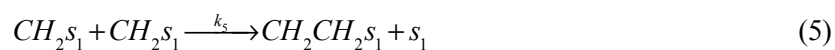
No.	P(bar)	H ₂ /CO (mol/mol)	T(°C)	GHSV (cm ³ (STP)/h/g _{cat})
1	20	2.1	230	5000
2	20	2.1	230	4000
3	20	2.1	235	5000
4	25	2.1	230	5000

2.2. Reaction scheme

Since the FT reactions were assumed to conform surface-catalyzed polymerization mechanism, they could be divided in three steps: 1) initiation step (the formation of monomer) 2) propagation step (joining monomers together and chain growth) and 3) termination step (consisting chain termination and readsorption of olefins).

In first step kinetic rates have been considered to be based on Eley-Rideal (ER) type. Therefore, carbon monoxide is absorbed on the catalytic active sites and reacts with hydrogen in the gas phase leading to formation of methylene species (CH_2^*). Propagation step also takes place by methylene insertion into the metal-alkylidene bond. For this step kinetic models based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) type were developed. In addition termination can occur by desorption of olefins from the catalyst surface or hydrogenation to form paraffins. Secondary reactions have also been considered in this proposed kinetic model. The olefins can readsorb on the active sites and terminate to paraffins by hydrogenation or propagate by methylene insertion into the metal-alkylidene bond.

This kinetic model has been represented by the following reactions:



Where, s_1 is an active site on the surface of catalyst. One reaction rate equation has been assumed for each elementary reaction over catalyst surface, leading a better prediction of initiation step and methane formation. It has also been assumed that the rate determining steps (RDSs) are steps of 5, 7 and 8. The remaining steps can be considered quasi equilibrium. The rates of formation of methane, ethane, ethylene, paraffins and olefins can be written as follow:

$$R_{\text{CH}_4} = k_{7M} \cdot [\text{CH}_3s_1] \cdot [\text{H}s_1] = k_{7M} \cdot K_6 \cdot [\text{CH}_2s_1] \cdot [\text{H}s_1]^2 / [s_1]$$

$$R_{\text{C}_2\text{H}_6} = k_{7E} \cdot [\text{C}_2\text{H}_5s_1] \cdot [\text{H}s_1] = k_{7E} \cdot K_6 \cdot [\text{C}_2\text{H}_4s_1] \cdot [\text{H}s_1]^2 / [s_1]$$

$$R_{\text{C}_n\text{H}_{2n+2}} = k_7 \cdot [\text{C}_n\text{H}_{2n+1}s_1] \cdot [\text{H}s_1] = k_7 \cdot K_6 \cdot [\text{C}_n\text{H}_{2n}s_1] \cdot [\text{H}s_1]^2 / [s_1]$$

$$R_{\text{C}_2\text{H}_4} = k_{8E}^+ [\text{C}_2\text{H}_4s_1] - k_{8E}^- P_{\text{C}_2\text{H}_4} \cdot [s_1]$$

$$R_{\text{C}_n\text{H}_{2n}} = k_8^+ [\text{C}_n\text{H}_{2n}s_1] - k_8^- P_{\text{C}_n\text{H}_{2n}} \cdot [s_1]$$

By solving the rate equations, rate expressions of the hydrocarbon formation can be written in the following form:

For methane:

$$R_{CH_4} = k_{7M} K_4 K_6 K_3' \frac{P_{H_2}^3 P_{CO}}{P_{H_2O}} / \left[1 + \sqrt{K_4 P_{H_2}} + K_1 P_{CO} + K_3' \frac{P_{H_2}^2 P_{CO}}{P_{H_2O}} + K_2 P_{H_2} K_1 P_{CO} + K_6 K_3' K_4^{0.5} \frac{P_{H_2}^{2.5} P_{CO}}{P_{H_2O}} + [C_2 H_4 s_1] / [s_1] \right. \\ \left. + [C_2 H_4 s_1] / [s_1] \cdot \sum_{i=3}^n \prod_{i=3}^n \alpha_i + [C_2 H_5 s_1] / [s_1] + K_6 \sqrt{K_4 P_{H_2}} \cdot [C_2 H_4 s_1] / [s_1] \cdot \sum_{i=3}^n \prod_{i=3}^n \alpha_i \right]^2$$

For ethane:

$$R_{C_2 H_6} = k_{7E} K_6 K_4 P_{H_2} \cdot [C_2 H_4 s_1] / \left[1 + \sqrt{K_4 P_{H_2}} + K_1 P_{CO} + K_3' \frac{P_{H_2}^2 P_{CO}}{P_{H_2O}} + K_2 P_{H_2} K_1 P_{CO} + K_6 K_3' K_4^{0.5} \frac{P_{H_2}^{2.5} P_{CO}}{P_{H_2O}} + [C_2 H_4 s_1] / [s_1] \right. \\ \left. + [C_2 H_4 s_1] / [s_1] \cdot \sum_{i=3}^n \prod_{i=3}^n \alpha_i + [C_2 H_5 s_1] / [s_1] + K_6 \sqrt{K_4 P_{H_2}} \cdot [C_2 H_4 s_1] / [s_1] \cdot \sum_{i=3}^n \prod_{i=3}^n \alpha_i \right]$$

For n-paraffins: (n≥3)

$$R_{C_n H_{2n+2}} = k_7 K_6 K_4 P_{H_2} \cdot [C_2 H_4 s_1] \cdot \prod_{j=3}^n \alpha_j / \left[1 + \sqrt{K_4 P_{H_2}} + K_1 P_{CO} + K_3' \frac{P_{H_2}^2 P_{CO}}{P_{H_2O}} + K_2 P_{H_2} K_1 P_{CO} + K_6 K_3' K_4^{0.5} \frac{P_{H_2}^{2.5} P_{CO}}{P_{H_2O}} \right. \\ \left. + [C_2 H_4 s_1] / [s_1] + [C_2 H_4 s_1] / [s_1] \cdot \sum_{i=3}^n \prod_{i=3}^n \alpha_i + [C_2 H_5 s_1] / [s_1] + K_6 \sqrt{K_4 P_{H_2}} \cdot [C_2 H_4 s_1] / [s_1] \cdot \sum_{i=3}^n \prod_{i=3}^n \alpha_i \right]$$

For ethylene:

$$R_{C_2 H_4} = k_{8E}^+ \cdot [C_2 H_4 s_1] - k_{8E}^- P_{C_2 H_4} / \left[1 + \sqrt{K_4 P_{H_2}} + K_1 P_{CO} + K_3' \frac{P_{H_2}^2 P_{CO}}{P_{H_2O}} + K_2 P_{H_2} K_1 P_{CO} + K_6 K_3' K_4^{0.5} \frac{P_{H_2}^{2.5} P_{CO}}{P_{H_2O}} + [C_2 H_4 s_1] / [s_1] \right. \\ \left. + [C_2 H_4 s_1] / [s_1] \cdot \sum_{i=3}^n \prod_{i=3}^n \alpha_i + [C_2 H_5 s_1] / [s_1] + K_6 \sqrt{K_4 P_{H_2}} \cdot [C_2 H_4 s_1] / [s_1] \cdot \sum_{i=3}^n \prod_{i=3}^n \alpha_i \right]$$

For 1-olefins: (n≥3)

$$R_{C_n H_{2n}} = k_8^+ \cdot [C_2 H_4 s_1] / [s_1] \cdot (1 - \beta_n) \cdot \prod_{j=3}^n \alpha_j / \left[1 + \sqrt{K_4 P_{H_2}} + K_1 P_{CO} + K_3' \frac{P_{H_2}^2 P_{CO}}{P_{H_2O}} + K_2 P_{H_2} K_1 P_{CO} + K_6 K_3' K_4^{0.5} \frac{P_{H_2}^{2.5} P_{CO}}{P_{H_2O}} + [C_2 H_4 s_1] / [s_1] \right. \\ \left. + [C_2 H_4 s_1] / [s_1] \cdot \sum_{i=3}^n \prod_{i=3}^n \alpha_i + [C_2 H_5 s_1] / [s_1] + K_6 \sqrt{K_4 P_{H_2}} \cdot [C_2 H_4 s_1] / [s_1] \cdot \sum_{i=3}^n \prod_{i=3}^n \alpha_i \right]$$

where

$$K_3' = K_1 \cdot K_2 \cdot K_3$$

$$\alpha_n = \frac{k_5 \cdot K_3' \cdot \frac{P_{H_2}^2 P_{CO}}{P_{H_2O}} \cdot [s_1]}{k_5 \cdot K_3' \cdot \frac{P_{H_2}^2 P_{CO}}{P_{H_2O}} \cdot [s_1] + k_7 \cdot K_6 \cdot K_4 \cdot P_{H_2} \cdot [s_1] + k_8^+ \cdot (1 - \beta_n)} \quad n \geq 3$$

$$\alpha_A = \frac{k_5 \cdot K_3' \cdot \frac{P_{H_2}^2 P_{CO}}{P_{H_2O}} \cdot [s_1]}{k_5 \cdot K_3' \cdot \frac{P_{H_2}^2 P_{CO}}{P_{H_2O}} \cdot [s_1] + k_7 \cdot K_6 \cdot K_4 \cdot P_{H_2} \cdot [s_1] + k_8^+}$$

$$\beta_n = (k_8^- / k_8^+) \times \left\{ P_{C_n H_{2n}} \cdot [s_1] / \left[\alpha_A^{n-2} \cdot [C_2 H_4 s_1] + \frac{k_8^-}{k_5 \cdot K_3' \cdot \frac{P_{H_2}^2 P_{CO}}{P_{H_2O}} \cdot [s_1] + k_7 \cdot K_6 \cdot K_4 \cdot P_{H_2} \cdot [s_1] + k_8^+} \right. \right. \\ \left. \left. \sum_{i=3}^n \left(\alpha_A^{i-2} P_{C_{(n-i+3)} H_{2(n-i+3)}} \right) \cdot [s_1] \right] \right\} \quad n \geq 3$$

2.3. Reactor Model

The model of the fixed-bed reactor used in this kinetic study can be described as:

$$\frac{dF_i}{dW_{cat}} = \sum_{k=1}^{NR} \alpha_{i,k} \cdot r_k$$

$$W_{cat} = 0, \quad F_i = F_{i,0}$$

Where $\alpha_{i,k}$ is the stoichiometric coefficient for the i th component in reaction k th, and r_k is the rate of reaction for each component. In addition number of the reactions is shown as NR . Rate constants and activation energies for each reaction are calculated according to the Arrhenius equation:

$$k_i(T) = k_{i,0} \cdot \exp\left(\frac{E_i}{RT}\right)$$

2.4. Parameter Estimation

The estimation of the kinetic parameters has been performed by the minimization of the objective function S :

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

Where N_{resp} is the number of responses and N_{exp} is the number of experiments. In addition $F_{ij,exp}$ is the observed value of i th response for j th experiment, whereas $F_{ij,cal}$ represents its calculated value of i th response for j th experiment [21]. Optimum parameters have been obtained by Genetic algorithms (GA).

Total deviation of the fitted response values from the experimental one has been measured by mean absolute relative residual (MARR) expressed as a percentage of the total:

$$MARR = \sum_{i=1}^{N_{resp}} \sum_{j=1}^{N_{exp}} \left| \frac{F_{ij,cal} - F_{ij,exp}}{F_{ij,exp}} \right| \frac{1}{N_{resp} \cdot N_{exp}} \times 100$$

3. Results and Discussion

The result of estimated parameters including activation energies and rate constants are listed in Table 2. To verify the accuracy of the results and the calculated parameters, several criteria were considered such as being positive obtained parameters, fitting model results with experimental data and physically meaningful values of the model. As shown in Table 2, the activation energy for methane formation is 84.60 kJmol⁻¹, which is in good agreement with that reported value by Vannice [22] (89 kJmol⁻¹) and smaller than reported value for paraffin (90.68 kJmol⁻¹). It can explain the higher selectivity of methane in comparison with those of other paraffins. The activation energy for ethylene is 105.24 kJ mol⁻¹ which is larger than that for other olefins (100.66 kJmol⁻¹) which could be a reason for the lower selectivity of ethylene among other olefins.

Table 2 - Estimated kinetic parameters in the present study

Parameter	Value	Unit	Parameter	Value	Unit
K ₁	0.4888	bar ⁻¹	E _{7E}	82.2410	kJ mol ⁻¹
K ₂	0.9336	bar ⁻¹	k _{7,0}	8.6151×10 ⁸	mmol s ⁻¹ g ⁻¹
K ₃	1.6472		E ₇	90.680	kJ mol ⁻¹
K ₄	0.8534	bar ⁻¹	k _{8E,0}	9.6428×10 ⁵	mmol s ⁻¹ g ⁻¹ bar ⁻¹
k _{5,0}	7.1821×10 ⁴	mmol s ⁻¹ g ⁻¹ bar ⁻¹	E _{8E}	105.24	kJ mol ⁻¹
E ₅	60.247	kJ mol ⁻¹	k _{8,0}	8.237×10 ⁵	mmol s ⁻¹ g ⁻¹
K ₆	0.0989		E ₈	100.66	kJ mol ⁻¹
k _{7M,0}	7.0452×10 ⁸	mmol s ⁻¹ g ⁻¹ bar ⁻¹	k _{8E⁻}	0.0142	mmol s ⁻¹ g ⁻¹ bar ⁻¹
E _{7M}	84.602	kJ mol ⁻¹	k _{8⁻}	0.0377	mmol s ⁻¹ g ⁻¹ bar ⁻¹
k _{7E,0}	5.1414×10 ⁷	mmol s ⁻¹ g ⁻¹ bar ⁻¹			

The estimated activation energies of the hydrocarbon formation are also within those reported in the literature [9,23] (80-90 kJ mol⁻¹ for paraffins and 100-110 kJ mol⁻¹ for olefins). In addition, the calculated activation energy for olefins formation is smaller than that for the paraffins which can explain the lower selectivity of olefins in comparison with of other paraffins.

Figures 1-4 show a comparison between the experimental and calculated product distributions for experimental data 1-4. Our results show that the calculated quasi equilibrium reaction rate constants are approximately 1. It can be concluded that the initial assumption for these reactions was close to reality. Moreover, it shows that the calculated results are in correspondence with those of experimental data and this comprehensive kinetic model satisfactorily predicts deviations from the ASF model.

The average error calculated on these data for total hydrocarbon, olefin and paraffin are 15.4, 27.5, 12.5%, respectively which are satisfactory and comparable to those of Visconti and Kwack [14,15], especially for paraffins, better results were observed. However, more investigation needs to be done for the model of olefin formation.

On the other hand, one of the advantages of this model is calculation up to carbon number 49 for paraffins, whereas it was 20 for model offered by Yang [9]. In addition, the other advantage of the proposed model in comparison to Visconti is that for every single reaction in initial step, a separate reaction rate was assumed.

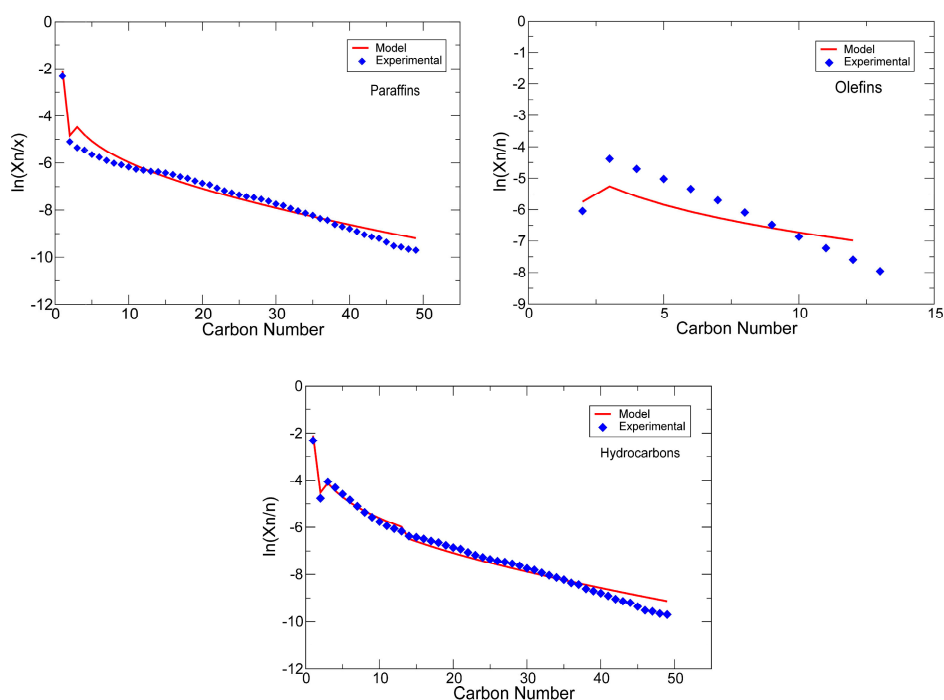


Figure 1 - Carbon number distributions of paraffin, olefin and total hydrocarbon for experiments 1: P= 20 (bar), H₂/CO= 2.1 (mol/mol), T=230 (°C) and GHSV= 5000 (cm³(STP)/h/g_{catalyst}).

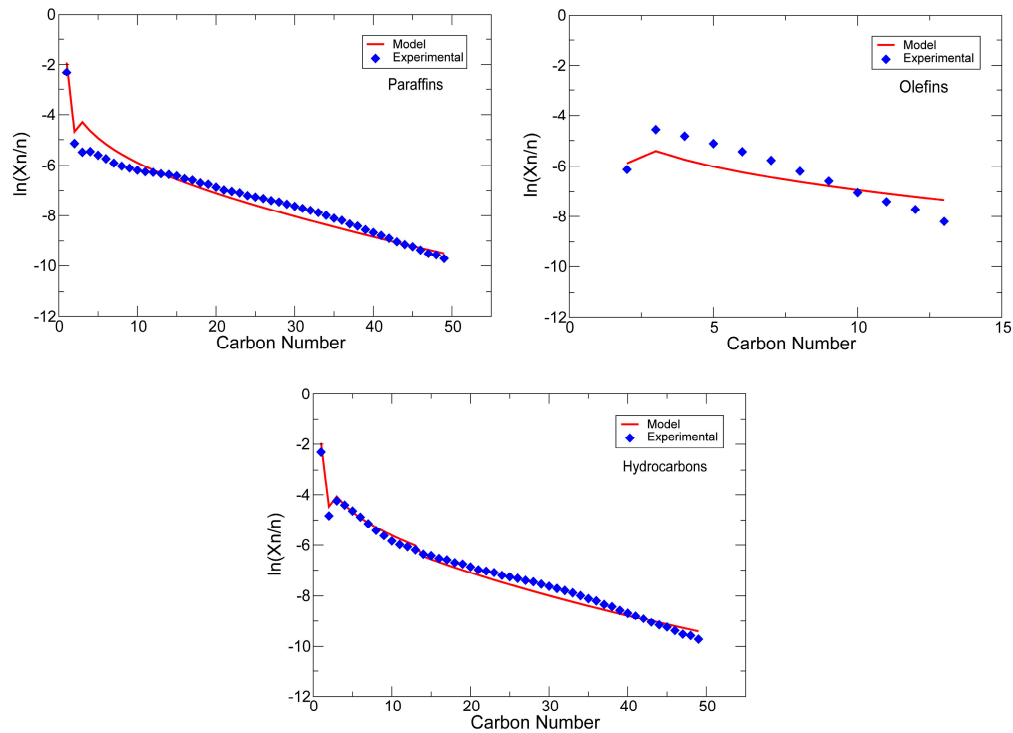


Figure 2 - Carbon number distributions of paraffin, olefin and total hydrocarbon for experiments 2: P= 20 (bar), $H_2/CO=2.1$ (mol/mol), T=230(°C) and GHSV= 4000 ($cm^3(STP)/h/g_{catalyst}$).

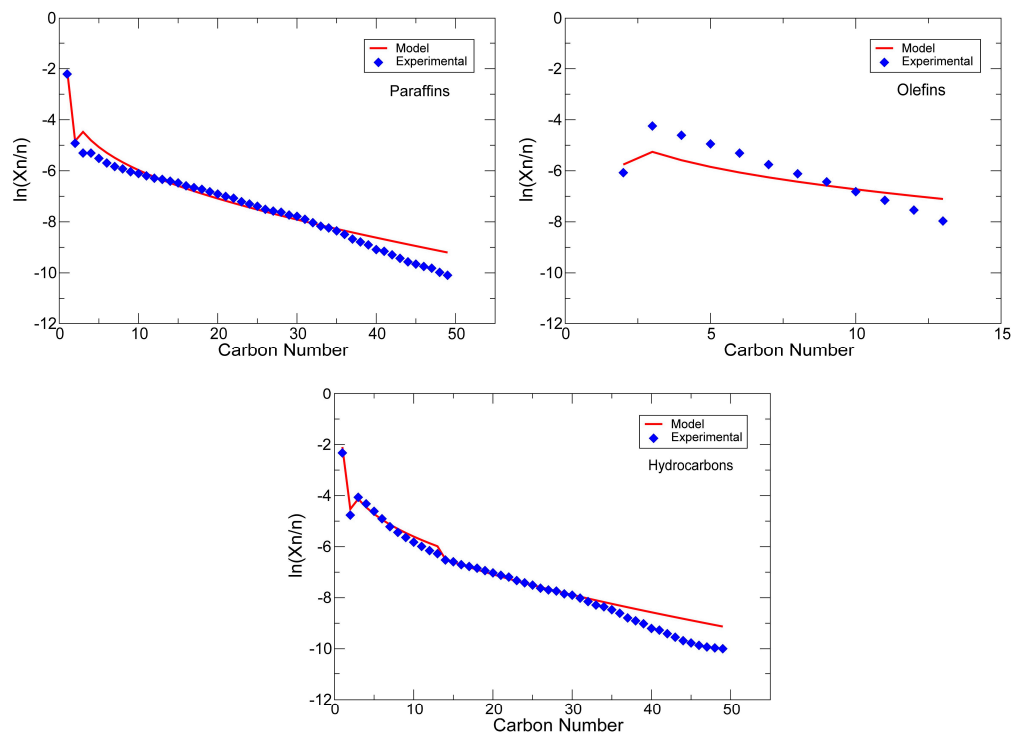


Figure 3 - Carbon number distributions of paraffin, olefin and total hydrocarbon for experiments 3: P= 20 (bar), $H_2/CO=2.1$ (mol/mol), T=235 (°C) and GHSV= 5000 ($cm^3(STP)/h/g_{catalyst}$).

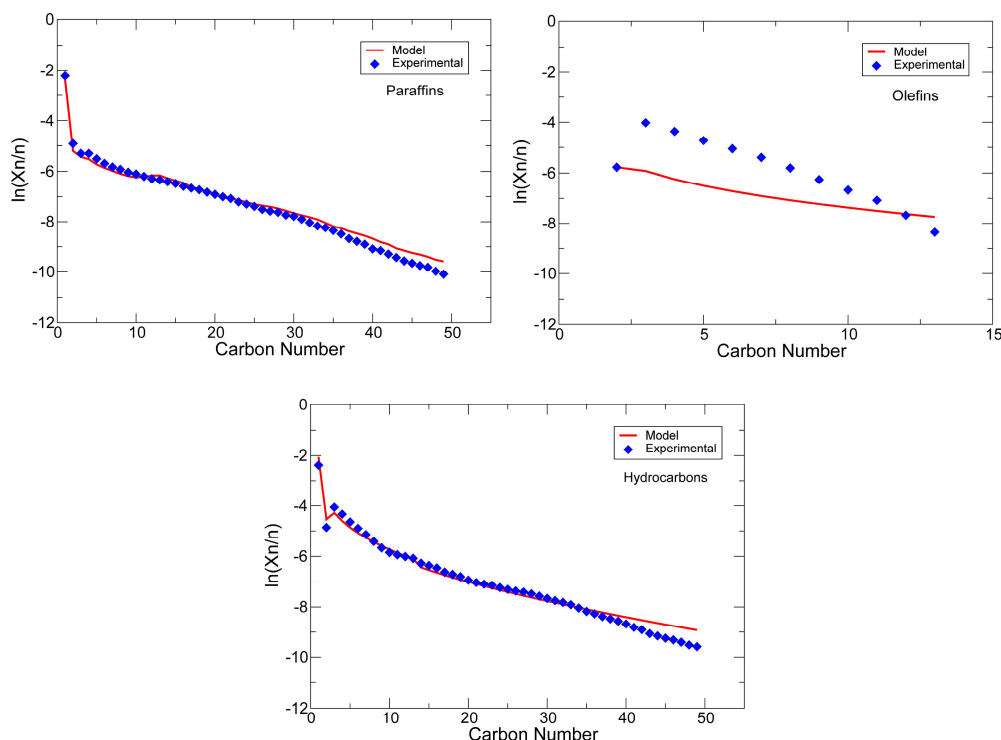


Figure 4 - Carbon number distributions of paraffin, olefin and total hydrocarbon for experiments 4: $P=25$ bar, $H_2/CO=2.1$ (mol/mol), $T=230(^{\circ}C)$ and $GHSV=5000$ ($cm^3(STP)/h/g_{catalyst}$).

5. Conclusions

A comprehensive mathematical model was developed for the Fischer-Tropsch synthesis reaction considering the olefin readsorption mechanisms and the ER type model for initiation step and LHHW type model propagation and termination steps. The developed model could fairly describe the product distribution up to $n = 49$ for paraffins and up to $n = 13$ for olefins.

Conflicts of Interest: The authors declare no conflict of interest.

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