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Kinetic modeling of the Fischer–Tropsch synthesis in a slurry phase bubble column reactor using Langmuir–Freundlich isotherm

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ABSTRACT

We employed the Langmuir–Freundlich isotherm for Fischer–Tropsch synthesis as a modification of the commonly used Langmuir isotherm, because the Langmuir–Freundlich isotherm can predict the adsorption of gases at solid absorbent more accurately than Langmuir isotherm. Several mechanisms for kinetic modeling of the Fischer–Tropsch synthesis have been developed in which the Langmuir isotherm is the basis of kinetic modeling of the catalytic reactions. Using Langmuir–Freundlich–Hinshelwood (LFH) model, the results of CO conversion in a slurry bubble column reactor show a very good agreement with the experiment. Moreover, we used fugacity instead of the pressure that leads to improve the accuracy of the new kinetic model. The fugacity term has been considered here by using Peng–Robinson Equation of State, modified by Gasem et al. The new kinetic model with fugacity is applied for modeling of a slurry bubble column reactor over the wide range of the reactor conditions of 523–563 K, 0.95–2.55 MPa and H_2/CO ratio: 0.65–1.51. The results of the new kinetic LFH-fugacity model shows the Average Absolute Deviation percentage (AAD%) of 4.25% for the CO conversion while this value is about 10.89% using the original equation based on Langmuir isotherm.

1. Introduction

Gas to liquid technology, Fischer Tropsch Synthesis (FTS), plays an important role in the production of ultra-clean transportation fuels, chemicals, and other hydrocarbon products. On the other hand, it is suitable for addressing the problem of environmental pollution and remote gas utilization [1] that Gas to Liquid (GTL) process may be accounted as an alternative solution to environmental issues. The FTS permits one to produce high quality fuel products that can be further processed to specific boiling-point fractions. Different types of reactor such as slurry three phase catalytic reactors, fluidized bed and fixed bed reactors have been utilized for FTS. The slurry bubble column reactors, SBC, have some advantages mainly include: nearly isothermal operation, small solids particle size that results in good productivity, good interface contacting, low pressure drop, and low construction and operation cost [2]. Moreover, although in view of the very different fluid dynamic conditions prevailing in the lab-scale slurry reactor and in the industrial slurry bubble column, one may also consider that the kinetic modeling of the FT process in SBC reactors is important in scale up to design industrial plants. In this area, many reactor kinetic models for the FTS in SBC reactors have been developed such as, recently two bubble class theory by Van der Laan et al. [3], De Swart [4], Maretto and Krishna [5] and Wang et al. [2]. According to the two bubble class theory, the gas phase is split up into two large and small bubbles class that the large bubbles rise straight up through the column as a plug flow, but the small bubbles are entrained in the slurry phase that have back mixing characteristics of the slurry phase [5].

The kinetics of the FT synthesis has been the main goal of many researches so that the different mechanisms have been proposed to analyze this process quantitatively. Huff and Satterfield [6], Zimmerman and Bukur [7], van der Laan and Beenackers [8] and the others have developed the kinetic equations for iron and cobalt catalysts in FT synthesis. These kinetic models are generally presented into two approaches [9]. One method describes the syngas consumption rate by using empirical equations or lumped kinetics on the basis of FTS reaction mechanism [10]. In the other approach based on the different mechanisms, the equations are developed to calculation of the product distribution of hydrocarbons. In FT synthesis, the product distribution data is needed for modeling and design of reactors, but due to lack of information about the polymerization like kinetics of FTS, a few researches have been worked in this field. Polymerization occurs through initiation, propagation and termination steps. Anderson–Schulz–Flory (ASF) theory is the first model that is widely used for product distribution in FTS [9], but many researchers reported deviation from this theory. Several studies have focused on improvement of product distribution model [11] and some of them have been successful. In this work, we follow the first approach to modeling of the CO conversion.

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The commonly used reaction rate equations for the FTS are based on Langmuir–Hinshelwood isotherm. In this work the Langmuir–Freundlich–Hinshelwood isotherm is used to develop a new kinetic model for both Fischer–Tropsch Synthesis and Water–Gas Shift reactions. Although the Langmuir–Freundlich isotherm should actually be named the Sips isotherm [12], but it seems the name of Freundlich isotherm is used more common.

In the most of the models a simplified model for the vapor–liquid equilibrium was used that the liquid phase has been assumed as an ideal solution. However, due to high pressure and presence of polar species such as water vapor, CO and CO_2, the nonideality of vapor phase may be taken into account to improve the accuracy of the modeling of FT reactors. Accordingly, the main objective of this work is to develop a new reaction rate equation for FTS that can correlate the CO conversion more accurate than the previous models such as Langmuir–Hinshelwood. Thus, the Langmuir–Freundlich isotherm is used to develop a new kinetic model for both Fischer–Tropsch and water–gas shift reactions. Moreover, to improve the accuracy of the results, the fugacity instead of the partial pressure of the species in the gas phase is used.

2. Fischer–Tropsch kinetic model

The main reactions of the Fischer–Tropsch synthesis for synthesis gas (syngas) conversion are presented as [11,13]:

$$CO + 2H_2 \rightarrow -(CH_2)- + H_2O \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

where the first and second equations are the Fischer–Tropsch, FT, and water–gas shift, WGS, reactions, respectively. It should be mentioned that using the iron catalyst, the WGS reaction is used in developing of the rate equation; nevertheless in the presence of cobalt catalyst this reaction may be neglected. Thus, the WGS reaction has been taken into account in this study, because the experimental data used in this work is based on the Fe catalyst. An accurate kinetic model for the both reactions allows one to estimate the CO conversion in a bubble slurry column reactor and correlate the experimental data more accurately. The reaction mechanism of Fischer–Tropsch Synthesis is similar to a polymerization reaction mechanism that includes initiation, propagation and termination stages. Most of the kinetic models, which have been applied for FT reaction, use the Langmuir isotherm such as Langmuir–Hinshelwood kinetic model that it considers the equilibrium mechanism of adsorption and desorption of reactants and products at the catalyst surface. The deficiency of these models is using Langmuir isotherm that results no accurate correlation, particularly, at high pressures. So using the Langmuir–Freundlich isotherm permits one to develop a new kinetic model for both FT and WGS reaction rates that can be applied to correlation of the CO conversion with more accurate results than the usual Langmuir–Hinshelwood kinetic model. Similar to development of the Langmuir–Hinshelwood model, during the hydrocarbon formation, using Langmuir–Freundlich, the following equations should be written for the adsorption and desorption at the catalyst surface of the absorbent as [14]:

$$\left(\frac{dn_A}{dt}\right)_{ads.} = K(1-\theta_A)^n P_A \tag{3}$$

$$\left(\frac{dn_A}{dt}\right)_{des.} = K'\theta_A^n \tag{4}$$

where parameter “n” is the Freundlich parameter, P_A is the partial pressure of species A and θ the surface coverage fraction, so at equilibrium one can write as:

$$K(1-\theta_A)^n P_A = K'\theta_A^n \tag{5}$$

Thus, by extending of the above relation one can obtain the Freundlich isotherm as:

$$\theta_A = \frac{K_A.P_A^{1/n}}{(1+K_A.P_A)^{1/n}}. \tag{6}$$

On the other hand, using Freundlich isotherm for the equilibrium reactions of adsorption and desorption, so for the chemisorptions mechanism of the FT synthesis one may express as:

$$H_2 + 2* \leftrightarrow 2H* \qquad K_H P_{H_2}(1-\sum\theta)^{2n} = \theta_H^{2n} \tag{7}$$

$$CO + * \leftrightarrow CO* \qquad K_{CO}P_{CO}(1-\sum\theta)^n = \theta_{CO}^n \tag{8}$$

$$CO* + * \leftrightarrow C* + O* \qquad K_C\,\theta_{CO}^n(1-\sum\theta)^n = \theta_C^n\,\theta_O^n \tag{9}$$

where the asterisk and θ denote the active sites and the surface coverage fraction, respectively. Using the Langmuir–Freundlich isotherm, the equilibrium equations between adsorption and desorption for hydrogen and carbon monoxide can be written as mentioned. Among the adsorbed species during chemisorptions, CH, CH_2 and OH coverage is too little so that these species can be neglected. As a result one could write the total area coverage fractions as:

$$\sum\theta = \theta_H + \theta_C + \theta_O + \theta_{CO}. \tag{10}$$

During the FT reactions, the rate of termination is much less than the propagation rate and may be ignored. The propagation of hydrocarbon chain is described as$C+H\rightarrow CH$ and the oxygen desorption from the surface is defined as$H+O\rightarrow OH$. So the reaction rate for the propagation reaction can be written as below:

$$r_{CO} = r_{C,org} = r_{C\rightarrow CH} = k_{C\rightarrow CH}\theta_H\theta_C. \tag{11}$$

On the other hand, the rate of desorption of oxygen from the surface of catalyst is expressed as:

$$r_{C,org} = r_{o-removal} = k_O\theta_H\theta_O. \tag{12}$$

So by combining Eqs. (7–9), (11) and (12), the area coverage fraction of species can be written as:

$$\theta_H = K_H \cdot P_{H_2}^{1/2n}(1-\sum\theta) \tag{13}$$

$$\theta_C = \frac{K_C\,.K_O\,.K_{CO}\,.K_H\,.P_{CO}^{1/n}\,.P_{H_2}^{1/2n}\,.(1-\sum\theta)^3}{r_{C,Org}} \tag{14}$$

$$\theta_O = \frac{r_{C,Org}}{K_O\,.\theta_H} = \sqrt{\frac{k_{C\rightarrow CH}k_C k_{CO}}{k_O}}P_{CO}^{1/2n}(1-\sum\theta) \tag{15}$$

$$\theta_{CO} = K_{CO}^{1/n}\,.P_{CO}^{1/n}(1-\sum\theta). \tag{16}$$

Finally, substituting Eqs. (13–15) into Eqs. (11) and (12) and finding the sum of the area fractions of species, one can obtain the rate equation for the CO conversion in FT synthesis as:

$$r_{CO} = \frac{k_{FT}P_{CO}^{1/2n}P_{H_2}^{1/2n}}{\left[1 + K_1P_{H_2}^{1/2n} + K_2P_{CO}^{1/2n} + K_3P_{CO}^{1/n}\right]^2} \tag{17}$$