A study on vapour-liquid equilibria in Fischer-Tropsch synthesis

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Abstract

Slurry phase Fischer-Tropsch synthesis is an important and promising route to produce clean fuels and valuable long chain hydrocarbons from synthesis gas. An important phenomenon in these kinds of reactors is the vapour-liquid equilibrium. Due to the complexity both in the reaction and hydrodynamics of these reactors, most of the reported work are on hydrodynamics and then on reaction and less attention has been paid to the vapour-liquid equilibria. This work shows an effort to present a reliable method for phase equilibria in slurry reactor for Fischer-Tropsch Synthesis. Different equation of states, and the empirical Henry’s correlation have been applied to a set of experimental data in non-reactive environment and it was tried to get a good fit, by introducing some adjustable parameters. It was shown that a modified SRK equation of state is the most appropriate for prediction the phase equilibria in Fischer-Tropsch synthesis reactor.

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Keywords: Fischer-Tropsch synthesis; vapour-liquid equilibrium; solubility correlation

1. Introduction

With the depleting of crude oil resources, Fischer–Tropsch synthesis (FTS), which supply an opportunity to obtain clean fuels from coal and natural gas, has attracted more attentions to meet the future energy demand. In the Fischer–Tropsch process, synthesis gas (a mixture of hydrogen and carbon monoxide) is converted into a broad range of valuable chemical products using either a cobalt-based or iron-based catalyst. The Fischer–Tropsch synthesis under typical industrial conditions is a three-phase
process, in which the solid catalyst is covered in a liquid through which the gas has to diffuse to access the catalytically active sites. From viewpoint of chemical engineering, vapour-liquid equilibria (VLE) play a significant role in the synthesis of hydrocarbons via the Fischer-Tropsch synthesis reaction, notably when the reaction is carried out in a three-phase slurry reactor. Caldwell and van Vuuren (1986) [1] were the first to realize the importance of vapor-liquid equilibrium (VLE) considerations in the Fischer–Tropsch (FT) synthesis modeling. They used Raoult’s law to describe VLE. Recently, a variety of VLE thermodynamic models have been used to model FT products. Thermodynamic studies in gas–liquid are often complicated by the non ideal behaviour of products that are partitioned between the liquid and the vapour phase. Therefore, the description of phase equilibria, is usually performed by means of an Equation of State (EOS). Especially, cubic equations of state are frequently used to develop the methods for calculating the vapour-liquid thermodynamic equilibrium in Fischer-Tropsch synthesis products. In recent years, some studies have been performed to present the most applicable equation of state for the Fischer-Tropsch synthesis. Li et al [2] showed that the solubility of gas solution in heavy paraffin can be described with extended form of SRK equation of state which modified by replacing the acentric factor with molecular weight.

In the present paper, in addition to the empirical methods for estimating the vapour-liquid equilibrium characteristics in multi component synthesis products, such as the Henry constants, the rigorous calculation method is based on the use equation of states with appropriate mixing rules will be used. For simple gases and hydrocarbons with a number of carbon atoms less than 20, critical thermodynamic constants can be found in the reference literature[3]. For heavier hydrocarbons, the data on the critical thermodynamic properties are fragmentary or not available at all. Then empirical methods like group contribution methods [4] or molecular level simulation [5] etc. are often used to estimate these critical parameters. Furthermore, Equation of states will have modified to calculate the fractions of the liquid and vapour phases in the mixture of hydrocarbons and simple gases in a Fischer-Tropsch reactor by replacing the acentric factor with molecular weight.

2. Thermodynamic Equilibrium

2.1. Equations of state

Equations of state are used to develop the methods for calculating the liquid-vapour thermodynamic equilibrium in Fischer-Tropsch synthesis products. Several equations of state, which can be used for this purpose, can be found in the literature. At present, there are numerous EOS in the literature [6], however, a cubic EOS such as the Soave–Redlich–Kwong [7] and the Peng–Robinson [8] are commonly used in engineering calculations. These EOS can be expressed, in a general functional form, as:

\[
P = \frac{RT}{v-b} - \frac{a\alpha}{(v+\xi_1 b)+(v+\xi_2 b)}
\]  (1)

Where \(\xi_1\) and \(\xi_2\), are typical constants for each EOS; parameters a, b represent the attractive and repulsive forces between molecules, being related to the critical properties of a pure substance. In addition, \(\alpha\) is expressed as a function of the reduced temperature, and the acentric factor [4].

The explicit form of the SRK equation of state can be written where constants a, b for pure-components is related to:
\[ P = \frac{RT}{v-b} - \frac{a\alpha}{(v+b)} \] (2)

\[ a = 0.42747 \frac{R_{c}T_{c}^{2}}{P_{c}} \] (3)

\[ b = 0.08664 \frac{RT_{c}}{P_{c}} \] (4)

And \( \alpha \) is expressed in terms of the acentric factor \((\omega)\) as:

\[ \alpha = [1 + (0.48508 + 1.55171\omega - 0.15613\omega^{2})(1 - T_{c}^{0.5})]^{2} \] (5)

Besides, PR EOS can be expressed, as:

\[ P = \frac{RT}{v-b} - \frac{a\alpha}{v(v-b)(v+b)} \] (6)

\[ a = 0.45724 \frac{R_{c}T_{c}^{2}}{P_{c}} \] (7)

\[ b = 0.0778 \frac{RT_{c}}{P_{c}} \] (8)

\[ \alpha = [1 + (0.37464 + 1.5422\omega - 0.26992\omega^{2})(1 - T_{c}^{0.5})]^{2} \] (9)

2.2. Vapour-Liquid Equilibrium

Vapour (v) and liquid (l) phases are in equilibrium at the same temperature and pressure, when the fugacity of each constituent i species is the same in all phases

\[ y_{i}\tilde{\phi}_{i}^{v}P = y_{i}\tilde{\phi}_{i}^{l}P \] (10)

Both, the vapour and liquid fugacity can be calculated using the corresponding fugacity coefficients as follows:

\[ \tilde{\phi}_{i}^{v} = \tilde{\phi}_{i}^{l} \] (11)

Where \( x_{i} \) is the mole fraction of species i in the liquid and \( y_{i} \) is the mole fraction of species i in the gas phase, and \( P \) is total pressure. This expression of the vapour-liquid equilibrium is very convenient and the relationship between gas and liquid composition can be expressed in terms of the so-called K-value:
\[ K_i = \frac{y_i}{x_i} = \frac{\phi_i}{\phi^*} \quad (12) \]

For multi component mixtures, the same EOS are used but the mixture parameters, \( a_m \) and \( b_m \), are calculated by the following mixing rules:

\[
a_m = \sum_i \sum_j y_i y_j (a_i a_j)^{0.5}(1-k_{ij}) \quad (13)
\]

\[ k_{ij} = k_{ji}; k_{ii} = 0 \quad (14) \]

\[
b_m = \sum_i y_i b_i \quad (15)
\]

Where \( a_{ii} \) and \( b_i \) are the parameters of the pure component and \( k_{ij} \) are the binary interaction parameters that take into account the interaction between each pair of different molecules. It has been found that binary interaction factors, which are typically large and/or strongly dependent on temperature in many proposed equations of state[9, 10], are mostly close to zero.

Based on the above parameters for the SRK and the PR EOS, the fugacity coefficients for the gas and liquid phases are given by

\[
\ln \phi_i = \frac{b_i}{b_m}(Z-1) - \ln(Z-B) - \frac{1}{(Z_i - \xi_1)} \times A \left( \frac{\partial a_m}{\partial y_i} \times \frac{1}{a_m} - \frac{b_i}{a_m} \right) \times \ln \left( \frac{Z + (1 + \xi_1)B}{Z + (1 + \xi_2)B} \right) \quad (16)
\]

Where \( A, B \) is mixture parameters and \( Z \) is the phase compressibility factors which are defined by the following relations:

\[
Z = \frac{PV}{RT} \quad (17)
\]

\[
A = \frac{a_m P}{R^2 T^2} \quad (18)
\]

\[
B = \frac{b_m P}{RT} \quad (19)
\]

2.3. Modification

Very little work has been performed to evaluate the applicability of the PR or any other EOS for F-T systems, even though they have been applied in recent slurry reactor models. Chao and Lin [11] improved the SRK EOS by redefining the expression used for \( \alpha \) by making the exponent of \( \alpha \) as a function of molecular weight. Li et al have been improved the term by replacing the acentric factor with molecular weight and have been showed that the modified version of the SRK equation of state is more suitable for correlating solubility data of FTS [2] and some literature indicated that molecular weight is feasible for correlating hydrocarbon properties[12-14].
It is remarkable that the acentric factor of the heavy n-paraffins is usually not accurate by estimated methods whereas the molecular weight of the heavy n-paraffins is an easily determined property in FTS. In this work, we improved both the SRK EOS and the PR EOS by replacing the acentric factor with molecular weight (M) as a characteristic parameter where M represents molecular weight of each component. The m term has been expanded by parameter estimation as a polynomial of molecular weight with the coefficient ($\psi_i$).

\[ m = f(m) = \sum_{i=1}^{n} \psi_i M^{i-1} \]  \hspace{1cm} (20)

By the optimization method, modified equation of states is obtained with the best correlation. For the SRK EOS and the PR EOS, m term expressed, respectively.

\[ m_{SRK} = 0.0375 + 0.0149M - 0.313 \times 10^{-4} M^2 + 0.186 \times 10^{-7} M^3 \]  \hspace{1cm} (21)

\[ m_{PR} = -0.006295 + 0.01296M - 0.2641 \times 10^{-5} M^2 + 1.398 \times 10^{-7} M^3 \]  \hspace{1cm} (22)

Details of calculation will be discussed in the next section.

3. Calculated results and comparison with experiment

In present work, several studies have been investigated for elucidating effects of EOS on VLE in FT synthesis. Original version of the SRK and the Peng-Robinson equation of states likewise the modified SRK and Peng-Robinson equation of states have been used to develop a method for calculating the fractions of the liquid and gaseous phases in the mixture of hydrocarbons and simple gases in a Fischer-Tropsch reactor. Further with using Henry’s constant VLE calculation has been repeated.

The solubility of gases in Fischer–Tropsch wax can be calculated with the assumption that the gas phase is wax-free by the following equation:

\[ S_i = \frac{X_i}{(1 - \sum X_i) M_w} \]  \hspace{1cm} (23)

Where $M_w$ is molecular weight of wax, and $x_i$ is molar fraction of each component in wax. The parameter estimation has been done by the minimization of the objective function. The objective function for optimization is designed as follows:

\[ f_{OBJ} = \sum_{i}^{N_{EXP}} \left( \frac{S_{i,EXP} - S_{i,CAL}}{S_{i,EXP}} \right)^2 \]  \hspace{1cm} (24)

Where $S_{CAL}$ is the calculated solubility, $S_{EXP}$ is the experimental solubility, and $N_{EXP}$ is the number of experimental points. The average absolute deviation (AAD) is defined as:
All estimating parameters including constants $\psi_i$ in Eq. (20) are optimized simultaneously. The result of calculating has been compared with the experimental data taken from the literature.

\[
\%AAD = \frac{1}{N_{\text{EXP}}} \sum_{i}^{N_{\text{EXP}}} \left| \frac{S_{i,\text{EXP}} - S_{i,\text{CAL}}}{S_{i,\text{EXP}}} \right| \times 100
\]  

(25)

Generally, the minimization of numbers and values of the binary interaction parameters is desirable because this produces better predictions when the binary interaction parameters are not known and are set to zero \[2\]. By setting the interaction factors equal to zero, it can be seen that the MPR equation gives an overall AAD of 12.36% and shows a better agreement than the original PR equation also the MSRK equation gives an overall AAD of 10.67% and shows a better agreement than the original SRK equation. Although in both cases modified equations of state give a better overall AAD than the original ones the best agreement belongs to MSRK. Henry’s equation which is the most reported one in the literature has the highest overall deviation from the experimental data, among others. Results of this comparison are shown in Table 1.

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<th>Data points</th>
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<th>MPR AAD%</th>
<th>SRK AAD%</th>
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Table 1: Comparison of solubility prediction among PR EOS, MPR EOS, SRK EOS, MSRK EOS and Henry Constants
It is seen that the calculated results in both modified cases and the experimental data satisfactorily correlate with each other. The comparison between predicted and experimental values is shown in Figure 1. A good agreement can be noted.

![Graph showing comparison of correlated solubility with literature values](image)

**Fig. 1.** Comparison of correlated solubility with literature values

Figure 2 illustrates the dependence of the mole fraction of carbon monoxide in heavy hydrocarbons. It is seen that the increase in the pressure causes an increase in the concentration of the dissolved gas. At the same time, the increase in the temperature causes a decrease in the solubility.

![Graphs showing solubility of carbon monoxide in hydrocarbons](image)

**Fig. 2.** Dependence of the solubility of carbon monoxide in (a) n-Octacosane and (b) n-Hexatriacontane on the pressure for temperature equal to (1) 100, (2) 200, and (3) 300°C.

Figure 3 illustrates the behaviour of the solubility of hydrogen in the heavy synthesized products. It follows from Figs. 2 and 3 that the concentration of syngas components in the liquid products is rather
high even at high temperatures, which is typical for the operating conditions of the Fischer-Tropsch reactor. This fact makes it possible to study the actual synthesis kinetics inside the porous catalyst pellets filled with liquid high molecular-weight products. It should be noted that it is impossible in principle to obtain similar results using the simple Raoult's law for solutions.

![Graph of solubility](image-url)

**Fig. 3.** Dependence of the solubility of Hydrogen in (a) n-Octacosane and (b) n-Hexatriacontane on the pressure for a temperature equal to (1) 100, (2) 200, and (3) 300°C.

4. Conclusions

In the present work, several equations of state including the Soave-Redlich-Kwong, the Peng-Robinson equations, and a modified form of them, also the empirical Henry’s equation have been examined for phase equilibria in Fischer-Tropsch synthesis. The solubilities of gaseous solutes in waxes predicted by the modified SRK are in good agreement with the experimental data collected from the literature. Other methods including the modified PR show higher deviations. It should be noted that the, Henry’s equation which is the most reported one in the literature has the highest overall deviation from the experimental data, among others.

References