

Predictive Thermodynamic Modelling of Liquid-Liquid-Vapor-Fluid (LLVF) Equilibrium in Synthetic Hydrocarbon Synthesis from Syngas

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The synthesis of synthetic hydrocarbons (HC) from syngas (a mixture of hydrogen and carbon monoxide), commonly named Fischer-Tropsch synthesis (FTS) appears as a promising technology to produce clean fuels from renewable sources. In this work, a predictive thermodynamic model was used to understand the phase behavior in a synthesis reaction using a multiphase (liquid-liquid-vapor-fluid, LLVF) thermodynamic model. The model was proposed as a linear programming and was solved using the software GAMS and CPLEX solver. A methodology has been developed based on Gibbs energy minimization method and the discretization of the molar fraction domain, which incorporates a thermodynamic model to describe the phase equilibria using a phi-phi approach. The fugacity coefficient of liquid and vapor phase was determined using Soave-Redlich-Kwong (SRK) equation of state in combination with van der Waals (vdW) mixing rule. A modified atom balance restriction was imposed to represent hydrogen and carbon monoxide as reactants in the system. Four compounds were considered to represent the possible products of the reaction: H₂O, CO₂, propane and octane. LLV and LL equilibrium conditions were observed at 373.15 K and 423.15 K for pressures between 15 and 50 bar, lower pressures resulted in organic compounds, only in vapor phase, and for higher temperatures the formation of liquid organic phase was not observed in any pressure. The model presented a good predictive ability to represent the phase behavior of hydrocarbon synthesis from syngas foreseeing the formation and the separation of an organic liquid phase and one aqueous liquid phase during FTS reaction with a relative low computational time.

1. Introduction

In the last years, significant efforts were applied in the development and optimization of several techniques for biofuels production from renewable sources. Among these options, the cellulosic and lignocellulosic materials appears as significant and abundant feedstocks for fuels production. These options includes cellulosic ethanol produced by biochemical and microbiologic transformation and synthetic fuels derived thermochemically, via biomass gasification, known as biomass to liquid (BTL) or Fischer Tropsch synthesis from syngas (FTS).

Synthesis gas or briefly, syngas, is a mixture mainly composed by carbon monoxide, carbon dioxide and hydrogen. Syngas can be produced from many sources, including natural gas, coal, biomass, or virtually any hydrocarbon feedstock, by reaction with steam or oxygen. Syngas is a crucial intermediate resource for production of hydrogen, ammonia, methanol, and synthetic hydrocarbon fuels.

FTS process from biomass has been given considerable attention in the last decade (Hamelinck et al., 2004). FTS process offers significant advantages over cellulosic ethanol and fuels derived from oil, like as: (1) no significant transportation fuel infrastructure changes would be required for widespread use; (2) the gasification technology can accommodate more easily the wide range of biomass feedstock's than biochemical based processes; (3) FTS fuels are totally free of sulphur and contain very few aromatics compared to gasoline and diesel (Tijmensen et al., 2002).

Although the FTS reaction has been extensively studied, only a few works dedicated some effort to understand the phase behavior observed during FTS reaction. Freitas and Guirardello (2015) studied the

phase behavior of FTS reaction using a multiphase (solid-liquid1 (organic)-liquid2 (aqueous)-vapor) thermodynamic Gibbs energy minimization model, using the consideration of ideal behavior for all phases involved and the consideration of immiscibility of water and hydrocarbons in two imposed liquid phases. This model showed to be interesting, because it enables a rapid assessment of phase behavior for FTS systems, however, the model do not present predictive ability to describe liquid-liquid equilibrium conditions in this kind of system.

Gibbs energy minimization thermodynamic models are extensively used to perform thermodynamic characterization of a large variety of systems. This class of model was previously used to understand the thermodynamic behavior of a large variety of glycerol reforming systems (Freitas and Guirardello, 2014a) and for a variety of supercritical water gasification reaction for hydrogen production from biomass (Freitas and Guirardello, 2014b). All of these works related a good predictive ability of Gibbs energy minimization model to represent chemical and phase equilibria in reactive multicomponent systems.

In this work, we used a predictive thermodynamic model, based on Gibbs energy minimization, to understand the phase behavior in a synthesis reaction using a multiphase (liquid-liquid-vapor-fluid, LLVF) model combined with Soave-Redlich-Kwong (SRK) equation of state and van der Waals (vdW) mixing rule to represent the non-ideal behavior during FTS reaction using a phi-phi ($\phi - \phi$) thermodynamic approach.

2. Methodology

2.1. Gibbs energy minimization – model formulation

The chemical and phase equilibrium, in a closed system with constant pressure and temperature, can be determined by the minimization of the Gibbs energy that can be written as:

$$G = \sum_{k=1}^{NP} \sum_{i=1}^{NC} \left[\mu_i^0 + RT \ln \frac{\hat{f}_i^k}{f_i^0} \right] \quad (1)$$

Where n_i^k is the number of moles of each component in each phase, NC is the total number of components considered in the systems and NP is the number of possible phases.

The Gibbs energy minimization must satisfy some restrictions to represent reactive systems, like as non-negativity of number of moles of each component in each phase, represented as:

$$n_i^k \geq 0 \quad \text{for } i = 1, 2, \dots, NC \quad \text{and} \quad k = 1, 2, \dots, NP \quad (2)$$

The molar balance was used in the calculations and was written as:

$$\sum_{i=1}^{NC} \sum_{k=1}^{NP} [n_i^k \cdot a_{mi}] = na_m \quad m = 1, \dots, NA \quad (3)$$

Where V represents vapor phase, L_1 represents one of the possible liquid phase, and L_2 represents the second possible liquid phase and F represents the fluid phase. The subscript m represents carbon, oxygen or hydrogen, once, this balance was written for each atom in the system. a_m represents the number of atoms present in the feed for each present atom (carbon, oxygen and hydrogen), NA represents the number of atoms considered during the simulations (for this system 3, carbon, oxygen and hydrogen) and am_{ik} represents the number of atoms of atom i present in the component k .

In this work, Soave-Redlich-Kwong (SRK) (Soave, 1972) equation of state was used to represent the non ideal behavior of both, liquid and vapor phases. The Gibbs energy minimization program was formulated as a linear programming model through a discretization of the molar fraction domain. This methodology was previous used by our research group with good results and the complete discretization procedure can be seen at Rossi et al., (2009) and Cunico and Guirardello (2015).

For liquid–vapor, liquid–liquid and liquid–liquid–vapor equilibrium conditions, the nonideality of all phases are given by the fugacity coefficients (ϕ_i^k) using the $\phi - \phi$ thermodynamic approach. The fugacities in Gibbs energy minimization model can be calculated by Eq 4 and Eq 5, for liquid and vapor phases. The differentiation between the phases (liquid, vapor and fluid) are made as presented in Cunico and Guirardello (2015).

$$\hat{f}_i^V = y_i \hat{\phi}_i^V P \quad (4)$$

$$\hat{f}_i^L = x_i \hat{\phi}_i^L P \quad (5)$$

Soave-Redlich-Kwong (SRK) equation of state was used for all phases. The thermodynamic properties of CO_2 , H_2O , propane and octane were obtained at DIADEM (2000) and in Polling et al. (2000). The model was implemented to study the reactive multiphase system composed by: CO_2 , water, propane and n-octane. The

critical properties of these components are presented in Table 1. Hydrogen and carbon monoxide are considered as reactants presenting a complete conversion to products during FTS process, this inclusion and consideration are made as presented in the restriction of atom balance (Eq 3) and is necessary to use the proposed thermodynamic formulation. These components are selected based on the main reactions that occurs in FTS reactions, general hydrocarbon synthesis from syngas (Eq 6) and Water Gas Shift reaction (Eq 7):



Table 1. Thermodynamic properties of selected components to represent FTS reaction.

Component	Chemical formula	T _c (K) ^a	P _c (bar) ^a	ω (-) ^a
Carbon dioxide	CO ₂	304.7	73.8	0.225
Water	H ₂ O	647.9	221.0	0.344
propane	C ₃ H ₈	369.8	42.48	0.152
n-octane	C ₈ H ₁₈	568.7	24.9	0.399

^a source: Polling et al. (2000) and DIADEM (2000).

In previous work of our group (Freitas and Guirardello, 2015), a simplified thermodynamic model, based on ideal behavior of liquid and vapor phase, with the consideration of immiscibility of liquid organic and aqueous phase, included as an imposition of two liquid phases (*l*₁ organic and *l*₂ aqueous) using a $\gamma - \phi$ approach. This model was used to study the hydrocarbon synthesis from syngas in a multicomponent (20 components) hydrocarbon synthesis from FTS reactions, minimizing the following objective function:

$$G = \sum_{i=1}^{NC} n_i^g (\mu_i^0 + RT(\ln P + \ln y_i + \ln \phi_i)) + \sum_{i=1}^{NC} n_i^{l_1} (\mu_i^0 + RT(\ln P_i^{sat} + \ln x_i^{l_1} + \ln \gamma_i^{l_1})) + \sum_{i=1}^{NC} n_i^{l_2} (\mu_i^0 + RT(\ln P_i^{sat} + \ln x_i^{l_2} + \ln \gamma_i^{l_2})) + \sum_{i=1}^{NC} n_{C(s)}^s \mu_{C(s)}^0 \quad (8)$$

In this work, pressures in the range of 5 bar and 150 bar and temperatures in the range of 353.15 K and 523.15 K were evaluated. Two H₂/CO molar ratios in the feed are tested: 2.0/1.0 and 2.125/1.0. The simulations were performed in a high performance computational station (Sun Microsystems – SPARC Enterprise M3000 server). The proposed model was solved using the software GAMS in combination with CPLEX solver. More details about the software and the solver can be found in Brooke et al. (1998).

3. Results and discussion

3.1. Model validation

The first step for the use of the proposed model was the validation. The validation was performed using experimental data obtained in Gallegos et al. (2006) for the thermodynamic equilibrium in CO₂+octane binary system, the results are presented in Figure 1. Figure 1 (a) present the validation for liquid phase (x) and Figure 1 (b) for vapor phase (y).

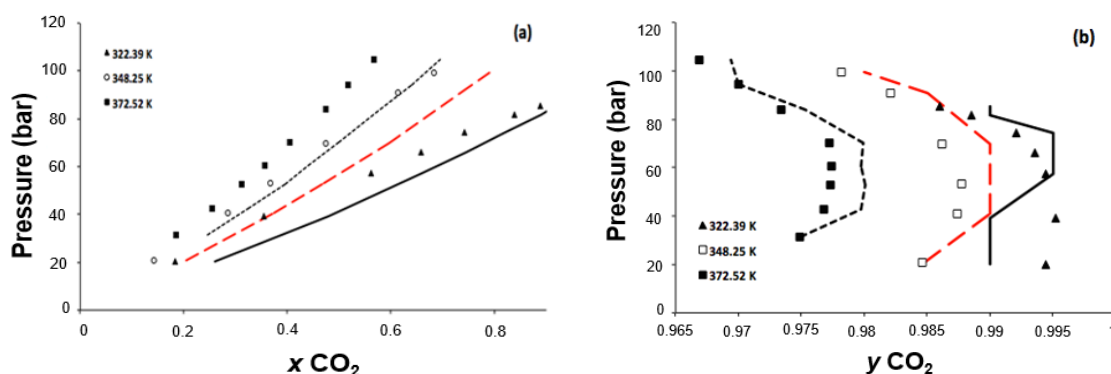


Figure 1. Model validation for the system CO₂ + n-octane. Experimental data from Gallegos et al. (2006). (a) Liquid phase; (b) vapor phase. Legend: lines: predictions obtained by the proposed model, solid black line – 322.39 K, dashed red line – 348.25 K and dashed black line – 372.52 K; symbols: experimental data obtained in the work of Gallegos et al. (2006).

The model was validated at three different temperatures, 322.39 K, 348.25 K and 372.52 K. It is important to emphasize that the model was validated without the use of binary interaction parameters (k_{ij} and l_{ij}) for van der Waals mixing rule, these parameters are fixed at zero.

The relative mean deviation ($RMD\%$) was determined by the following equation:

$$RMD\% = \frac{1}{NEP} \cdot \sum_{i=1}^{NEP} \left| \frac{x_i^{lit} - x_i^{pred}}{x_i^{lit}} \right| \cdot 100\% \quad (9)$$

Where NEP is the number of experimental points, x_i^{lit} is the value obtained from literature and x_i^{pred} is the predicted value from the thermodynamic model.

Analyzing the Figure 1, it is possible to verify that the proposed model presented a satisfactory ability to represent the liquid vapor equilibrium in CO_2 + octane binary system. RMD of 23.87% was observed for liquid phase and RMD of 0.2458% was observed for vapor phase. This behavior was expected due to the fact that we are not using the binary interaction parameters for mixing rule, and we are using a $\phi - \phi$ thermodynamic approach. However, it is important to emphasize that the model is completely predictive and presents these results without the use of any experimental data or previous adjustment, therefore, their performance in representing the liquid vapor equilibrium can be considered satisfactory for this kind of system. After this, the model was used to perform the calculation of combined chemical and phase equilibrium during FTS reaction.

3.2. Study of chemical and phase equilibrium during FTS reaction

After the validation, the model was used to perform the calculations of combined chemical and phase equilibrium during FTS reaction for hydrocarbon production. Effects of temperature, pressure and reactants composition are analyzed with respect to octane yield (%) (Eq 10) and with respect to the total number of moles of hydrocarbons (represented by propane and octane) during FTS process.

$$\text{octane yield (\%)} = \frac{n_{\text{octane}}}{\sum_{i=1}^{NC} n_i} \cdot 100\% \quad (10)$$

Figure 2 (a) presents the results for octane yield as a function of pressure and temperature, when a H_2/CO molar ratio of 2/1 was used in the feed and Figure 2 (b) presents the results for a total number of moles formed in the organic liquid phase for the same operational conditions. Figures 3 (a) and (b) present the same effects for the studied systems, at the same conditions of pressure and temperature, but this time for a H_2/CO molar ratio of 2.125/1.

Analyzing Figure 2 (a) it is possible to verify that conditions of higher pressures (higher than 35 bar) and lower temperatures (lower than 423.15 K) were thermodynamically responsible for the increase of octane yield obtained in the products. These conditions are associated with the formation of two liquid phases in the simulated systems (one organic and one aqueous).

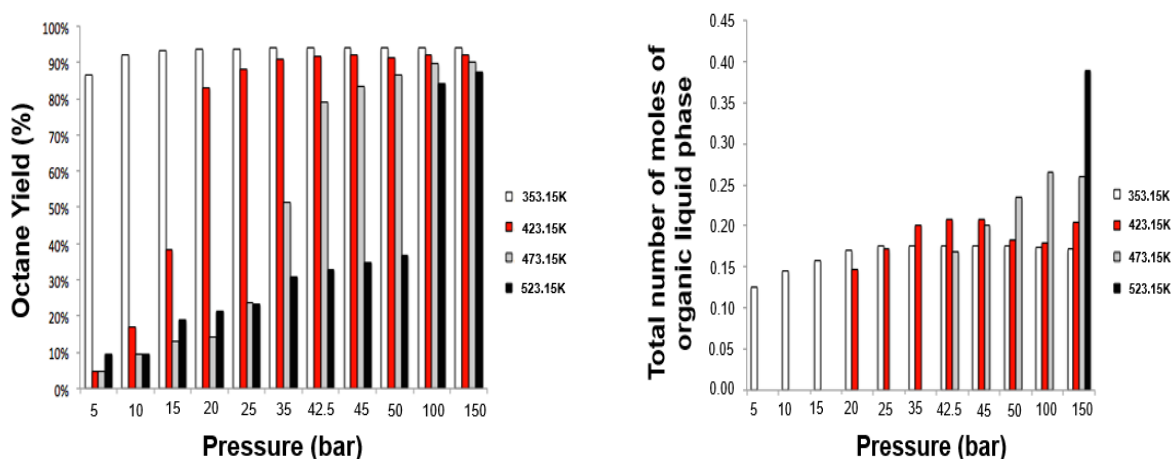


Figure 2. Effects of pressure and temperature under (a) octane yield; (b) total number of moles observed in organic phase for a H_2/CO molar ratio of 2/1 in the feed.

Organic liquid phase are observed for all range of pressure tested, only for 353.15 K, however, at these temperature, lower kinetics tend to be observed due to low activity of the reaction under these temperature

condition (see Figure 2 (b)). Significant amounts of octane are obtained for higher temperatures only for pressures above 100 bar. For a system at 100 bar and 473.15 K, the following molar composition are observed: CO₂ – 14.8%; water – 35.5%; propane – 7.6%; and octane – 42.1%. these results emphasized that the production of higher hydrocarbons are favored by higher pressure conditions in the reactor, similar results are observed in the experiments of Das et al. (2003) for temperature effects and in Pirola et al. (2014) for pressure effects.

The formation of a fluid phase are observed only at 150 bar and 523.15 K; at these operational conditions, the total number of moles are computed as an organic phase, but a significant amount of water was observed at the system. When this condition was used, the composition of this phase was majority represented by water (around 55% of the molar composition). The composition of octane was around 28%, presenting a significant reduction when compared with simulations where the fluid phase was not observed, such behavior could result in subsequent problems in the separation steps necessary for FTS process.

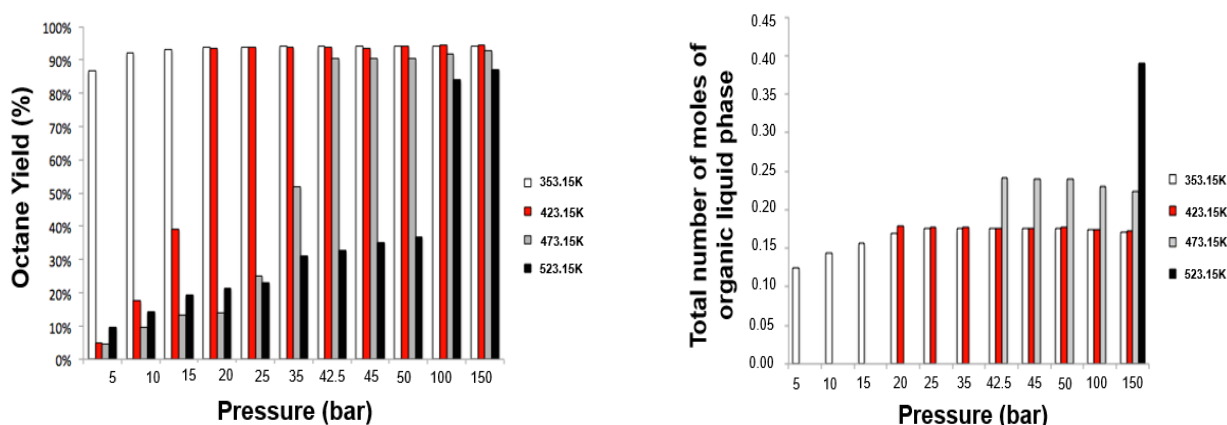


Figure 3. Effects of pressure and temperature under (a) octane yield; (b) total number of moles observed in organic phase for a H₂/CO molar ratio of 2.125/1 in the feed.

Figure 3 presents the trends for the simulations with H₂/CO molar ratio in the feed of 2.125/1. The general behavior observed for this system is very similar to that observed with a H₂/CO molar ratio of 2/1. However, it is possible to verify that the general yield of octane was higher for the system with H₂/CO molar ratio of 2.125/1, in comparison with the system where a H₂/CO molar ratio of 2/1 was used. It is important to emphasize that H₂/CO molar ratio did not present significant effects under octane production during FTS reaction in the range tested by the present work.

In respect with the obtained results it is possible to verify that higher hydrocarbon production are favored by conditions of pressures higher than 35 bar and temperatures lower than 473.15 K. Lower temperatures may result in slow reactions for hydrocarbon synthesis, due to the low kinetics observed under these operational conditions (Van der Laan and Beenackers, 1999). It is also possible to observe that conditions where organic liquid phase are synthesized stay related with larger yields of octane (higher hydrocarbons). This behavior was previous observed by our research group using more simplified thermodynamic models in Freitas and Guirardello (2015) and Silva and Guirardello (2010). However, none of these works relates these papers relates this thermodynamic behavior using a complete predictive thermodynamic model combined with an equation of state.

Similar trends are observed with the use of simplified thermodynamic formulations, presented in Freitas and Guirardello (2015), but the model proposed by this work are more robust when compared with the model used in Freitas and Guirardello (2015), that used the objective function presented in Eq 7. In this work, the immiscibility of organic and aqueous phase are predicted only by the use of SRK equation of state (in combination with van der Waals mixing rule).

As mentioned before, the simulations were performed in a high performance computational station (Sun Microsystems – SPARC Enterprise M3000 server). However, even using this high performance computational station, elevated computational times were observed during the simulations (about 13 minutes) for one delta of 0.005 in the molar fraction domain (which results in 1,373,701 points in simulation grid). The observed high computational times are directly associated with high number of variables associated with the resolution of this class of problem.

4. Conclusion

The thermodynamic evaluation of combined chemical and phase equilibria for the system involved in hydrocarbon synthesis from FTS process was performed using a predictive thermodynamic model based on Gibbs energy minimization combined with Soave-Redlich-Kwong equation of state and van der Waals mixing rule. The model presented a good predictive ability to represent the thermodynamic behavior of FTS system. Conditions of liquid-liquid-vapor equilibrium are well predicted and the phase description was done without the use of binary interaction parameters. Conditions of high pressure (higher than 35 bar) and low temperature (around 423.15 K) proved to be the best conditions for high chain hydrocarbon (in this work represented by octane) synthesis from syngas. These conditions are associated with the formation of liquid-liquid-vapor equilibrium during FTS reaction. The proposed thermodynamic model performs the calculation in a complete predictive way, reporting the complete description of chemical and phase equilibria for the complex FTS reaction system.

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