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Analysis and Characterization of Fischer-Tropsch Products through Thermodynamic Equilibrium using Global Optimization Techniques

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The Fischer-Tropsch (FT) based Gas-to-Liquid (GTL) technology presents as an opportunity to obtain clean fuels from coal, natural gas and more recently from biomass. The process has been attracting more attention to meet future energy demand. In the Fischer-Tropsch process, synthesis gas (a mixture of hydrogen and carbon monoxide) is converted to a wide variety of valuable chemicals, either using an iron-based or cobalt based catalyst. The composition and the productivity of products are controlled by different mechanisms and kinetic factors. The catalyst employed, the type of reactor and operating conditions (temperature, pressure and composition of the syngas) has significant effects on the composition and characteristics of the products. The condition for thermodynamic equilibrium is the minimum Gibbs energy of the system, therefore such system can be modeled as an optimization problem in order to solve the chemical and phase equilibrium and determine the most thermodynamic favorable phases and compositions of the formed FT products. The set of nonlinear equations was solved in GAMS/CONOPT using the non-stoichiometric formulation. The non-ideal behavior of the vapor phase was evaluated using the second virial correlation. The immiscibility of two liquid phases (organic and aqueous) takes into account the non-ideal behavior in the liquid phase. The effects of temperature (450-750 K), pressure (5-60 bar) and H_2:CO ratio (1:1-3:1) were evaluated on the composition and phases of products, conversion and yield. The FT system is not at global chemical equilibrium, only some subsystems are. However, the thermodynamic distributions predict chain growth probability values, independent of mechanism and catalyst representing a generic distribution.

1. Introduction

Fischer-Tropsch synthesis (FTS) is an industrial process which converts synthesis gas, composed mainly of H_2 and CO, into a large number of products, such as alkanes and alkenes (Dry 2004). The aforementioned technology is comprehended into a group of processes called Gas-to-Liquid technologies (GTL). GLT involve the chemical conversion of natural gas, biomass or coal into synthetic crude oil that can be further refined and separated into different fractions of useful hydrocarbons, including liquid transportation fuels (Yang et al. 2014; Onel et al. 2015). The synthesis of hydrocarbons from the hydrogenation of carbon monoxide over a metal-based catalyst was discovered early last century, in 1923 by Fischer and Tropsch. Following the initial findings, considerable effort has led to the development of different catalysts to this process, improvement in reactor design and process operating conditions in order to reach higher selectivity (Steynberg et al. 1999; Dry 2002; Davis 2005; Elbashir et al. 2009).

FTS is a particularly complex system, wherein a number of different reactions are combined to a single mechanism: irreversible Fischer-Tropsch reaction. The hydrocarbons formed during the synthesis are distributed between the two phases (vapour and liquid). The lighter components preferentially accumulate in the vapour phase while the heavy oils and waxes in the liquid phase (Muleja et al. 2016). The reaction happens in steps and the products follow an Anderson-Schulz-Flory model (ASF) distribution, the probability of chain growth (α) is independent of the size of the chain. Thus, hydrocarbon selectivity may be predicted based simply on the statistical distribution calculated by α-value and the number of carbon (Flory 1936; Anderson et al. 1984).

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Some equilibrium reactions are also present, among them the equilibrium between carbon monoxide, carbon dioxide, methane and carbon, such as the reaction of water gas shift (WGS) and Boudouard equilibrium (van der Laan & Beenackers 1999). Studies on kinetics have been widely approached, one of the pioneers were Friedel & Anderson (1950). Several authors proposed numerous kinetic models (Dry 1976; Sarup & Wojciechowski 1989; Yates & Satterfield 1991). On the other hand, there are few studies about the thermodynamic approach. Stenger & Askonas (1986) have studied the product distribution using the free energy minimization, with a full CO and H_2 conversion. Torrente-Murciano et al. (2014) studied the thermodynamic equilibria of hydrocarbon synthesis via CO and/or CO_2 reduction. Lu et al. (2012a) performed a series of experiments and concluded that distribution in FTS might be determined by thermodynamics. The process parameters impose important role on catalytic activity, molecular weight of the products and selectivity, the study of the effect of variation in temperature, time and other parameters is imperative for process development, design and optimization (Junhu Gao et al. 2012)

This paper presents the thermodynamic analysis and characterization of FT synthesis for hydrocarbon production. The method of Gibbs energy minimization were used, including in the calculation thirty three chemical species (paraffin, olefins, CO, CO_2, H_2O, H_2). The effect of temperature (in the range of 450-750 K), pressure (in the range of 5-60 bar) and H_2:CO ratio (1:1 and 3:1) were evaluated on the composition of products, conversion and yield.

2. Methodology

2.1 Reaction Synthesis Modelling

Once the system reaches thermodynamic equilibrium, it is possible to identify phases and compositions in a multicomponent system. At constant temperature, pressure and initial composition, the minimization of the Gibbs energy of the system, Eq (1), with respect to the number of mols of each substance in each phase, leads to the condition of the chemical potential of each substance being equal in all phases. It allows to determine not only the concentration of components in a multicomponent system but also the phases in equilibrium (O'Connell & Haille 2005).

$$G = \sum_{i=1}^{NC} \sum_{k=1}^{NP} \mu_i^k . n_i^k \tag{1}$$

where NC represents the number of chemical species (*i*), NP the number of phases (*k*), G the Gibbs energy, n_i^k the number of moles and μ_i^k the chemical potential.

The chemical potential can be expressed in terms of fugacity and the Eq (1) can be rewritten as:

$$G = \sum_{i=1}^{NC} n_i^G\left(\mu_i^0 + RT(lnP + ln\, y_i + \ln \phi_i)\right) + \sum_{k=1}^{LP} \sum_{i=1}^{NC} n_i^L\left(\mu_i^0 + RT(lnP_i^{sat} + ln\, x_i + \ln \gamma_i)\right) \tag{2}$$

where y_i stands for the composition in gas phase, x_i is the composition in the liquid phase, μ_i^0 is calculated from the formation properties under a reference condition, R gas constant, P pressure and T is temperature. The equation represents the Gibbs energy for the chemical and phase equilibrium in the case of a mixture that allows the possible formation of a gas and two liquid phases. The non-ideality of the two liquid phases (organic and aqueous) was modeled by considering total immiscibility between water and hydrocarbons, and by considering ideal behavior (γ_i=1) for the components allowed in each individual liquid phase.

The fugacity for the gas, Eq (3), was calculated using the virial equation truncated at the second coefficient, using the correlation of Pitzer and Curl (1957), and further modified by Tsonopoulos (1974). The following relation determined the fugacity coefficient:

$$ln\hat{\phi}_i = \left[2\sum_{i=1}^{NC} y_i B_{ij} - B\right]\frac{P}{RT} \tag{3}$$

The problem can be solved by employing optimization techniques minimizing Eq (3). For the direct minimization some restrictions must be fulfilled (Smith & Missen 1982). The non-negativity of the number of moles of each component in each phase ($n_i^k \geq 0 \ \forall\, i$). The non-stoichiometric formulation, Eq (4), was used for the mass balance constraint:

$$\sum_{i=1}^{NC} a_{mi}(n_i^G + n_i^{L1} + n_i^{L2}) = \sum_{i=1}^{NC} n_i^0 \cdot a_{mi} \qquad m = 1, \cdots, N \tag{4}$$

where n_i^0 is the initial number of moles, a_{mi} is the number of atoms of the element m. The non-stoichiometric formulation is equivalent with the stoichiometric formulation if the number of independent reactions is equal to the difference between the number of components and the number of atoms (Smith & Missen 1982).

This methodology, together with optimization techniques has been used by various researchers for the phase equilibrium calculation. White et al. (1958) was one of the first to study the minimization approach; the author used the minimization of the Gibbs energy involving a series of ideal systems. Gao et al. (2012) conducted a thermodynamic analysis of CO and/or CO_2 methanation using the same methodology.

2.2 Model Implementation

The non-linear set of equations was solved using the software GAMS (General Algebraic Modelling System) and the solver CONOPT, in order to determine the combined chemical and phase equilibrium. In the study, thirty three possible chemical species (linear paraffin, linear alpha alkenes and alcohols besides carbon monoxide, carbon dioxide, water and hydrogen) were considered (Satterfield et al. 1985; Norval & Phillips 1990; Lu et al. 2012). The thermodynamic data have been selected from Poling et al. (2001). The effects of temperature (in the range of 450-750 K), pressure (in the range of 5-60 bar) and H_2:CO ratio (in the range of 1:1-3:1) were evaluated on the composition and phases of products, conversion and yield.

3. Results and Discussions

The influence of the operational conditions, such as temperature, pressure and H_2:CO ratio, were evaluated. The effect of the catalyst must be assessed by restriction of components formed in the synthesis, when the reactions are based on the thermodynamics (Raje et al. 1997), therefore the component methane has shown limited formation. Figure 1 shows the temperature and pressure effects on the H_2 thermodynamic equilibrium conversion, considering all inlet compositions case studies.

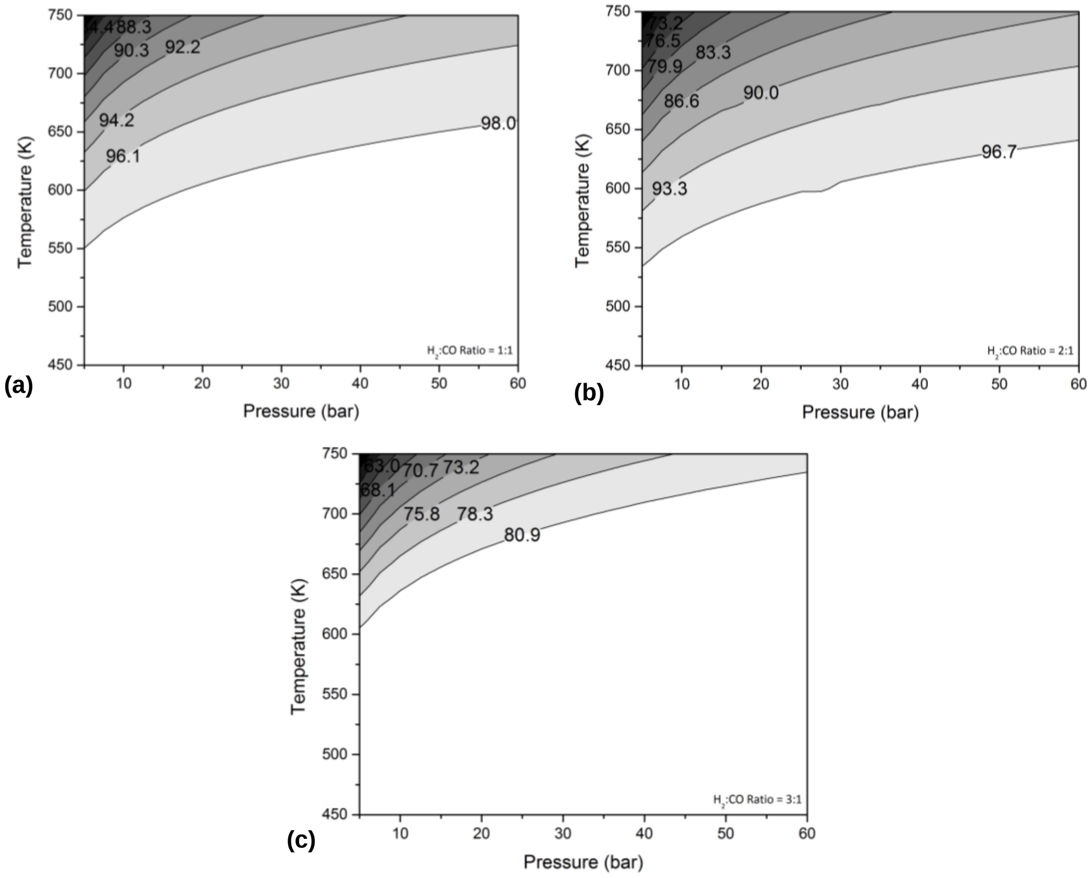

Figure 1: Effect of temperature and pressure on the H_2 thermodynamic equilibrium conversion. Inlet composition H_2:CO ratio of (a) 1:1, (b) 2:1 and (c) 3:1.

The parameter temperature is inversely proportional of H_2 conversion. The elevation of temperature leads to the reduction of H_2 conversion. For instance, keeping a constant pressure (e.g. 30 bar), the change in temperature from 450 K to 750 K reduces the H_2 conversion in 7.40, 14.79 and 8.88 % for an inlet composition with H_2:CO ratio of 1:1, 2:1 and 3:1, respectively.

Regarding the effect of the pressure, keeping a constant temperature (e.g. 600 K), the modification in pressure from 5 bar to 60 bar increases the H_2 conversion in 3.16, 7.21% and 2.48% for an inlet composition H_2:CO ratio of 1:1, 2:1 and 3:1, respectively. This behavior is less pronounced in lower temperatures; below 500 K no significant effect of pressure has been observed.

The CO conversion shows similar pattern for temperature and pressure, the increase in temperature reduces the conversion. Similar results have been reported by Torrente-Murciano et al. (2014), below 500 K the CO conversion follows the FT reaction pathway with near no water-gas shift (WGS) activity, due to the equilibrium shift to CO formation.

According to Bukur et al. (2016) high syngas conversions are only achieved under thermodynamic equilibrium. However, under experimental conditions one cannot achieve high conversion, since the maximum syngas conversion is limited when usage ration (defined as a ratio of moles of H_2 consumed and moles of CO consumed) is different from feed composition.

Concerning the effect of the feed ratio, the increase in hydrogen contend increases CO conversion. Govender et al. (2006) study the usage ration and the recycle in a FTS, their results illustrate the effect of feed ratio, between 1.08 and 2.01, on the exit H_2/CO ratio and CO conversion on experiments. They found that CO conversion is 30–45% (increasing with increase in feed H_2/CO ratio).

Figure 2 shows the temperature and pressure effects on the H_2 yield to hydrocarbons, considering all inlet compositions case studies.

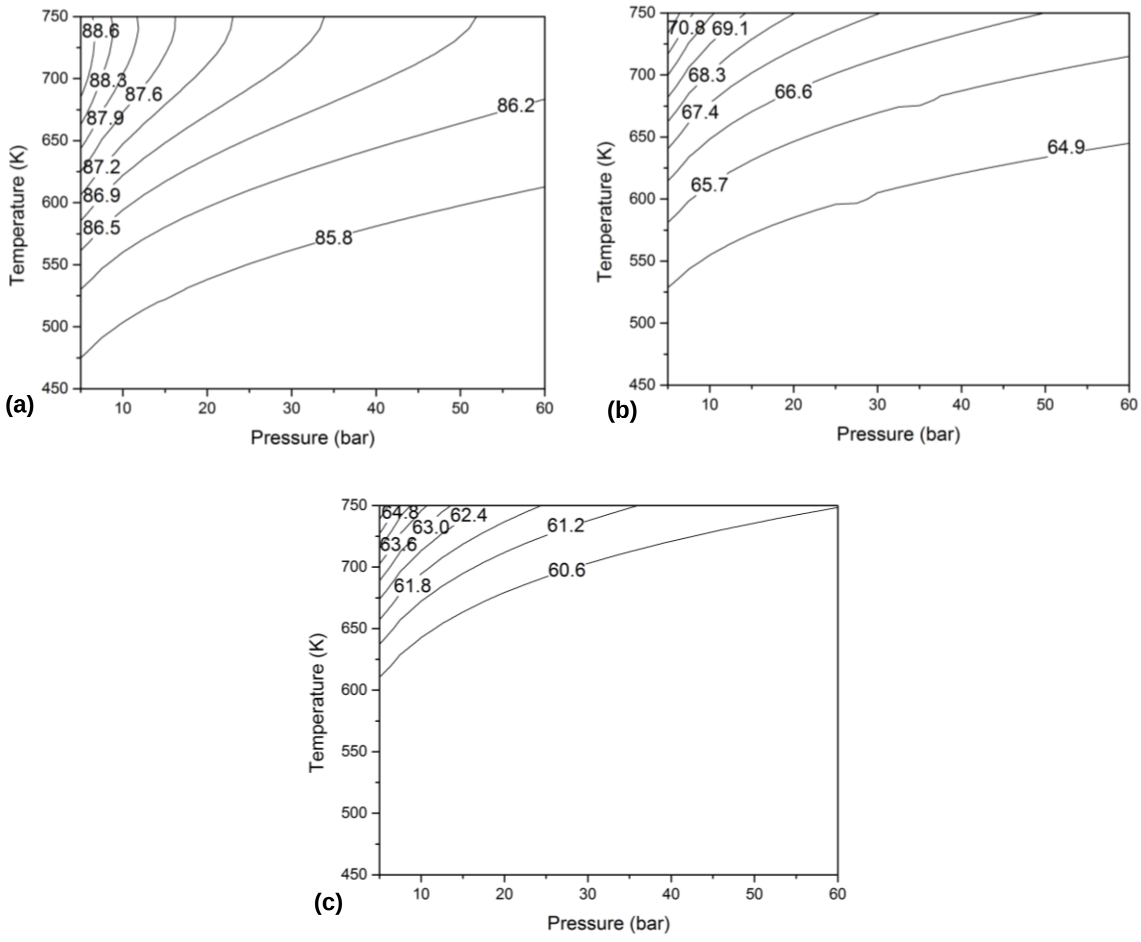

Figure 2: Effect of temperature and pressure on the H_2 yield to hydrocarbon. Inlet composition H_2:CO ratio of (a) 1:1, (b) 2:1 and (c) 3:1.

The reaction temperature has shown a positive effect in the yield to hydrocarbons. The pressure has no significant effect in the H_2 yield to hydrocarbons in temperatures below 550 K (< 1%), however at higher temperatures there is a more pronounced effect. For instance at 700 K, the variation in pressure from 5 bar to 60 bar, reduces the yield in 2.8 %, 8.1% and 8.2% for an inlet composition H_2:CO ratio of 1:1, 2:1 and 3:1, respectively.

The effect of the feed ratio on the H_2 yield to hydrocarbons in negative, the increase in such variable reduces de yield. The maximum yield is 88.9%, 72.4% and 66.1%, for an inlet composition H_2:CO ratio of 1:1, 2:1 and 3:1, respectively.

Similar trends were reported by Torrente-Murciano et al. (2014), where the authors achieved 100% H_2 yield into hydrocarbons under these reaction conditions when the H_2:CO molar ratio is 1 or below, due to the lack of water gas shift reaction activity.

The equilibrium calculations performed are close to the predicted in the literature; however, under typical experimental conditions FT reactions have not reached the thermodynamic equilibrium. According to Norval (2008), the FT system is not at global equilibrium, a partial equilibrium implies that some species have achieved the equilibrium, while other have not. FT can be considered a system with three partial equilibrium: homologous series, the water shift reaction (WGS), and the redox behavior of the catalyst with the H_2:CO ratio.

As expected according to the Anderson–Schulz–Flory theory, the FT log-linear product distribution shows a straight line with small chain growth probability factors (α), between 0.001 and 0.2. For instance, at 600 K and 25 bar the α-value is 0.024, 0.015 and 0.006 for a H_2:CO ratio of 1:1, 2:1 and 3:1, respectively. When the pressure is raised to 40 bar, at constant temperature (600 K) the α-value is 0.028, 0.017 and 0.006 for a H_2:CO ratio of 1:1, 2:1 and 3:1, respectively. However, this indicates that the controlling step based only in thermodynamic analysis is termination rather than propagation, different from the kinetics where the growth probability factor vary between 0.4 and 0.7 (van der Laan & Beenackers 2000; Das et al. 2007; van der Laan et al. 1999; Nakhaei Pour et al. 2014).

The alkenes should be almost completely hydrogenated to alkanes under the thermodynamic point of view, indicating primary FT products. Another important aspect of the system regarding the temperature is that the increase in such variable increments the production of not only linear alpha alkenes but also alcohols. The production is less pronounced under higher pressures.

4. Conclusions

The Fischer Tropsch synthesis is a process where the syngas is converted into hydrocarbons under catalytic conditions. The operational conditions play an important role in the composition of the mixture formed. The problem was solved by the minimization of the Gibbs energy of the system, in order to find the more thermodynamic stable phases and compositions. The effects of operational conditions on the product were evaluated. The effect of temperature is negative in CO and H_2 conversion, however is positive in the H_2 yield to hydrocarbons. The pressure has shown a positive effect in conversion. The Fischer Tropsch reaction is not at global chemical equilibrium, only some subsystems are. However, the thermodynamic distributions predict a chain growth probability factor value, independent of mechanism and catalyst representing a generic distribution. Once this approach calculates the equilibrium of the system, it is important to identify tendencies under different operational conditions to further increase productivity or reduce costs.

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