



Thermodynamic Characterization of Hydrocarbon Synthesis from Syngas using Fischer-Tropsch Type Reaction

Antonio C.D. Freitas, Reginaldo Guirardello*

School of Chemical Engineering, University of Campinas (UNICAMP), Av. Albert Einstein 500, 13083-852, Campinas-SP, Brazil
guira@feq.unicamp.br

The synthesis of hydrocarbons (HC) from syngas (a mixture of hydrogen and carbon monoxide), commonly named Fischer-Tropsch synthesis (FTS), allows making valuable products from relatively cheap substrates, such as biomass, natural gas or coal. Furthermore, synthetic HC are reported to be useful, cleaner (lower in sulphur and heavier metals than crude oil), easier and cheaper to transport. FTS reaction is normally conducted on metal supported catalysts (Fe, Co and Ru) and the production of higher HC is directly related with the reaction conditions. In this work, optimization techniques are applied in Gibbs energy minimization method in a multiphase model that considers the potential formation of coke (S), a water phase (L₁), an organic phase (L₂) and a gas phase (V) (S+L₁+L₂+V model) to perform the thermodynamic characterization of FTS process. The software GAMS 23.2.1 and the solver CONOPT are used to solve the proposed problems. The restrictions of non-negativity of the number of moles and the stoichiometric balance are used. The effect of the catalyst is considered by restricting the products that can be formed, since the actual system is not in thermodynamic equilibrium. Twenty-three (23) compounds are selected to represent the possible products in FTS reaction, including aliphatic hydrocarbons in the range of C₂-C₂₀, H₂O, H₂, CO and CO₂. The effects of reaction conditions are analyzed, effects of temperature (in the range of 350-550 K), pressure (in the range of 5-30 bar) and H₂/CO ratio used in the feed (in the range of 1.0-2.0/0.5-1.0) are tested in terms of HC production and products composition. The reaction yields proved to be highly dependent on the reaction conditions; low temperature, high pressure and H₂/CO molar ratio of 2.0/1.0 are achieved as the best conditions to promote HC production in FTS process.

1. Introduction

Currently the energetic resources from oil represents approximately 75 % of the global matrix of energy. Several factors points to more extensive use of renewable energy source like as biomass, mainly because of the high demand for fuels and by the alarming levels of CO₂ released in the atmosphere around the world.

These different economic and environmental factors resulted in renewed interest in the development and improvement of manufacturing gas-to-liquid technologies (GTL), via Fischer-Tropsch process (FTS), over the past few years, to produce hydrocarbons (HC) from syngas (Dry, 2002).

The synthetic HC produced by this technology are usable, cleaner, presenting lower contents of sulfur, nitrogen, aromatics and heavy metals than petro-derived HC. Furthermore, these HC are reported as easier and cheaper to transport. Due to these features synthetic fuels produced from FTS technology are considered as green fuels (Gill et al., 2011).

The composition and yield of the products of FTS processes are controlled by different mechanisms and kinetic factors. The catalysts used, the type of reactor and operating conditions like as temperature, pressure and composition of the syngas used to promote the reaction had a significant effect on the composition and characteristics of the obtained products (Farias et al., 2007).

In this paper, optimization techniques were applied in Gibbs energy minimization method to perform the thermodynamic characterization of FTS reaction for HC production. The software GAMS 23.2.1 and the solver

CONOPT are used in the resolution of the optimization problem. The restriction of stoichiometric balance and non-negativity of number of moles were imposed to the proposed solid-liquid-liquid-vapor (S+L₁ (water)+L₂ (organic phase)+V) model.

Twenty-three (23) compounds are selected to represent the possible products in FTS reaction, including linear aliphatic hydrocarbons from C₂-C₂₀. The effects of reaction conditions are analyzed under HC production and products composition, effects of temperature (in the range of 350-550 K), pressure (in the range of 5-30 bar) and H₂/CO ratio used in the feed (in the range of 1.0-2.0/0.5-1.0) were evaluated.

2. Methodology

2.1. Model development

Gibbs energy minimization method is based in the fact that the equilibrium state is reached when the total Gibbs energy of the system reach a minimum value. The total Gibbs energy can be determined by the following equation:

$$G = \sum_{i=1}^N \sum_{k=1}^F n_i^k \mu_i^k \quad (1)$$

where i represent the compounds and k the phases in the system. G represents the Gibbs energy, n_i^k represents the number of moles of component i in phase k and μ_i^k represents the chemical potential of component i in phase k .

Equation 1 can be rewritten as:

$$G = \sum_{i=1}^{NC} n_i^g (\mu_i^0 + RT(\ln P + \ln y_i + \ln \phi_i)) + \sum_{m=1}^{NL} \sum_{i=1}^{NC} n_i^l (\mu_i^0 + RT(\ln P + \ln x_i^l + \ln \gamma_i^l)) + \sum_{i=1}^{NC} n_{C(s)}^s \mu_{C(s)}^0 \quad (2)$$

where y_i represents the composition of component i in gas phase and x_i represents the composition of component i in liquid phase. P is the pressure, R the universal constant of gases and T the temperature, NC represents the number of components and NL is the number of liquid phases. In this paper we considered a total immiscibility model between two liquid phases (aqueous and organic) present in the system, to represent the nonideality in the liquid-liquid equilibrium between water and HC. Also, in the simulations each phase is considered as an ideal phase with respect to the components in them ($\phi_i = 1$ and $\gamma_i = 1$).

Equation 2 can be minimized to determine the equilibrium compositions of the system, but some additional restrictions needs to be imposed to perform the calculations. The first restriction is imposed by non-negativity of number of moles, given by:

$$n_i^k \geq 0 \quad (3)$$

In this paper we used the stoichiometric formulation to represent the restriction imposed by mass balance. This restriction is represented by:

$$\sum_{k=1}^{NP} n_{ik} = n_i^0 + \sum_{j=1}^{NR} \nu_{ij} \xi_j \quad (4)$$

Where NP is the number of phases and NR is the number of reaction involved in the process ν_{ij} is the stoichiometric coefficient of component i in reaction j and ξ_j represents the extent of the reaction j .

In this paper, was developed a model with the consideration of total immiscibility of two liquid phases (one composed by HC and one composed only by water), the model also considers a possible formation of one solid phase, composed only by solid carbon (coke, C_(s)), and one gas phase. This model, was mathematically represented by Equation 5.

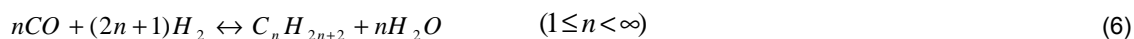
$$\min G = \sum_{i=1}^{NC} n_i^g (\mu_i^0 + RT(\ln P + \ln y_i)) + \sum_{i=1}^{NC} n_i^{l1} (\mu_i^0 + RT(\ln P + \ln x_i)) + \sum_{i=1}^{NC} n_i^{l2} (\mu_i^0 + RT(\ln P + \ln x_i)) + \sum_{i=1}^{NC} n_{C(s)}^s \mu_{C(s)}^0 \quad (5)$$

Similar models were developed in previous works of our research group. Silva and Guirardello (2010) developed a Gibbs energy minimization model to study the hydrocarbon production from syngas. This kind of model was used to study other reactions too. Glycerol reforming methods, supercritical water gasification of different

biomass material and methane reforming were tested in previous works of our research group, and good representation of experimental data were found for these systems (Freitas and Guirardello, 2012, 2014 a, b, c).

2.2. Model implementation

The software GAMS (General Algebraic Modeling System) with the CONOPT solver was used to solve the combined chemical and phase equilibrium problem. A description of GAMS software can be found in Brooke et al. (1998). The general equation, used to represent the formation of hydrocarbons from syngas, by FTS type process, was presented in Equation 6. Besides this reaction, the water gas shift reaction was also considered (Equation 7).



Twenty-three (23) possible compounds are considered during the simulations, including linear hydrocarbons in the range composed by C₂-C₂₀ plus CO, CO₂, H₂O and H₂ (Khodakov et al., 2002). These compounds are selected based in experimental composition presented in papers from literature (Marvast et al., 2005).

All thermodynamic data used in calculations are obtained in Reid et al. (1988). CH₄ formation was inhibited to represent the catalyst effect in the system (Raje, et al., 1997). In next sections the effects of temperature, pressure and H₂/CO molar ratio used in the feed are studied under reactants (CO and H₂) conversion, HC yield and high HC (with more than 5 carbons in the chain, C₅₊) production.

3. Results and discussion

3.1. Temperature effect

Table 1 depicts the temperature effect in the FTS system, for reactants (H₂ and CO) conversion, H₂ yield to HC and total number of moles of HC produced during the reaction. For these simulations, pressure and H₂/CO molar ratio in the feed are kept constant at 10 bar and 2.0/1.0, respectively.

Table 1. Effect of reaction temperature under FTS reaction for HC production

Temp. (K)	CO conv. (%)	H ₂ conv. (%)	H ₂ yield to HC	C ₅₊ (mol)
350	92.0	100.0	54.0	0.09139
400	82.7	100.0	58.7	0.01065
450	80.5	100.0	59.7	0.00016
500	80.4	100.0	59.8	0.00007
550	80.3	99.9	59.8	0.00004

Analyzing this data is possible to verify that the elevation of reaction temperature results in reductions in both, CO and H₂ conversion. The H₂ yield to HC increased with the elevation of reaction temperature.

This behavior can be explained due the fact the total number of moles of short chain (C₂ to C₄) HC produced increase at these conditions, thus, the H₂ yield to HC increases, but the HC produced does not present good quality for application as fuels. This behavior can be visualized observing the last column in Table 1, that presents the sum of the total number of moles of HC, with more than 5 carbons in the chain, produced in the system. The production of these HC reduced with the increase in reaction temperature.

Figure 1 shows the molar fraction of HC produced (considering only the HC phase, L₂ in the model) as function of the number of carbons in HC chain and reaction temperature in logarithmic scale. From this figure is interesting to emphasize that, conditions of liquid-liquid-vapor (L₁+L₂+V) equilibrium are reached only at 350 and 400 K, and at these conditions, more significant production of high chain HC are observed. At temperatures higher than 400 K only vapor phase are formed in the systems.

Analyzing the data, it is possible to verify that, high chain HC are produced at low temperature conditions in liquid phase. C₂₀ was formed only at 350 K, the hydrocarbon produced with high carbon chain, at 400 K was C₁₄, at 450 K was C₉, at 500 K was C₈ and at 550 K was C₆. This behavior was expected, because high temperature conditions are related to present negative effect under high chain hydrocarbon production in synthesis processes from syngas (Pirola et al., 2014). In none of tested conditions solid carbon formation was observed.

3.2. Pressure effect

Pressure is related to present significant effect in FTS systems. The effect of pressure was evaluated again for reactants (CO and H₂) conversion, H₂ yield to HC and total number of moles of C₅₊ produced in the system, and

these results are presented in Table 2. All simulations presented in this section were performed at constant temperature (373.15 K) and H₂/CO molar ratio (2.0/1.0) in the feed.

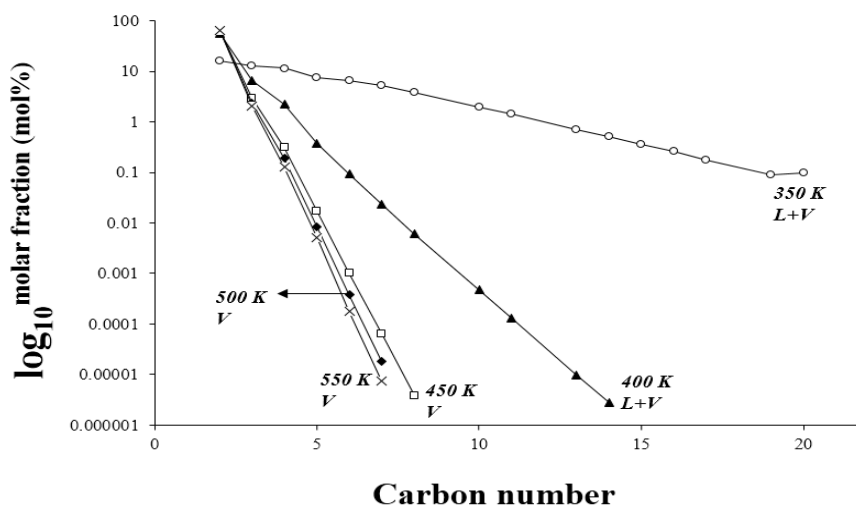


Figure 1. Molar fraction of HC produced by FTS reaction as function of number of carbons in the molecule and temperature

Table 2. Effect of system pressure under FTS reaction for HC production.

Pressure (bar)	CO conv. (%)	H ₂ conv. (%)	H ₂ yield to HC	C ₅₊ (mol)
5	81.5	100.0	59.3	0.00317
10	84.4	100.0	57.8	0.02701
15	88.4	100.0	55.8	0.06708
20	90.3	100.0	55.0	0.08171
30	90.8	100.0	54.6	0.08799

For pressures from 5 to 20 bar are observed conditions of L₁+L₂+V equilibrium. At 30 bar, only the liquid phases (L₁ + L₂) are formed. In none of tested conditions solid carbon formation was observed. High H₂ and CO conversions are observed in all range of pressure analyzed, but is possible to see that the elevation of pressure resulted in increased CO conversion. H₂ conversion was 100% in all conditions analyzed. The yield of H₂ into HC decreased with the increase of reaction pressure, this behavior was expected and desired in FTS systems, mainly because this means that HC with high chain are being produced at these conditions. This behavior is emphasized by the moles of C₅₊ produced during the FTS process, this number increases significantly and directly with the pressure.

The molar fraction of the HC produced in logarithmic scale, as a function of the number of carbons in the chain and system pressure effects are presented in Figure 2. Analyzing Figure 2 is possible to verify that the elevation of pressure results in increases in high chain HC production. From the pressure of 10 bar, the formation of C₂₀ (large HC possible to be formed in simulations) was observed for all pressures tested (15, 20 and 30 bar). Furthermore, was observed that the major part of the HC produced stays at liquid phase, only short chain HC remains at vapor phase. Similar behavior was related in the experiments performed by Das et al. (2003).

3.3. H₂/CO molar ratio effect

In this section the effect of H₂/CO ratio used in the feed were evaluated on the behavior of HC synthesis in FTS reaction. The effects of CO and H₂ suppression are studied, pressure and temperature are kept constant for all simulations at 15 bar and 373.15 K, respectively. The results for reactants (CO and H₂) conversion, H₂ yield to HC and total moles of C₅₊ HC produced are presented in Table 3.

Analyzing the results presented in table 3 it is possible to verify that CO conversion reduces significantly with the reduction of H₂ ratio in the feed. Similar trend was observed for H₂ conversion in the cases where CO was suppressed.

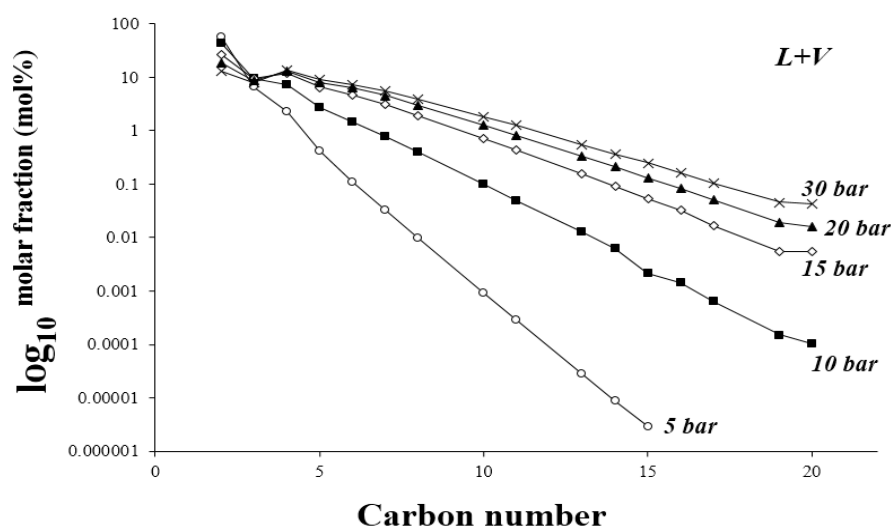


Figure 2. Molar fraction of HC produced by FTS reaction as function of number of carbons in the molecule and pressure

Table 3. Effect of H_2/CO molar ratio used in the feed under FTS reaction for HC production

H_2/CO ratio	CO conv. (%)	H_2 conv. (%)	H_2 yield to HC	Moles of C_{5+}
2.0/1.0	88.4	100.0	55.8	0.0671
1.5/1.0	63.8	100.0	57.5	0.0259
1.0/1.0	41.5	100.0	58.5	0.0072
2.0/0.75	100.0	93.7	60.0	0.0000
2.0/0.5	100.0	62.5	60.0	0.0000

The hydrogen yield increases with H_2 suppression, this behavior can be explained by the fact the total number of moles of short chain HC (C_2 to C_4) produced increase at these conditions. Thus, the H_2 yield to HC increases, but as mentioned before for temperature effect, this behavior was not interesting, because the HC produced presents very low quality for further application as fuel. The total number of moles of C_{5+} produced emphasizes this trend, as can be seen at last column in Table 3. For all studied systems, conditions of L_1+L_2+V equilibrium are observed and no solid carbon formation was observed.

Figure 3 presents the effects of H_2/CO ratio used in the feed and the carbon number in the HC chain in logarithmic scale. Analyzing the results presented it is possible to verify that both, CO and H_2 suppression resulted in negative effects for HC production in FTS reaction. H_2 suppression resulted in reduced production of long chain HC, but CO suppression proved to be more expressive in this inhibition effect, the largest HC produced in the cases where CO was suppressed in the feed stream was C_4 (for H_2/CO ratio of 2.0/0.75).

This effect can be explained due to mandatory effect that CO represents for HC production in FTS type reaction, the behavior of CO in FTS processes was better explained in some papers in literature that studied the reaction mechanism of FTS (Davis, 2001). Analyzing this figure it is possible to verify that H_2/CO molar ratio presented a significant effect under HC production in FTS reaction, and the effect of CO suppression proved to be more significant and detrimental for the system than the H_2 suppression.

4. Conclusion

The effects of reaction conditions are evaluated in FTS for HC productions from syngas. The effects of temperature, pressure and H_2/CO molar ratio in the feed are studied and show to have significant effects on HC production and under products characteristics. High chain HC production demonstrated to be viable in conditions of high pressure (higher than 15 bar), low temperature (lower than 400 K) and H_2/CO molar ratio of 2.0/1.0. Solid carbon formation was not observed in conditions analyzed by this paper to promote FTS reaction. The proposed thermodynamic model, considering a solid-liquid-liquid-vapor ($S+L_1+L_2+V$) equilibrium, showed to be reliable to perform equilibrium calculations using Gibbs energy minimization method in FTS systems. For all studied systems, low computational times (lower than 10 s) are observed.

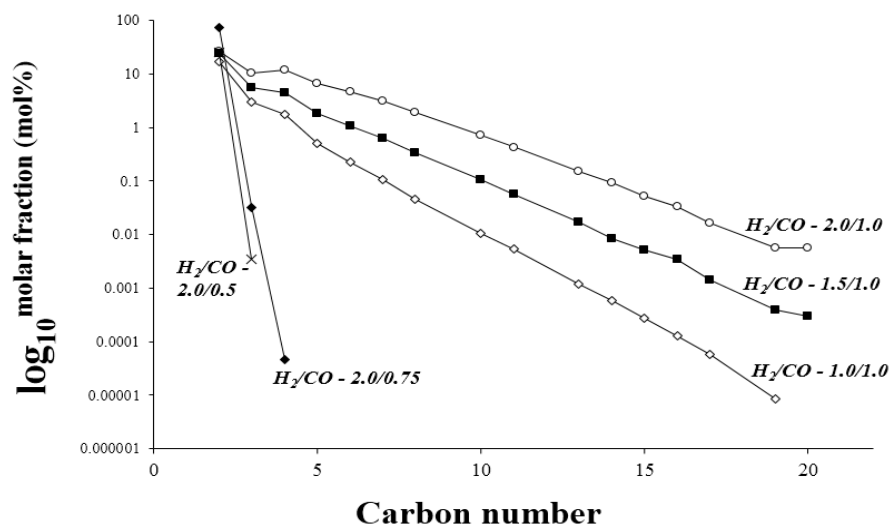


Figure 3. Molar fraction of HC produced by FTS reaction as function of number of carbons in the molecule and H_2/CO molar ratio used in the feed

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