

Thermodynamic Analysis for Fischer-Tropsch Synthesis Using Biomass

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The use of biomass to produce environmental cleaner fuels has been gaining more attention in the past decades due to the socio-economic benefits over the petrochemical route. For instance, the conversion of synthesis gas (H_2 and CO) obtained from biomass into fuel using Fischer-Tropsch (FT) process and catalysts, which is conventionally based on iron and cobalt. This process generates a mixture of light olefins, wax, gasoline, diesel, and alcohols. In fact, operating conditions (such as temperature, pressure, H_2/CO ratio and catalyst composition) can predict the FT products range. The thermodynamic modeling of this system is calculated by phase and chemical equilibrium, applying global optimization techniques to minimize the Gibbs energy of the system, subject to the restrictions of stoichiometric balances for each reaction considered and non-negativity of the number of moles. In addition, the catalytic effect is taken into account in the constraints of the model. Thus, the purpose of this work is the evaluation of the chemical equilibrium for the multiphase mixture (alkenes, alkanes, alcohols, CO_2 , H_2O , H_2 , and CO) in order to provide the phase composition for the FT process. The thermodynamic modeling was developed with a non-linear program (NLP) and solved by GAMS (General Algebraic Modeling System) software with the CONOPT3 solver. Moreover, we analyzed the effect of operating conditions (temperature, pressure, and H_2/CO molar ratio), considering an ideal system (Raoult's law) in the liquid phase for the thermodynamic characterization.

1. Introduction

Consume of fuels has been increasing; according to Ail & Dasappa (2016), the energy demand will increase average about 1.6% annually until 2035. These facts lead to a future with more renewable resources, instead of fossil energy, due to socio-economic benefits and environmental impact. The biomass has been a promising energy source towards generation of biofuels like ethanol and diesel. One of these technologies to get fuels from biomass is to convert biomass to synthesis gas (H_2 and CO), followed by the conversion into fuels via Fischer-Tropsch Synthesis (FTS) (Swain et al. 2011).

Fischer-Tropsch Synthesis is a catalytic process that produces a large mixture of hydrocarbons (HC), which includes light olefins, wax, gasoline, diesel and alcohols. This process is particularly complex due to different serial reactions that occur, producing alkanes, alkenes, alcohols, and some equilibrium reactions, such as water-gas-shift (WGS), methane reaction and Boudouard reaction (Dry 2002).

Fischer-Tropsch products are cleaner than fossil fuels, and quality of them depend on operational conditions in which the process occurs, on catalyst composition, and the reactor design. The practical conditions that affects the FT process are temperature, pressure and the feed ratio of syngas (i.e., H_2/CO ratio). The commercial catalysts employed in this process are based in cobalt and iron; although there is an abundance of research wherein include different promoters in the catalyst to increase the product selectivity (Everson et al. 1978; Iglesia et al. 1992). The FT reactors can be separated in two classes, corresponding to work conditions, which are: the High Temperature Fischer-Tropsch (HTFT) and the Low Temperature Fischer-Tropsch (LTFT).

The HTFT process involves two phases: one gas phase (reactants and products) and one solid phase (catalyst), operating in a temperature range of 300 to 350 °C. In the LTFT process there are three phases associated; these reactors, known as slurry phase bubble column reactor, consist in gas, solid, and a liquid

phase where the catalyst particles are immersed. These reactors run in a temperature range of 200 to 250 °C (Espinoza et al. 1999).

There are several studies and investigations to comprehend the mechanisms and improving the FT products selectivity based on kinetics and thermodynamic models. According to Norval (2008), an approach based in the thermodynamic equilibrium can describe the FT process performance. This method is simpler than kinetics models and can predict the products phase behaviour. Besides, it is possible to evaluate the effect of operating conditions, such as the temperature, pressure and H₂/CO ratio (Pacheco & Guirardello 2017).

Stenger & Askonas (1986) observed that the thermodynamic product distributions is similar to the experimental. In a recent research, Freitas & Guirardello (2016) developed a study for FT system combining Gibbs energy minimization and Soave-Redlich-Kwong equation of state as optimization problem using linear programming; and concluded that high pressure and low temperature provided the best conditions for formation of high chain hydrocarbons. Marano & Holder (1997) have formulated a vapor-liquid equilibrium model for FTS whereby the solubility of gas and light hydrocarbons was calculated using a correlation of pseudocomponent, as n-paraffin solvent, in the liquid phase for an individual solute.

For these reasons, this paper aimed to evaluate the effect of operating conditions (temperature, pressure and feed composition) in the FT process, using a thermodynamic analysis, in a reactor containing a solvent as the liquid phase in the feed, like a slurry phase reactor (three-phase). The method employed optimization techniques, based in the minimization of the Gibbs energy, with simultaneous phase and chemical equilibrium. We considered the possibility of a system that may contain up to four phases: solid, gas, organic liquid and aqueous liquid phases. The thermodynamic analysis allowed to predict the products formed in the chemical equilibrium for the FTS, and from that, it was possible to define better operating conditions to produce high weight hydrocarbons (diesel and gasoline) and alcohols.

2. Methodology

The thermodynamic equilibrium of a multicomponent and multiphase system can be calculated via Gibbs energy minimization, by Eq (1). When the system is in equilibrium, the Gibbs energy reaches a minimum value (Smith & Missen 1982).

$$G = \sum_{i=1}^{NC} \sum_{\pi=1}^{NP} n_i^{\pi} \mu_i^{\pi} \quad (1)$$

where n_i^{π} and μ_i^{π} represent the number of moles and the chemical potential of component i in phase π , respectively. NC and NP are the number of compounds and the number of phases, respectively. The chemical potential can be calculated by Eq (2).

$$\mu_i^{\pi} = \mu_i^0 + RT \ln \left(\frac{\hat{f}_i^{\pi}}{f_i^0} \right) \quad (2)$$

In Eq (2), μ_i^0 is the chemical potential in the reference state, and it is calculated from the formation properties under a reference condition, as well as the fugacity in the reference state (f_i^0). R represents the universal constant of gases, and T is the system temperature. The fugacity of each component (\hat{f}_i^{π}) in the gas phase (\hat{f}_i^g) is obtained from Eq (3), while in the liquid phase (\hat{f}_i^l) it is calculated by Eq (4).

$$\hat{f}_i^g = y_i \cdot \hat{\phi}_i^g \cdot P \quad (3)$$

$$\hat{f}_i^l = x_i \cdot \gamma_i \cdot P_i^{sat} \quad (4)$$

where y_i and x_i are the mole fraction of each component i in the gas and liquid phases, respectively; P is the pressure of the system and P_i^{sat} is the saturation pressure. In this paper, we have treated each individual phase as an ideal phase ($\hat{\phi}_i^g = 1$ and $\gamma_i = 1$), using Raoult's law in the liquid phase below the critical point.

When the critical temperature of one component is lower than the temperature of the system, then this species leaves its vapor behavior, and becomes a gas, there being no more vapor-liquid equilibrium, but a gas-liquid equilibrium due to the high temperature being over the critical temperature of some components. Hence, Eq (4) cannot represent the fugacity in the liquid phase when the temperature of the system is higher than the critical temperature of some component of the system, because there is no more saturated vapor pressure.

Thus it is possible to predict the species dissolved in the liquid phase by using Eq (5), also known as Henry's law, where H_i is the Henry constant for component i .

$$\hat{f}_i^l = x_i \cdot H_i \quad (5)$$

To determine the fugacity in the liquid phase, we use a conditional expression between the Raoult's law and Henry's law. The Henry constants for some compounds in the organic liquid phase was calculated from data published by Marano & Holder (1997), considering n-hexadecane as pseudo-solvent. The Henry constants for the compounds dissolved in the aqueous liquid phase were obtained from NIST Standard Reference Database. In this paper, we considered the partial miscibility between the two liquid phases through the Henry's law to represent liquid-liquid equilibrium.

The Gibbs energy minimization was modeled as an optimization problem, and we considered the following constraints for this model: the non-negativity of the number of moles – Eq (6) – and the material balance represented by stoichiometric formulation – Eq (7), instead of the atom balance.

$$n_i^\pi \geq 0 \quad (6)$$

$$\sum_{\pi=1}^{NP} n_i^\pi = n_i^0 + \sum_{j=1}^{NR} \nu_{ij} \xi_j \quad (7)$$

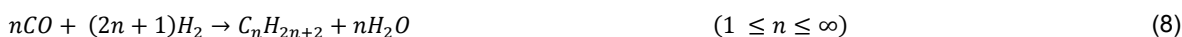
where n_i^0 is the initial number of moles of the component i , ν_{ij} represents the stoichiometric coefficient of the component i in reaction j , ξ_j is the extent of reaction j , and NR is the number of independent reactions. Other constraints included in this problem are the inhibition of methane formation (Freitas & Guirardello 2015) and the limitation of CO₂ formation as catalyst effect of cobalt (van Berge & Everson 1997).

We also considered the possible formation of one solid phase, composed by coke. We assumed the solid phase as ideal. In this way, the system may present up to four phases: one gas phase, two immiscible or partially miscible liquid phases (organic and aqueous, each one modeled as an ideal phase), and one solid phase. The Gibbs energy minimization approach disregard any kind of flow, since it is a closed system, or kinetic effect. According to Pacheco & Guirardello (2017), with the thermodynamic analysis, its possible to predict the chain growth probability values, independent of the mechanism and the catalyst.

This optimization problem, formulated as nonlinear program (NLP), was solved by the software GAMS (General Algebraic Modeling System) using the CONOPT algorithm. For the thermodynamic analysis of the system in the chemical equilibrium, we have considered the possibility of formation of 20 linear alkanes (C₁ – C₂₀), 7 alpha alkenes (C₂-C₈), 3 alcohols (C₁-C₃), water, solid carbon and carbon dioxide; plus the reactants hydrogen and carbon monoxide. These compounds were selected based on the literature (Dry 2002). From this model, we evaluated the effect of the temperature (400 – 900 K), the pressure (5 – 50 bar) and the H₂/CO inlet molar ratio for 2.0 and 2.3, representing a slurry phase bubble column reactor.

3. Results and discussion

The model given by Eq (8)-(10) describes the generic reactions that occurs during the FTS to produce paraffins, olefins and alcohols, respectively; followed by the water-gas-shift reaction – Eq (11). From these equations, the prediction of the best operating conditions to generate hydrocarbons, with higher carbon number, was possible. Under all conditions analyzed in this work no formation of solid carbon was observed.



First, we have compared the effect of carbon monoxide conversion for the temperature range of 400 to 900 K, pressure range of 5 to 50 bar and the H₂/CO molars ratio in the feed equal to 2.0 and 2.3, representing the usually H₂/CO molar ratio applied in the LTFT process (Ail & Dasappa 2016).

Figure 1 shows the conversion of carbon monoxide as function of temperature and pressure for the H₂/CO inlet molars ratio of 2.0 and 2.3, respectively. As can be seen, the increase of temperature leads to the decrease of the CO conversion, while the increase of pressure causes a rise in the CO conversion. However,

this pressure effect is more accentuated for high temperatures than low temperatures. Considering the temperature of 400 K, from the pressure of 5 to 50 bar, there is an increase of 1.89%, while the temperature of 900 K shows an increase of 43.65% at the same pressure range.

Comparing the CO conversion to both H_2/CO molar ratio, we noted that the CO conversion is bigger for H_2/CO molar ratio equal to 2.3 than to 2.0. This obviously occurs because in the thermodynamic equilibrium, the increase of hydrogen inlet causes the elevation of carbon monoxide consume, promoting high CO conversions. Pirola et al. (2014) also have reported the molar ratio effect at CO conversion in their experimental work using iron loaded supported catalysts for H_2/CO molar ratio range of 1 to 2.

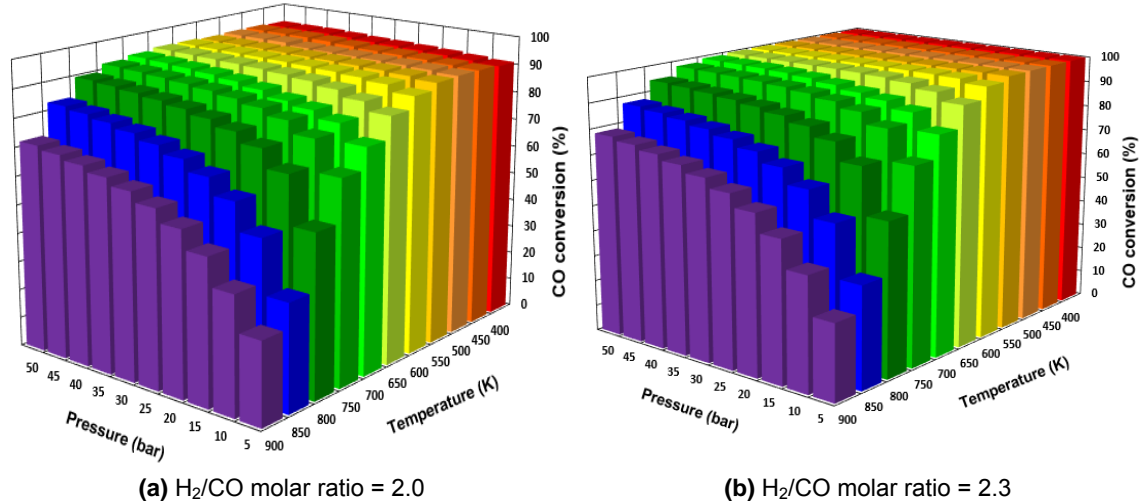


Figure 1: The effect of temperature, pressure and H_2/CO inlet molar ratio on the carbon monoxide conversion

The hydrogen yield to hydrocarbon for both H_2/CO inlet molar ratio is greater than 57% for all temperature and pressure ranges (Figure 2). The pressure likewise does not significantly affect the hydrogen yield to hydrocarbon as well as the carbon monoxide conversion, as observed above. The H_2 yield to HC decreases with the increase of H_2/CO inlet molar ratio from 2.0 to 2.3. Pacheco & Guirardello (2017) related the maximum yield to HC as 72.4% and 66.1% for a feed molar composition of H_2/CO of 2.0 and 3.0, respectively. While in this work, the maximum hydrogen yield to hydrocarbon corresponds to 62.3% and 61.3% for H_2/CO inlet molar ratio of 2.0 and 2.3, respectively.

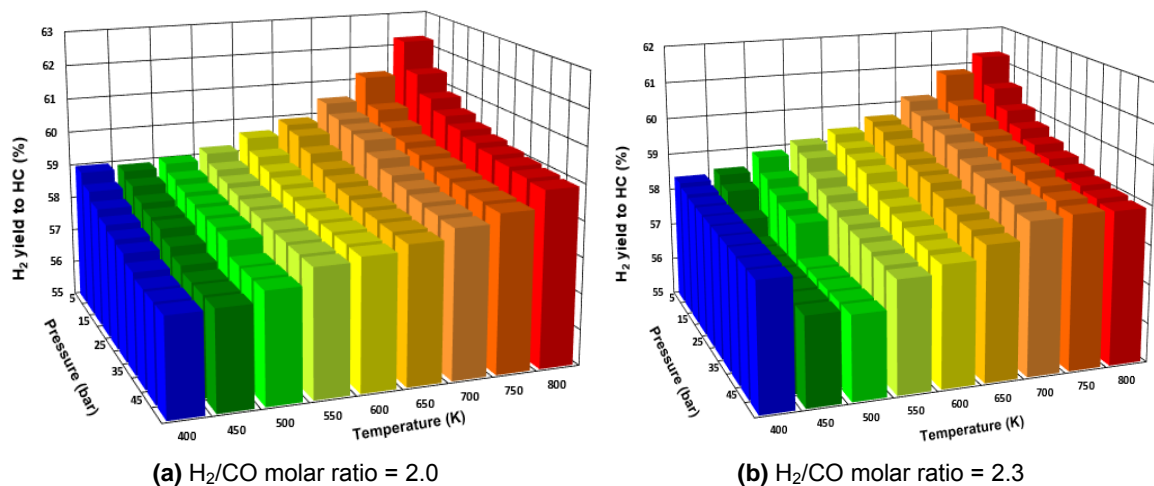


Figure 2: The effect of temperature, pressure and H_2/CO inlet molar ratio on the hydrogen yield to hydrocarbon

As seen in the Figure 2, high temperatures exhibit an increase in the hydrogen yield to hydrocarbon. However, this feature does not lead to a good operational condition, because high temperatures increase the formation

of hydrocarbons with short chains. Whereas the high quality fuels expected through FTS are hydrocarbons with long chain, greater than C_{5+} , in the cuts of gasoline and diesel. The Figure 3 shows how the temperature and the pressure influence the distribution of C_{5+} Fischer-Tropsch products.

As noted before, high temperatures have a negative influence on the production of long chain hydrocarbons during Fischer-Tropsch process. The maximum C_{5+} molar fraction of FT products (36.6% of the FT products) is achieved at the temperature of 370 K, as shown in the Figure 3. While temperatures above 490 K have a distribution of C_{5+} Fischer-Tropsch products lower than 5%. Pressures greater than 25 bar do not affect the product distribution. Also, the product distribution was fitted by the chain growth probability factor (α) from a log-linear straight line (Norval, 2008). Alpha values for H_2/CO molar ratio of 2/1 and 530 K, at pressures of 25 and 40 bar is 0.081 and 0.082, respectively.

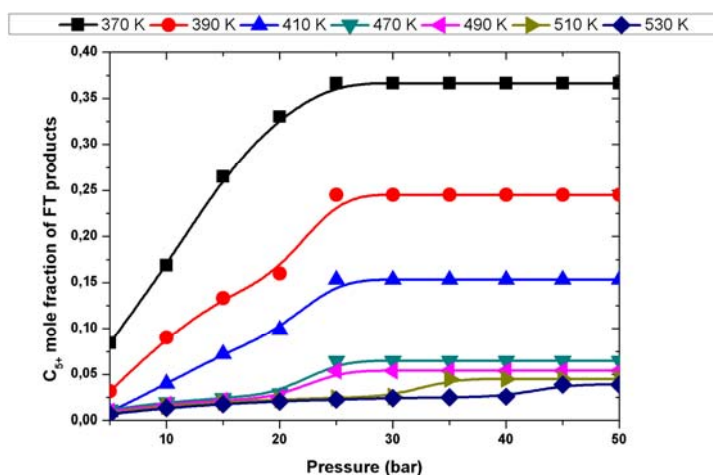


Figure 3: The effect of temperature and pressure in the distribution of C_{5+} Fischer-Tropsch products for H_2/CO inlet molar ratio of 2.0. (The calculations were applied only at the points, and the curves were fitted)

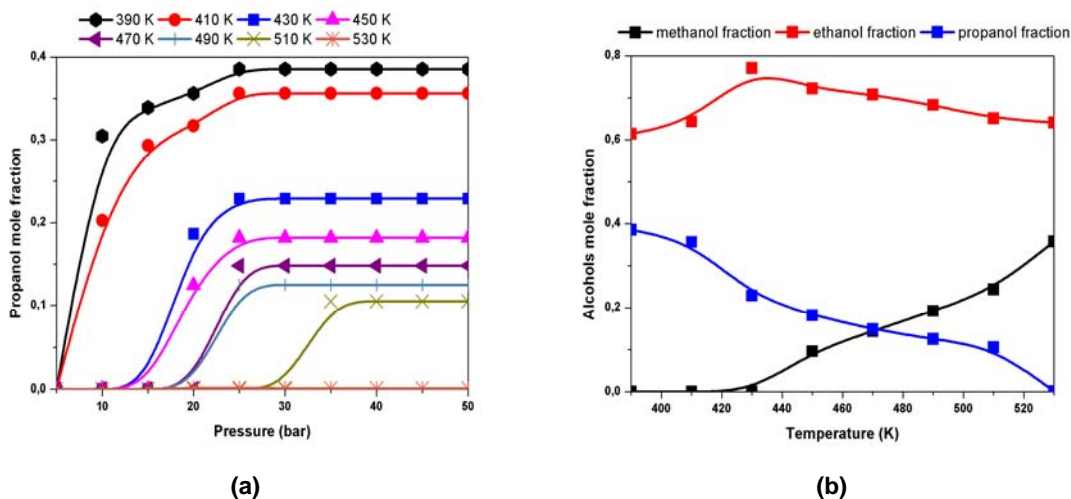


Figure 4: (a) Effect of temperature and pressure on the propanol formation during FTS for H_2/CO inlet molar ratio of 2.0. (b) Effect of temperature in the distribution of alcohols during FTS for pressure of 50 bar and H_2/CO inlet molar ratio of 2.0. (The calculations were applied only at the points, and the curves were fitted)

For all conditions analyzed, the majority of products formed during Fischer-Tropsch process are alkanes. These alkanes are present in the gas and liquid organic phase. The liquid solvent exhibited a high influence to C_{5+} be in the liquid phase in the equilibrium. But, in high temperatures ($T > 450$ K), only gas phase was formed, even in the presence of solvent. Moreover, we noticed the presence of small traces of some hydrocarbons (from ethane to pentane) in the aqueous liquid phase, as result of the pressure increase.

Usually, alcohols are co-products in the Fischer-Tropsch process, but they have a high value. Hence, we also evaluated the influence of operational conditions in the alcohol production. The Figure 4a shows that the

pressure has an important influence in the propanol formation, such high levels of propanol mole fraction are achieved at pressures above 25 bar. Among the three alcohols considered in this analysis, the ethanol exhibited the larger mole fraction, over 60% for all temperatures, as can be viewed in the Figure 4b. High temperatures have a positive impact on the formation of methanol, unlike propanol, that shows a negative effect over high temperatures.

4. Conclusions

The thermodynamic analysis for Fischer-Tropsch synthesis conducted by a conditional expression in the liquid phase between the Raoult's law and Henry's law had an accurate effect to represent both liquid phases (organic and aqueous). The temperature range of 370 to 510 K shows the best conditions for production of paraffins, and co-products, such as alcohols. Moreover, we concluded that a higher hydrogen yield to HC at high temperatures does not mean a more favourable operating condition, because the best conditions tested in this work to achieve a desirable distribution of long chain hydrocarbons are temperatures below 410 K, pressures above 25 bar, and H₂/CO inlet molar ratio of 2.0. Although a real FT system is not at chemical equilibrium, the Gibbs energy minimization with the constraints of methane reaction and cobalt catalyst effect, on the WGS reaction, was able to predict the formation of FT products under different operating conditions.

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Reference

- Ail, S.S. & Dasappa, S., 2016. Biomass to liquid transportation fuel via Fischer Tropsch synthesis - Technology review and current scenario. *Renewable and Sustainable Energy Reviews*, 58, pp.267–286.
- van Berge, P.J. & Everson, R.C., 1997. Cobalt as an alternative Fischer-Tropsch catalyst to iron for the production of middle distillates. *Studies in Surface Science and Catalysis*, 107(15), pp.207–212.
- Dry, M.E., 2002. The Fischer-Tropsch process: 1950-2000. *Catalysis Today*, 71(3–4), pp.227–241.
- Espinoza, R.L. et al., 1999. Low temperature Fischer–Tropsch synthesis from a Sasol perspective. *Applied Catalysis A: General*, 186(1–2), pp.13–26.
- Everson, R.C., Woodburn, E.T. & Kirk, A.R.M., 1978. Fischer-Tropsch reaction studies with supported ruthenium catalysts. *Journal of Catalysis*, 53, pp.186–197.
- Freitas, A.C.D. & Guirardello, R., 2016. Predictive Thermodynamic Modelling of Liquid-Liquid-Vapor- Fluid (LLVF) Equilibrium in Synthetic Hydrocarbon Synthesis from Syngas. *Chemical Engineering Transactions*, 50(3), pp.313–318.
- Freitas, A.C.D. & Guirardello, R., 2015. Thermodynamic characterization of hydrocarbon synthesis from syngas using fischer-tropsch type reaction. *Chemical Engineering Transactions*, 43, pp.1831–1836.
- Iglesia, E., Soled, S.L. & Fiato, R.A., 1992. Fischer-Tropsch synthesis on cobalt and ruthenium. Metal dispersion and support effects on reaction rate and selectivity. *Journal of Catalysis*, 137(1), pp.212–224.
- Marano, J.J. & Holder, G.D., 1997. Characterization of Fischer-Tropsch liquids for vapor-liquid equilibria calculations. *Fluid Phase Equilibria*, 138(1–2), pp.1–21.
- National Institute of Standards and Technology, 2017. NIST Standard Reference Database 69: NIST Chemistry WebBook. Available at: <http://webbook.nist.gov/chemistry/> [Accessed October 31, 2017].
- Norval, G.W., 2008. Notes on the issues of equilibrium in the Fischer-Tropsch synthesis. *Canadian Journal of Chemical Engineering*, 86(6), pp.1062–1069.
- Pacheco, K.A. & Guirardello, R., 2017. Analysis and Characterization of Fischer-Tropsch Products through Thermodynamic Equilibrium using Global Optimization Techniques. *Chemical Engineering Transactions*, 57, pp.1669–1674.
- Pirola, C. et al., 2014. Biosyngas conversion by fischer-tropsch synthesis: Experimental results and multi-scale simulation of a pbr with high fe loaded supported catalysts. *Chemical Engineering Transactions*, 37, pp.595–600.
- Smith, W.R. & Missen, R.W., 1982. *Chemical Reaction Equilibrium Analysis: theory and algorithms*, New York: Wiley New York.
- Stenger, H.G. & Askonas, C.F., 1986. Thermodynamic product distributions for the Fischer-Tropsch synthesis. *Industrial & Engineering Chemistry Fundamentals*, 25(3), pp.410–413.