

Reliability of an Open-source Continuous Chemical Process Simulator to Demonstrate a Complex Transesterification Reaction

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Abstract— Reaction mechanisms are usually simulated as a mechanistic study on simulators that require a mathematical model to be entered manually. Models that simulate reaction mechanisms are of the stochastic/deterministic or continuous/discrete nature that generates data once the variables are fixed. This is a tedious task as it requires observing the reaction mechanism - no further investigation just observe how the mechanisms behave and whether the results are accurate or not and if not then to what extent. This research tries to minimize this tediousness by simulating the reaction mechanisms for a complex reaction such as transesterification, to observe the accuracy of the simulator. It does so by simulating two different reaction mechanisms using a formulated model while observing the %conversion as a way to determine the accuracy of the model. This paper also performs an unorthodox reactor setup, in which the reactor is made to simulate Eley-rideal/ Langmuir-Hinshelwood mechanisms of reaction. After manipulating the parameters of the model, the results of the simulation were compared to those obtained from lab experiments for purpose of validation. A Comparison between lab and simulation experiments show that amongst the two prevalent mechanisms of reaction, the simulation of the E-R mechanism provided more accurate and realistic results than the simulation of the L-H mechanism.

Keywords— Eley-Rideal Mechanism, Langmuir-Hinshelwood Mechanism, Mass Transfer Kinetics, Reaction Mechanism, Reaction Setup.

I. INTRODUCTION

Modeling is a tiresome process but can demonstrate the functioning of a hypothetical system, to observe its workings. It is necessary to solve a model after its development the complexity of the model makes it difficult to obtain converging solutions. This is where a computer can help. Using a mathematical model, a computer can simulate a hypothetical system and successfully observe its behavior. Computer simulations have become a useful tool for the mathematical modeling of many natural systems including but not limited to climatology, economics, social science, physics, biology, astrophysics, chemistry, psychology, and engineering. Simulation of a system is the convergence of a model for that system. They can help gain insight into prospective technology and approximate the performance of systems too complex for analytical solutions [1].

Computer simulations can either be small or large scale programs running for brief instances or hours or days, respectively, the latter requiring a network-based group of computers [2]. The behavior of the modeled system inside a computer simulation is captured using algorithms and equations, performing a vast number of calculations in a matter of seconds. Computer simulation requires the actual running of a program that contains these equations or algorithms to provide for a variety of behaviors to be observed. Simulation, therefore, is the process of running a model. Thus one would not "build a simulation"; instead, one would "build a model", and then either "run the model" or equivalently "run a simulation [2].

There are various types of computer models depending on the attributes. These include [3]:

- Stochastic
- Deterministic
- Continuous
- Discrete
- Dynamic system simulation,
- Dynamics simulation of field problems,
- Local
- Distributed

A continuous dynamic simulation performs numerical solution of differential-algebraic equations or differential equations (either partial or ordinary). Periodically, the simulation program solves all the equations and uses the numbers to change the state and output of the simulation. Applications include flight simulators, construction and management simulation games, chemical process modeling, and simulations of electrical circuits. Originally, these kinds of simulations were implemented on analog computers, where the differential equations could be represented directly by various electrical components such as op-amps. By the late 1980s, however, most "analog" simulations were run on conventional digital computers that emulate the behavior of an analog computer [4].

This paper studies whether an established model for an equilibrium reactor can be manipulated as accurately as possible to demonstrate reaction mechanisms. The study simulates the transesterification reaction for the production of biodiesel and uses results from lab experiments as a comparison to validate the manipulations made to the equilibrium reactor model.



II. LITERATURE REVIEW

A. Transesterification

Transesterification is an oil treatment process that reduces the viscosity of inedible oil to an extent where they are ready for use in a diesel engine. For the process to occur, the oil is treated with an alcohol in the presence of a catalyst, to Fatty acid alkyl ester (Biodiesel) and Glycerol. The FAAE is the desired product, biodiesel, from the reaction. The reaction can be shown as follows:

$$\begin{array}{c} CH_2OCOR''' & CH_2OH & R'''COOR \\ \vdots & \vdots \\ CH_2OCOR'' + 3ROH & \xrightarrow{catalyst} & CH_2OH + R''COOR \\ \vdots & \vdots \\ CH_2OCOR' & CH_2OH & R'COOR \end{array}$$

$$Oil + Alcohol \rightarrow Glycerol + Biodiesel$$

The most common catalyst configuration used for the reaction is homogenous catalysis either acid or base. However, as discussed in the previous section, homogeneous catalysis is not preferred due to the following reasons [5]:

1) Water formation inhibits the process. To remove this water, product drying will be required, adding to the cost of the biodiesel produced.

2) Catalyst recycling is not possible or even if possible, has never been done on a production scale due to high costs.

3) Corrosive nature of the catalysts – acid H_2SO_4 and base SMO – involves extremely careful handling. The SMO tends to absorb water and needs to remain under a nitrogen blanket. For shorter storage durations or when the liquid has a short turnaround, blanketing is not necessary. SMO tends to settle and potentially lose its original power over a while if unused and sitting. The related troubleshooting and fixing are extremely time-consuming and expensive.

4) Multiple stages of processes (multi-stage esterification, and multi-stage transesterification). With multiple stages involved, there is a loss of heat, transfer time, wear/tear, and employee training time to address all processes happening simultaneously.

While investigating multiple catalyst types available for the transesterification processes, MK Lam et al. reported preference in utilizing heterogeneous and biological enzymes for the transesterification process [6]. This was due to an industry shift towards the use of inedible oil to produce biodiesel. However, unlike edible oil with its low Free Fatty Acid (FFA) content, inedible oil has a relatively higher FFA content [7]. Because of this, homogeneous catalysis lost preference for transesterification of inedible oil as discussed earlier.

Heterogeneous catalysts are recognized for transesterification of inedible oil, as a prospective technology for obtaining green diesel fuel, neck in neck with mineral diesel fuel. Metal oxides of Magnesium or Calcium are widely considered due to their general availability, although; on their own, have a lower oil to biodiesel conversion. Other heterogeneous catalysts such as zeolites are also available for use [8]. Hydrotalcites, Lithium doped catalysts, a mixture of a solid base, and solid acid catalysts were also tested and observed to give almost complete conversion of oil to biodiesel [9,10]. Tang, Ying et al. focused on reducing the variety of catalysts while simultaneously providing an increased conversion. A solid base catalyst, Calcium oxide, modified by attaching bromoocatane to the catalyst surface and washing with hexane was able to produce a 99.5 % yield of biodiesel from soybean oil employing an oil to alcohol ratio of 15 [11].

B. Mass Transfer Kinetics

Mass transfer kinetics is the study of the effects of certain parameters that will reduce mass transfer resistance and increase the amount of oil converted to biodiesel. It also entails the study of the mechanisms of reaction that is supposedly taking place during the process.

1) Effect of process parameters

Like any other chemical process, in which various parameters both internal and external affect the conversion of the reactants. The study will observe the effect of two process parameters on the amount of reactant. These parameters include:

- 1- Temperature
- 2- Concentration

Previous studies show the effect of these parameters on the amount of inedible oil conversion to biodiesel. Tarik M., et al. observed conversion of Jatropha seed oil under various conditions of temperature, catalyst loading, and concentration of reactants. Optimum conditions for heterogeneous transesterification was observed to be at 70°C at a molar concentration of methanol 9 times greater than that of oil in the feed and a catalyst loading of 1.5wt percentage [12]. Another study, experimenting with sunflower oil, was able to achieve an oil conversion of greater than 90% using CaO as a base catalyst at a temperature of 60°C, 1wt % catalyst loading, and molar alcohol to oil ratio of 13 [13].

Chawalit et al. studied the conversion of palm kernel and achieved a conversion of 49 and 98 % for limestone and dolomite as catalyst materials respectively. Experiments were performed and optimum conditions were observed at 60°C at 6wt % catalyst and methanol to oil ratio of 30 [14]. Viriya-Empikul, N., et al. used eggshells as a CaO source to produce biodiesel from palm olein. At optimum conditions of 18 methanol to oil ratio, 65°C, and 10wt % catalyst, a conversion exceeding 90% was achieved [15].

As can be seen, the process parameters do not give a maximum conversion at a constant value all the time. The conversion of raw oil to biodiesel is also dependent on:

- a) Type of Oil used
- b) Type of alcohol used
- c) Catalyst used
- d) Catalyst treatment method

e) Reaction phase etc.

The study keeps in focus, the effect of the parameters as well as the effect of the reaction mechanism, the latter being a function of the type of alcohol used, as discussed in the upcoming section. Parameters investigated in this study are



Temperature and Oil-Alcohol ratio and their combined effect on Oil conversion to biodiesel.

2) Reaction mechanism

The type of alcohol used for the transesterification reaction determines the yield of the process along with the type of reaction mechanisms that will take place. Two mechanism types vastly govern the transesterification reactions i.e. the Langumiur-hinshelwood (L-H) mechanism and the Eley-Rideal (E-R) mechanism.

To understand the reaction mechanisms as discussed above, knowledge about nucleophilic and electrophilic properties of the carbonyl group, present in triglycerides and alcohol is necessary.

For homogenous base catalysis, by the action of the catalyst, molecules of alcohol become nucleophilic and attack the electrophilic part of the triglyceride molecule [16]. Triglyceride molecules are broken down into three-steps. The first step produces an intermediate tetrahedral. The second step breaks down the unstable intermediate tetrahedral, producing a diglyceride ion and a fatty acid ester. The final step recovers the catalyst by proton transfer.

These steps occur continuously until three fatty acid alkyl esters (if Methanol is being used, the term is fatty acid methyl ester or FAME for short) and a glycerol molecule is formed. In base-catalyzed transesterification, free fatty acid concentration needs to be low to avoid soap formation [17].



Figure 1: L-H mechanism of Transesterification with TG [18, 19]

Homogeneous acid catalysis differs from the basecatalyzed reaction in that, over here, the triglyceride is more electrophilic and susceptible to attack by alcohol, although the process is slower and reaction rate differs for both types of catalysts.

Now focusing on Heterogeneous base catalysis. Like homogeneous catalysis, both the acidic and basic characteristics of heterogeneous catalysts are important properties for the transesterification of triglyceride molecules. However, both the adsorption and desorption of reactants and products must occur, for a faster rate of reaction. [16].

Two views that cover this aspect of the reaction, as discussed above, namely L-H mechanism (dual-site) and E-R mechanism (single site), are as shown in Figures 1 and 2 respectively.

Dossin et al. studied the L-H model for the transesterification of ethyl acetate with methanol over a magnesium oxide catalyst. As is the case for the dual-site mechanism, both reactants will be adsorbed and then react on the catalyst surface [19]. Figure 1 shows the L-H model describing the transesterification reaction. As can be seen, the reaction is divided into four steps.

Figure 2, shows the adsorption of both reactants on the catalyst surface. Production of a tetrahedral intermediate takes place in the second step (2), giving off a fatty acid alkyl ester in (3) and a diglyceride molecule in (4).



Figure 2: E-R mechanism of Transesterification with TG [20, 21]

The E-R mechanism of reaction constitutes of three-steps. Other than the first step i.e. adsorption of only the alcohol molecule on the catalyst site, the rest of the procedure is almost the same as L-H mechanism.

In layman's terms, for the dual-site mechanism (L-H), adsorption occurs on the catalyst active sites leading to a reaction between the two adsorbed species. For the single site mechanism (E-R) the alcohol is protonated and attacks the triglyceride molecule in the liquid phase. The type of reaction mechanism during transesterification depends on the number of carbon atoms on the alcohol used, according to Suwannkarn et al. [22]. Observation of the transesterification reaction



process shows alcohols with a higher carbon count prefer L-H mechanism while alcohols with a lower carbon count (such as methanol) preferred E-R mechanism [22]. Most often then naught, the process of transesterification prefers lower carbon alcohols, therefore the E-R mechanism is dominant here.

Several authors have investigated the kinetics of transesterification under the influence of homogeneous base catalysts [19]. Still, there is very little information regarding the mass transfer kinetics for transesterification under solid base catalysts. Hattori et al. [23] proposed a reaction mechanism for the transesterification of ethyl acetate with a variety of alcohols catalyzed by a variety of solid base catalysts, particularly alkaline-earth-metal oxides. However, this mechanistic study did neither provide values of activation energies nor rate constants. Another study proposed a kinetic model to describe the transesterification of ethyl acetate using methanol as the alcohol, in the presence of magnesium oxide as a heterogeneous catalyst [19]. The model is based on the E-R mechanism, applied in the liquid phase where methanol adsorption is assumed as the rate-determining step.

When it comes to simulation of the transesterification reaction on a free chemical simulation software only two studies [24, 25], to the best of our knowledge, have been carried out. However, even in that study, only the feasibility of the process to run on a simulator with limited resources is checked. No validation is provided for the results obtained.

The current research simulates the reaction on the same software and provides for validation with experiments performed in the lab at the same conditions. It also shows that for reactions involving different reaction mechanisms, it is possible to set up the reactor in a way to correctly simulate the reaction.

III. MATERIALS AND METHODS

A. Raw Material

For this research, to simulate the transesterification reaction, raw materials included Triolein and Methanol as components for the overall transesterification reaction while Triolein, Methanol, Di-olein, and Mono-olein were components to simulate the systematic transesterification reaction.

B. Simulation Software

The following study uses an Open-source Chemical Simulation Software – Cape Open to Cape Open (COCO). Inside the software, various components help in the successful execution of the simulation. These components include COFE (Cape Open Flow sheeting Environment), TEA (Thermodynamics Engineering Applications package), CORN (Cape Open Reaction Numeric package), and COUSCOUS (the CAPE-OPEN Unit-operations Simple package)

C. Component Addition in the Simulation Database

The component database or the compound library included inside COCOs' installation software is a mere list of 430 compounds. To carry out the desired simulation, it was necessary to add compounds integral to the study using the pure component database manager. A. J. de ASSIS et al. [22] provided sufficient data for the desired components as shown in Figure 3.

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Figure 3: PCD Manager: Compound Database, courtesy of A. J. de Assis et al. [25].

Compounds selected for the simulation are as follows:

- a) Triolein (Reactant)
- b) Di-olein (Intermediate Reactant)
- c) Mono-olein (Intermediate Reactant)

- d) Methanol (Reactant)
- e) Methyl oleate (Product)
- f) Glycerol (By-product)



D. Property Package Selection

Various property packages are available in the COCO TEA library; however, these property packages are only for compounds that are already present in the TEA library – by default. For compounds added using the PCD manager, there will be some error due to data missing from the integrated packages. So amongst the following packages most suitable for the transesterification process, the study moved forward with the UNIFAC VLE property package.

The UNIFAC method (UNIQUAC Functional-group Activity Coefficients)[45] is a semi-empirical system for the prediction of non-electrolyte activity in non-ideal mixtures.

Where data for the UNIQUAC model is not available, as is the case in the present study, the UNIFAC model is the next best pick.

E. Reaction Setting

Using the CORN environment, the transesterification process was selected to consist of three equilibrium reactions and a single overall reaction as well. Simulations on the reaction/s settings were carried out to see whether some of the previously formulated speculations about the reaction mechanism could be tested or not. Reactions were set up as shown in Figures 4 and 5.



Figure 4: Three-step Transesterification reactions setup in CORN (simulation of LH mechanism)



Figure 5: Single-step Transesterification Reaction setup in CORN (simulation of E-R mechanism)

F. Reactor Selection and Setup

For the simplicity of the simulation, the following assumptions were considered:

- 1) The presence of excess methanol reactant minimizes the reversibility of the transesterification reaction, therefore the reaction is assumed as a pseudo first-order reaction.
- The reaction mixture is a homogeneous phase. Solid catalyst is in powder form and at a very low concentration in comparison to the whole volume of the reaction mixture.
- 3) Reaction mixture volume remains constant.
- 4) Reaction temperature remains constant.

Under these assumptions, the Equilibrium reactor far suited the needs of the simulation. The reactor was set to carry



out reactions in the liquid phase and to show the conversion value of Triolein. Furthermore, the reactor was set to operate at isothermal conditions with zero pressure drop.

IV. RESULTS AND DISCUSSION

To validate the results of the study, it is necessary to perform a comparison between lab and simulation results. Operating Parameters selected for comparison are:

- 1- Temperature effect
- 2- Concentration effect

A. Lab results

To demonstrate the effect of operating parameters on oil conversion to Biodiesel, experimentation at a lab-scale is necessary to give real-life results as well. Biodiesel production takes place using Jatropha Oil and Methanol – using CaO as a catalyst in the lab experiments – under various operating conditions to check for the conversion of oil. Table 1 shows the results of these experiments.

TABLE 1: Effect of operating parameters on oil conversion.

Temperature V	s Oil conversion	Oil-Alcohol Ratio Vs Oil Conversion	
55	66	1:03	58
60	78	1:05	69
65	86	1:07	78
70	67	1:09	87
75	58	1:11	80
15		1:13	72.5

The results of Table 1 have their plots in Figures 6 and 7 respectively.



Figure 6: Effect of temperature on oil conversion

As seen in Figure 6, the raw oil conversion increases up to a specific temperature after which it starts to decrease. The irregularity of the curve is due to the phase change of the mixture. As the reaction temperature increases, the molecules receive more energy, allowing extra molecules to achieve activation energy and react. Consequently, a reaction occurs and spawns a variety of products. Now, this increase in temperature allows more molecules to react, and hence the triolein conversion increases. The decrease in the conversion is due to the vaporization of methanol as the operating temperature rose all the while keeping the oil-alcohol ratio constant.



Figure 7 shows the results of the lab experiments demonstrating the effect of the oil-alcohol ratio on oil conversion. The trend obeys Le Chatelier's principle and in retrospect, the trend typically follows an increasing logarithmic curve. Following a logarithmic curve usually means that the initial increase is fast but with time the instantaneous gains start decreasing and the curve approaches an asymptote.

Explaining the curve for this experiment needs an understanding of Le Chatelier's principle. Le Chatelier's principle states that "If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change." In this case, the change in equilibrium change is due to increasing the concentration of one of the reactants to move the reaction equilibrium forward. Therefore, as the concentration of the reactant increases in the reacting mixture, the amount of oil converted automatically increases until there is no more oil left to react with methanol.

B. Simulation Results

Results of the simulation are as shown in Figure 8 – Simulating the effect of Temperature on Oil Conversion – and Figure 9 – Simulating the effect of Oil-alcohol ratio on Oil conversion.



Figure 8: Effect of Temperature on oil conversion. Single-step reaction (E-R mechanism) three-step reaction (L-H mechanism)



Simulation for the first set of experiments investigates the effect of Temperature on the amount of oil converted to product. The Simulation included reactions at equilibrium and the equilibrium constant, a function of Temperature, calculated using the Arrhenius Equation. The reactor was set up in a way that it simulated the same reactor model to demonstrate two different sets of reaction mechanism to account for the inhibition effect.



Figure 9: Effect of Concentration on oil conversion. Single-step reaction (E-R mechanism) three-step reaction (L-H mechanism)

C. Comparison between Simulated and Lab Results

Figures 10 and 11 show a comparison between simulated and lab results. These figures only compare the plots of the results. As can be seen, the simulated plots very closely mimic the experimental results. This shows proof that the reaction model and simulation setup are accurate in simulating a complex reaction such as transesterification.



Figure 10: Comparison of experimental and simulation results (Temperature)

Real-life reactions for both the mechanism are the same and form the same products and by-products. The mechanism that takes place during the reaction only depends on the type of alcohol used. Therefore, for Methanol the reaction mechanism is the Eley-Rideal type.

Further statistical analysis of the data may be performed for more accuracy, but even without that, the simulated results are very promising for understanding the E-R and L-H mechanism of adsorption in a transesterification reaction. It should be clear that the single-step reaction setup mimics the E-R type mechanism for transesterification while the threestep reaction setup mimics the L-H mechanism for transesterification.



Figure 11: Comparison of Simulated and Lab results (Concentration Effect)

V. CONCLUSIONS

The research studies the effectiveness of an open-source chemical simulation software, possible to demonstrate a complex reaction such as transesterification accurately with limited data. Experiments, both lab, and simulation, were performed studying the effect of two parameters – temperature and oil-alcohol ratio – on oil conversion. Two adsorption reaction models – Eley-Rideal and Langmuir-Hinshelwood – were simulated on a Chemical Simulation Software (COCO) using an equilibrium reactor.

Since the reactor model used in the simulation accounts for reactions at equilibrium, it becomes a little difficult to simulate the reaction for the Eley-Rideal mechanism with exact accuracy. The concept behind the research is to be able to simulate a reaction with high accuracy without being able to use an exact model for that reaction. Since the equilibrium model is best suited for reactions at equilibrium, hence the reaction for transesterification can be simulated as it is an equilibrium reaction.

Results from experiments were tabulated and then plotted for a better understanding. Lab results were compared with simulation results to check for the accuracy of the assumptions used during the simulation and in the process helped validate the results of the simulation

The study is quite new and shows promise in making it easy to demonstrate a reaction mechanism accurately, on an open-source Chemical Simulation software such as COCO



without the need for buying expensive and pricey simulation software.

Regression analysis may be performed to analyze the plotted simulation and lab data more accurately and further validate results from this study.

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REFERENCES

- [1] Strogatz, Steven (2007). "The End of Insight". In Brockman, John. What is your dangerous idea?. HarperCollins.
- Researchers stage largest Military Simulation ever" Archived 2008-01-22 at the Wayback Machine, Jet Propulsion Laboratory, Caltech, December 1997
- [3] Bratley, Paul; Fox, Bennet L.; Schrage, Linus E. (2011-06-28). A Guide to Simulation. Springer Science & Business Media.
- [4] Available at: https://en.wikipedia.org/wiki/Computer_simulation Accessed on: 13/09/2020.
- [5] Available at: http://www.biodieselmagazine.com/articles/7793/homogenous-catalystand-effects-on-multifeedstock-processing Accessed on: 12/08/2020.
- [6] Lam, Man Kee, Keat Teong Lee, and Abdul Rahman Mohamed. "Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review." Biotechnology advances 28.4 (2010): 500-518.
- [7] Javidialesaadi, A., and S. Raeissi. "Biodiesel production from high free fatty acid-content oils: experimental investigation of the pretreatment step." APCBEE Procedia 5 (2013): 474-478.
- [8] Simonetti, E. A. N., G. P. Thim, and G. G. Cortez. "Ca-Al hydrotalcites as catalysts for methanolysis and ethanolysis of soybean oil." Modern Research in Catalysis 3.04 (2014): 117.
- [9] Borugadda, Venu Babu, and Vaibhav V. Goud. "Biodiesel production from renewable feedstocks: Status and opportunities." Renewable and Sustainable Energy Reviews 16.7 (2012): 4763-4784..
- [10] Endalew, Abebe K., Yohannes Kiros, and Rolando Zanzi. "Heterogeneous catalysis for biodiesel production from Jatropha curcas oil (JCO)." Energy 36.5 (2011): 2693-2700.
- [11] Tang, Y., Xu, J., Zhang, J., & Lu, Y., Biodiesel production from vegetable oil by using modified CaO as solid basic catalysts. Journal of Cleaner Production, 42, 198-203, (2013).
- [12] Labib, Tarik M., S. I. Hawash, K. M. El-Khatib, Abbas M. Sharaky, G. I. El Diwani, and E. Abdel Kader. "Kinetic study and techno-economic

indicators for base catalyzed transesterification of Jatropha oil." Egyptian Journal of Petroleum 22, no. 1: 9-16, (2013).

- [13] Granados, M. López, MD Zafra Poves, D. Martín Alonso, R. Mariscal, F. Cabello Galisteo, R. Moreno-Tost, J. Santamaría, and J. L. G. Fierro. "Biodiesel from sunflower oil by using activated calcium oxide." Applied Catalysis B: Environmental 73, no. 3-4: 317-326, (2007).
- [14] Ngamcharussrivichai, Chawalit, Wipawee Wiwatnimit, and Sarinyarak Wangnoi. "Modified dolomites as catalysts for palm kernel oil transesterification." Journal of Molecular Catalysis A: Chemical 276.1, 24-33, (2007).
- [15] Viriya-empikul, Nawin, Pawnprapa Krasae, Buppa Puttasawat, Boonyawan Yoosuk, Nuwong Chollacoop, and Kajornsak Faungnawakij. "Waste shells of mollusk and egg as biodiesel production catalysts." Bioresource technology 101, no. 10: 3765-3767, (2010).
- [16] Endalew, Abebe K., Yohannes Kiros, and Rolando Zanzi. "Inorganic heterogeneous catalysts for biodiesel production from vegetable oils." biomass and bioenergy 35.9: 3787-3809, (2011)
- [17] Demirbas, Ayhan. "Comparison of transesterification methods for production of biodiesel from vegetable oils and fats." Energy Conversion and Management 49.1: 125-130, (2008).
- [18] Hattori, Hideshi, Masaomi Shima, and Hajime Kabashima. "Alcoholysis of ester and epoxide catalyzed by solid bases." Studies in surface science and catalysis 130: 3507-3512, (2000).
- [19] Dossin, Tanguy F., Marie-Françoise Reyniers, and Guy B. Marin. "Kinetics of heterogeneously MgO-catalyzed transesterification." Applied Catalysis B: Environmental 62.1: 35-45, (2006).
- [20] Di Serio, Martino, Riccardo Tesser, Lu Pengmei, and Elio Santacesaria. "Heterogeneous catalysts for biodiesel production." Energy & Fuels 22, no. 1: 207-217, (2008).
- [21] Kulkarni, Mangesh G., Rajesh Gopinath, Lekha Charan Meher, and Ajay Kumar Dalai. "Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification." Green Chemistry 8, no. 12: 1056-1062. 12, (2006).
- [22] Suwannakarn, Kaewta, Edgar Lotero, and James G. Goodwin. "Solid brønsted acid catalysis in the gas-phase esterification of acetic acid." Industrial & Engineering Chemistry Research 46.22: 7050-7056, (2007).
- [23] Hattori, Hideshi, Masaomi Shima, and Hajime Kabashima. "Alcoholysis of ester and epoxide catalyzed by solid bases." Studies in surface science and catalysis 130: 3507-3512, (2000).
- [24] RODRIGUES, F., and A. J. de ASSIS. "Biodiesel Process Simulation: 1. Computational Implementation of Chemical and Physical Properties." Blucher Chemical Engineering Proceedings 1.2: 12712-12720, (2015).
- [25] RODRIGUES, F., and A. J. de ASSIS. "Biodiesel Process Simulation: 2. Process Synthesis and Design Case Study." Blucher Chemical Engineering Proceedings 1.2: 12704-12711, (2015).