Biodiesel Production Optimization From Triolein Through Esterification Process Using Dwsim Software Simulation

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ABSTRACT

Biodiesel is a renewable fuel that does not pollute the air, is easily biodegradable and can be renewed. Biodiesel can be used in almost all diesel engines without undergoing significant changes. This makes it one of the best options today to replace diesel. Biodiesel is generally made from vegetable oils, animal fats or algae. Esterification of vegetable oil fatty acids with short-chain alcohol is one of the methods used to make biodiesel. According to SNI 7182:2015, a purity of at least 96.5% of biodiesel must be met. Therefore, optimum biodiesel production process planning is needed. The optimization is done by considering the type of process, the composition of materials, the kind of reactors, the temperature that can affect the biodiesel produced. The aim of this research is to optimize using process simulation to produce biodiesel with a set standard of purity. Biodiesel or methyl oleate ($C_{19}H_{36}O_2$) from triolein feed ($C_{57}H_{104}O_6$). The simulation was done in three different PFD using DWSIM version 8.6.0. The results are expected to provide an overview of the initial engineering design of biodiesel production process.

Keywords: biodiesel, esterification, production optimization, reaction kinetics, DWSIM version 8.6.0.

1. Introduction

One of the vital human needs is energy. Most of the energy needs are filled by non-renewable natural resources such as natural gas, oil and coal, but these resources are gradually running out of stock. Renewable energy sources can be divided into several sections: wind energy, marine energy, solar energy, hydro energy, geothermal energy and bioenergy. *Bioenergy is divided again into bioenergy for electricity/heat and bioenergy in the form of biofuels, Ellabban O. et al. [1].*

The limited resources of fossil fuels and on the other hand the need to reduce greenhouse gas emissions are one of the key drivers in the search for alternative fuels. So now more attention is given to biofuels in this case of biodiesel that can be used as alternative fuels. *Biodiesel has become a clean alternative diesel fuel and one kind of green alternative energy source, whose physical and chemical properties are similar to diesel, Kumar Sunil [2].* Now several methods for producing biodiesel such as pyrolysis process, catalytic, non-catalytic, supercritical processes, esterification, transesterification, pre-treatment and others have been discussed and developed. *Biodiesel is an air-free, easily biodegradable and renewable fuel so it is considered one of the best candidates today as a replacement for diesel from petroleum because it can be widely used in all biodiesel engines without the need for significant modifications, Vijayakumar C. et al. [3].*

Biodiesel has advantages over diesel that is non-toxic, environmentally friendly because the raw material contains no sulphur as well as low emissions, high cetane numbers, and has good lubricating properties. Biodiesel can be produced from vegetable oils, animal fats and algae. The world's increased consumption of biodiesel from various sources, including those generally consumed by humans, has resulted in a reduction in raw materials for the production of biodiesel itself. Therefore, biodiesel from vegetable oil sources that are literally not humanly consumed are very prospective to develop in addressing the problem of reduced oil production. Biodiesel manufacturers in various parts of the world are now in various stages of development such as the initial design phase, the final technical specification phase of the equipment or the stage of producing biodiesel. Decisions about what type of process to use, what raw materials to use and how flexible the process can be used for other raw materials and what equipment to use can be made "offline" with accurate simulation models. *Process flow diagrams (PFDs) with energy and material balance in a chemical process simulator can enable efficient process design for the desired optimum level, Chemstations, Inc. Biodiesel in Chemcad page 1 [4].*

Biodiesel (methyl oleate) can be defined as a mono-alkyl ester of long-chain fatty acids contained in vegetable oils or animal fats that are allocated as fuel for diesel engines. Quoted from the book *Chemical Process Design: Computer-Aided Case Studies by Dimian C. A. and Bildea Sorin C. page 409-416 [5], in general, the process of making biodiesel can be divided into several process groups namely: Batch Process, Continuous Catalytic Process, Superkritical Process, Hydrolysis and Esterification Process, Enzymatic Process and Triglyceride Hydropyrolysis Process*. Besides, there is also a non-catalytic process of producing biodiesel.

The non-catalytic production process of biodiesel has been reported at least by *Dasari et al. [6]* and *Han et al. [7]*. The process has several advantages, including that it does not require the removal of FFA by refining or pre-esterification. Besides, because without the use of catalysts, the process of separating and purifying products becomes simpler and more environmentally friendly. However, non-catalytic processes typically use excess methanol with higher operating temperature and pressures when compared to catalytic, even some researchers conduct experiments on conditions above the supercritical metanol.

Biodiesel can be obtained from the processing of a variety of vegetable oils, for example in Germany it is extracted from rapeseed oil, whereas in other parts of Europe it is derived from sunflower seed oil and also from rapseed oil, in the United States and Brazil it is produced from soybean oil, in Malaysia it is from palm oil and in Indonesia it is gained from palm oil, jatropha, coconut and soya oil. Vegetable oils generally contain 90–98% triglycerides (TG) as the main component and small amounts of mono and diglycerids (MG and DG). Triglyceride is an ester of three long-chain fatty acids (C_8–C_{22}) that are bound to a single group of glycerols. The FFA content in vegetable oils ranges between 1–5%, but there are also greater than 5% depending on the type of oil and the way it is processed.

1.1. Esterification Process

An ester is an organic compound with the symbol R 'which replaces one hydrogen atom (H) or more. Esterification is the reaction of the transformation of a carboxylic acid and alcohol into an ester using an acid catalyst. Ester is a compound that contains a group -COOR with R can be in the form of alkyl or aryl. The esterification reaction is a reversible reaction.

Esterification is the stage of conversion of free fatty acids into esters or reacting fatty oils with short chain alcohols. In the catalytic process, a suitable catalyst is a substance characterized by strong acids such as organic sulfonic acid, H_2SO_4 and H_2PO_4. Esterification is generally aimed at making biodiesel from oil with a high free fatty acid ratio with an acidity of more than 5 mg-KOH/g. The process of esterification of biodiesel is preceded by a process of hydrolysis between triglycerides and water as seen in the reaction below (figure 1).

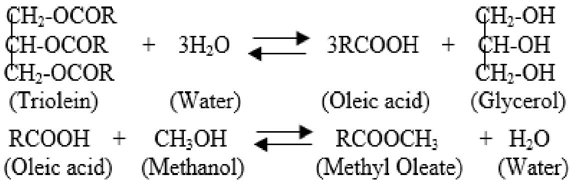


Figure 1: Methyl Oleate Formation Reaction (Hydrolysis & Esterification)

The esterification phase is usually followed by the transesterification phase, but before the esterification product is transferred to the transesterification stage, the water elements and acid catalysts contained therein must be removed first. If the water content is high then biodiesel will be of poor quality, because it still contains soap, FFA and high triglycerides.

1.2. Transesterification Process

Biodiesel synthesis uses transesterification reactions with short-chain alcohols. The process basically aims to convert the compounds (TG, MG and DG) of glycerides with high molecular weight and high viscosity that dominate the composition of refined fatty oil into FAME. In the catalytic process of transesterification of vegetable oils reacted with NaOH/KOH and methanol to produce FAME and glycerol, the reaction can be seen in figure 2, below.

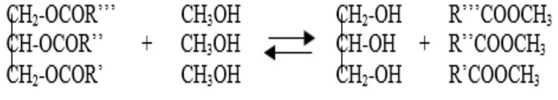


Figure 2: Transesterification reaction of triglycerides with methanol

The transesterification reaction runs in three stages of reaction. Each of these stages is a long chain reaction with methanol, the reaction can be seen in figure 3, below.

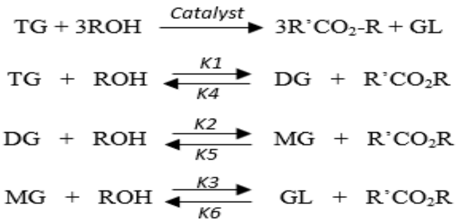


Figure 3: Overall reaction and stage reaction of transesterification process

The esterification/transesterification reaction is a reaction of a reversible nature so that excessive alcohol addition is intended to stimulate the reaction to lead more to the product and also aims to convert as many triglycerides as possible into methyl oleates, so that the reversal reaction can be considered ignored as almost all the reagents turn into the product. Basic catalyst transesterification occurs between methanol and triglycerides through sequential DG and MG formation which produces methyl oleates at each stage. *The rate of conversion of monoglyceride (MG) to methyle oleate is faster than DG and TG in transesterification, Darnoko and Cheryan, [8], because MG is more soluble in the polar phase (glycerol) where the catalyst is located and MG has lower activation energies than DG or TG.*

The biodiesel product discussed in this study is methyl oleate ($C_{19}H_{36}O_2$) with a feed of triolein ($C_{57}H_{104}O_6$). Triolein is selected as a raw material in this simulation of optimization of the production of biodiesel because triolein has the properties and characteristics of symmetrical triglycerides derived from glycerol and three uninsaturated fatty acids, namely oleic acid, as seen in figure 4, below.

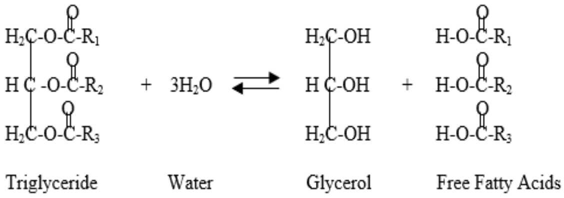


Figure 4: Triglyceride Hydrolysis Reaction

Several previous studies on optimizing the production of biodiesel from a variety of raw materials have been carried out extensively. *Saputri et al. [9]* optimized the production of biodiesel from jatropha curcas seeds by using an activated natural zeolite catalyst at the transesterification stage, this study showed that in conditions with a concentration of 3%, the activated naturally zeolite catalyst, the purity achieved reached 92,04%. Then *Putri et al. [10]* used a reactive extraction process to optimize the process of making biodiesel from jatropha curcas seeds with a yield of 12.80%. The use of a process simulator such as Aspen HYSYS for simulating the optimization of production of biodiesel has also been previously done by *Abdurakhman et al. [11]* with a membrane reactor to make biodiesel from waste cooking oil. Also with *Giwa et al. [12]* using Aspen HYSYS to evaluate the best options for biodiesel production effectively and efficiently. Furthermore, *Adeniyi et al. [13]* found factors to be considered in the simulation of biodiesel production processes using HYSYS process simulators such as temperature, methanol-oil ratio, and the use of catalysts.

Furthermore there is *Firda D. et al. [14]* in her journal has conducted research on optimization of production of biodiesel based on vegetable oil using Aspen HYSYS with the optimal purity obtained of 96.5% using fluid package NRTL and Gibbs reactor for its hydrolysis process. According to *Abdulloh et al. [15], one attempt to increase the economic value of vegetable oils is to hydrolyze the oil into its fatty acids so that the fatty acid contained in the oil can be further exploited. Adhani et al. [16], stated that high levels of free fatty acids can inhibit the reaction of biodiesel formation, as the catalyst will react with free fat acids forming soaps, thus making it difficult to separate and purify biodiesel. Joelianingsih et al. [17], reported that the non-catalytic transesterification reaction of palm oil works at atmospheric pressure.* With a methanol feed flow rate of 4 grams per minute and an initial oil mass of 200 grams shows the influence of reaction temperatures at 250°C, 270°C and 290°C on the reaction rate constant (k) and transesterification reaction conversion. The perfect conversion of methyl oleate occurs at an operating temperature of 290°C and the required time is 7.25 hours.

With more developing chemical process simulator technology available, it is worth putting a hypothesis that process simulators other than HYSIS or Aspen Plus can definitely also be used as an alternative simulator calculation in determining the purity of biodiesel by applying a model of fluid thermodynamics (property package) in a process simulation that can be the same or different. For this purpose, the use of the DWSIM Process Simulator version 8.6.0. using UNIFAC as its property package in the optimization of biodisel production is done to know how far the results are obtained when compared with other process simulations.

This research is closely related to the kinetics of reactions such as determining the values of reaction rate constant (k), activation energy (Ea) and impact frequency factor (A) applied in the Arrhenius equation, where these values will be used in running a DWSIM process simulator to determine the methyl oleate content obtained. In order to ensure that the reactive substance can collapse well in the process of hydrolysis, mixing is required. *According to Patle et al. [18], an increase in temperature will increase the inter-particle impact, which means the reaction will run faster and the resulting conversion will be greater,* so the result of mixing triolein and water in a mixer will be first heated to a temperature between 70°C – 90°C before entering the reactor to accelerate its hydrolysis process.

Generally, optimization of biodiesel production processes is done using catalyst processes with a variety of catalyst concentrations, then there are also non-catalytic processes or by modifying processes. However, process optimization by performing simulation processes first can help give the opportunity to benefit to know the optimal condition of a process before the production process is actually applied in the industry.

The mixture between triolein and water is a mixture of polar and non-electrolyte nature. The polar molecules have dipole moments, which means there is an unequal load distribution in the molecule. This charge distribution creates both positive and negative poles in the molecule. So the selection of the thermodynamic model for this simulation process can use the UNIFAC model as the application of the UNIFAC has been implemented by *Adeniyi et al. [13].* In this study, the reactors used for the hydrolysis process are equilibrium reactors and CSTR for the esterification/transesterification process.

2. Material and Methods

The stages in conducting research using this process simulation include the determination of the Block Flow Diagram (BFD), Process Flow diagram (PFD) and simulation using the DWSIM chemical process simulator software version 8.6.0.

2.1. Block Flow Diagram (BFD)

BFD is the simplest form of flow diagram used in an industry. A block in a BFD can represent anything from a single device to a whole factory. A BFD can be used to break down a complex system into stages or sectors of smaller and more sensible principles. The manufacture of BFD was one of the first steps in the development of a chemical process. Once the BFD alternative has been selected from the literature on biodiesel production, the next, BFD is used as a benchmark for the creation of a complete process flow diagram (PFD).

2.2. *Process Flow Diagram (PFD)*

Process Flow Diagram (PFD) is a type of flow diagram that shows the relationship between the main components in a factory, PFD can be used to model a new process, improve the output of a process or document a process. PFDs contain information about mechanical equipment, operating data, and interconnections to other systems.

PFD offers several benefits, including clarifying the working procedures of a equipment, and simplifying the scope of processes and basic information, making important data such as raw materials, process parameters and flow rates easier to understand. PFD is the primary method of communicating process and design information. The PFD shows the sequence of flow through various equipment and details the composition, flow connections, flow rates and operating conditions. The PFD is more detailed and provides more information than the BFD, which only provides a general overview of the data stream.

2.3. Simulation with DWSIM

In this study, the process simulation was done using DWSIM version 8.6.0. (2023). The simulation is based on three PFD scenarios, starting with a literary study of the factors affecting the production of biodiesel then determining the fluid packages to be used in the simulation of the production. The fluid packages used are UNIFAC (UNIQUAC Functional-group Activity Coefficient). UNIFAC is a thermodynamic model based on the model of predictive activity coefficients, while NRTL and UNIQUAC are semi-predictive models. To run the simulation, the data used included BFD, reaction kinetics data, input operating parameters, input composition, and unit operating condition obtained from calculations and related literature studies.

Data information for all components of substances used in simulations using this DWSIM has been available in the ChemSep library, such as for: Hydrolysis processes where the reactant is triolein and water and its products are oleate acids. Esterification & transesterification process where the reactant is oleate acid and methanol with the main product is methyl oleate and its by-product is glycerol. Three BFDs have been selected by the authors as references in the selection of biodiesel manufacturing processes to be summarized in a proposal and continued with the creation of a process flow diagram (PFD), as seen in the figure 5-7 below.

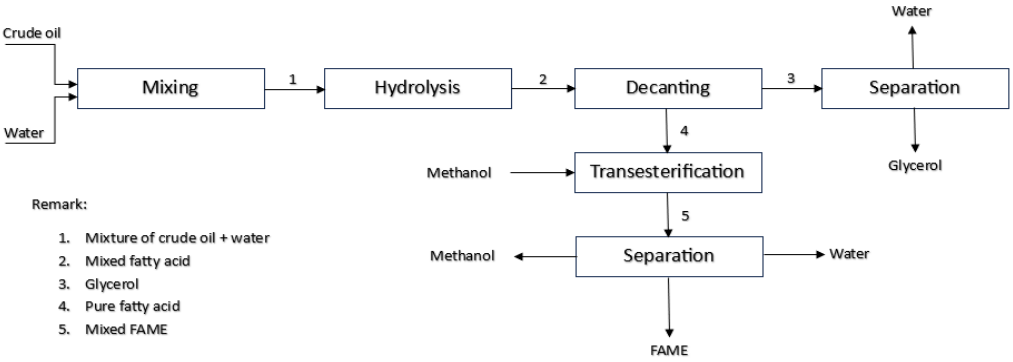


Figure 5: BFD-1, Biodiesel Production Hydrolysis-Transesterification Process-*Adeniyi et al. [13].*

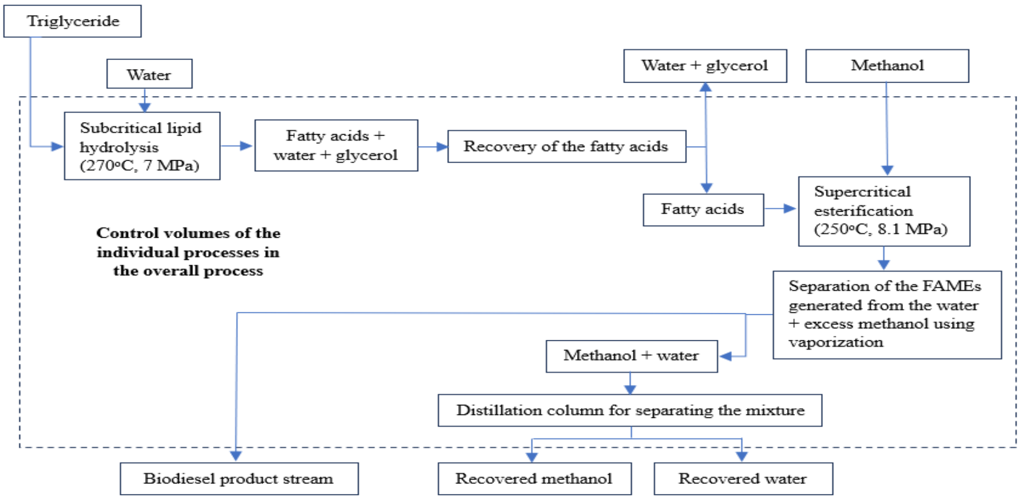


Figure 6: BFD-2, Biodiesel Production Integrated Subcritical lipid hydrolysis & Supercritical Esterification *Okoro et al. [19].*

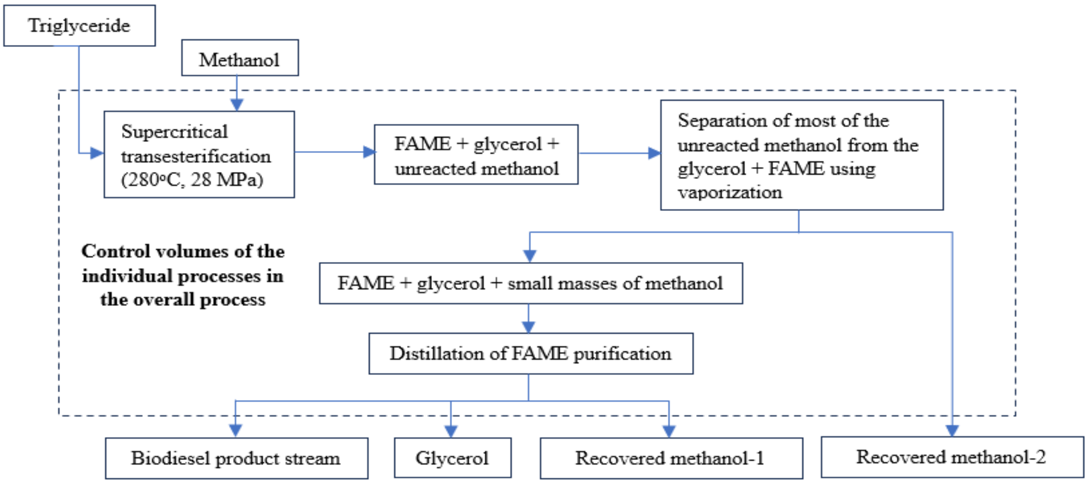


Figure 7: BFD-3, Biodiesel Production with DST (Direct Supercritical Transesterification - *Okoro et al. [19]*

In BFD No. 1 (Figure 5) the production process of biodiesel is carried out through hydrolysis and esterification/ transesterification process. In the process of hydrolysis, the triglyceride structure is dissolved so that the fatty acids are formed, the reduction of free fatty acid levels in the purification phase is very important to obtain high-quality biodiesel. Thus, the production process with the application of separation twice so that the purification of biodiesel from its fatty acids can be performed well is shown in this BFD.

On the BFD no. 2 (Figure 6) shows the production of biodiesel ISHSE (Integrated Subcritical Lipid Hydrolysis & Supercritical Esterification) as a whole involves the initial subcritical water-triglyceride hydrolysis at a temperature of 270°C and a pressure of 7 MPa (70 bar). The resulting fatty acids are then separated by decantation with the residues of a liquid containing glycerol and hydrolysis water. At the end of this supercritical esterification reaction, the FAME product is purified by separating from methanol and non-reacting water residues through the evaporation process of methanol and boiling water.

Further on BFD no. 3 (Figure 7) the line 'breaking-out' shows the whole process and the solid block line shows the process per individual. BFD No. 3 shows that the entire process of production of DST (Direct Supercritical Transesterification) involves a supercritical triglyceride transesterification reaction with the addition of methanol at 280°C and pressure 28 MPa (280 bar), it can be concluded from this transesterification reaction that the excess methanol and non-reacting methanol can be recovered through the evaporation process of FAME and by-products such as glycerol. Further refining of the FAME product to remove the glycerol and a small portion of the remaining methanol is carried out through the distillation process.

From the three BFDs discussed above, it can be seen that in general the selection of both conventional biodiesel production processes and the addition of reactive distillation afterwards all involve hydrolysis-esterification-transesterification processes. In addition to BFD-1 and BFD-2, there are two main processes, the first is the hydrolysis process followed by the decantation process and the second is the esterification /transesterification process, so that the author in this case is determined to summarize and make a proposal for the production of biodiesel based on the process of hydrolysis and esterification/transesterization, this is because the process is perceived to be relatively simpler.

3. Result and Discussion

3.1. BFD Proposal for Biodiesel Production

The PFD optimization of the biodiesel production process was made based on the main process summary of the three BFDs selected above. The proposed BFD in the design of the PFD/flow sheet in the DWSIM simulator version 8.6.0. as shown in figure 8 below:

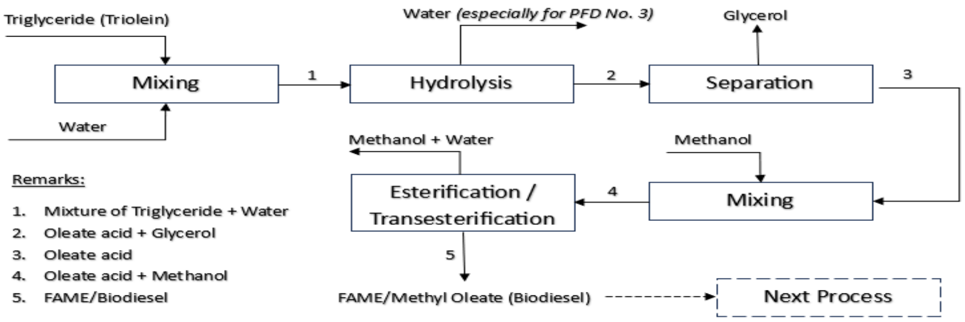


Figure 8: BFD Biodiesel manufturing process through hydrolysis, esterification/transesterification process

3.2. Activation Energy & Frequency Factor Determination

To determine the kinetic values of reactions such as rate constant (k), activation energy (Ea) and frequency factor (A) triglycerides taken reference data from the results of the study that have been described by *Darnoko and Cheryan [8]* as shown in table 1 & 2:

Table 1: Reaction rate constant data for TG, DG and MG for hydrolysis at different temperatures (GL*=Glycerol)

Glyceride	Temperature °C	Reaction rate constant (wt%··min)$^{-1}$	R^2
TG → DG	50	0.018	0.9865
	55	0.024	0.9966
	60	0.036	0.9822
	65	0.048	0.9903
DG → MG	50	0.036	0.9940
	55	0.051	0.9974
	60	0.070	0.9860
	65	0.098	0.9678
MG → GL^a	50	0.112	0.9733
	55	0.158	0.9619
	60	0.141	0.9862
	65	0.191	0.9843

Table 2: Activation Energy Data for Hydrolysis TG, DG and MG during Transesterification of Palm Oil

Reaction	E_a (kcal/mol)	R^2
TG → DG	14.7	0.9959
DG → MG	14.2	0.9998
MG → GL	6.4	0.7457

Based on the reaction equation in figure 3, which produces methyl oleate and glycerol, the rate constant (k) of the MG ➔ GL* reaction as seen in table 1 above can also be applied to determine the k value at other experimental temperatures by using a linear equation regression as shown in the figure 9 below. The *k* value is required to calculate the activation energy value (Ea) and the frequency factor (A) by applying the values to the Arrhenius equation.

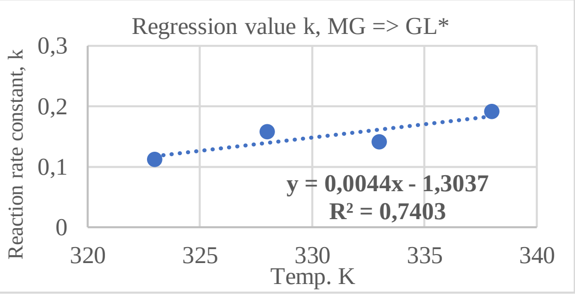


Figure 9: Diagram MG➔GL* Reaction Rate Constant

Using the regression equation in figure 9, then will be obtain the the reaction rate constant values (k), the value of 1/T (K) and ln *k* for the other defined temperatures at 65, 70, 75 and 80°C used for the simulation of calculations against alternative PFD 1, the data obtained is as table 3 below:

Table 3: Data k, 1/T and ln k for Alternative Sim-1

Data for the 1st alternative PFD simulation

Temp. °C	Temp. K	k	1/T	Ln k
65	338	0.184	0.002959	-1.69554
70	343	0.206	0.002915	-1.58231
75	348	0.228	0.002874	-1.48061
80	353	0.250	0.002833	-1.3883

Then the activation energy value (Ea) of the esterification/transesterification reaction can be determined from the plot graph ln *k* versus 1/T (order one reaction rate) as seen in the figure 10 below.

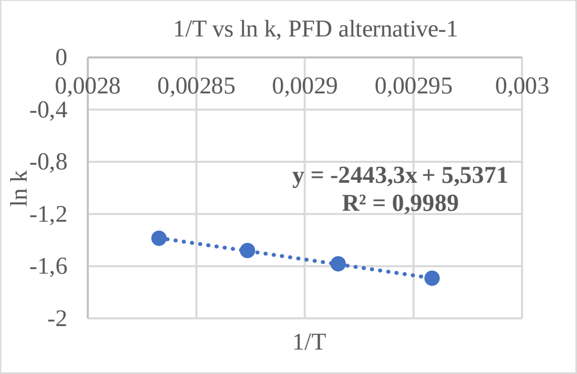


Figure 10: Diagram 1/T vs ln *k* for Alternative PFD Simulation-1

Based on a linier equation obtained from the figure 10 above y = -2443.3x + 5.5371 with a value of R^2 = 0.9989, then it is possible to determine the value (-Ea/R) which is the slope of this equation of -2443.3 then the value R (ideal gas constant) is known as 8.314 J/molK. This data is then applied to the Arrhenius equation below to obtain the value of activation energy (Ea) and the frequency factor (A).

$$\mathbf{k = A * \exp^{(-Ea / RT)} \Rightarrow A = k / \exp^{(-Ea/RT)}}$$

where: k = reaction rate constant, A = pre-exponential impact frequency factor, Ea = activation energy (J/mol), R = ideal gas constant (8.314 J/molK) and T = temperature in Kelvin (K). Using the equation (1) then the activation energy (Ea) obtained of 20.314 KJol/mol. then the calculation of the value of the impact frequency factor (A) for each temperature (65, 70, 75 and 80°C) simulated on the 1st alternative PFD as shown in table 4.

Table 4. Frequency Factor Data for Alternative Simulation-1

Temp. °C	Frequency factor, A
65	252.941
70	254.936
75	254.773
80	252.961

By applying the same method, the data will be obtained as calculated and mentioned above for the simulation of the 2nd and the 3rd alternative PFD with each temperature as shown in table 5–8 and figure 11-12 below:

Table 5: Data k, 1/T and ln k for Alternative Simulation-2

Data for alternative 2nd PFD simulation

Temp. °C	Temp. K	k	1/T	Ln k
85	358	0.272	0.002793	-1.30379
90	363	0.294	0.002755	-1.22588
95	368	0.316	0.002717	-1.15360
100	373	0.338	0.002681	-1.08619

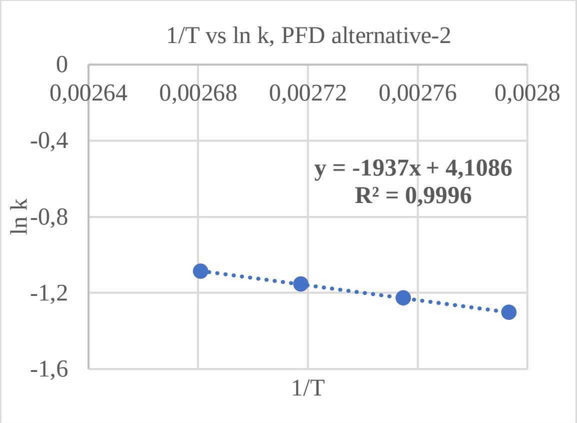


Figure 11: Diagram 1/T vs ln k for Alternative PFD Simulation-2

By applying linier equation obtained from the figure 11 above where y = -1937x + 4.1086 with the value $R^2 = 0.9996$ then the value (-Ea/R) that is the slope of the above equation is -1937, so that the activation energy (Ea) is obtaining of 16.104 KJol/mol and the frequency factor value for each temperature (85, 90, 95 and 100°C) simulated on the 2nd alternative PFD as shown in table 6.

Table 6: Frequency Factor Data for Alternative Simulation-2

Temp. °C	Frequency factor, A
85	60.753
90	60.960
95	60.946
100	60.754

Further for the data-simulation PFD alternative-3 is solved as shown in table 7.

Table 7: Data k, 1/T and ln k for Alternative Simulation -3

Data for 3rd alternative PFD simulation				
Temp . °C	Temp. K	k	1/T	Ln k
210	483	0.822	0.002070	-0.19662
216.2	489.2	0.849	0.002044	-0.16396
219.5	492.5	0.863	0.002030	-0.14699
220	493	0.866	0.002028	-0.14445
240	513	0.954	0.001949	-0.04762
250	523	0.998	0.001912	-0.00250

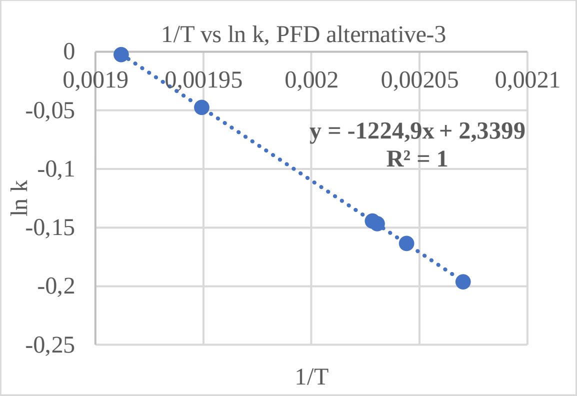


Figure 12: Diagram 1/T vs ln k for Alternative PFD Simulation-3

By using the same method then based on the linier equation obtained from the figure 12 above y = -1224.9x + 2.3399 with the value $R^2 = 1$, then the value (-Ea/R) that is the slope of the above equation is -1224.9 so that the activation energy (Ea) is obtaining 10.184 KJol/mol, as well as the frequency factor values for each temperature (210, 216.2, 219.5, 220, 240, and 250°C) simulated on the 3rd alternative PFD as shown in table 8.

Table 8: Frequency Factor Data for Alternative Simulation-3

Temp. °C	Frequency factor, A
210	10.375
216.2	10.380
219.5	10.382
220	10.383
240	10.382
250	10.377

The overall activation energy values (Ea), R^2 and A values for esterification /transesterification reactions in CSTR on each PFD simulation can be summarized in the table 9. (simulation no. 3 for each PFD).

Table 9: Ea, R^2 and A values for each PFD

Alternative Simulation	Activation energy (Ea) (kJol/mol)	R^2	Frequency factor, (A) for each temp.
PFD-1	20.314	0.9989	254.773 (at 75°C)

PFD-2	16.104	0.9996	60.946 (at 95°C)
PFD-3	10.184	1	10.382 (at 219.5°C)

3.3. Optimization Through Process Simulation

In the discussion of the results of the simulation research with DWSIM this will describe the research scenario results from the PFD alternatives to 1, 2 and 3 for the 3rd simulation only of each PFD, whereas for the other simulation results of each PFD parameters can be seen more detail in table 11 and table 12.

The hydrolysis process is carried out using an equilibrium reactor, the fatty acids that are produced are still mixed with glycerol, but only the pure fatty acid is needed for the production of biodiesel. Therefore, pure fatty acids are separated from glycerol using a separator. Glycerol as a by-product can still be used because it has a high economic value especially as a raw material in various industrial applications.

The resulting pure oleate acid cannot be directly processed at the esterification or transesterification stage due to its still high temperature (around 70-90°C). Therefore, a cooler is needed to lower the temperature of the pure fatty acid to 25°C. After that, in sequence, methanol at a temperature of 25°C and a set flow rate of 1030 kg/h is discharged into a closed reactor and then added pure oleic acid. The system must be completely closed so that methanol evaporation can be avoided. The reaction will occur at an initial temperature of 25°C with a duration of reaction between 1 and 8 hours. Excess methanol donation is meant to make the conversion take place perfectly. Methanol will react with oleic acid in an esterification & transesterification reaction and produce methyl oleate and the non-reacting methanol residues will evaporate or separate.

The best kinetic reaction model for data taken from the *Darnoko-Cheryan [8]* study is the second-order kinetic model for the initial stage of the reaction followed by the first order or the zero order at the subsequent reaction stage. Through the esterification /transesterification reaction that occurs at CSTR, methyl oleate is produced as a biodiesel product and methanol does not react in the vapor phase separately. Then the methyl oleate is stored in the storage tank. The process stages of the BFD are created into a PFD which is subsequently simulated using DWSIM version 8.6.0. Figure 13. depicts the PFD for the first alternative scenario of the 3rd simulation, which is the entire engineering process based on the proposal of the BFD.

Based on the simulation results, alternative PFD 1-(3) appears to produce a mixture of biodiesel solutions that still contain other components such as oleate acid, methanol, methyl oleate, water and non-exhausted triolein residues. From this alternative 1-(3) PFD simulation, the methyl oleate mol fraction in the biodiesel solution mixture was only 0.18889 with a total flow rate of 1066.19 kg/h and a total molar flow of 2.8830 kgmol/h, so that the purity of methyl oleate obtained from the calculation results is only 15.075%. This purity is still very far from the standard of purity for biodiesels set by SNI. The purity calculation method in this study is based on the equation of chemical stoichiometry reaction in the production of biodiesel *Yusuf et al. [20]* as shown in Figure 14.

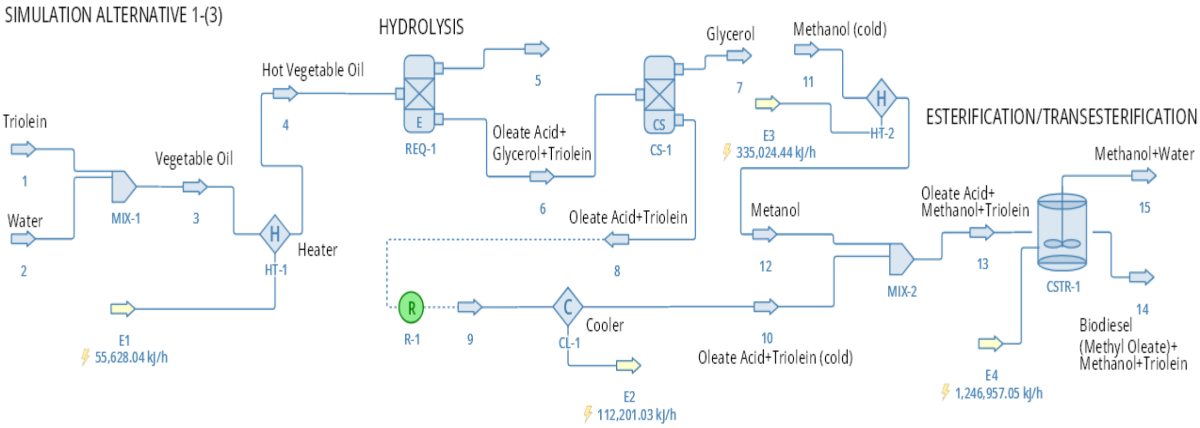
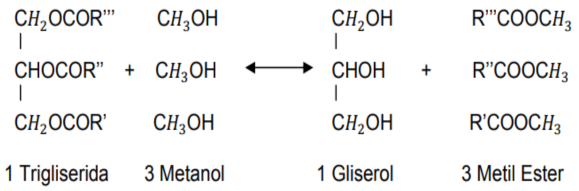


Figure 13: Simulation of PFD Biodiesel Production Alternative 1-(3)



$$\begin{array}{lclcll}
CH_2OCOR''' & & CH_3OH & & CH_2OH & & R'''COOCH_3 \\
| & & & & | & & \\
CHOCOR'' & + & CH_3OH & \longleftrightarrow & CHOH & + & R''COOCH_3 \\
| & & & & | & & \\
CH_2OCOR' & & CH_3OH & & CH_2OH & & R'COOCH_3
\end{array}$$

Figure 14: Stoichiometry Reaction of Biodiesel Formation

Based on the reaction in figure 14, the ratio of the molecule of vegetable oil (triglyceride/ triolein) to the methyl ester (biodiesel) is 1 versus 3 (1:3), thus an example of calculating the purity of biodiesel for scenario 1-(3) can be written as follows:

Mol triolein = 1.1520 $kgmol/h$/1020 kg/h
= 1.129 x 10^{-3} mol

Mol biodiesel = 2.8830$kgmol/h$/1066.19 kg/h
= 2.704 x 10^{-3} mol

methyl oleate mol fraction = 0.18889 (from simulation)

$$\text{Purity} = \frac{1\ x\ mol\ methyl\ oleate}{3\ x\ mol\ triolein} \text{ x } 100\% \tag{2}$$

$$= \frac{1\ x\ 0.18889\ x\ 2.704\ x\ 10^{-3}\ mol}{3\ x\ 1.129\ x\ 10^{-3}\ mol} \text{ x } 100\%$$

= 15.075 %

DWSIM also displays the energy requirements and the amount of energy that comes out of the system. Based on the information on the energy flow, the first heater that heats the vegetable oil requires an external energy of 55,628.04 kJ/h, then the cooler that cools the oleate acid produces an energy of 112,201.03 kJ / h, the second heater which heats up the methanol requires external power of 335,024.44 kJ per hour and the energy required by the process in the CSTR is 1,246,957.05 Kj/h. Further for the 2nd alternative PFD the 3rd simulation (figure 15) also appears to still produce a mixture of biodiesel solutions that still contain other components such as oleic acids, methanol, methyl oleates, water, and unreacting triolein residues. With a triolein flow rate equal to the alternative-1 simulation of 1020 kg/h and a molar flow of 1.1520 kgmol/h, and a water flow rate of 9.98 kg/hr and a methanol flow rate of 1030 kg/hour, from the results of the alternative 2-(3) simulation a methyl oleate mol fraction in a biodiesel mixture of 0.26690 with a total flow rate for biodiesels of 1038.28 kg/h and a total molar flow for biodiesel of 2.0457 kgmol/h is obtained, so by following the same calculation steps as in the alternative-1 above, the purity of biodiesel is 15.520%.

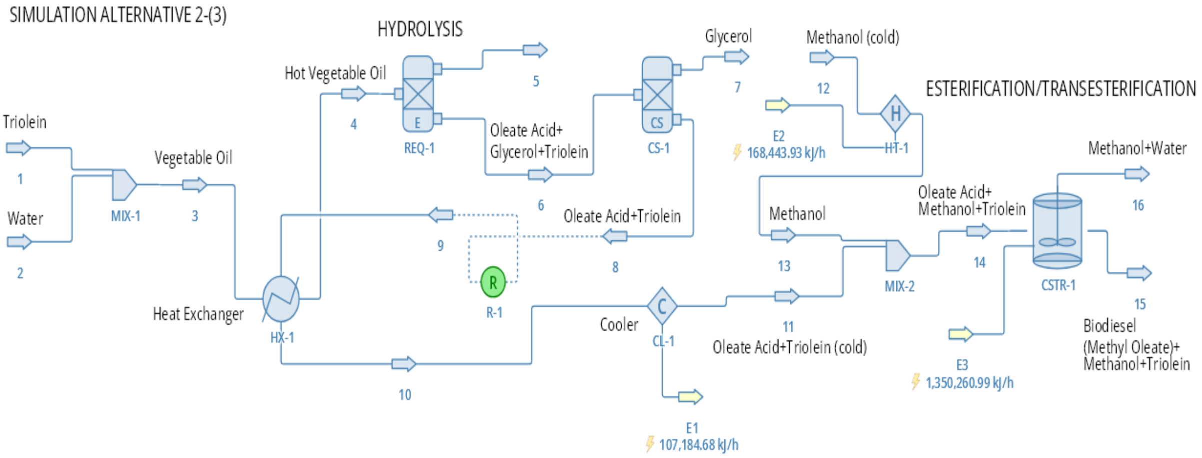


Figure 15: Simulation of PFD Biodiesel Production Alternative 2-(3)

Thus, there has been a slight increase in the amount of purity produced compared to alternatives-1. However, the purity still does not meet the standard of biodiesel purity set by SNI. According to the analysis of mol fractions of the composition of biodiesel products in alternative PFD 1 and 2, the mol fraction content of triolein and methanol is still very high. This is due to the fact that the water added with triolein in the hydrolysis reaction has been converted exhausted so that not all triolein are converted into fatty acids. The remainder of the non-reacting or unconverted triolein is brought to the end product of biodiesel. Besides because of the triolein not fully converted, the oleate acid produced is also not optimum so that when reacted with methanol, the acid is converted and the metanol is still abundantly contained in the biodiesel product. Based on the results of the 2nd alternative PFD simulation with DWSIM, the composition of mol fractions of triolein in biodiesel product is 0.4741 and the mol fraction of methanol in biodiesel product as 0.2501 (see table 12).

The energy wasted for this 2nd alternative is the energy that comes out of the cooler of 107,184.68 kJ/h, but the energy required from outside the system is energy for the heater as a methanol heater of 168,443.93 kJ /h and the energy needed for the process at the CSTR of 1,350,260.99 kJ./h. The biodiesel purity obtained from the 2-(3) alternative PFD simulation is still low due to the inoptimum reaction, so it is proposed to use the 3rd alternative simulation-(3). In order to overcome the water depletion observed at the hydrolysis stage, changes were made to the feed, i.e. an increase in the water mass flow rate to 80 kg/h with molar flow of 4.4407 kgmol/h and a reduction in the triolein feed to 950 kg/hour with molar flow of 1.07293 kg.mol/h as well as a methanol flow rate of 1030 kg/h. With such changes in composition expected to affect triolein in order to react optimally. Figure 16. shows a 3-(3) scenario PFD simulation focused on purity optimization.

Based on the results of this 3-(3) alternative PFD simulation, a mixture of biodiesel solutions is produced with a composition that is dominated by methyl oleate and only a small amount of oleate acid, methanol and water. The methyl oleate mol fraction in the biodiesel mixture was 0.96292 with a mass flow rate of 699.235 kg/h and a molar flow of 2.3827 kg.mol/h. With the same method of calculation, the purity of biodiesel obtained was 96.843%. Thus, the purity obtained already met the standard of purity established by the SNI. Still using PFD No. 3 for simulations of calculations 4, 5 and 6 (see table 12) the methyl oleate content was actually higher than the third simulation of 97.115% for the fourth simulation, then 99.501% for the fifth simulation and

99.461% for the sixth, but the results obtained in the form of mass flow rate were less optimal because only 693.931 kg/h (simulation-4), 388.959 kg/hr (simulation-5) and only 140.240 kg/hr (simulation-6) compared to the third calculation simulation at 699.235 kg/h. Thus, simulation 3 is the most optimal calculation to be chosen because in addition to having met the purity standard set by SNI it also has the highest mass flow rate among other simulations.

In terms of the energy flow, the 3rd alternative PFD indicates that the heat energy generated from the oleate acid cooling process of 40.196.25 kJ/h is fully reused for the energy required in the CSTR process, while the heat power generated by the hydrolysis process is reused to heat the resulting mixture of triolein feed and water (vegetable oil) through a heat exchanger with a counter current flow, this is the same as in scenario 2.

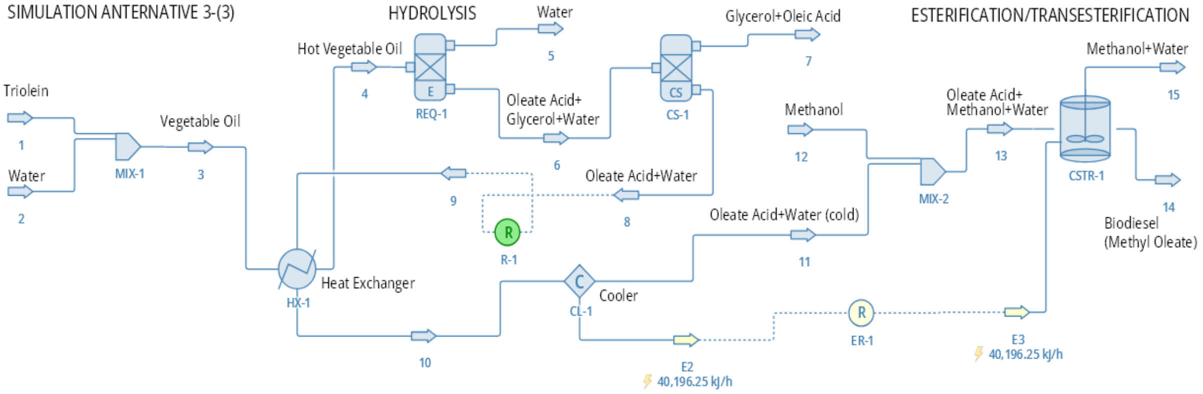


Figure 16: Simulation of PFD Production of Alternative Biodiesel 3-(3)

Table 10. below is a summary of the energy flow comparison generated by each alternative 1, 2 and 3 PFD simulation. For the total energy requirements of alternative 1 and 2 (calculated on the basis of the total power requirements of each processing device, then the energy required is approximately the same, which are -1.27751 x 10^6 kJ/h for PFD-1 and -1.36447 x 10^6 KJ/h for PFD-2. Whereas the energy needs of alternative-3 are much lower when compared with the two above alternatives because alternative-3 PFD does not use a heater to heat methanol and also the heat produced by the cooler is fully reused for the CSTR process so that the total external energy requirement is only -312519 kJ/h. Table 11 and table 12 below show the material composition of the stream and the summary in terms of mol fractions for each feed and final product for each alternative.

3.4. Tabulation and Graphics of DWSIM Simulation Result

Table 10: Mass and Energy Balance Data for each PFD Simulation Outcome

Equipment	Type	Energy consumption (-) / Generation (+) kJ/h			Efficiency (%)			MBR (kg/h)		
Process		PFD-1	PFD-2	PFD-3	PFD-1	PFD-2	PFD-3	PFD-1	PFD-2	PFD-3
MIX-1	Stream Mixer	1.27529E-06	1.27529E-06	1.54316E-05				7.99361E-13	7.99361E-13	7.99361E-13
CSTR-1	Continuius Strirred Tank Reactor	-1246960	-1350260	-40196.3				0	0	3.39728E-12
CS-1	Compound Separator	-388860	-304033	-58817.1				9.99201E-13	-1.9984E-13	2.59792E-12
MIX-2	Stream Mixer	148970	-0.00406246	-5.04568E-05				0	0	0
HT-1	Heater	-55628	-168444	-	100	100		0	0	-
CL-1	Cooler	112201	107185	40196.3	100	100	100	0	0	0
REQ-1	Equilibrium Reactor	487783	351083	-243795				0.000203092	0.00020389	0.00120155
HT-2	Heater	-335024	-	-	100			0	-	-
HX-1	Heat Exchanger		-168444	-9906.79		80.857	100		-1.9984E-13	-3.59712E-12
Total Energy Consumption:		-1277510	-1364470	-312519	Residual Mass Balance:			0.000203092	0.00020389	0.00120155

Table 11: Tabulation of simulation results with DWSIM

PFD	Simulation no.	Temp. inlet Equil. Reactor °C	Temp. outlet Equil. Reactor °C	Oleate acid outlet Equil. Reactor (mol fraction)	Conversion (%)		Temp. outlet CSTR °C	Frequency factor (A)	Methanol conversion at CSTR (%)	Residence time at CSTR (second)		Molar flow Triolein (kgmol/h)	Mass flow Triolein (kg/h)	Mol Triolein (a)	Molar flow Biodiesel (kgmol/h)	Mass flow Biodiesel (kg/h)	Mol Biodiesel (b)	Mol fraction Methyl Oleate (c)	Purity of Biodiesel (%) (1xcxb)/(3xa) x100 %
					Water	Triolein				Liquid	Vapor								
Alternati	1	70	69.2	0.31	9	15	65.	252.9	1.750	134	0.0	1.15	102	0.00	33.6	2044	0.01	0.01	7.857
	2	70	69.2	0.31	9	15	70.	254.9	1.778	263	0.4	1.15	102	0.00	3.54	1087	0.00	0.15	14.78
	3	70	69.2	0.31	9	15	75.	254.7	1.800	270	0.4	1.15	102	0.00	2.88	1066	0.00	0.18	15.07
	4	70	69.2	0.31	9	15	80.	252.9	1.819	275	0.3	1.15	102	0.00	2.53	1055	0.00	0.21	15.23
Alternati	1	90	109.	0.32	9	15	85.	60.75	1.6990	278	0.3	1.15	102	0.00	2.31	1046	0.00	0.23	15.39
	2	90	109.	0.32	9	15	90.	60.96	1.6990	280	0.3	1.15	102	0.00	2.15	1041	0.00	0.25	15.46
	3	90	109.	0.32	9	15	95.	60.94	1.6989	281	0.3	1.15	102	0.00	2.04	1038	0.00	0.26	15.52
	4	90	109.	0.32	9	15	100	60.75	1.6989	282	0.3	1.15	102	0.00	1.95	1035	0.00	0.27	15.56
Alternative 3	1	90	184.	0.96	7	99	210	10.37	9.205	335	0.2	1.07	950	0.00	2.67	781.	0.00	0.91	92.02
	2	90	184.	0.96	7	99	216	10.38	9.510	355	0.2	1.07	950	0.00	2.49	731.	0.00	0.94	95.12
	3	90	184.	0.96	7	99	219	10.38	9.672	370	0.2	1.07	950	0.00	2.38	699.	0.00	0.96	96.84
	4	90	184.	0.96	7	99	220	10.38	9.698	372	0.2	1.07	950	0.00	2.36	693.	0.00	0.96	97.11
	5	90	184.	0.96	7	99	240	10.38	9.908	653	0.2	1.07	950	0.00	1.31	388.	0.00	0.99	99.50
	6	90	184.	0.96	7	99	250	10.37	9.908	178	0.2	1.07	950	0.00	0.47	140.	0.00	0.99	99.46

Table 12: Parameters and Material Composition Results of the 3rd Simulation for each PFD

Material Stream or No. Of stream	PFD no. (for simulation 3)	Parameter				Mol Fraction					
		Temp. (°C)	Pressure (kPa)	Molar flow (Kgmole/h)	Mass flow (kg/h)	Oleate Acid	Methanol	Methyl Oleate	Water	Glycerol	Triolein
Triolein (feed)	1-(3*)	25	101.325	1.1520	1020	0	0	0	0	0	1
	2-(3)	25	101.325	1.1520	1020	0	0	0	0	0	1
	3-(3)	25	101.325	1.0729	950	0	0	0	0	0	1
Water (feed)	1-(3)	25	101.325	0.5540	9.98	0	0	0	1	0	0
	2-(3)	25	101.325	0.5540	9.98	0	0	0	1	0	0
	3-(3)	25	101.325	4.4407	80	0	0	0	1	0	0
Vegetable Oil	1-(3)	35.27	101.325	1.7060	1029.98	0	0	0	0.3247	0	0.6753
	2-(3)	35.27	101.325	1.7060	1029.98	0	0	0	0.3247	0	0.6753
	3-(3)	49.76	101.325	5.5136	1030	0	0	0	0.8054	0	0.1946
Hot Vegetable Oil	1-(3)	70	101.325	1.7060	1029.98	0	0	0	0.3247	0	0.6753
	2-(3)	90	101.323	1.7060	1029.98	0	0	0	0.3247	0	0.6753
	3-(3)	90	101.323	5.5136	1030	0	0	0	0.8054	0	0.1946
(6) Oleate Acid (+) Glycerol	1-(3)	69.29	101.275	1.7060	1029.98	0.3188	0	0	0.0058	0.1063	0.5690
	2-(3)	109.6	101.298	1.7060	1029.98	0.3201	0	0	0.0046	0.1067	0.5686
	3-(3)	184.9	101.298	3.6686	1007.14	0.9646	0	0	0.0165	0.0188	0
(8) Oleate Acid	1-(3)	69.29	101.275	1.5395	1014.65	0.3533	0	0	0.0065	0.0097	0.6305
	2-(3)	109.6	101.298	1.5387	1014.58	0.3549	0	0	0.0051	0.0096	0.6303
	3-(3)	184.9	101.298	3.2535	901.837	0.9789	0	0	0.0174	0.0036	0
Glycerol (by-Product)	1-(3)	69.29	101.275	0.1664	15.3368	0	0	0	0	1	0
	2-(3)	109.6	101.298	0.1672	15.4022	0	0	0	0	1	0
	3-(3)	184.9	101.298	0.4151	105.303	0.8526	0	0	0.0095	0.1379	0
Methanol (feed)	1-(3)	25	101.325	32.145	1030	0	1	0	0	0	0
	2-(3)	25	101.325	32.145	1030	0	1	0	0	0	0
	3-(3)	25	101.325	32.145	1030	0	1	0	0	0	0
Methanol (output)	1-(3)	75	101.275	30.770	978.466	0	0.9827	0	0.0173	0	0
	2-(3)	95	101.299	31.639	1006.3	0	0.9826	0	0.0173	0	0
	3-(3)	219.5	101.274	33.016	1232.6	0.0003	0.8788	0.0247	0.0958	0.0004	0
Biodiesel (product)	1-(3)	75	101.275	2.8830	1066.19	0	0.4612	0.1889	0.0078	0.0051	0.3370
	2-(3)	95	101.299	2.0457	1038.28	0.0032	0.2501	0.2669	0.0032	0.0057	0.4741
	3-(3)	219.5	101.274	2.3827	699.235	0.0270	0.0095	0.9629	0.0005	0	0

1-3*) calculation result for PFD alternative-1 simulation-3

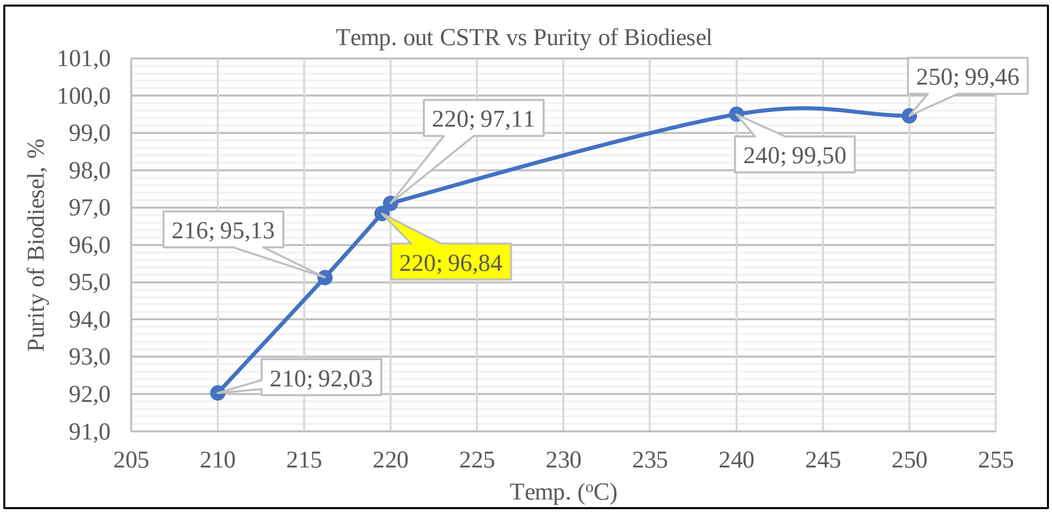


Figure 16: CSTR Output Temperature vs. Biodiesel Purity Level

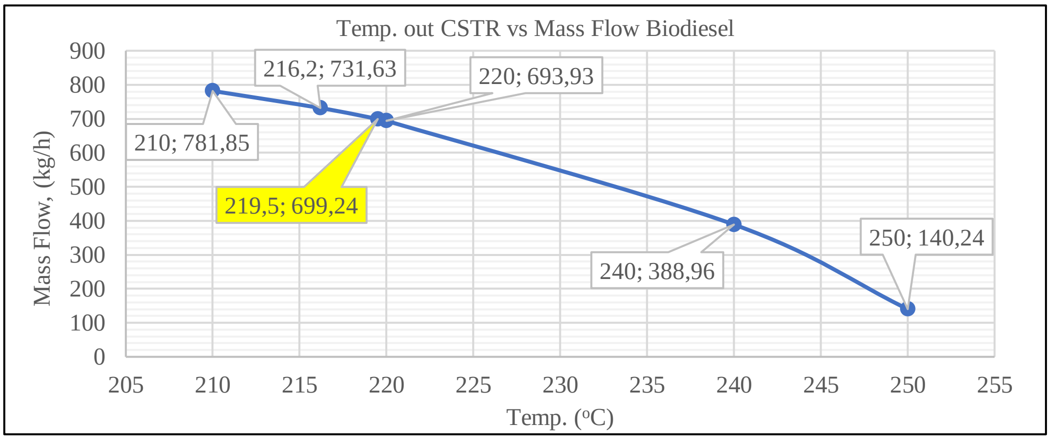


Figure 17: CSTR Output Temperature vs. Biodiesel Mass Flow

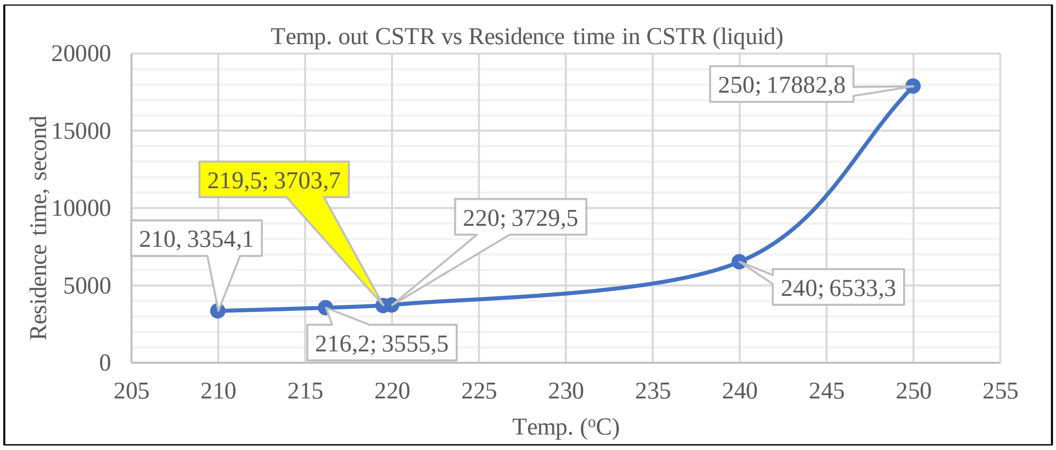


Figure 18: CSTR Output Temperature vs. CSTR Residence Time (liquid)

4. Conclusion

1). The optimization of the purity of the production of biodiesel was carried out on three PFDs based on the proposed BFD. The 3rd alternative simulation of the PFD was the process chosen for this optimization because it was able to produce an optimum purity for biodiesels of 96.843% at CSTR temperature at 219.5°C, with a residence time of 3703.7 seconds and a mass flow rate of 699.235 kg/h. This purity achievement has been in accordance with the standard of purity set by SNI.

2). The activation energy obtained from the 3rd simulation was 10.184 kJol/mol with a frequency factor value (A) of 10.382 L/mol.min at 219. 5°C.

3). The use of heat exchangers in the 2nd and 3rd PFDs has a positive impact on energy efficiency and indirectly has an impact in reducing production costs. By using heat exchanger, the heat energy needs can be reduced as this device can take advantage of the thermal energy generated by the system and replace the role of additional using of heater. Specifically for the simulation in the 3rd PFD, the heating energy produced by the cooler is fully utilized for the processes that take place in the CSTR, so the total energy needs for the 3rd PFD simulation are much smaller compared to the PFD-1 and PFD-2.

5. Suggestion

Recommendations for further research that will lead to optimization of production through process simulation should be carried out with catalytic processes using catalysts, thus obtaining a distinction of the results obtained between catalytical and non-catalytical processes. In addition, it is necessary to consider supplementing the process equipment in the simulated PFD such as the addition of pumps for the required flow and other process equipment.

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