Simulation of a Reactive Distillation Process for Biodiesel Production

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ABSTRACT

Biodiesel production has received global attention for its potential to replace the conventional diesel because of the diminishing petroleum reserve and pollution caused by petroleum distillates. Reactive distillation of biodiesel can reduce the number of process equipment and the amount of energy required to power a biodiesel process plant. This study uses Aspen HYSYS to simulate a reactive distillation column for biodiesel synthesis. The reactive distillation column yielded 69.60% and 20.82% biodiesel and glycerol respectively. The product upgrading process produced 99.33% biodiesel and 78.24% glycerol.

Keyword: Reactive distillation, biodiesel, glycerol, pressure, reflux ratio, boil-up ratio, draw stage, Aspen HYSYS

1.0 INTRODUCTION

The major part of worldwide energy consumption comes from petroleum, charcoal and natural gas with exception of nuclear and hydroelectric energy. However, these sources are limited, and could be depleted by the end of the next century [1]. The concern that these fossil fuel sources are diminishing, coupled with environmental degradation, have intensified the need to identify alternative energy sources. This is because it is widely recognized that renewable and non-conventional sources of energy for transportation could play a key role in energy generation and consumption patterns in the future [2]. In search of such alternatives, the potential utilization of plant seed oil and animal fats as substitutes for biofuels like biodiesel, bioethanol and biolubricant has received attention globally. Biodiesel is as an alkyl ester obtained from the seeds of plant and fats of animal. The oil obtained from several plant seeds and animal fats are long chain hydrocarbons which are generally environmentally friendly [3]. The demand for biodiesel increased more recently as a result of price increase for petroleum fuel products and also due to biodiesel's advantage of reduced net carbon dioxide and sulfur oxide emissions on a life cycle basis in comparison to petroleum diesel [4].
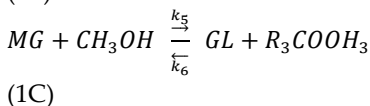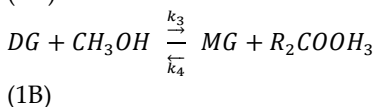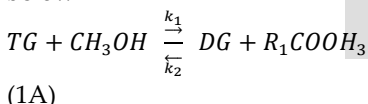
Among several methods for biodiesel synthesis are pyrolysis, esterification, micro emulsification and transesterification. Transesterification which is the most adopted process for biodiesel synthesis involves the reaction of the oil with an alcohol. The reaction can be catalyzed by bases, acids, enzymes or carried out under supercritical conditions in the absence of catalysts. The alcohol used is of low molecular weight with ethanol having most consideration due to its low cost and ready availability. However, greater conversion into biodiesel can be reached using lower chain alcohols like (≤C2) than the longer chain alcohols (≥C3), this is because lower chain alcohols tend to produce better products with no side chains than the longer ones [5]. Due to impurities, the glycerol must be refined before commercial use in other industries. The first step usually employed to recover biodiesel after transesterification reaction is separation of crude biodiesel from this by-product. The reaction being an equilibrium limited reaction can have its conversion increased far beyond chemical equilibrium conversion due to the constant removal of products of reaction from the reactive zones if the reaction and separation are combined in a single process. This may lead to a subsequent reduction of investment and capital cost and may be applicable for sustainable development due to low consumption of resources [6].
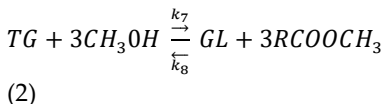
Conventional chemical plants mainly consist of reaction and separation processes. Reactive distillation is growing as an innovative industrial technology by combining both of these processes into a single comprehensive unit. Reactive distillation is a process where the chemical reactor also acts as the still [7]. Separation of the product from the reaction mixture does not require multi-separation distillation steps. This technique reduces both energy and equipment costs. A single reactive distillation column could replace the conventional reactor and distillation processes, which consume five times more energy and capital costs than the single unit alternatively [8]. In comparison to the conventional process for biodiesel synthesis, reactive distillation results in higher conversion, selectivity and yield, avoid equilibrium restrictions, aids in the removal of

unnecessary side reactions, helps in complete removal or reduction in number of recycle streams, avoidance of non-reactive azeotropes, reduce total plant investment cost and reduce process energy requirement (heat integration). In employing reactive distillation for biodiesel production, certain criteria need to be considered in order to have a reasonable conversion of reactants to product. Firstly, the location of the feed in the column is paramount as it will control the residence time for product formation [9]. Secondly, the column configuration such as a simple column for conventional separation with a condenser and reboiler, reboiled absorber with no condenser and zero reflux, Refluxed absorber with reflux and no reboiler etc. to suit the type of reactions and the conditions for product formation in the column. However, the effect of pressure, temperature, concentration and flowrates of the reactants are also very important as, individual feed conditions will affect the rate of product formation [10].

The kinetic model developed for the synthesis of biodiesel from soybean oil shows that biodiesel is produced from three stage wise reversible reactions [11]. Noureddini and Zhu were showed that for every production of biodiesel, the triglyceride is converted to diglyceride and monoglyceride intermediates before biodiesel synthesis. The overall behavior of the reaction according to [11] exhibit a second order kinetics. The reactions are shown in the equations below

$$TG + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftarrows}} DG + R_1COOH_3$$

(1A)

$$DG + CH_3OH \underset{k_4}{\overset{k_3}{\rightleftarrows}} MG + R_2COOH_3$$

(1B)

$$MG + CH_3OH \underset{k_6}{\overset{k_5}{\rightleftarrows}} GL + R_3COOH_3$$

(1C)

The overall reaction is as thus;

$$TG + 3CH_3OH \underset{k_8}{\overset{k_7}{\rightleftarrows}} GL + 3RCOOCH_3$$

(2)

The equations led to the development of the rate equation for biodiesel synthesis.

For many applications, a lighter reactant is fed at the bottom stage of the reactive zone, whereas a heavier reactant is fed at the top stage of the reactive zone [12]. However, for the transesterification reaction of vegetable oil with methanol to produce biodiesel, it is shown that introducing both the reactants to the column at the first reactive stage results in better performance [13]. Moving the feed stage of methanol down to the bottom of the reactive distillation column decreases the conversion of the vegetable oil and the yield of biodiesel. Although a higher amount of methanol is

observed at the upper stage of methanol feed location, the transesterification is less pronounced due to the absence of catalyst. The reaction mechanism is shown in figure 1. Higher feed temperatures also bring about higher conversion of the vegetable oil but when the temperature becomes too high, the amount of methanol required for the reaction decreases which brings about reduction in the conversion of the oil and the yield of biodiesel. This research is aimed at using Aspen HYSYS V10 to simulate the reactive distillation for biodiesel production.
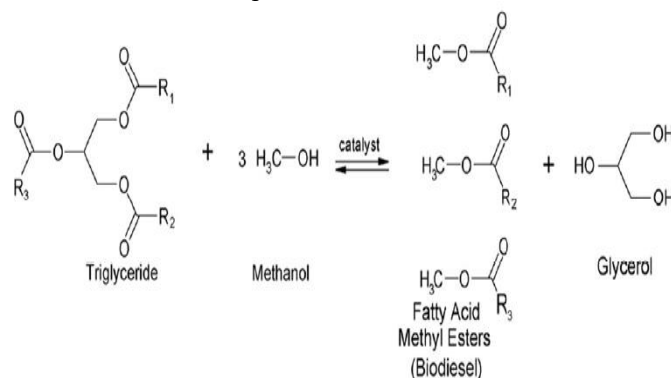

Figure 1: Transesterification of triglyceride with methanol to biodiesel and glycerol

2.0 METHODS

No laboratory work was carried out on this research. The physio-chemical properties were obtained from literature.

2.1 Simulation Process

The use of modern simulation packages due to their extensive thermodynamic properties will provide reliable information for plant operations. The Advance System for Process Engineering (ASPEN) Hyprotech System (HYSYS) V10 was used to carry out the process simulation.

The basic pure components like methanol, triolein (oil), glycerol and methyl-oleate were available from HYSYS properties. Monoolein and diolein intermediate components were added from Aspen properties. The universal quasichemical (UNIQUAC) thermodynamic fluid package was selected for activity coefficient of the phases in the system, this formed the basis of the result obtained after the simulation had been completed [14]. The kinetic reaction was inputted with all the rate constant as developed by [11]. Table 1 shows the kinetic constants for transesterification of soybean oil and methanol at 60 ^{0}C.

TABLE 1
KINETIC CONSTANT FOR TRANSESTERIFICATION OF
SOYBEAN OIL AND METHANOL AT 60 ^{0}C [11]

Rate Constant	$k_0(Lmol^{-1}s^{-1})$	E_a $(cal\ mol^{-1})$
k_1	3.9×10^7	13,141

k_2	5.7×10^5	9,932
k_3	5.906×10^{12}	19,860
k_4	9.88×10^9	14,639
k_5	5.335×10^3	6,421

2.2 Unit Operations and Operating Conditions

The oil was fed at 1000 kg/hr and the methanol stream was set to calculate the required amount of methanol which amounted to 217.1 kg/hr (4.6:1). Both streams were heated to 60 °C which is the required temperature of reaction for biodiesel synthesis. The feeds were fed to the first stage of the reactor with fifteen theoretical stages. The transesterification reaction was activated and set to start at the first stage and stop at stage fourteen (14). The distillate was the recovered methanol (at 61.56 °C) and the bottom product (at 317.8 °C) comprised the mixture of methyl-oleate and glycerol with few compositions of unreacted triolein, diolein, monoolein and methanol. Table 2 shows the properties and composition of streams. The bottom product was sent to the second column for separation and product upgrading into three process streams i.e. heavier bottom and the glycerol as the lighter component with biodiesel drawn from stage nine (9). The hot biodiesel from stage 9 was sent to the hot inlet of the plate heat exchanger (E01) to preheat the incoming oil, the hot outlet of E01 was sent to a shell and tube heat exchanger (E02) to preheat the methanol. The model flowsheet as described is shown in figure 2 below.

TABLE 2
PROPERTIES OF FEED AND PRODUCT STREAMS OF REACTIVE DISTILLATION COLUMN AND BIODIESEL PURIFICATION COLUMN

S/No	Component	Properties	Value
1	Triolein	Pressure (kPa)	95.00
		Temperature (°C)	60.00
		Mass flow (kg/hr)	1000.00
2	Methanol	Pressure (kPa)	95.00
		Temperature (°C)	60.00
		Mass Flow (kg/hr)	217.10
3	Mixed Bottom	Pressure (kPa)	95.00
		Temperature (°C)	317.80
		Mass Flow (kg/hr)	1084.00
		Composition (B/G) (%)	69.60/20.82
4	Recovered Methanol	Pressure (kPa)	90.00
		Temperature (°C)	61.56
		Mass Flow (kg/hr)	132.90
		Composition (%)	99.98
5	Glycerol at top	Pressure (kPa)	30.00
		Temperature (°C)	178.00
		Mass Flow (kg/hr)	133.00
		Composition (%)	78.08
6	Heavy Bottom	Pressure (kPa)	35.00
		Temperature (°C)	325.30
		Mass Flow (kg/hr)	301.10
		Composition (B) (%)	42.46
7	Biodiesel at tray 9	Pressure (kPa)	34.44
		Temperature (°C)	299.80
		Mass Flow (kg/hr)	650.10
		Composition (%)	99.33
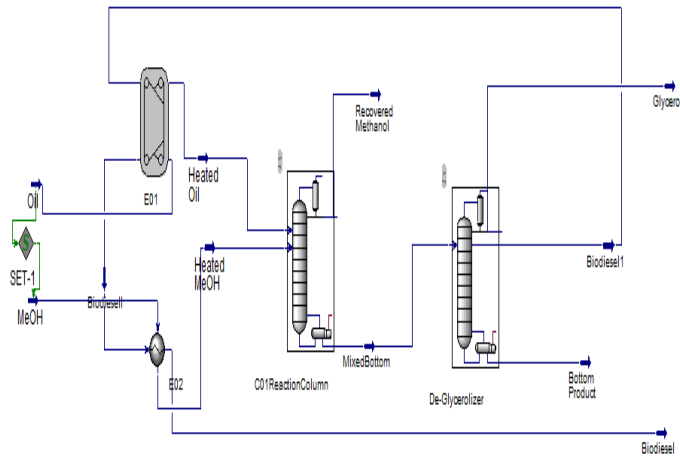
Fig. 2: Model flowsheet for reactive distillation of biodiesel

3.0 RESULT AND DISCUSSION

3.1 Parametric Study of the Reactive Distillation Column (Reaction Column)

3.1.1 Effect of Pressure on Biodiesel Formation in the Reaction Column

Figure 3 shows the effect of the feed pressure from 80-103.5 kPa on the formation of biodiesel. 80-90 kPa recorded the maximum biodiesel composition of 64.33 %. A drastic drop in composition was recorded as the pressure approached atmospheric. This indicates that higher pressure decreases the rate of reaction in the column resulting to poor product formation. The best practice in attaining higher conversion in the column is operating at relatively low pressure (vacuum feed system).

Fig, 3: Effect of pressure on the formation of biodiesel

3.1.2 Effect of Column Reactor Condenser and Reboiler Pressure on Biodiesel Formation

The condenser and reboiler pressure profiles were studied from 0 to 110 kPa, keeping the condenser pressure lower than the reboiler pressure. Between 0 to 69 kPa condenser and reboiler pressures, no convergence was recorded. However, at 70 kPa condenser pressure and 75 kPa reboiler pressure, convergence was recorded and the composition of biodiesel was found to be 67.05% which was relatively higher. All time higher composition of 67.43% was recorded at 75kPa and 80kPa condenser and reboiler pressures respectively. The composition dropped continuously with an increase in pressure from 80 and 90 kPa up to 105 and 110 kPa condenser and reboiler pressures. Therefore, 75 and 85 kPa condenser and reboiler pressures are the optimal operational pressures for higher yield of biodiesel in the column.
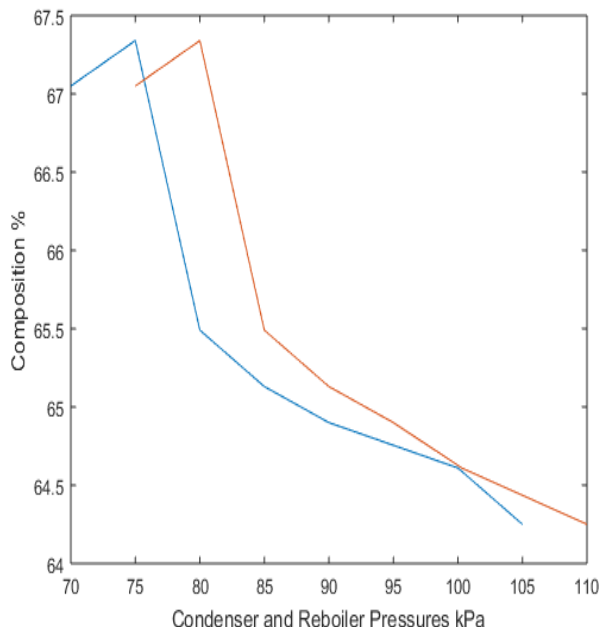
Fig. 4: Effect of condenser and reboiler pressure on the composition of biodiesel

3.1.3 Effect of Reflux Ratio on Biodiesel Formation

Figure 5 shows the effect of reflux ratio studied from 0.0001-1 versus the composition of biodiesel at constant pressure and temperature. From the figure, at very low reflux ratios, higher compositions of biodiesel are realized but drastically drops as it approaches unity. However, it is paramount to know that the degree of cooling affects the conversion of reactants to product. Reflux ratios will therefore, decrease the composition of the biodiesel formed as they possess lower temperature than the reactive distillation still and favor the formation of the glycerol byproduct. In this regard, the best reactive distillation practice for biodiesel synthesis is the reboiled absorber which only comprises a reboiler and zero reflux.
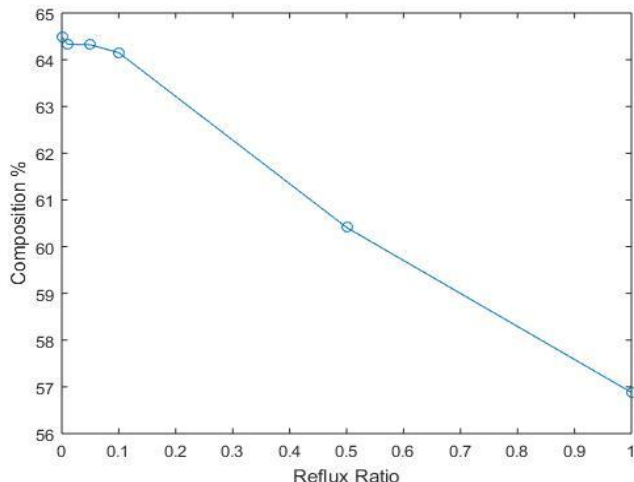

Fig. 5: Effect of reflux ratio to biodiesel composition

3.1.4 Effect of Number of Trays to the Formation of Biodiesel

Figure 6 shows a plot of number of trays versus the composition of biodiesel. The addition of five number of trays from 15 to 20 raises the composition from 64.33% to 64.39% which is a 0.06% increase. Additional five trays raise the composition by 0.12%. It can be seen that the maximum tray number is 25 and additional trays will only add up to equipment cost. The lesser increase in composition renders tray addition irrelevant. Therefore, fifteen number of trays is sufficient for reactive distillation.
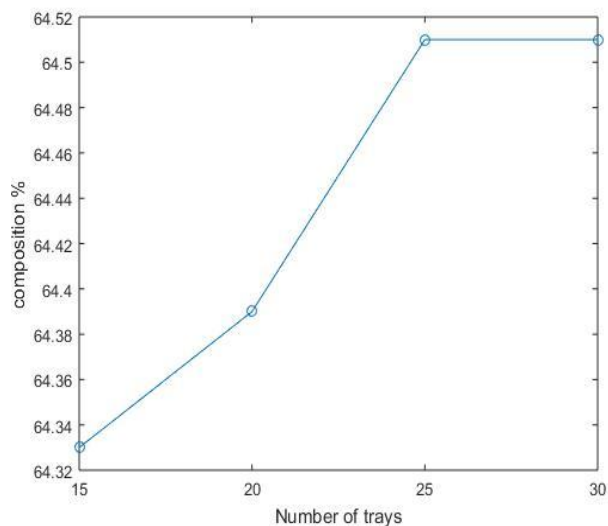

Fig. 6: Effect of Numbers of trays to the composition of biodiesel

3.1.5 Reaction Extent of Biodiesel across Stages

Figure 7 shows the extent of conversion of triolein to biodiesel from the condenser (represented as 0) to the reboiler (represented as 16). At the condenser, no feasible reaction was observed which might be due to the suppression of reaction temperature at the colder regions by reflux ratios. At tray one, the composition of biodiesel rose to 46.83% and gradually increased down the column. This was due to the sufficient residence time and available reaction temperature allowed to favor the forward reaction. The peak conversion of 64.90% was recorded at the reboiler (at a temperature of 203.7 ℃). This shows that continuous boil-up of reboiler feed increases the composition of biodiesel in the reactive distillation column. Therefore, it can be asserted that the transesterification reaction increases down the column and vice versa.
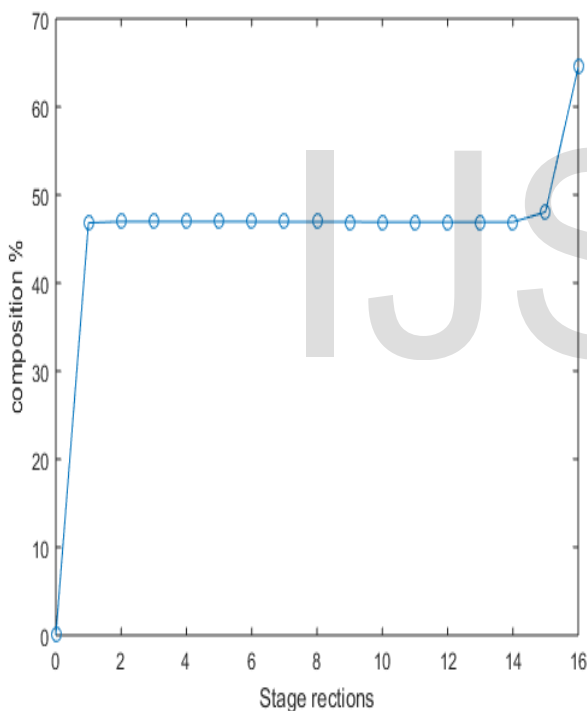
greater than 0.46. It can be deduced that at 0.46, a reasonable amount of liquid was reboiled back to the reboiler that improved the composition. At boil-up ratios greater than 0.46, a reduction in composition of biodiesel was observed. This was as a result of more of the liquid returning to the reboiler than those leaving. Therefore, to achieve a higher composition of biodiesel, the optimal boil-up ratio of 0.46 should be adopted. This verify the fact that in the selection of the column, column configuration of a reboiled absorber is preferable to handle reactive distillation of biodiesel as the decrease in composition of biodiesel even at higher boil up is far more significant than its composition at higher reflux ratios.
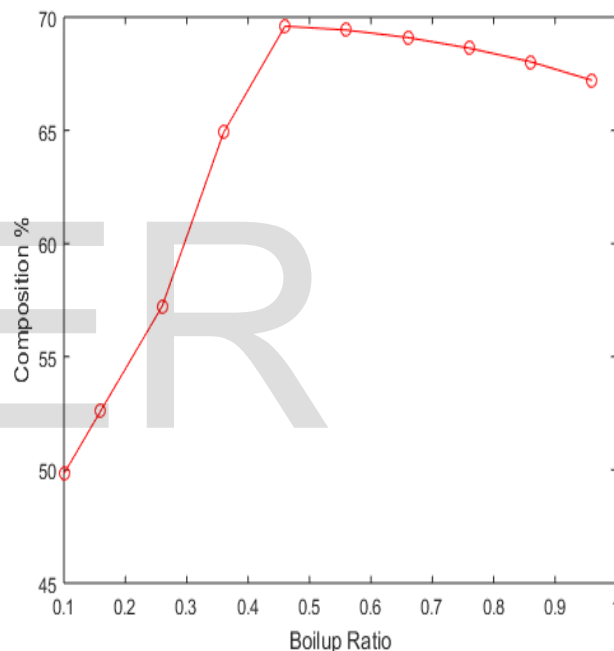

Fig. 8: Effect of boil-up Ratio to the composition of biodiesel

Fig. 7: Reaction Extent at all 15 stages with condenser and reboiler

3.1.6 Effect of Boil-up Ratio to the formation of Biodiesel

The boil-up ratio was studied from 0.1 to 1 to determine its effect to the production of biodiesel. At 0.1, the composition of 49.83 was recorded. Increase in composition was observed as the boil-up increased from 0.1 to 0.46. That is to say more liquids leave the reboiler than they are reboiled back. A very higher conversion of 69.60 % was recorded at 0.46 boil up ratio before drastically dropping at higher boil up ratio

3.2 Parametric Study of Biodiesel and Glycerol Fractionation Column (Deglycerolizer)
3.2.1 Condenser and Reboiler Pressure Effect of Biodiesel Seperation Column

Figure 9 shows the effect of condenser and reboiler pressure on the separation of biodiesel from glycerol, studied from 0 to 110 kPa condenser and reboiler pressure. The composition at vacuum pressures tended to be slightly higher than the composition at higher pressures. Nevertheless, the pressure difference seemed to be insignificant as the percentage increase was not more than 0.01%. It is more convenient to stick to safe working pressures in the column.
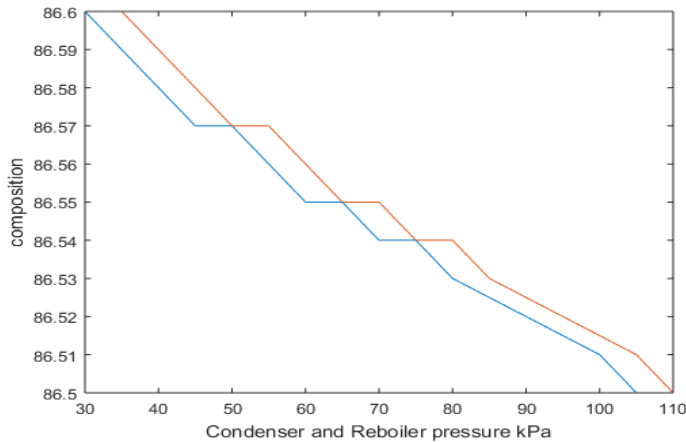
 Fig. 9: Effect of condenser and reboiler pressure to Biodiesel purity

3.2.2 Stage Composition of Biodiesel and Glycerol

Figure 10 shows the composition distribution of biodiesel and glycerol at all the stages with the condenser and reboiler. It can be seen that biodiesel composition increased down the column from the condenser and attained a maximum composition of 99.81 at tray nine (9). Therefore, the desired draw stage for pure composition of biodiesel was in tray 9. For glycerol, a purity of 78.24% was achieved at the condenser, but decreased immensely on going down the column. The composition of 78.24% sufficiently qualifies the condenser to be the actual draw stage of glycerol.
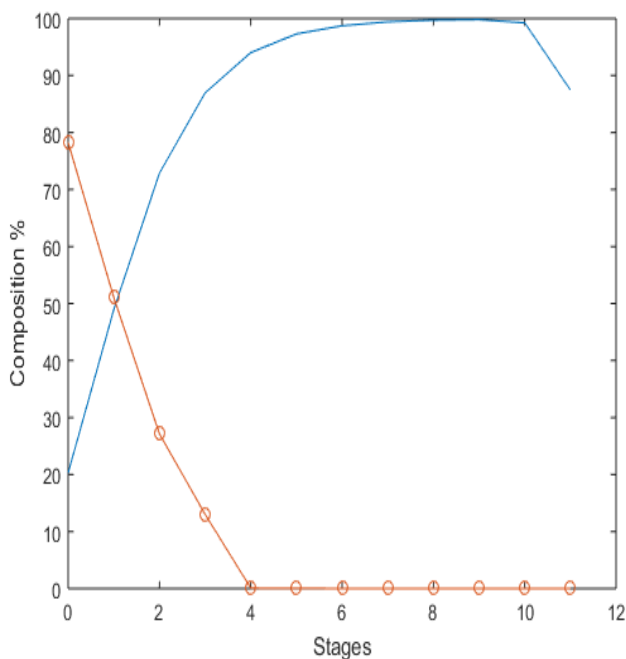

Figure 10: Composition of biodiesel and glycerol at each stage

4.0 CONCLUSIONS

The following conclusion can be drawn from the result of this work

1. The reactive distillation of biodiesel reduces the number of process equipment as seen in [4].
2. The reactive distillation bottom product yielded 69.60% biodiesel and 20.82% glycerol with 3.33% and 1.89% of diolein and monoolein respectively. 3.97% and 0.39% were the composition of unreacted oil and methanol respectively.
3. Moderate pressure of 75 kPa and 80 kPa condenser and reboiler pressures producing a reasonable yield of biodiesel suggest that lower pressures give better conversion.
4. Column configuration of a reboiled absorber gives reasonable conversion due to its zero-reflux configuration
5. Boil-up ratio of 0.46 gave a maximum conversion of 69.60% biodiesel in the reactive distillation column
6. Purer draw stage of biodiesel is at stage nine (9)
7. The purity of biodiesel at the purification column (De-Glycerolizer) was found to be 99.33% at 650.10 kg/hr while Glycerol at the top was found to be 78.06% at 133.10 kg/hr

REFERENCES

[1] O. O. Babajide, "Optimisation of Biodiesel Production via Different Catalytic and Process Systems.," University of Ibadan., 2011.

[2] N. M. Atadashi, I. M., Aroua, M. K., Aziz, A. R. A., & Sulaiman, "Refining Technologies for the Purification of Crude Biodiesel," *Appl. Energy*, vol. 88, no. 12, pp. 4239–4251, 2011.

[3] T. K. Pradeep and R. T. Rahul, "Properties of Neem, Jatropha,Mahua and Karanja Seed Oil as Potential Feedstock for Biodiesel Production.," vol. 2, pp. 93–98, 2015.

[4] A. Okullo and N. Tibasiima, "Process Simulation of Biodiesel Production from Jatropha Curcas Seed Oil," *Am. J. Chem. Eng.*, vol. 5, no. 4, pp. 56–63, 2017.

[5] U. S. Ubam, "Production of Bio-Lubricant from Neem Seed Oil Using Acetic Acid as an Oxygen Carrier," Ahmadu Bello University-Zaria, 2017.

[6] M. S. Radhaa, K. A. Sukkar, J. M. Ali, Z. M. Shakoor, and N. Manwel, "Hydrodynamics , Mass and Heat Transfer in Reactive Distillation," vol. 4, no. 2, pp.

1–9, 2008.

[7]   G. Towler and R. K. Sinnott, *Chemical Engineering Design Principles, Practice and Economics of Plant and Process Design*. Butterworth-Heinemann, 2008.

[8]   G. Rionugroho, F. Ahmad, and M. Lee, "A Hybrid Reactive Distillation Process with High Selectivity Pervaporation for Butyl Acetate Production via Transesterification," *J. Memb. Sci.*, vol. 543, pp. 49–57, 2017.

[9]   R. M. Dragomir, "Synthesis and Design of Reactive Distillation Columns," University of Manchester, 2004.

[10]   H. S. Fogler, *Elements of Chemical Reaction Engineering*, 4th ed. Prentice Hall Professional Technical Reference, 2006.

[11]   H. Noureddini and D. Zhu, "Kinetics of Transesterification of Soybean Oil," *Biocatal. Artic.*, vol. 74, no. 11, 1997.

[12]   O. Levenspiel, *Chemical Reaction Engineering*, 3rd ed. John Wiley & Sons, 1999.

[13]   T. Poddar, A. Jagannath, and A. Almansoori, "Use of reactive distillation in biodiesel production : A simulation-based comparison of energy requirements and profitability indicators," *Appl. Energy*, 2016.

[14]   K. A. Hamid, *HYSYS : An Introduction to Chemical Engineering Simulation*, 1st ed. Universiti Teknologi Malaysia, 2009.