Process Design of Mixed Flow Reactor for Lye-Catalysed Transesterification Reaction

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Abstract
The design of a continuous transesterification process for biodiesel production was carried out using ASPEN HYSYS software. The feed consisted of castor oil and methanol in the ratio 1:6 with catalyst (lye) loading of 1 wt % of oil. A conversion of 99.97 % was achieved. The transesterification reaction took place at 60 ^oC and atmospheric pressure. The basis for the process design was 1 kmolhr^{-1} of castor oil feed which gave 1.107 m^{3}hr^{-1} of biodiesel and 0.08 m^{3}hr^{-1} of glycerol. Based on the studies carried out, the process proved to be feasible with biodiesel purity of 99.7 % and methanol recovery of 99.71%. Glycerol was also obtained as a by-product with a purity of 89.09 %. The HYSYS process modelling tool generated heat and material balance data for the process as well as the sizing of the continuous stirred tank reactor and other equipment. The data obtained were used in the cost estimation of biodiesel production. The total production cost of biodiesel was set at $9,502,813.40 per annum (NGN 4,513,836,365) at the prevailing exchange rate of $1 to NGN475. The single greatest contributor to this value was the cost of the castor oil feedstock, which accounted for 84.2 % of the total estimated production cost. This is, however, on a high side therefore impairing the financial feasibility of the biodiesel production from castor oil.

Keywords: Biodiesel, Castor-Oil, Catalyst, Methanol, Mixed Flow Reactor,

1.0 INTRODUCTION

A LYE catalysed esterification reaction is a sodium methoxide-fatty acid chemical interaction for the synthesis of environmental benign fuel known as biodiesel. The studies over the past decade have studded both open and patent literature in a bid to furthering conserve and supplement the depleting fossil fuel reserve coupled with the campaign against global climate change (Cheng and Timilsina, 2011; Zhang et al., 2012; Giarola et al., 2012; Karatepe et al., 2012; Zabeti et al., 2009; Lam et al., 2010; Luque et al.,2010; Borges and Diaz, 2012; Lou et al.,2008; Di Serio et al., 2008; Loreto et al., 2005). For the process feasibility at localized regions of the globe, several biodiesel feedstocks have received special attention. These included waste cooking oil (Wang et al., 2006; Owolabi et al., 2011; Canakci and Van Gerpen, 2001), pawpaw seed oil (Owolabi and Osiyemi, 2013), Jatropha oil (Berchmans and Hirata, 2008; Shuit et al.,2010; Sahoo et al.,2009). Other studies used Karanja oil (Naik et al.,2008; Sahoo et al., 2009), Polanga seed oil (Sahoo et al.,2007), cotton seed oil (Demirbas, 2008), rubber seed oil (Ramadhas et al.,2005), tobacco seed oil (Veljkoviv et al.,2006), jimson weed oil (Wang et al.,2012) and poon oil (Devan and Makalakshmi,2009). However, several advantages of biodiesel have been reported in the literature (Ong et al., 2012; Azam, 2005; Singh and Singh, 2010; Agarwal and Rajamanoharan, 2007; and Dermibas and Dermibas, 2007). Series of trials on automobiles using biodiesel have also been conducted by some institutions in India (Sudarsan and Anupama, 2006) with high degree of success. Similarly, at the University of Ilorin, Kwara State, Nigeria, Jatropha seed oil biodiesel was used to test run a fossil diesel generator for a few hours (Belewu, 2011). The biodiesel process is, however, fraught with its high cost of production (Ibrahim, 2015; Canakci and Van Gerpen, 2001). This has thus militated largely against industrial scale biodiesel

production and wide acceptance as a complete substitute for fossil fuel. West et al., (2008) in their assessment of four biodiesel production processes submitted that the high cost of the process is largely attributed to the cost of virgin vegetable oil as feedstock. Exploring methods to reduce the production cost of biodiesel should therefore be the focus of current research trends. Hence, in this study, castor oil, a readily available and inedible oil (Santana et al., 2010) from rapidly growing castor plant, has been considered as the major feedstock for biodiesel production.

The other aspects of biodiesel production such as the biodiesel process simulation studies and reactor design toward industrial scale biodiesel production have been reported (Haas *et al*., 2006; Zhang *et al*., 2003; West *et al*., 2008, Ibrahim *et al*., 2013) but with little success. Haas *et al*. (2006) developed a process simulation model to estimate biodiesel production cost. Their model was found to be limited to a traditional alkali catalysed production method (West *et al*., 2008). Zhang *et al*., (2003) also developed a HYprotech SYStems (HYSYS) based process modelling to assess the technological feasibility of four biodiesel plant configurations where they found that one step (i.e. acid catalysed process) was the most economical. Ibrahim *et al*. (2013) carried out a research on simulation, design and construction of a continuous heterogeneous Jatropha based biodiesel pilot plant using calcium (II) oxide as catalyst. Similar reports with respect to castor oil to the best of our knowledge is either unavailable or in closed literature. The objectives of this work are to carry out the design of a process for the lye-catalysed synthesis of castor oil-based biodiesel in mixed flow reactor (MFR) at the rate of 1 kmolhr^{-1} of castor oil feed, to evaluate the process financial feasibility at mild operating conditions and to design a mini-reactor for the process

2.0 METHODOLOGY

This section discusses the design of the transesterification process. Each of the subsections describes some of the key units of the process flow diagram.

2.1 *Process Simulation*

A complete process design was carried out as depicted in **Figure 1** for the lye-catalysed transesterification of castor oil in order to obtain the process feasibility and to obtain both material and heat requirements of the process for subsequent economic analysis. All the streams are notated with a running number followed by main function. The first step in the design using HYSYS is the selection of all components that will participate in the formation of biodiesel. These components are castor oil (triricinolein, $C_{57}H_{104}O_9$), methanol (CH_3OH), sodium hydroxide (NaOH), methyl ricinoleate ($C_{19}H_{36}O_3$), glycerol ($C_3H_8O_3$) and water (H_2O). Triricinolein and methyl ricinoleate are not contained in the HYSYS component library and as such were generated using the HYSYS hypothetical component generator. The properties of these components (such as molecular weight, critical temperature, critical pressure and acentric factor) used in the creation of these hypothetical components are presented in **Table 1**. The presence of polar organic materials such as methanol and glycerol in the process, necessitated the selection of extended non-random two-liquid (extended NRTL) thermodynamic model for use as the property package for calculation of activity coefficient of the liquid phase. Since some binary interaction parameters were not available in the databank, they were estimated using the UNIFAC liquid-liquid equilibrium methods (Ndiaye *et al*., 2006). Similarly, the Wilson fluid package was also selected for design in both the methanol recovery and the glycerol purification units. As earlier stated, they were also estimated using the UNIFAC vapour-liquid equilibrium methods.

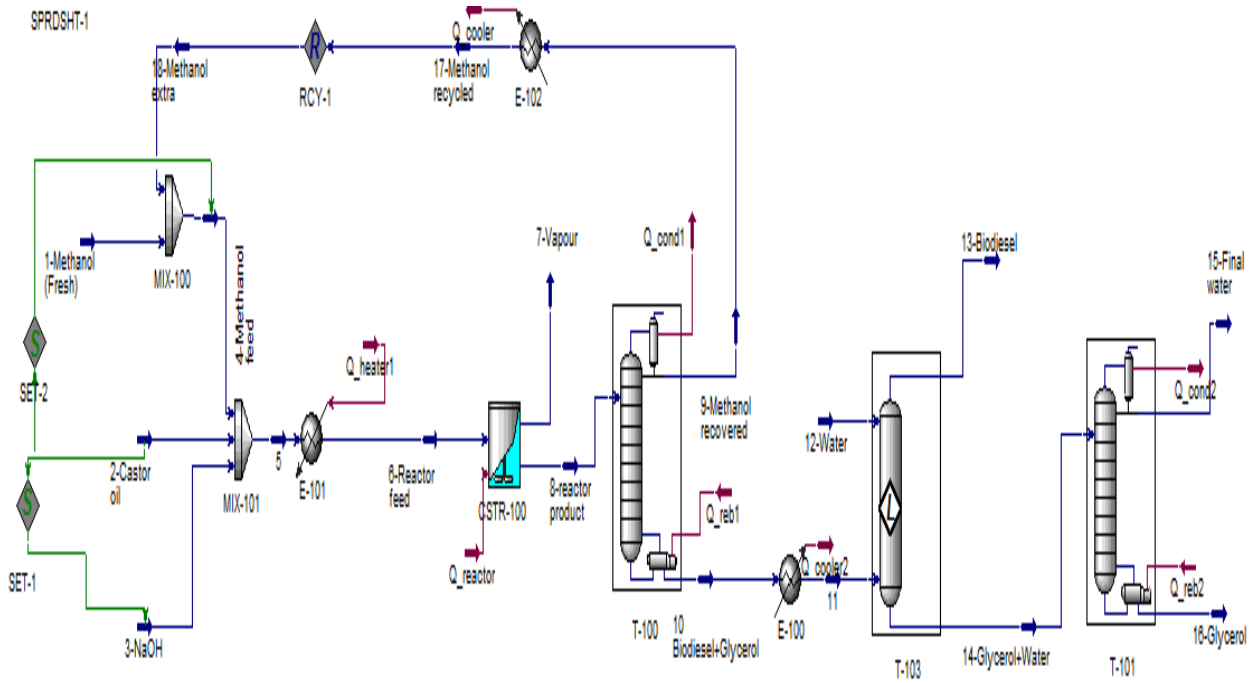


Figure 1: Process flow diagram of biodiesel production process in HYSYS.

Table 1. Properties for hypothetical molecules creation (Ndiaye *et al*., 2006).

Properties	Castor Oil (Triricinolein)	Methyl ricinoleate
Molecular weight (ggmol^{-1})	925.9	312.5
Critical temperature (K)	993.4	-
Critical pressure (K)	3.3	-
Acentric factor	2.542	-
Density (kgm^{-3})	-	926
Boiling point (^{o}C)	-	412

2.2 Process design

The plant was designed to produce 1.107 m^{3}hr^{-1} of biodiesel and 0.08 m^3 hr^{-1} of glycerol as by-product. The main operations' units include continuous stirred tank reactor (CSTR), mixers, pumps, valves, extractor, distillation column and storage tank. The simulation was carried out with a 6:1 molar ratio of methanol to castor oil, 1% sodium hydroxide (lye catalyst) based on the mass of oil, at 60 ^{o}C and 1 atmosphere.

2.2.1 Mixer I

Having selected the components and thermodynamic model, the process design commenced. The first step was to mix a fresh methanol stream and the recycled methanol stream, both at room temperature of 25 ^{0}C and atmospheric pressure of 1 atm, in a mixer, as shown in **Figure 2**.

2.2.2 Mixer II

The single methanol stream leaving mixer I then entered into another mixer with the castor oil stream and NaOH catalyst at the same temperature and pressure, as revealed in **Figure 3**.

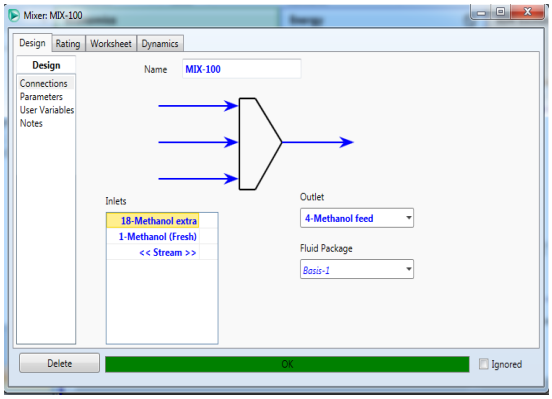


Figure 2: Installation of Mixer I.

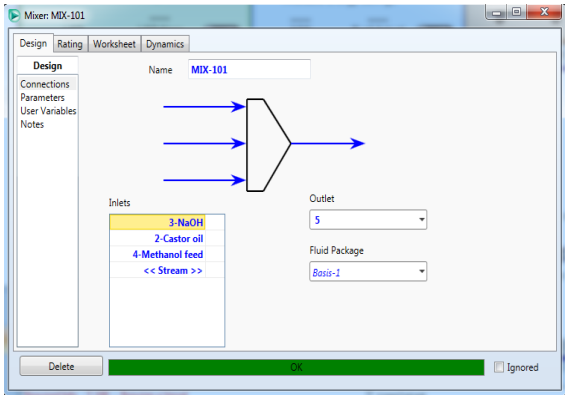


Figure 3: Installation of Mixer II.

2.2.3 Set Block I

The set block was installed to ensure that the amount of catalyst being fed into the process was at the stipulated 1.0 wt. % of the castor oil feed. The mass flow of the target variable (NaOH) was set, as indicated in **Figures 4(a)** and **4(b)**.

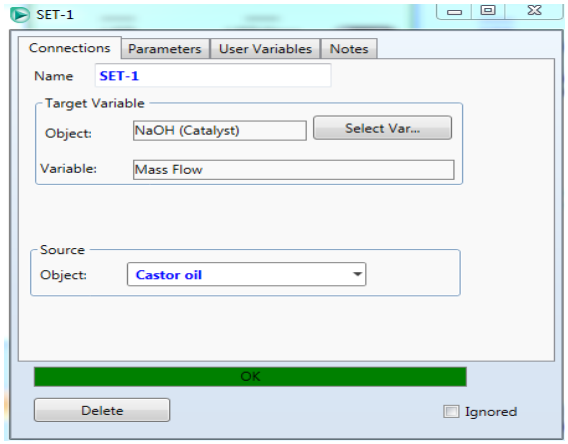


Figure 4(a): Installation of set block I.

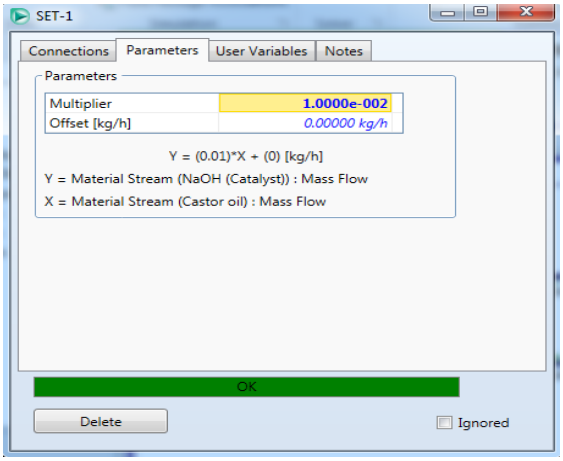


Figure 4(b): Installation of set block I.

2.2.4 Set Block II

The second set block was put in place to set the molar flow rate of the mixed methanol stream in tune with the castor oil stream, as given in **Figure 5**.

2.2.5 Heater

The heater was installed to increase the temperature of the reactor feed from room temperature (25 ^{o}C) to the temperature required in the reactor (60 ^{o}C), as depicted in **Figure 6**.

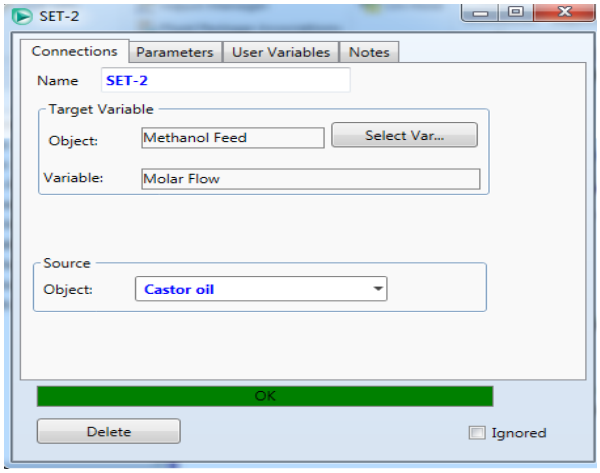


Figure 5: Installation of set block II.

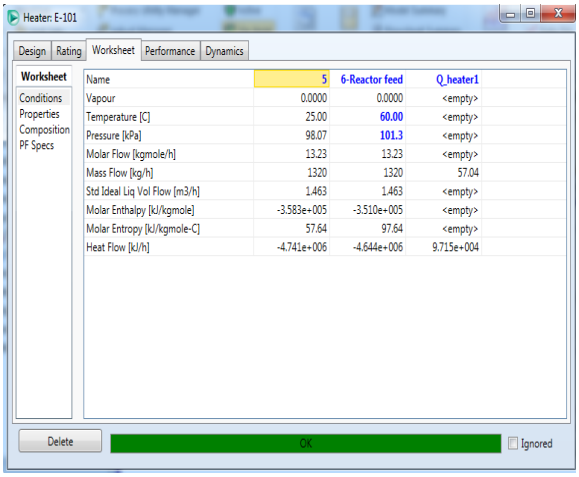


Figure 6: Worksheet of heater.

2.2.6 CSTR

The heated sodium hydroxide-methanol-castor oil mixture goes into the CSTR. A reaction set earlier created was added. In the creation of the reaction set and for the kinetics of the transesterification reaction, kinetics data (activation energy and Arrhenius pre-exponential factor) for the production of biodiesel from castor oil and methanol using sodium hydroxide as catalyst at 60 ^{o}C and 1 atm was entered for both forward and backward reactions. The conventional equation for the reaction is given by Eq. 1:

$$C_{57}H_{104}O_9 + 3CH_3OH \rightarrow 3C_{19}H_{36}O_3 + C_3H_8O_3 \quad (1)$$

However, for the purpose of this study, to drive equilibrium to the product side and ensure that the castor oil is completely used up (limiting reactant), the methanol to oil ratio is set at 6:1. The stoichiometry of the new equation as balanced by HYSYS is presented in **Figure 7**.

2.2.7 Methanol Recovery Unit

The product from the CSTR was sent into a methanol recovery unit, as shown in **Figure 8**. Methanol was input in excess and so the unreacted methanol can be recycled into the process. A distillation column was used as the methanol recovery unit, where methanol being the most volatile constituent was obtained as the overhead product and the biodiesel-glycerol mixture obtained as bottoms product. The methanol recovery column has its condenser operating at total reflux. The number of theoretical stages used was 3. This was chosen because at higher number of stages, the amount of methanol recovered did not change significantly. Reflux ratio was estimated by HYSYS as 1.73. Pressure drop across reboiler and condenser was assumed to be zero.

The compositions obtained for both top and bottom output streams are seen in **Figure 9**, where 99.9 % of the total methanol was successfully recovered.

2.2.8 Cooler

The bottoms product from the distillation column (biodiesel and glycerol) was expected to be at a high temperature and so it was first sent into a cooler to reduce the temperature to 25 ^{o}C, as given in the worksheet of cooler in **Figure 10**.

2.2.9 Biodiesel Purification Unit

The cooled mixture of biodiesel and glycerol was then sent into a liquid-liquid extraction column, as depicted in **Figure 11**, while **Figure 12** presents the compositions of all input and output streams of biodiesel purification unit. The mixture was washed countercurrently with water in this column using 3 extraction stages to ensure high level of purity of the biodiesel stream (which is the raffinate) while the extract was obtained as the glycerol-water mixture at the bottom of the column.

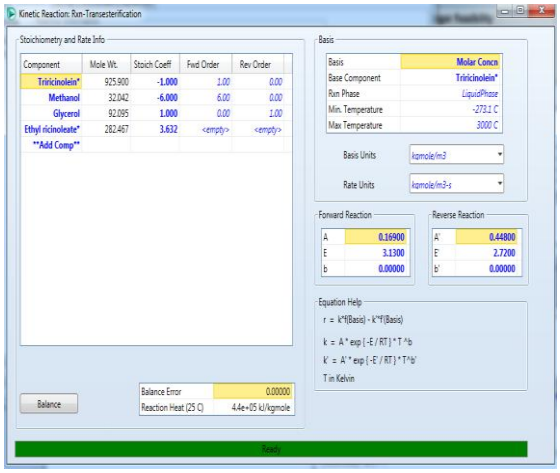


Figure 7: Reaction set for methanol to oil ratio of 6:1.

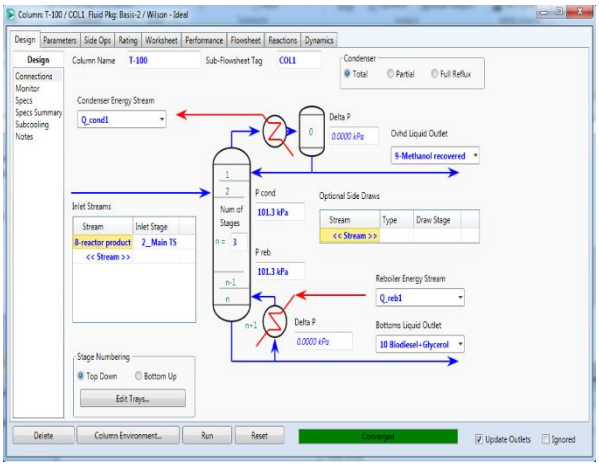


Figure 8: Installation of methanol recovery column.

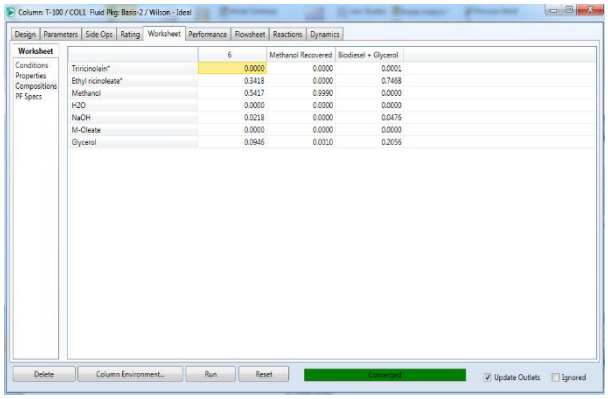


Figure 9: Compositions of all components in input and output streams of column.

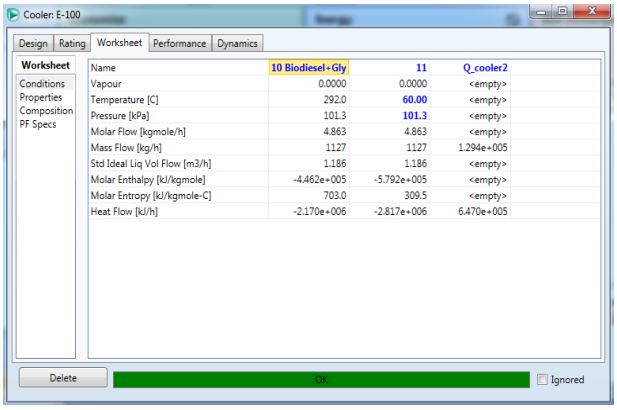
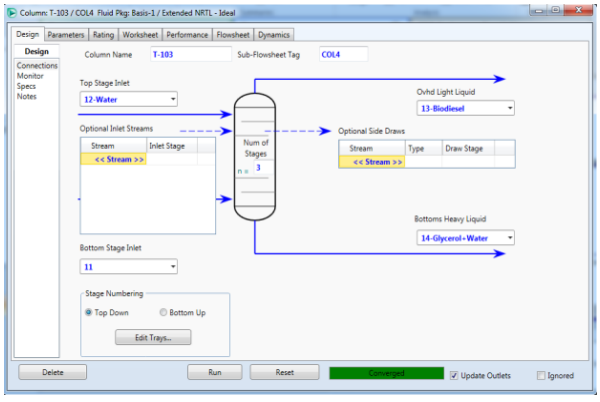


Figure 10: Worksheet of cooler.



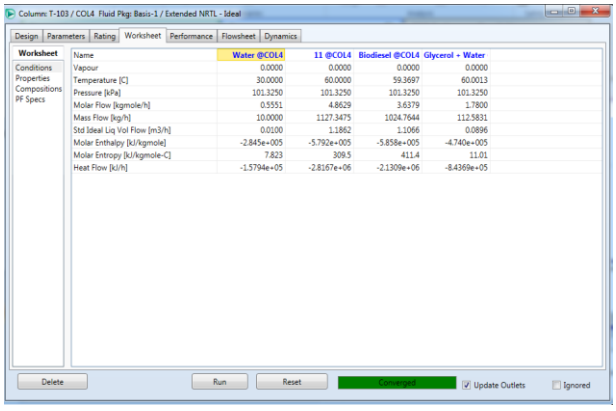
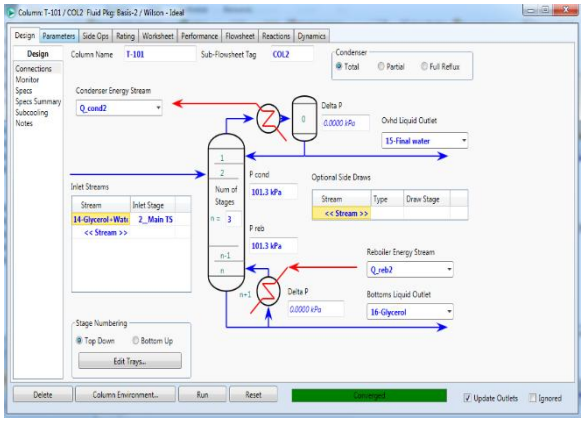


Figure 11: Installation of biodiesel purification unit.

Figure 12: Compositions of all input and output streams of biodiesel purification unit.

2.2.10 Removal of water from glycerol

A distillation column, as illustrated in **Figure 13**, was designed for the removal of water from glycerol, glycerol being a useful by-product. The column was used to obtain this product with water leaving as overhead and glycerol as bottoms, with its compositions depicted in **Figure 14**. This column has 3 theoretical stages with a reflux ratio of 0.5. Pressure drop across condenser and reboiler was assumed to be zero.



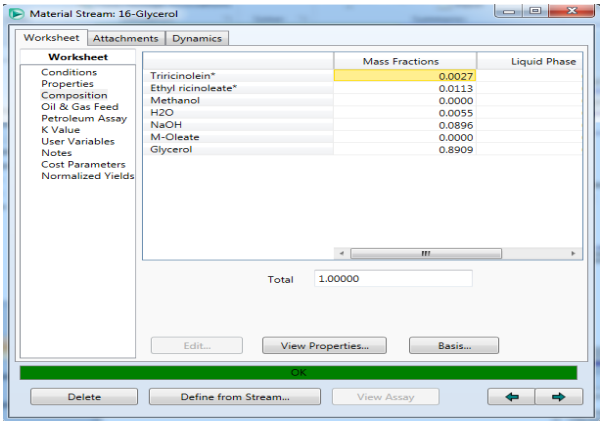


Figure 13: Installation of glycerol purification unit.

Figure 14: Composition of glycerol stream.

2.2.11 Methanol Recovery Stream

Figure 15 depicts the recovered excess methanol being recycled into the process after being cooled to the initial temperature of 25 °C.

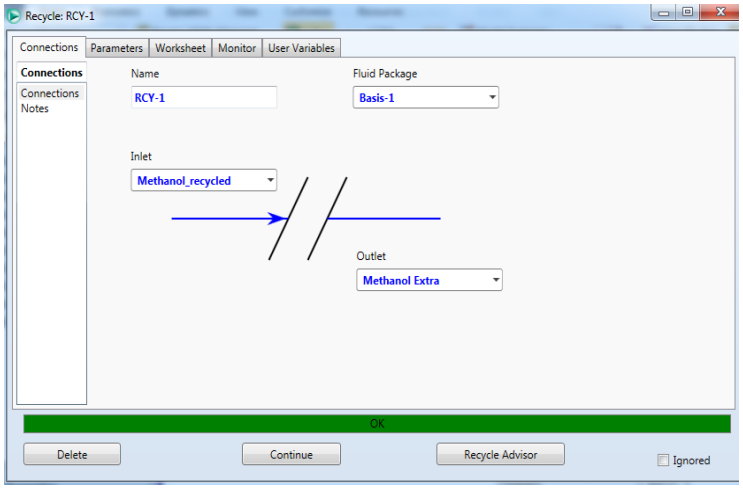


Figure 15: Installation of recycle stream.

3.0 RESULTS AND DISCUSSION

This section presents the results of the reactor design and the cost analysis of the tranesterification reaction.

3.1 Reactor Sizing

The sizing of the CSTR was carried out by ASPEN HYSYS and the results obtained are presented in **Table 2**. A conversion of 99.97 % was achieved in the CSTR.

Table 2. Results of CSTR sizing.

Reactor Parameters	Specification obtained from HYSYS
Vessel temperature (°C)	69.64
Vessel pressure (kPa)	101.32
Vessel pressure drop (kPa)	0
Vapour outlet pressure drop (kPa)	0
Tank volume (m^3)	0.5
Liquid volume (m^3)	0.25
Liquid volume percent	50
Vessel diameter (m)	0.75
Vessel height (m)	1.13
Material type	carbon steel
Mass density (kgm^{-3})	7861.09
Allowance stress (kPa)	94458.20
Shell thickness (mm)	6.35
Corrosion allowance (mm)	3.18
Efficiency of joints	1

3.1 Cost Analysis

From the studies carried out, it can be established that the process is technically capable of producing biodiesel at the required purity and operating conditions. Therefore, it is, of interest, to carry out a cost analysis to determine the total investment needed for the biodiesel production from castor oil feed. According to Perlingeiro (2005), the total investment corresponds to the sum of the materials needed to implement the process, resulting from stages of a project known as fixed investment, and the sum of the resources necessary for initiating the production activities and maintaining them, referred to as working capital. The fixed investment includes direct and indirect investment (25 % of direct investment). Total investment, however, is established only as a function of the values of inside battery limits (ISBL). This refers to the resources applied to the acquisition, transportation and installation of equipment directly used in the processes, as given by Eq. 2 (Santana *et al.*, 2010):

$$\text{Total investments} = 1.81(ISBL) \tag{2}$$

Similarly, according to Kasteren and Nisworo (2007), the ISBL can be estimated based on the total cost of equipment needed for the process:

$$ISBL = \text{ total cost of equipment } \times 5 \tag{3}$$

A depreciation rate of 10 % per year was assumed. Thus, equipment was assumed to have a useful life of 10 years. The annual equivalent cost (AEC) of the total investment is given by:

$$AEC = I_{total}\left[\frac{(1+j)^t j}{(1+j)^t - 1}\right] \tag{4}$$

AEC, which represents the annual equivalent cost, is the average useful life of the equipment and *j* is the annual interest rate of the current financial markets. The useful life for a piece of

equipment for our process was taken as 10 years and annual interest rate was estimated at 15%. The costs of items of equipment for the plant were obtained from HYSYS (Santana *et al.,* 2010) as well as from Sinnott and Towler (2009). The costs of CSTR (as obtained from HYSYS), two distillation columns, one extraction tower, two mixers and others were \$7390.67, \$200,000 \$3000, \$3000 and \$100,000 respectively. Hence, the total cost of equipment was \$313,390.67 and the value of inside battery limits, ISBL, was estimated using Eq. 3 to be \$1,566,953.35 and the total investment, according to Eq. 2, was estimated to be \$2,836,185.56. The total operating cost was estimated based on the raw materials used, catalyst, labour, utilities, and maintenance. The labour cost was estimated as 11 % of the total investment, which was \$311,980.41, and the maintenance cost was estimated as 6 % of the total investment, which gave \$170,171.13. The total cost of biodiesel production was therefore \$9,502,813.40, as **presented** in **Table 3**. The cost of materials was estimated by obtaining cost per unit from Sinnott and Towler (2009), and multiplying by actual amount needed as obtained from HYSYS. **Table 4** presents the total cost of raw materials and utilities.

Table 3. Total cost of biodiesel production.

	Cost (\$)	% Participation
CAE	565,114.60.00	5.94
Castor oil	7,999,766.00	84.2
Methanol	420,174.00	4.40
NaOH	2,666.00	0.20
Electricity and steam	32,932.00	0.35
Labour	311,980.00	3.30
Maintenance	170,170.80	1.80
Total	9,502,813.40	100

Table 4. Total cost of raw materials and utilities.

Specification	Cost per unit (\$)	Amount required per year	Cost (\$)
Castor Oil	1.2/kg	6,666,480	7,999,776
Methanol	232.5/ m^3	1807	420,174
NaOH	0.4/kg	6667	2,666
Electricity	4.5508/kWh		32,766
Steam at 100 psi	0.023		166

The annual equivalent cost, *AEC*, of the total investment was obtained, using Eq. 4, as follows:

$$AEC = \$2836185.56\left[\frac{(1+0.15)^{10}\times 0.15}{(1+0.15)^{10}-1}\right] = \$565{,}115.82$$

Estimating the cost of production of biodiesel per gallon for plant operation of 300 days per year (having taken cognisance of public holidays, start-up and shut-down times and some inevitable circumstances) with biodiesel production rate of 1.107 m^3hr^{-1} we have:

$$\frac{\$9{,}502{,}813.40}{1\,year}\left(\frac{1\,year}{300\,days}\right)\left(\frac{1\,day}{24\,h}\right)\left(\frac{1\,h}{1.107\,m^3}\right)\left(\frac{0.003785\,m^3}{1\,gallon}\right) = \$4.51/\,gallon$$

Hence, the cost of production of biodiesel was estimated to be \$4.51/gallon. This is a relatively high cost when compared to the market value of biodiesel which is currently set at \$3.03/gallon. This high cost estimate is largely attributed to the cost of castor oil used as feedstock which takes up 84.2 % of the total yearly cost of producing biodiesel. Castor oil is in high demand as it is widely used as a starting material for many industrial chemical products such as paints, coatings,

inks, lubricants (Ogunniyi, 2006) and as such its use for the production of biodiesel is in competition with these other products. Supply is not as surplus as it should be and so cultivation of the castor bean seed should be encouraged. Extensive research is being carried out in search of ways to reduce the high cost of production of biodiesel from castor oil. Alternatives include production from cheaper sources of oil and waste vegetable oil being the choice option.

With regard to glycerol, a by-product obtained from the biodiesel production process, glycerol currently has a relatively low market price. The current price of crude glycerol ranges between 3 and 10 cents per Ib glycerol. While this helps to reduce the total cost of biodiesel production, it is still relatively high when compared to diesel obtained from fossil fuels (₦200 per L of diesel). As at 2014, over 65 % of glycerol was obtained as a by-product of biodiesel production (Shorey, 2016). Sales of glycerol can be grossly increased to further reduce cost of biodiesel production by producing even purer glycerol that can be used in the pharmaceutical industry. The purity of glycerol in the simulated process is currently set at 89.09 % with a large portion of the impurity present being the NaOH catalyst. To attain purity of 99.5 % or more as required by the pharmaceutical industry, it is necessary to introduce a catalyst neutralization stage into the process**.**

Considering the current situation, the high cost of production of biodiesel does not allow it to easily compete economically with diesel obtained from fossil fuels. However, the use of biodiesel will provide environmental benefits as well as economic benefits if supply of castor oil is increased.

4. CONCLUSION

The design of a biodiesel production process through transesterification of castor oil at a flow rate of 1 $kmolhr^{-1}$ and methanol with sodium hydroxide catalyst was carried out using HYSYS simulation software. The production cost for the process was estimated, taking into consideration equipment sizing and flow rate obtained from the investigation. From a technical perspective, the process proved to be feasible producing biodiesel of high purity (99.7 %) to be blended with diesel or biodiesel from other sources. However, cost analysis of the process does not prove the process to be feasible mainly due to the high cost of castor oil.

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