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MODELING, SIMULATION AND OPTIMIZATION OF TRANSESTERIFICATION OF CITRULLUS LANATUS OIL TO BIODIESEL USING ASPEN PLUS SOFTWARE

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ABSTRACT
Biodiesel is one of the renewable energy resources which is suitable to replace the fossil fuel due to the depletion of fossil fuel in the future. The modeling and optimization of biodiesel production process from citrullus-lanatus oil is conducted by using Aspen-plus software version 8.8. This process is modeled and simulated in order to optimize the biodiesel production with significant parameters that affect the biodiesel production process. The sensitivity analyses and the optimization of the process were accomplished using the Sensitivity and the Optimization sections of Model Analysis Tool of Aspen Plus. The results obtained revealed that; with increase in temperature biodiesel yield increases at first and started falling at 64.5^{o}C. An increase in resident time gives rise to increase in biodiesel yield, at 2hr 30min the increases in the yield becomes slower. Increase in Catalyst concentration and methanol-oil ratio give rise to a decrease in biodiesel yield. The sensitivity analyses of the process carried out shows that optimization was necessary to obtain the operating variables that would yield maximum biodiesel flow. The result of the optimization indicated increase in biodiesel flow from 9.04 to of 9.8kmol/hr, Temperature from 50 to 58^{o}C, Methanol-Oil ratio increases from 3 to 4.5, the time of reaction increases from 30 to 90 min while catalyst-concentration decreases from 0.0852 to 0.0853. The model developed gives an optimum values of methanol-oil ratio, catalyst concentration and reaction temperature which can be successfully adopted in oil industry to maximize the yield of methyl esters.

KEYWORDS: Transesterification, Aspen Plus, Sensitivity Analysis, Optimization, Biodiesel.

1.0 INTRODUCTION
In this modern technological age, one of the challenges facing the transportation industry, is finding a less polluting substitute for diesel. Meanwhile, any kind of fuel with the cetane number specified in a diesel cycle cannot be utilized. One of the alternatives for this is biodiesel which is indirectly obtained from vegetable oil or animal fat in the presence of alcohol. (Goharimanesh et al. 2016).

Biodiesel is a cleaner fuel than petroleum diesel and an exact substitute for existing compression engines. (Yathish et al. 2013). Biodiesel refers to a vegetable oil- or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, propyl or ethyl) esters (Yathish et al. 2013). Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, animal fat (tallow)) with an alcohol.

Biodiesel is liquid which varies in color between golden and dark brown depending upon the production feedstock. It is immiscible with water, has a high boiling point and low vapor pressure. Typical ethyl ester biodiesel has a flash point of about 130ºC, biodiesel has a density of about 0.88 gm/cm^3, less than that of water (Chen, et al., 2008). A biodegradable transportation fuel that contributes no net carbon dioxide or sulfur emission to the atmosphere and is low in particulate emission. Ultra Low Sulfur Diesel fuel (ULSD) fuel, which is advantageous because it has virtually no sulfur content. Biodiesel has very good lubricating properties, significantly better than standard diesel which can prolong engine's life, (Ranganathan , et al., 2008). As a result, biodiesel can now compete with other alternative fuels and clean-air options for urban transit fleets and government vehicles across the country. It is safe, biodegradable and reduces air pollutants such as particulates, carbon monoxide and hydrocarbon. A variation in biodiesel energy density is more dependent on feedstock used than the production process (Chen, et al., 2008).

Biodiesel is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils

used; it can be used alone, or blended with petro-diesel; biodiesel can also be used as a low carbon alternative to heating oil.

Alternative fuel derived from vegetable oil and animal fat have increasingly important due to decrease in petroleum resources and increase in pollution problems. Scarcity of fossil fuel increases the searching of new biomass to trap renewable energy sources more attractively. Currently biodiesel is prepared from oil like soybean, canola, palm, sunflower etc. throughout the world (Bringi 1987; Altun 2011). It is now believed that the world food crisis will occur as the result of using food crops for producing biodiesel (Kalam et al. 2008). This lead to search for excavation of biodiesel feed stocks from unconventional, nonedible oil and fats like, waste grease, waste cooking oil, waste tallow, jatropha seed oil, tobacco seed oil, rubber seed oil, polanga seed oil, Citrullus *lanatus* etc.

Citrullus lanatus belongs to the family of Cucurbitaceae which has a tremendous genetic diversity, extending to vegetative and reproductive characteristics (Ng 1993). They thrive in tropical, subtropical, arid deserts and template locations. Citrullus lanatus is an annual herbaceous, monoecoius plant with a non-climbing creeping habit. After planting, they completely cover the soil surface within three weeks and flowering starts. Often the fruits are ready to harvest 3 - 4 months after sowing (Ng 1993).

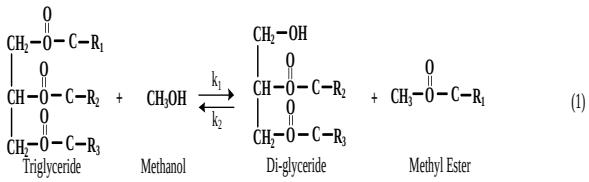
Cost of biodiesel is more than that of conventional fuels, The cost of raw materials accounts for 75– 85% of the production cost of biodiesel (Van et al. 1997; Demirbas 2009); therefore, optimization of industrial production of biodiesel is with major importance. There are several methods to obtain the optimum operating condition for biodiesel production process. In this work, Aspen plus Software is used to optimize the production of biodiesel from Catullus *lanatus.*

2.0 Biodiesel Production Process

Vegetable oils can be chemically modified to produce biodiesel fuel. All oils in nature are made-up of triglyceride; which is compose of glycerin molecule and three fatty-acid chain bonded together to form a very large molecules. These molecules can be broken in the present of a catalyst (such as Alkaline, Acid or Lipase-catalyzed etc.) which allow methanol molecule to bond with the freely fatty acid chain (when subjected to heating while mixing) forming Fatty-Acid Methyl Ester (FAME) otherwise known as Biodiesel and a by-product glycerol, this process is called Trans-esterification.

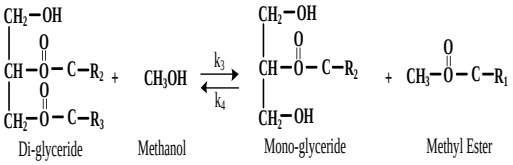
The reaction progresses in three reversible steps: (Allen, et al., 2006)

1. The Tri-glyceride reacts with the alcohol to form a Di-glyceride and a fatty acid ester,



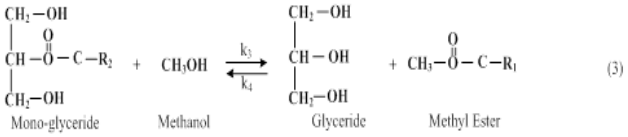
(1)

2. The Di-glyceride reacts with the alcohol to form a mono-glyceride and a fatty acid ester.



(2)

3. The mono-glyceride reacts with the alcohol to form glycerin and a fatty acid ester.



(3)

For example, if citrullus lanatus oil, with at least 5 different fatty acid groups, is used, there could potentially be 125 different triglycerides, 25 different di-glycerides, and 5 different mono-glycerides present.

3.0 Procedure

The Aspen plus V8.8 software was used for the simulation of the biodiesel production as shown in Figure 1. In this work, it assumed that the feedstock is the citrullus lanatus oil whose composition profile was determined by Edidiong et al. (Essien, Eduok 2012). Table 1 lists the Fatty acid composition of the refined citrullus lanatus seed oil.

Table. 1: Fatty acid composition of citrullus lanatus seed oil (Essien, Eduok 2012).

Fatty acid	Percentage composition
palmatic	10.57
Stearic	8.333
Oleic	13.65
Linoleic	62.15
Linolenic	5.297

Table 2 list the components used in the model to represent the chemical species present.

Di-glycerides such as DILEIC, DIPALMIT, DISTEAR, DILENIC and DIOLE-01 and Mono-glycerides such as MONOO-01, MONPALMA, MONSTEAR, MONLEIC and MONLENIC are the intermediates of the transesterification reaction.

MSTEARAT, MEPALMIT, MELINOLE, MEOLEIC and MLINOLEN are the biodiesel products, with glycerol as a by-product.

Sodium hydroxide is used as the catalyst, and is removed by adding H3PO4 to precipitate Na3PO4.

3.1 Process Description

Methanol and catalyst (NaOH) were first mixed under ambient condition and pumped to the reactor where oil which was initially preheated to the reactor temperature was combined and allowed to react for an hour to form glycerol and methyl ester. The product of the reactor was then passed through DIST1 where un-reacted methanol were removed and recycled. The bottom product of the DIST1 was preheated (to aid the separation of the remaining methanol) before moved to the washer, where most of the methanol was absorbed in water at the bottom product. The overhead product was rectified to obtain FAME (biodiesel). The bottom product was neutralized in NEUTRILZ by NaOH, to remove the used catalyst from the by-product glycerol which was then stripped in GLYRCOL.

Table. 2. Components Used in the Biodiesel production process.

Component ID	Type	Component name	Formula
METHANOL	Conventional	METHANOL	CH4O
NAOH	Conventional	SODIUM-HYDROXIDE	NAOH
GLYCEROL	Conventional	GLYCEROL	C3H8O3
PALMITIC	Conventional	TRIPALMITIN	C51H98O6
STEARIC	Conventional	GLYCEROL-TRISTEARATE	C57H110O6
LINOLEIC	Conventional	TRILINOLEIN	C57H98O6
LINOLENI	Conventional	TRILINOLENIN	C57H92O6
MSTEARAT	Conventional	METHYL-STEARATE	C19H38O2-N1
MEPALMIT	Conventional	METHYL-PALMITATE	C17H34O2-N1
MELINOLE	Conventional	METHYL-LINOLEATE	C19H34O2
MEOLEIC	Conventional	METHYL-OLEATE	C19H36O2
MLINOLEN	Conventional	METHYL-LINOLENATE	C19H32O2
WATER	Conventional	WATER	H2O
H3PO4	Conventional	ORTHOPHOSPHORIC-ACID	H3PO4
NA3PO4	Conventional	TRISODIUM-PHOSPHATE	NA3PO4
DIOLE-01	Conventional	DIOLEIN	C39H72O5
MONOO-01	Conventional	MONOOLEIN	C21H40O4
DIPALMIT	Conventional	1,3-DIPALMITIN	C35H68O5-1
MONPALMA	Conventional	1-MONOPALMITIN	C19H38O4
MONSTEAR	Conventional	1-MONOSTEARIN	C21H42O4
DISTEAR	Conventional	1,2-DISTEARIN	C39H76O5-2
MONLEIC	Conventional	1-MONOLINOLEIN	C21H38O4-1
MONLENIC	Conventional	1-MONOLINOLENIN	C21H36O4-1
DILENIC	Conventional	1,2-DILINOLENIN	C39H64O5-2
OLEIC	Conventional	TRIOLEIN	C57H104O6
DILEIC	Conventional	1,3-DILINOLEIN	C39H68O5-1

3.2. Reactions: A kinetic reaction model named CIT-OIL was created for use in the REACTOR (see Table 3). In addition, catalyst removal is modeled with a fixed conversion reaction in NEUTR using hydrogen phosphate (H_3PO_4).

Table. 3: Transesterification Kinetics: CIT-OIL.

Rxn No.	Reaction type	Stoichiometry
1	Kinetic	OLEIC + METHANOL --> MEOLEIC + DIOLE-01
2	Kinetic	DIOLE-01 + MEOLEIC --> OLEIC + METHANOL
3	Kinetic	DIOLE-01 + METHANOL --> MEOLEIC + MONOO-01
4	Kinetic	MEOLEIC + MONOO-01 --> DIOLE-01 + METHANOL
5	Kinetic	MONOO-01 + METHANOL --> GLYCEROL + MEOLEIC
6	Kinetic	GLYCEROL + MEOLEIC --> METHANOL + MONOO-01
7	Kinetic	LINOLEIC + METHANOL --> MELINOLE + DILEIC
8	Kinetic	MELINOLE + DILEIC --> LINOLEIC + METHANOL
9	Kinetic	DILEIC + METHANOL --> MELINOLE + MONLEIC
10	Kinetic	MELINOLE + MONLEIC --> DILEIC + METHANOL
11	Kinetic	MONLEIC + METHANOL --> GLYCEROL + MELINOLE
12	Kinetic	GLYCEROL + MELINOLE --> METHANOL + MONLEIC
13	Kinetic	PALMITIC + METHANOL --> MEPALMIT + DIPALMIT
14	Kinetic	MEPALMIT + DIPALMIT --> PALMITIC + METHANOL
15	Kinetic	DIPALMIT + METHANOL --> MEPALMIT + MONPALMA
16	Kinetic	MEPALMIT + MONPALMA --> METHANOL + DIPALMIT
17	Kinetic	MONPALMA + METHANOL --> GLYCEROL + MEPALMIT
18	Kinetic	GLYCEROL + MEPALMIT --> METHANOL + MONPALMA
19	Kinetic	STEARIC + METHANOL --> MSTEARAT + DISTEAR
20	Kinetic	MSTEARAT + DISTEAR --> STEARIC + METHANOL
21	Kinetic	DISTEAR + METHANOL --> MSTEARAT + MONSTEAR
22	Kinetic	MSTEARAT + MONSTEAR --> DISTEAR + METHANOL
23	Kinetic	MONSTEAR + METHANOL --> GLYCEROL + MSTEARAT
24	Kinetic	GLYCEROL + MSTEARAT --> MONSTEAR + METHANOL
25	Kinetic	LINOLENI + METHANOL --> MLINOLEN + DILENIC
26	Kinetic	MLINOLEN + DILENIC --> LINOLENI + METHANOL
27	Kinetic	DILENIC + METHANOL --> MLINOLEN + MONLENIC
28	Kinetic	MLINOLEN + MONLENIC --> DILENIC + METHANOL

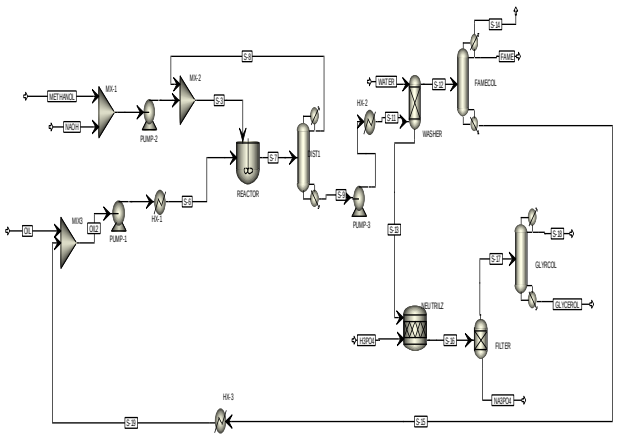


Figure. 1: Aspen Plus model of biodiesel process.

4.0 RESULTS AND DISCURSSION

In this section, results from the steady-state simulation of biodiesel production from citrullus lanatus using Aspen Plus (base on Figure 1) is presented, Stream FAME has the highest fraction of the methyl ester (i.e mixture of MSTEARAT, MEPALMIT, MELINOLE, MEOLEIC and MLINOLEN) which gives a biodiesel of 99.4 (mol%) purity.

4.1 Sensitivity Analysis

Sensitivity analysis was carried out on the developed model, to investigate the responses of some of the major components. The results obtained from the sensitivity studies carried out by finding out how the mole fractions of the components obtained from the product of the reactor responded to some input variables of the process are given in Figures 4.1 – 4.4. The input variables considered in the sensitivity analysis were the reactor temperature, Methanol:Oil ratio, catalyst concentration and resident time.

4.2 Variation of Operating Temperature of the Reactor

Figure 2 presents the responses of the mole fractions of Methyl Esters to the reactor temperature. From the Figure, it was noticed that, the mole fractions of methyl-Palmitate decreases with increase in temperature of the reactor while methyl Oleate, methyl Stearate, methyl lenoleate and methyl linolenate increases rapidly and latter decrease at 64^{o}C due to the vaporization of the methanol (at 64^{o}C).

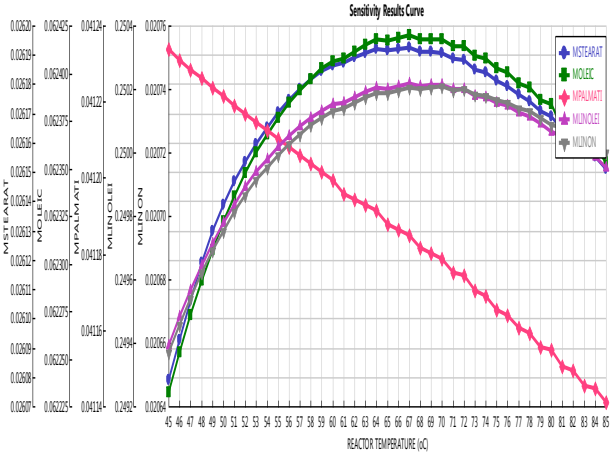


Figure. 2: Responses of the mole fractions of methyl Esters (Biodiesel) formed to reactor Temperature.

4.3 Variation of Resident time of the Reactor

The results obtained from the sensitivity analysis of the mole fractions of Methyl Esters with changes in reactor resident time is shown in Figure 3. It was observed from the results that the mole fractions of methyl- Palmitate decreases with time (which is due to the fact that backward reaction is favored in the reaction of Palmitate with methanol) while methyl Oleate, methyl Stearate, methyl lenoleate and methyl linolenate increases with increase in time.

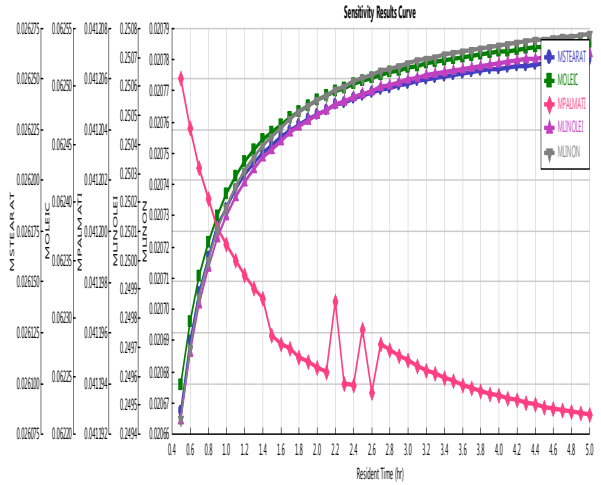


Figure 3: Responses of the mole fractions of methyl Esters (Biodiesel) formed with increase in resident time (hr).

4.4 Variation of Catalyst Concentration

Figure 4 shows the responses of the mole flow of Methyl Esters to the variation of reactor catalyst concentration. From the Figure, it was noticed that the methyl esters decreases with increase in catalyst concentration of the reactor, this is properly due to the formation of soap from part of the oil which is facilitated by the excess catalyst.

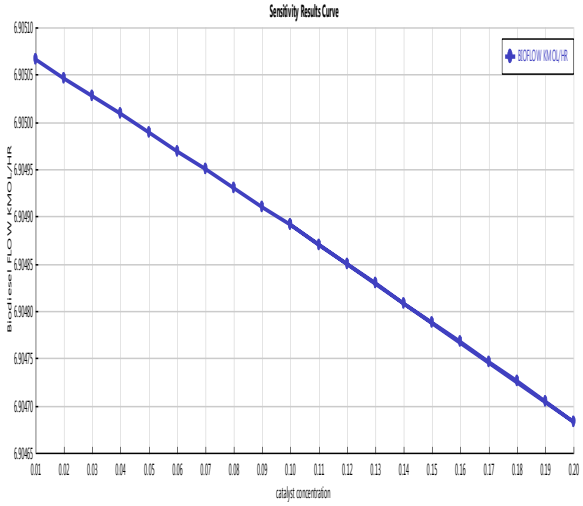


Figure. 4: Responses of the mole fractions of methyl Esters (Biodiesel) formed with increase in Catalyst concentration.

4.5 Variation of Methanol-Oil ratio

The changes that occurred in the mole flow of methyl-ester (biodiesel) as the methanol-oil ratio was varied (increased) are shown in Figure 5. From this figure it was discovered that the responses of the mole flow of methyl-ester decreases gradually as methanol-oil ratio increases from 3.8 to 11.2.

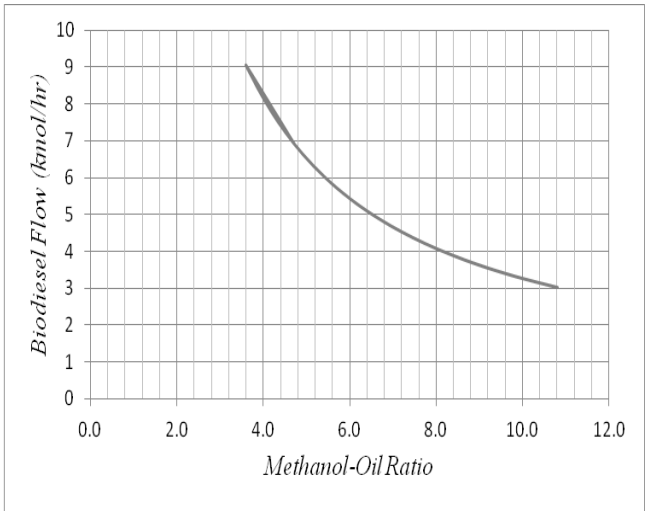


Figure 5: Responses of the mole fractions of methyl Esters (Biodiesel) formed with increase in Methanol-Oil Ratio (the horizontal axis read the moles of Oil per mole of Methanol).

To obtain the optimum input variables that will give the highest yield of methyl-ester, optimization of the process was carried. The optimum input variables obtained from the optimization carried out and those of the steady-state simulated before the optimization are given in Table 4. From the Table, it was discovered that the input values obtained from the optimization were different from those of the steady-state simulation carried out prior to the optimization except that of the resident time. Also noticed from the values of the optimum values given in

Table 4 were that the values given by the optimization are within the ranges specified for the input variables during the optimization. This was an indication that the function of the optimization tool of Aspen Plus used to obtain the optimum conditions of this process was good.

Table. 4: Steady-state and optimum parameters obtained from the process.

Parameter	Values obtained from	
	Steady state	Optimization
Biodiesel Flow (kmol/hr)	9.04	9.8
Temperature (^{o}C)	50	58
Time (min)	30	90
Methanol Oil Ratio	3	4.5
Catalyst Concentration	0.0853	0.0852

From Table 4, it was also noticed that the optimized values of some of the parameters were different from their steady-state values. Specifically, the value of the mole flow of biodiesel before optimization was actually obtained to be 9.04 kmol/hr. After the optimization, that is, with the simulation of the model carried out with the optimum input values, as can be seen from the results shown in Table 4, biodiesel flow increases to 9.8 kmol/hr.

CONLUSSION

In this work, biodiesel production process from Citrullus lanatus oil was developed and simulated using Aspen Plus software. Sensitivity analysis was carried out on the results of the simulation to investigate the response of biodiesel yield on some of the factors like; reactor temperature, resident time, methanol-oil ratio and catalyst concentration. The results of the sensitivity analysis reveal that; with increase in temperature biodiesel yield increases at first and started falling at 64.5^{o}C. An increase in resident time gives rise to increase in biodiesel yield, at 2hr 30min the increases in the yield becomes slower. Increase in catalyst concentration and methanol-oil ratio give rise to a decrease in biodiesel yield. Furthermore, the sensitivity analysis of the process carried out pointed out that optimization was necessary to obtain the operating variables that would yield maximum biodiesel flow and the result of the optimization gave a value of 9.8 kmol/hr as the mole flow of biodiesel produced when the reactor temperature, the reactor resident time, the catalyst concentration and methanol-oil ratio were approximately 58^{o}C, 90 min, 0.085254544 and 4.5, respectively. The result of this work defines a strategy for industrial biodiesel production planning.

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