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DEPLOYING MATHEMATICAL MODELS FOR MONITORING THE QUALITY OF BIODIESEL PRODUCTS IN BIODIESEL PROCESSING PLANTS

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Abstract

This research was carried out to produce biodiesel from waste vegetable oil using homogenous and heterogeneous catalysis and hence obtain a good basis for effective comparison of the two processes. The percentage conversion of the waste vegetable oil to biodiesel and its fatty acid methyl ester (FAME) content were determined using established correlations. Potassium hydroxide (KOH) and calcium oxide (CaO) were respectively used for the homogenous and heterogeneous catalysis. From the results obtained, the highest conversion obtained from the homogeneous catalysis was 85.63% while 88.51% conversion was obtained from the heterogeneous process. FAME contents of the biodiesel produced from the homogenous and heterogeneous process was 89% while the yield from the heterogeneous process was 75.1%. The average densities were 0.874g/mL and 0.892 g/mL of biodiesel produced using homogenous and heterogeneous catalysis respectively. The average viscosity was 4.59 cSt at 65° C at 150 minutes reaction time for biodiesel produced using the heterogeneous process.

Keywords: Biodiesel; quality; monitoring; models; processing.

1. Introduction

Biodiesel is one of the many energy alternatives that can help in reducing the over dependence on fuels from fossil origin ^[1-3]. It is derived from renewable sources such as vegetable oil or animal fats which can complement the conventional petroleum diesel fuel ^[1]. The increasing use of fossil fuels has caused several social and environmental challenges over the years such as high levels of land, air and water pollutions, global warming through the release of greenhouse gases (GHG) (CO₂, CH₄), coupled with increasing cost of production leading to high energy and transportation costs ^[4]. In comparison to fossil fuel, greenhouse gases emissions are reduced by about 41% during production and combustion of biodiesel ^{[5],} e.g. B20 reduces CO₂ by 15%. Thus, biodiesel is increasingly becoming the most attractive alternative energy source to petroleum diesel ^[2, 6-7]. It can be produced based on need with less pollution problems ^[8].

Generally, though, biofuels only offer a partial solution to many of the problems associated with fossil fuel usage. Hence there is the need to encourage more stakeholders' involvement in the full development of biodiesel production in order to mitigate the associated problems with fossil fuel usage. At the moment, there are a few hundreds of persons, industries, and agencies that are into biodiesel production using diverse processes such as homogeneous alkali-catalysed trans-esterification, acid esterification followed by base catalysed trans-esterification of vegetable oils or animal fats, heterogeneous catalysis (solid acid catalyst) or enzymatic process ^[9-16]. Biodiesel is the end product of all these processes.

The major reaction taking place is that between the vegetable oil and alcohol in the presence of a catalyst to form esters and glycerol ^[17]. Thus, the quality of biodiesel obtained from these varied processes is expected to vary considerably. Amongst the factors affecting biodiesel quality are, fatty acid content ^[6], the processing methods, conditions of processing (temperature, catalyst type, and dosage, agitation speed and time), water content, the type and quality of raw materials ^[9, 18]. Any change in the feed source especially that of vegetable oils, the composition of the biodiesel and consequently the properties of the biodiesel also change ^[9]. ASTM D6751 and EN 14214 are two specification types for standardizing the properties of biodiesel products and some of these properties include: viscosity, cold flow, flash point, cetane number, oxidative stability, iodine value, density, acid value, Free and total glycerol, Na, K, Mg, Ca, P, S, water and sediment, sulphated ash, carbon residue ^[2, 19].

More often than not, monitoring, testing and setting biodiesel standards require very sophisticated machines such as the nuclear magnetic resonance (NMR) spectrometer, high performance liquid chromatograph (HPLC), gas chromatograph-mass spectrometer, flame ionization detector (FID) or electron capture detector (ECD), Fourier Transform Infrared Spectrometer (FTIR) and a host of others, which are cost prohibitive and inaccessible to most biodiesel producers in developing countries. Mostly affected are the rural farmers who cannot afford this very expensive analytical equipment. It has been shown that when biodiesel is well processed, its quality and efficiency become more significantly better than petro diesel ^[9].

For predicting the properties of biodiesel, various models have been developed using various feed oils and their blends to determine the quality of biodiesel ^[9, 20]. Each model is used for the prediction of a given property of the biodiesel ^[10]. Literature reveals that there is a great volume of work done in the process design and manufacturing of biodiesel from various vegetable oils and a few prediction models for the very important properties of biodiesel ^[10]. The acid value (AV) is one of the analytical parameters usually employed to evaluate the quality of biodiesel ^[21]. Quality control of biodiesel fuel based on an acid value is very important in the determination of the rate and extent of conversion of the vegetable oil or fat to biodiesel.

Biodiesel is essentially composed of fatty acid methyl (or ethyl) ester (FAME or FAEE) depending on the alcohol (methanol or ethanol) used during the trans-esterification process and varying amounts of fatty acids. The fatty acid content is usually quantified or quoted as an acid number ^[22]. The acid-number limit for biodiesel, ASTM D 6751, has been set at 0.5. As the acid value (AV) of the biodiesel/oil system decreases, the percentage conversion of the oil to biodiesel increases. It is advantageous to have an acid value that is as low as possible signifying a high level of conversion of the triglycerides to biodiesel. The acid number of biodiesel fuel is measured according to JIS, ASTM D 664 or ISO standards either by potentiometric or volumetric titration [21-22]. Regulating bodies have established specifications for AV obtained from biodiesel analyses so as to set the quality of biodiesel obtained from the numerous production techniques used by biodiesel producers ^[21, 23]. The high acid value is an indication of the presence of unreacted vegetable oil in the biodiesel product which invariably affects the overall quality or properties (viscosity, cetane number, cold flow, pour point, flash point, density, etc.) of the biodiesel. Thus, with a single quality parameter (acid value), the percentage conversion of vegetable oil to biodiesel can be estimated using proven mathematical models. Consequently, during in-process checks in biodiesel processing plants, progressive monitoring of the acid number of biodiesel will give an indication of the level of completeness or extent of the trans-esterification reaction. This approach can then be popularized and used by many biodiesel producers especially with the rural populace who cannot afford the expensive and most times sophisticated biodiesel testing machines. In this study, the acid values of biodiesel formed were monitored against the reaction time and the values obtained were used to calculate the corresponding percentage conversion of waste frying oil (WFO) using Wang's correlation ^[24] and Fame content using Felizardo's correlation ^[25]. Both the homogenous and heterogeneous catalytic processes were employed at different reaction temperatures and times.

2. Materials and method

2.1. Materials

The waste frying oil used in this study was sourced from the Covenant University cafeteria, Ota, Nigeria. Reagents such as methanol (technical grade), potassium hydroxide pellets (85.0 % minimum assay, Qualikems), anhydrous calcium oxide (Sigma-Aldrich, >99.99% purity), were obtained from authorized manufacturers. Hot plate magnetic stirrer (JENWAY 1000 ST15 OSA, UK), weighing balance (Scout Pro SPU2001, China), Petroleum products kinematic viscosity tester (SYD-265D-1), stopwatch (Samsung tab clock), Mercury-in-glass 0-360° thermometer (UNISCOPE), reflux condenser. All glassware was J-SIL Borosilicate glass.

2.2. Experimental procedures

2.2.1. Pre-treatment of waste frying oil

1 litre of the waste frying oil (WFO), was filtered using sieve cloth to remove bits of food residues and 500 mL of it was then heated at 115° C to a constant weight to remove its water/moisture content.

2.2.2. Catalyst preparation (homogenous catalyst)

Potassium hydroxide pellets (1.1g of 0.8 w/w of WFO) were placed in a conical flask containing 144.4g of methanol. The conical flask was stoppered and agitated to ensure complete dissolution of the pellets in the methanol.

2.2.3. Trans-esterification of oil using a homogenous catalyst

The method earlier described ^[26-27] was used for the trans-esterification reaction in this study. In doing this, a fixed amount of freshly prepared and well stirred KOH-methanol mixture was first added into the reactor (3-necked flat-bottom flask) equipped with a reflux condenser, a quick fit thermometer and a port for charging of the feed and then preheated to 40° C. The measured pre-treated WFO which was also pre-heated to the same temperature in a beaker on a hot plate was then carefully charged into the reactor under constant agitation and heating until the reaction temperature was achieved. The time of reaction started when the reaction reached the required temperature (40, 50, 55, 60, 65° C). The reaction was stopped after the present reaction times of between 30 to 150 minutes were respectively achieved.

2.2.4. Transesterification of oil using a heterogeneous catalyst

The same experimental set up as in section 2.2.3 was used. Except that instead of KOH - ethanol mixture, a fixed amount of freshly prepared well stirred CaO-methanol mixture was used at a ratio of 9:1 methanol to oil. The best reaction temperature obtained from the homogeneous process (60° C) was used here but at a varied reaction time of between 30 and 150 minutes.

2.2.5. Separation of biodiesel and glycerol phases

The products of reaction from the above sections were transferred to a separating funnel and allowed to settle for between 6 to 12 h to give two distinct phases of biodiesel on top and glycerol or aqueous phase at the bottom. The glycerol was then carefully drained out into a container while the biodiesel was left in the separating funnel for the washing stage.

2.2.6. Biodiesel washing and drying

The biodiesel phase obtained was then washed with warm deionized water several times until the washing water became very clear. Water was then drained out from the separating funnel while the washed biodiesel was drained into a beaker for drying. The washed biodiesel was dried by heating to 115° C until a constant weight was obtained.

2.2.7. Determination of acid value of biodiesel

Methanol was neutralized with 0.1N NaOH using phenolphthalein as indicator. Ten (10) g of the biodiesel was weighed into a beaker. Then 50 ml each of benzene and the neutral alcohol were poured into the beaker containing the biodiesel sample. The mixture was stirred vigorously to ensure proper mixing and was then titrated with 0.1M KOH which was previously prepared using 3-4 drops of phenolphthalein indicator until a colour change (pink) was persistently observed for 15 s. The steps were repeated, and the average values were calculated. The acid value was calculated using equation 1 shown below;

$$Acid value = \frac{Q \times 56.1 \times M}{W}$$
(1)

where: W = weight of sample; M = strength of KOH; Q = average titre value.

2.2.8. Determination of percentage conversion of WFO to biodiesel

The determination of the percentage conversion of WFO to biodiesel was based on Yong's correlation ^[24] as given in equation 2:

% conversion = $\left(1 - \frac{AV_{biodiesel}}{AV_{WFO}}\right) \times 100\%$

(2)

where: AV_{WFO} is acid the value of the waste frying oil (WFO); $AV_{biodiesel}$ is acid value of the biodiesel.

2.2.9. Specific gravity/density

A dry cleaned empty 50 ml density bottle was weighed and the mass recorded as M, it was then filled up with distilled water and subsequently with the sample with their weights taken as M_1 and M_2 respectively. The densities of the distilled water and biodiesel were then calculated from equation 2. Hence, the specific gravity was evaluated as shown below:

 $Density(g/cm^3) = \frac{weight of (density bottle and content) - weight of empty bottle}{weiht of equal volume}$ (3)

2.2.10. Cloud and pour points

A sample of the biodiesel was placed in a test jar to a mark and then placed inside a cooling bath. The temperature at the bottom of the test jar which is the temperature at which the biodiesel starts to form cloud was taken as the cloud point while the lowest temperature at which the fuel continues to flow was recorded as the pour point.

2.2.11. Kinematic viscosity

A viscometer was inserted into a water bath with a set temperature and left for 30 min. The sample was added to the viscometer and allowed to remain in the bath to equilibrate or attain the test temperature. The sample was then allowed to flow freely and the time required for the lower meniscus of the biodiesel sample to pass from the first to the second mark was taken using a stop watch. The procedure was repeated a number of times and the average time values were recorded. The kinematic viscosity of each sample was then calculated from equation 4.

Kinematic viscosity = $t \times K$

where K is 0.4959, the viscometer calibration factor.

2.2.12. Estimation of the FAME content of biodiesel

The Felizardo's correlation ^[25] (equation 4) was used to estimate the percentage FAME content of the biodiesel samples produced.

 $FAME\% = -45.055 \ln \mu + 162.85$

where μ is the viscosity of the biodiesel sample produced ^[25].

(4)

3. Results and discussion

3.1. Effect of variation in temperature and time on yield for biodiesel produced using homogenous and heterogeneous catalysis

From Table 1, the free fatty acid content of the WFO gave 1.74%. The value was far less than 5% and hence the choice of a single step trans-esterification process using KOH as the catalyst.

Table 1. Physiochemical prop	perties of waste frying	oil used for the	production of biodiesel
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Property	Value	Property	Value
Colour	Dark brown	Molecular weight of FA(g/mol)	263.92
Density (g/cm ³)	0.91	Pour point (⁰ c)	-3
Specific gravity	0.911	Cloud point(⁰ c)	20
FFA value (%)	1.74	Acid value (mg KOH/g)	3.48
Saponification value	148.7	Kinematic viscosity (cSt) at 40°c	54

The research was designed so as to compare the extent of conversion of WFO to bio-diesel between two catalytic processes - heterogeneous and homogenous catalysis. Potassium hydroxide was used as the homogeneous catalyst while CaO was used as the heterogeneous catalyst. From Table 2, varied reaction temperatures and times were investigated principally to decide the overall best optimal reaction conditions in the trans-esterification of WFO to its corresponding biodiesel using the homogeneous catalytic process. The highest yield of 89% was obtained at 60°C. Hence it was this condition that was imposed on the heterogeneous trans-esterification of the WFO to its bio-diesel, (see Table 3).

Sample	Temp. (°C)	Time of reaction (min)	Yield (%)	Conver- sion (%)	Density (g/cm ³)	FAME	Pour point (°C)	Cloud point (°C)
A1		30	78.87	24.14	0.878	74.73	2	11
A2		60	79.9	37.07	0.878	75.63	3	11
A3	40	90	83.5	50.00	0.876	77.35	3 3 3	12
A4		120	82.6	66.09	0.872	78.31	3	12
A5		150	83	74.14	0.870	78.93	5	12
B1		30	71.1	31.90	0.882	76.42	3	11
B2		60	77.5	45.11	0.882	76.88	5	11
B3	50	90	79.1	56.61	0.874	78.45	5	12
B4		120	76.6	67.82	0.880	80.43	5	12
B5		150	75.9	79.02	0.884	81.08	5	12
C1		30	72	40.23	0.872	84.51	3	11
C2		60	78.5	54.89	0.878	85.96	4	12
C3	55	90	85.2	74.14	0.882	78.45	4	13
C4		120	82.8	77.30	0.882	80.43	4	13
C5		150	83.7	83.91	0.884	81.08	5	13
D1		30	72.6	53.16	0.876	85.96	1	11
D2		60	76.1	72.70	0.878	86.70	2	12
D3	60	90	89	77.30	0.878	87.20	3	12
D4		120	87.5	80.75	0.882	90.70	3	13
D5		150	88.1	83.91	0.884	92.84	4	13
E1		30	70.9	67.82	0.864	87.54	1	11
E2		60	74.00	75.86	0.868	89.36	2	11
E3	65	90	76.50	80.75	0.870	91.90	4	12
E4		120	75.20	83.91	0.876	93.03	4	12
E5		150	75.70	85.63	0.884	94.19	5	13

Table 2. Results for biodiesel produced using a homogenous catalyst

S/N	Temp. (°C)	Time of reaction (min)	Yield (%)	Conversion (%)	Density (g/cm ³)	FAME	Pour point (°C)	Cloud point (°C)
F1		30	67.6	69.25	0.9	85.07	2	11
F2		60	67.9	77.30	0.900	89.09	2	11
F3	60	90	69.2	87.07	0.902	91.16	2	11
F4		120	71.3	88.51	0.900	94.39	2	12
F5		150	75.1	77.30	0.882	97.87	3	12

Table 3. Results for biodiesel produced using a heterogeneous catalyst

From Table 2, the trend shows an appreciable rise in biodiesel yield from between 30 and 100 minutes getting to their maxima in about 90 minutes before they began to decline after that. The drop in yield after 90 minutes could be adduced to possible soap formation and backward reaction that may have been triggered after the residence time was exceeded ^[28]. It was observed that there was no well-defined trend of yield versus temperature. The highest yields were obtained at 60° C this agrees with a similar study done by Mathiyazhagan *et al.* ^[29] while the lowest yields were obtained at 65°C (the boiling point of methanol). The low yield at this temperature may be attributed to the continuous evaporation and condensation of methanol in the reaction medium leading to (i) equilibrium shift to the left (ii) imbalance in the methanol-oil molar ratio (iii) reduced contact time between the methanol and oil. It is this cumulative effect that gave rise to the reduced yield in biodiesel. In comparison (Table 2), the homogeneous catalysis produced the highest biodiesel yield (89.5%) in 90 minutes than the heterogeneous catalysis (75% in 150 minutes) at the same temperature (60° C) as shown in Table 3. The trend for biodiesel produced using heterogeneous catalyst agrees with the work of Bourney *et al.* ^[30].

3.2. Effect of variation in temperature and time on the physico-chemical properties of biodiesel produced using homogenous and heterogeneous catalysis

3.2.1. Density

Table 2 and 3 shows the densities obtained at 60° C in response to temperature and time variations for both homogeneous and heterogeneous catalysis. The densities obtained from the heterogeneous catalysis were generally higher and remained practically the same at an average value of 0.90g/ml between 30 and 120 minutes but with a sharp fall to 0.882g/ml. While for homogeneous catalysis the densities rose steadily from 0.876 to 0.882 g/ml within the reaction time of 30 to 150 minutes. From Table 2 and 3, it was observed that temperature variations had only a little or no effect on densities of biodiesel produced. However, the densities of all of the biodiesel produced fell within EN 14214 standards (0.86-0.90) g/cm³.

3.2.2. Viscosity

From Figure 1, it was observed that as reaction temperature and time increased there was the corresponding drop in the viscosity values of the biodiesel obtained. The results correspond to the work reported by Demirbas ^[3]. At 40° C, when compared with the kinematic viscosity (54cSt) of the waste frying oil, there was a significant drop in kinematic viscosity of the biodiesel obtained from the homogeneous catalysis within the reaction time considered. This may be attributed to the fact that the fatty acid bonds in the triglyceride structure have been broken and reacted with the methoxide to produce three moles of biodiesel. It is the formation of the biodiesel that leads to the viscosity drop as shown in Figure 1. Viscosity is a very important parameter in the production of fuels because it determines the burning efficiency, lubricity, and atomization of the fuel. From Figure 1, the viscosity (4.502) of biodiesel produced in 150 minutes and at 65° C gave the best. It falls within ASTM D6751 standards (1.9-6.0) cSt and EN 14214 standards (3.5-5.0) cSt. From Figure 2, it was observed that biodiesel produced with heterogeneous catalyst (CaO) at 60° C was less viscous (4.23cSt) than the viscosity (4.55cSt) biodiesel produced using a homogenous catalyst (KOH) at the same temperature.

Both viscosities, however, falls within ASTM D6751 standards (1.9-6.0) cSt and EN 14214 standards (3.5-5.0) cSt.

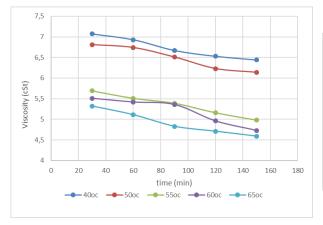


Figure 1. Variation in temperature and time on the density of biodiesel produced using a homogenous catalyst

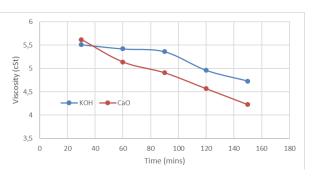


Figure 2. Variation in time on the viscosity of biodiesel produced using homogenous catalyst and heterogeneous catalyst at 60°C

3.2.3. The effect of reaction time and temperature on the acid value of biodiesel

Table 4 respectively describe the effect of reaction time and temperature on the acid values of biodiesel. From Table 4, the effect of temperature was most vividly portrayed at different times horizontally across the table. As the temperature increased from 40 to 65° C while holding each time constant, the acid values reduced. This may be due to the fact that the rate of reaction generally increases as reaction temperature increases. This agreed with the work of other researchers ^[29, 31].

Table 4. The effect of temperature and time on the acid value of bio-diesel using homogenous and heterogeneous catalysts

Time (min)		Heterogeneous catalysis				
	40°C	50°C	55°C	60°C	65°C	60°C
		Acid value				
30	2.64	2.37	2.08	1.63	1.12	1.07
60	2.19	1.91	1.57	0.95	0.84	0.79
90	1.74	1.51	0.90	0.79	0.67	0.45
120	1.18	1.12	0.79	0.67	0.56	0.40
150	0.90	0.73	0.56	0.56	0.50	0.40

Increased reaction rate means conversion of more of the oil into biodiesel and ultimate reduction in its acid number. The effect of reaction time (30 to 150 minutes) on the acid number of biodiesel followed the same decreasing trend for all the trans-esterification reactions at a constant temperature. All the acid numbers tended to lower values at higher reaction time. It was observed from Table 4, that lower acid values and hence higher conversions were obtained using heterogeneous catalysis than homogeneous catalysis at 60° C.

The acid values of biodiesel produced at 40° c and 50° c within the reaction time of 30 - 150 minutes did not meet the acceptable standard of ASTM D6751 (<0.8) while the acid values of biodiesel produced at 60° C and 65° C within 90 to 120 minutes met the acceptable standard of ASTM D6751. Also, the acid values of biodiesel produced from the heterogeneous catalysis using calcium oxide at 60° C and between 60 - 150 minutes fell within an acceptable standard of ASTM D6751.

3.2.4. Effect of variation in temperature and time on conversion of biodiesel produced using a homogenous catalyst

The conversion was calculated by determining the amount of fatty acid that was converted and comparing it to the amount of fatty acid initially present in the waste frying oil that was used. The acid values of the biodiesel obtained were calculated using equation 1. From Table 4 it was observed that the acid value of biodiesel was inversely proportional to its percentage conversion (see Tables 3 and 4). With increasing reaction time, all acid values (Table 4) of the biodiesel assumed decreasing trends while the percentage conversion of the corresponding biodiesel assumed increasing trends (Table 2 and 3). The lower the acid values of the biodiesel produced the higher is its corresponding percentage conversion. This observation corresponds to the work of of Pinto et al. ^[32]. From Table 2 and 3, it was observed that conversion of oil to biodiesel using the heterogeneous catalysis (CaO) was higher than that of the homogeneous catalysis (KOH) at 60° C and within the reaction time of 30 – 120 minutes. This finding agrees with the work of other researchers ^[33]. From Table 5 the qualities of two of the best biodiesel samples E5 and F5 are compared. They had 85.63 and 88.5% percentage conversions respectively. On comparing E5 and F5 with biodiesel standards of ASTM D6751 and EN 14214, the conformity level of the various parameters was high to pass for biodiesel. The relatively low % conversion (85.63% for E5 and 88.5% for F5) only indicates that there is room for improvement and optimization of the biodiesel batch processes used for the trans-esterification reactions. The attention and target would be at obtaining greater than 95% oils conversion to their corresponding biodiesel, which should automatically translate to better and improved biodiesel properties.

Properties	Petro-diesel ASTM D0975	Biodiesel ASTM D6751	Biodiesel EN 14214	Biodiesel Sample E5	Biodiesel Sample F5
Density at 30°C (g/cm ³)	0.876	0.875-0.90	0.86-0.90	0.884	0.9
Viscosity at 40°C (cSt)	1.9-4.1	1.9-6.0	3.5-5.0	4.59	4.57
Pour point °C	-35 to -15	-15 to 16	-	5	3
Cloud point °C	-15 to 5	-3 to 12	-	13	12
Acid value (mg KOH/g)	0.35	<0.8	<0.5	0.5	0.4
FAME content (%)	-	-	-	94.19	97.87
Conversion (%)	-	-	-	85.63	88.51

 Table 5. Comparison of biodiesel samples with biodiesel standards

3.2.5. Effect of variation in temperature and time on FAME content of biodiesel produced using a homogenous catalyst

From Table 2 and 3, it was observed that the FAME contents represented by the different curves assumed increasing trend with increasing reaction time and temperature. The effect of time and temperature were more pronounced at increasing time and temperature. The set of values represent the two lowest temperatures of 40 and 50° C (after about 150 minutes of reaction) gave 79 and 81% FAME contents respectively. The implication of this is that the impurity level or unconverted WFO is still very high and may thus not be suited for use as biodiesel. At the same reaction time of 150 minutes, the FAME contents obtained at 55, 60 and 65°C were 90.3, 93 and 94.2% respectively. Table 2 and 3 helps us to compare the FAME contents of biodiesel obtained from heterogeneous and homogeneous catalysis at 60° C. From the reaction time of 40 to 150 minutes, the percentage FAME contents of biodiesel samples obtained from the corresponding biodiesel samples obtained from the homogeneous catalysis under the same set of temperature and time. At 60, 90, 120 and 150 minutes, the percentage FAME contents of provide the same set of temperature and time. At 60, 90, 120 and 150 minutes, the percentage FAME contents of provide the same set of temperature and time.

samples obtained from heterogeneous catalysis while they were 86.6, 87.3, 91 and 93% respectively for biodiesel samples obtained from homogenous catalysis.

4. Conclusion

The study of the production of biodiesel using homogeneous and heterogeneous catalysis at varied temperature and time revealed that:

- Temperature and time were two critical factors to obtaining good quality biodiesel.
- Higher percentage conversions of WFO to biodiesel were obtained at higher temperatures of 55, 60 and 65°C than at 40 and 50° C.
- At 60° C, heterogeneous performed better than homogeneous catalysis in the conversion of WFO to biodiesel. The percentage conversion and FAME content of biodiesel from the heterogeneous catalysis were higher than that of heterogeneous catalysis.
- Quality of biodiesel may be determined per time by monitoring the change in acid value as the trans-esterification reaction progresses.
- The acid value of biodiesel is inversely proportional to the % conversion of oils to biodiesel. The lower the acid value of biodiesel sample the higher is its % conversion.
- Well formulated mathematical models that relate acid value or number to oil conversion to biodiesel can be deployed to monitoring and obtaining the progress of trans-esterification reactions. At higher % conversion, conformity of the quality of the biodiesel products is assured.

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References

- [1] Kumar V, and Kumar J. Kinetics of Jatropha Curcas transesterification in batch reactor. in Proceedings of the World Congress on Engineering and Computer Science. WCECS 2008, October 22 24, 2008, San Francisco, USA, ISBN: 978-988-98671-0-2.
- [2] Saini RD. Conversion of Waste Cooking Oil to Biodiesel. International Journal of Petroleum Science and Technology, 2017. 11(1): 9-21.
- [3] Demirbas A. Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. Energy Conversion and Management, 2009. 50(4): 923-927.
- [4] Dahunsi SO, Oranusi S, and Efeovbokhan VE. Cleaner energy for cleaner production: Modeling and optimization of biogas generation from Carica papayas (Pawpaw) fruit peels. Journal of cleaner production, 2017; 156: 19-29.
- [5] Hill J, Nelson E, Tilman D, Polasky S, Tiffany D. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. in Proceedings of the National Academy of Science of the United States of America (PNAS), 2006; 103(30): 11206-11210.
- [6] Lamaisri C, Punsuvon V, Champrame S, Liangsakul P. Relationship between fatty acid composition and biodiesel quality for nine commercial palm oils. Songklanakarin Journal of Science & Technology, 2015. 37(4) 389-395.
- [7] Ved K, and Padam K. Study of physical and chemical properties of biodiesel from sorghum oil. Research Journal of Chemical Sciences, 2013; 3(9): p. 64-68.
- [8] Tschakert P, Huber-Sannwald E, Ojima DS, Raupmn MR. Holistic, adaptive management of the terrestrial carbon cycle at local and regional scales, in Glob. Environ. Change., 2008; 18(1):128-141.
- [9] Saxena P, Jawale S, and Joshipura MH. A review on prediction of properties of biodiesel and blends of biodiesel. Procedia Engineering, 2013; 51: 395-402.
- [10] Puspa Asri N, Budikarjono K, and Roesyadi A. Kinetics of Palm Oil Transesterification Using Double Promoted Catalyst CaO/KI/γ-Al₂O₃. Journal of Engineering & Technological Sciences, 2015; 47(4): 353-363.
- [11] Borges M, and Díaz L. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: a review. Renewable and Sustainable Energy Reviews, 2012; 16(5): 2839-2849.
- [12] Chouhan AS, and Sarma A. Modern heterogeneous catalysts for biodiesel production: A comprehensive review. Renewable and Sustainable Energy Reviews, 2011; 15(9): 4378-4399.

- [13] Ramírez-Ortiz J, Medina-Valtierra J, and Rosales MM. Used frying oil for biodiesel production over kaolinite as catalyst. Engineering and Technology, 2011; 80: 977-980.
- [14] Lam MK, Lee KT, and Mohamed AR. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. Biotechnology advances, 2010; 28(4): 500-518.
- [15] Ghaly AE, Dave D, Books MS, Budge S. Production of biodiesel by enzymatic transesterification. Am J Biochem Biotechnol, 2010; 6(2): 54-76.
- [16] Chai F, Cao F, Zhai F, Chen Y, Wang X, Su Zh. Transesterification of vegetable oil to biodiesel using a heteropolyacid solid catalyst. Advanced Synthesis & Catalysis, 2007; 349(7): 1057-1065.
- [17] Okullo A, Temu A, and Ntalikwa J. Transesterification Reaction Kinetics of Jatropha Oil for Biodiesel Production. in Second International Conference on Advances in Engineering and Technology. 2011: 221-227.
- [18] Corral Bobadilla M, Lorza RL, Garcia RE, Gomez FS, González EPV. An Improvement in Biodiesel Production from Waste Cooking Oil by Applying Thought Multi-Response Surface Methodology Using Desirability Functions. Energies, 2017; 10(1): 130.
- [19] Knothe G. "Designer" biodiesel: optimizing fatty ester composition to improve fuel properties. Energy & Fuels, 2008; 22(2): 1358-1364.
- [20] Ruiz-Méndez M, Marmasat S, Liotta S, Doberganes MC. Analysis of used frying fats for biodiesel production. Grasas y aceites, 2008. 59(1): 45-50.
- [21] Gonzaga FB, and Sobral SP. A new method for determining the acid number of biodiesel based on coulometric titration. Talanta, 2012; 97: 199-203.
- [22] Mahajan S, and Konar SK. Determining the acid number of biodiesel. Journal of the American Oil Chemists' Society, 2006; 83(6): 567-570.
- [23] Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. 2012: ASTM International.
- [24] Wang Y, Zhao M, Ma S, Kuang L, Han X, Tang S. Preparation of biodiesel from waste cooking oil via two-step catalyzed process. Energy conversion and management, 2007; 48(1): 184-188.
- [25] Felizardo P, Correia MJ, Raposo I, Mendes JF, Berkemeier R, Bordado JM. Production of biodiesel from waste frying oils. Waste management, 2006; 26(5): 487-494.
- [26] Efeovbokhan VE, Ayoola A, Anawe PAL, Oteri O. The effects of trans-esterification of castor seed oil using ethanol, methanol and their blends on the properties and yields of biodiesel. International Journal of Engineering and Technology, 2012; 2(10): 1734-1742.
- [27] Enontiemonria EV, Abiodun OJ, and Eric KE. Extraction and Use of Potassium Hydroxide from Ripe Plantain Peels Ash for Biodiesel Production. Journal of Biobased Materials and Bioenergy, 2016; 10(1): 1-9.
- [28] Anitha A, and Dawn S. Performance characteristics of biodiesel produced from waste groundnut oil using supported heteropolyacids. International journal of chemical engineering and applications, 2010; 1(3): 261.
- [29] Mathiyazhagan M, Ganapathi A, Jaganath B, Benganayaki N, Sasireka N. Production of biodiesel from non-edible plant oils having high FFA content. International Journal of Chemical and Environmental Engineering, 2011; 2(2) 119-122.
- [30] Bournay L, Casanave D, Delfort B, Hillio G. New heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerin produced by biodiesel plants. Catalysis Today, 2005; 106(1-4): 190-192.
- [31] Jagadale S, and Jugulkar L. Review of various reaction parameters and other factors affecting on production of chicken fat based biodiesel. International Journal of Modern Engineering Research, 2012; 2(2): 407-411.
- [32] Pinto AC, Guarieiro LLN, Rezende MJC, Ribeiro NM, Torres EA, Lopes WA, Pereira PAP, de Andrade JB. Biodiesel: an overview. Journal of the Brazilian Chemical Society, 2005; 16(6B): 1313-1330.
- [33] Kim H.-J, Kang BS, Kim MJ, Park YM, Kim DK, Lee JS, Lee KY. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. Catalysis Today, 2004; 93: 315-320.

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