Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 57(4) 336-345, 2015

BIODIESEL PRODUCTION FROM HIGH ACID WASTE VEGETABLE OIL USING HOMOGENEOUS CATALYST

A. P. Tchameni, Lin Zhao*, R. D. Nagre, Ma Chao

College of Petroleum Engineering, Yangtze University, Wuhan, 430100,China
**Corresponding author's Email address: linzhao2000@126.com*

Received April 21, 2015; Corrected June 28, 2015, Accepted June 29, 2015

Abstract

Biodiesel is an environmental-friendly petroleum product currently being adopted by Oil and Gas companies in the formulation of drilling fluids. Its production cost is mostly related to the price of its raw materials. This work investigated suitable methods of biodiesel production from cheap high acid value feedstock oil (AV: 83.07mgKOH/g) using three steps. First, acid esterification at the optimum condition of: 35vol% (ethanol to oil ratio) 1.1vol%(HCl to oil ratio) at 65°C for 5 hours which reduced the acid value to 3.36 mgKOH/g of esterified oil, followed by ethanolic de-acidification**.** using 60% of the mass of the esterified oil as the volume of the base (0.1NKOH) needed plus 5% alkali excess at 50°C for 10min. the acid value was reduced to 0.56 mg KOH/g de-acidified oil. Lastly, transesterification at the optimum condition of: 35wt% ethanol, 1.5wt% KOH at 70°C after 6 hours. The biodiesel yield obtained was 91.25%. The biodiesel was characterized by determining some of its basic physico-chemicals properties. The flash point was measured as 185°C, its specific gravity was 0.86, the acid value and viscosity were 0.44 mgKOH/ g oil and 4 centipoises respectively.

Keywords: Waste vegetable oil; Esterification; Ethanolic de-acidification; Transesterification; Biodiesel.

1. Introduction

In early 1990s, people became conscious of the problems related to the use of diesel oil based drilling mud. Although it provides good lubrication and wellbore stability, minimises formation damage and risk of differential sticking in addition to high temperature stability and faster rate of penetration. It causes environmental hazards by disposal of oil-contaminated drill cutting produced from the drill well [1].

For this purpose, governments and Environmental Protection Agency (EPA) have imposed tighter regulations to ensure the use of environmental-friendly drilling mud [2-3]. Consequently, researchers in the field and Oilfield companies have over the past few decades tasked with the challenge to develop oil based drilling mud, base on additives which are less detrimental to effect the environment and the ozone layer. To overcome the hazardous effect of diesel fluid and others mineral oils and vegetable oils have been used in the drilling mud formulations. However, in recent years, biodiesel production from the vegetable oil has become vogue [4-5].

Biodiesel has been found to exhibit comparable properties to petroleum fuels with additional advantages such as being derived from a renewable source, non-toxic and biodegradable [6]. Biodiesel has more favorable combustion emission profile, such as low emissions of carbon monoxide since carbon dioxide as its main combustion product can be recycled by photosynthesis, thus minimizing the impact of its combustion on the greenhouse effect, reflecting its environmentally friendly features. Biodiesel also has a relatively high flash point and exhibits good lubricating properties [7].

Biodiesel is derived from vegetable oil or animal fats and consists of long chain alkyl (methyl, ethyl, or propyl) esters. Triglycerides or triacylglycerols are the main components of fats and oils, and can be defined as a hydrophobic ester of glycerol reacting with fatty acid. They are relatively viscous and less denser than the water at room temperature. Many researchers have developed methods to increase the density or reduce the viscosity of triacylglycerols through emulsification, pyrolysis, transesterification and leaning. The common method used for this purpose is the transesterification.

Transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol in the presence of catalyst(base) to form esters and glycerol [8]. Preferably, short chain alcohol are used such as methanol and ethanol to form respectively Fatty Acid Methyl Esters (FAMEs) or Fatty Acid Methyl Esters *(FAEEs)* [9].

Currently, biodiesel consumption is increasingly becoming more attractive worldwide, although the main challenge is related to the cost of raw materials. Indeed, it has been reported that slightly 60-95% of the total cost of the biodiesel production arises from the initial cost of the raw materials [10].

To address the issue of cost of biodiesel, low-priced feedstock oils (non-edible oil) in some cases with high acid value such as waste vegetable oil, tung oil, *Jatropha curcas L*., and acidified oil are used to produce biodiesel instead of used edible palm, soybean or rapeseed oils which are more expensive and rather available for human consumption. The acidity of the waste vegetable oil is attributed to the hydrolysis of the triglyceride to diglyceride/monoglyceride/ glycerol and free fatty acids while frying process at high temperature.

For the transesterification process, FFAs should be first removed otherwise they will de-activate the base-catalyst by reacting with the base to form soaps (saponification reaction). Thus, decreasing the yield of the biodiesel production, rendering the process unprofitable [11]. Feedstock with acid value greater than 2 mg KOH/g oil are not recommended for the base catalyzed transesterification. Esterification should first be carried out to reduce the FFAs content by converting the acid content to esters prior to transesterification reaction.

Ghadge *et al.* [12] in their work observed that after the initial esterification of the mahua oil, the acid value was still very high, a second esterification was then necessary to further reduce the acidity to an acceptable level. Ding *et al.* [13] also reached at the same conclusion, but after the first esterification the acid value was 3.76mgKOH/g, alkali-de-acidification was performed at the optimum condition of 0.5N alkali plus 15% excess alkali at 60°C after 40 min and the soapstock was removed by mechanical separation, the acid value was 0.86mg KOH/g.

In this research work, the optimum condition of the esterification of FFAs contained in the feedstock (*AV*:83.07mg KOH/g oil) was studied. Followed by ethanolic de-acidification, prior to transesterification process.

2. Experimental

2.1 Materials and reagents

The Waste Vegetable Oil (WVO) was supplied by Wuhan Mejie Feiyou Chuli Limited Liability Company (Wuhan, china), was dried for 3h in the oven at 103°C to remove water, and hot-filtered to remove others solid impurities. Acid value of oil was determined according to the china standard method GB/T5530-2005 [14] and the value calculated using the following formula.

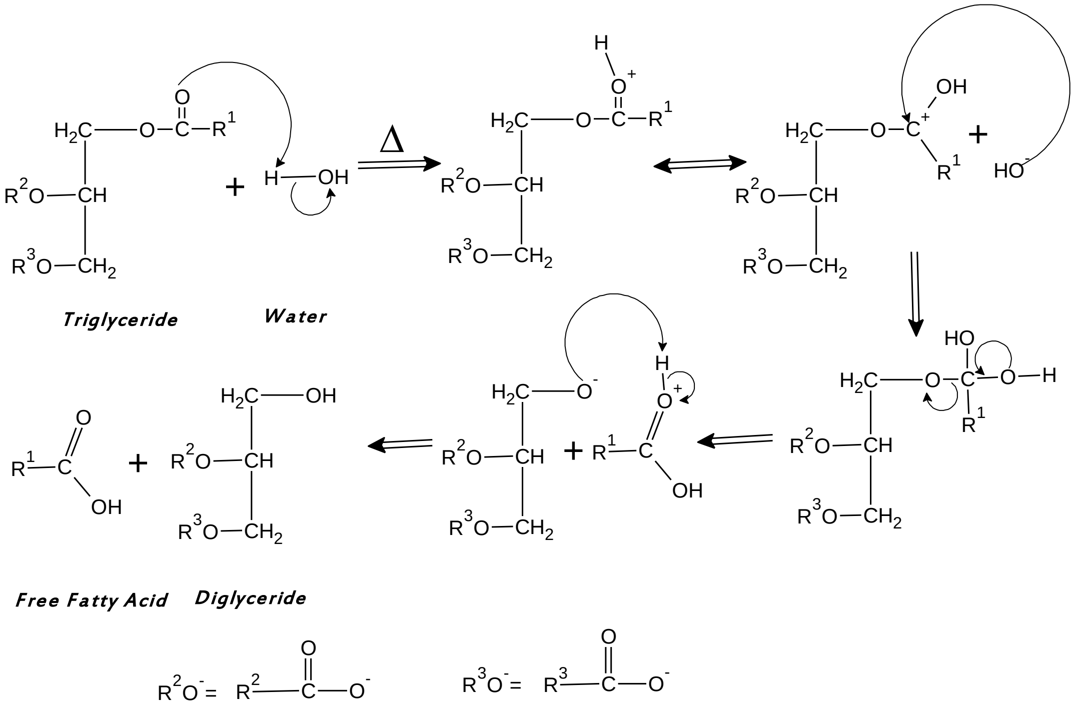
$$AV = \frac{56.1.[Base].V}{w}$$

where AV is acid value, V is volume of base, [base] is concentration of base, w is mass of oil sample. The initial WVO acid value was found as 83.07 mg KOH/g oil.

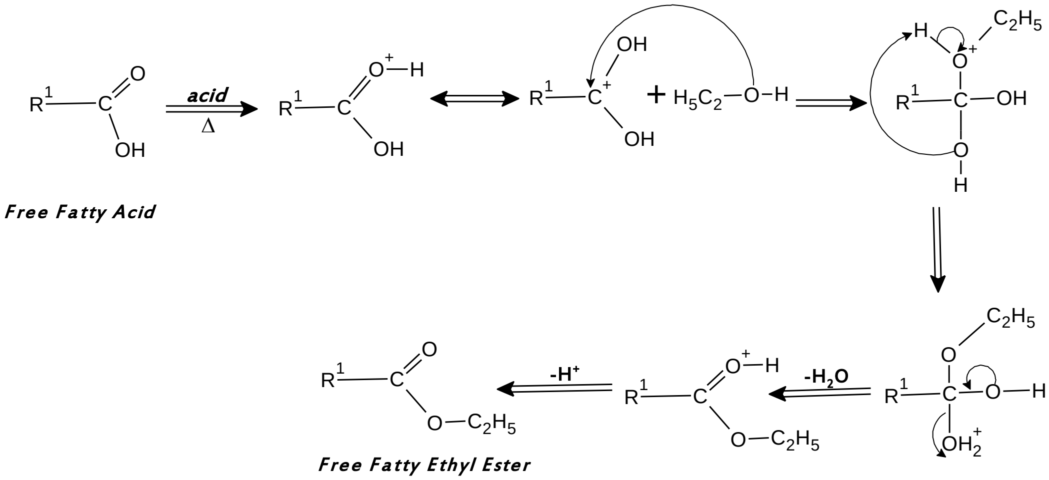
Ethanol, hydrochloric acid, KOH and de-ionized water were of analytic grade and used without any further purification.

2.2 Acid-catalyzed esterification procedure

The aim of this step was to reduce the FFAs produce during frying process as shown in scheme 1 (mechanism of triglyceride hydrolysis to diglyceride) in the oil by converting it into esters using ethanol, hydrochloric acid respectively as a reagent and catalyst as described by the mechanism in scheme. 2



Scheme 1 General mechanism of triglyceride hydrolysis to diglyceride



Scheme 2 General mechanism of esterification reaction-

Forty millilitres (40 mL) of WVO was mixed with the desired quantity of hydrochloric acid and mixed with ethanol in a three-necked flask equipped with a reflux condenser, placed in a water bath. The reaction mixture was stirred under reflux condition at atmospheric pressure. Volume ratios of diluted hydrochloric acid catalyst were: 0.5, 0.7, 0.9, 1.1 and 1.3% (v/v) to volume of WVO. The volume ratio of ethanol were: 15, 20, 25, 30, 35 and 40%(v/v) to the volume of the WVO. The reaction time and temperature were: 2, 4, 5, 6 hours and 55, 65, 70, 75°C respectively. The reaction mixtures were cooled to room temperature, it was then transferred in the separating funnel and allowed to settle overnight. Water and excess ethanol were settled at the bottom of the funnel and later drained out. The oil was washed three times with de-ionized water (50°C) for further purification, it was then dried, the acid value of the EO was determined while the percentage conversion was estimated by the relationship stated below.

$$\phi(\%) = \frac{AV_{WVO} - AV_{EO}}{AV_{WVO}} \times 100$$

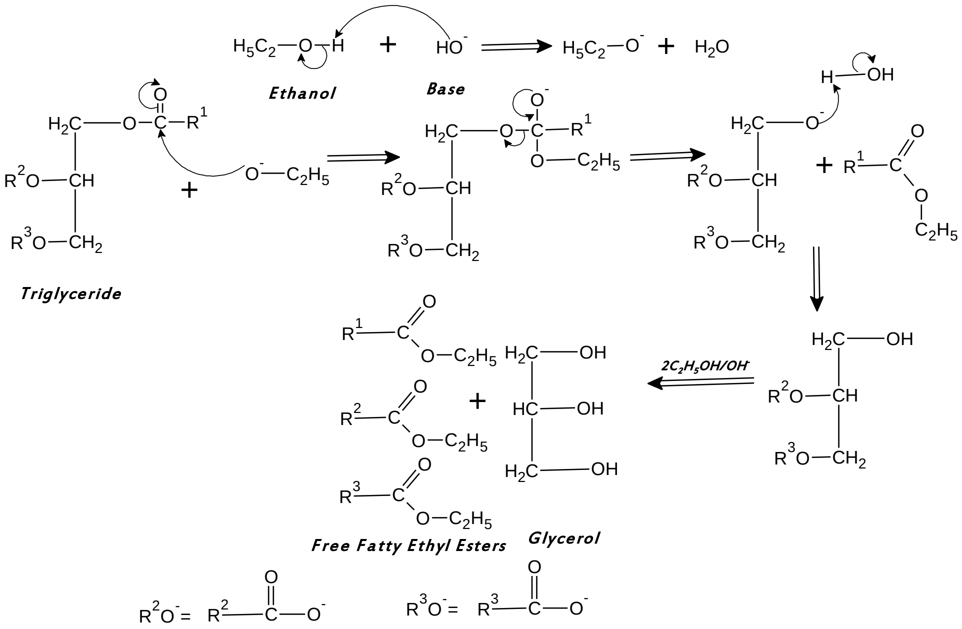
2.3 Ethanolic de-acidification of the esterified oil

In order to enhance the yield of the transesterification, the AV of the EO should be less than 2 *mgKOH/g* prior to transesterification, however, the AV of the EO after acid-catalyzed esterification was 3.32 *mgKOH/g* EO. Therefore, ethanolic de-acidification was necessary to reduce the free fatty acid content in the EO as followed.

The required volume of the base(0.1NKOH) for the de-acidification was first determined by titration using phenolphthalein indicator at 50°C. Hence, 60% mass of the oil was estimated as the volume of the base necessary for the de-acidification. The ethanolic de-acidification was then carried out by weighing 5g of the EO dissolved in ethanol and adding the required volume of base plus 5% excess to ensure complete neutralization. The mixture was stirred slowly at 50°C for 10 min, transferred into the separating funnel for the separation by gravity. The lower layer was drained off, the oil left in the funnel was then washed out with a warm (50°C) de-ionized water for further purification. The AV of the dried de-acidified oil (DAO) was obtained as 0.56 *mg KOH/g* DAO

2.4 Base-catalyzed transesterification

Following a favorable acid value of the DAO, the transesterification reaction of the DAO was then performed. As described in Scheme 3



Scheme 3 General mechanism of transesterification reaction

To achieve optimum yield, reactions conditions were investigated by varying the time, the temperature of the reaction, the mass ratio of KOH to DAO and mass ratio of ethanol to DAO. It should be noted that, because of the low polarity of ethanol, KOH was first dissolved in 10vol% de-ionized water (based on DAO). During this step, 40 g of the DAO was used, the amount of KOH catalyst was varied from 1 to 2.5% (w/w), ethanol from 15 to 45% (w/w), reaction time 2 - 7 hours and temperature from 55 to 75°C. The reaction was performed under constant stirring in a three-neck flask under reflux conditions whilst the temperature regulated using a water bath. The reaction was terminated at desired, cooled to room temperature and poured in the separating funnel to effect separation. After about 8 hours, two layers were then formed, the glycerol at the bottom was drained off, upper layer biodiesel was washed several times with warm de-ionized water, dried with Na_2SO_4, then filtered to remove solid particles. The yield of the product was calculated according to the formula stated below.

$$\text{Biodiesel yield(\%)} = \frac{W_{FAEEs}}{W_{DAO}} \times 100$$

2.5 Evaluation of the properties of the oil and the biodiesel samples

2.5.1 Acid value

The acid value of the sample was determined according to China standard method GB/T5530-2005. The procedure is outlined as follows: 0.5g of the oil sample was weighed and completely dissolved in a neutralized ethanol at 50°C after adding a few drops of phenolphthalein, stirred and titrated against 0.1N KOH. The acid level was then determined using the formula above.

2.5.2 Specific gravity

The specific gravity was determined using JA5003N digital precision electronic analytical balance, according to *ASTM D4052* at 15°C using the specific gravity bottle. The steps are outlined as follow: an empty bottle was weighed, filled with water and reweighed. The water was poured out and dried. The same procedure was followed using the different oil samples [15].

2.5.3 The viscosity

The viscosity was estimated using Brookfield DV3T rheometer equipped with a temperature controller at 40°C in accordance with *ASTM D455.* The oil sample was poured into a temperature regulating container and the viscosity was then determined using spindle 61[16].

2.5.4 Moisture content

Moisture content can be defined as the weight loss of the sample, dried at 103°C for 12 hours[17].

2.5.5 Flash point

The flash point was estimated using Pensky-Martens closed cup method *ASTM D93*. The oil was poured into a container and tightly closed. Equipped with a thermometer, the temperature was increased gradually until a flash appeared and the temperature was immediately noted [18].

2.5.6 Free fatty acid

By the same method as that of acid value determination, the %FFA was determined by applying the formula, since it is related to the acid value.

$$\%\text{FFA} = \frac{28.2 \times [Base] \times V}{w}$$

3. Results and discussion

3.1 Acid catalyst-esterification

Acid catalyst-esterification was crucial because of the relatively high acid value of the WVO in order to avoid soap formation during transesterification. This step considerable reduced the oil acidity from 83.07 mg KOH/g oil to 3.36 mg KOH/g EO.

3.1.1 Effect of hydrochloric acid ratio on the esterification

The hydrochloric acid used as a catalyst was varied at different volume ratio: from 0.5%vol to 1.3%vol whilst other parameters were kept constant, ethanol ratio 25%vol, the temperature of 65^{o}C and the reaction time at 4 hours. As shown in Fig.1, as the amount of HCl was increased the acid value decreased. The optimum value was attained as 1.1%vol of HCl resulting in acid value of 13.46 mgKOH/g oil, corresponding to 83.79% conversion. Thus, any further increase in the catalyst amount up to 1.3% did not reduce the FFAs content in the WVO.

3.1.2 Effect of alcohol ratio on the esterification

The amount of ethanol was varied from 15% to 40%(v/v). Others variables were kept invariant: hydrochloric acid ratio 1.1%, reaction time 4 hours, reaction temperature 65^{o}C. In the Fig. 2*,* it was observed that as the amount of ethanol was increasing, the acid content of the oil was gradually reducing. The percentage conversion of 91.89% was obtained using 35% ethanol ratio. Beyond this, no further decrease in the FFAs content of the WVO was achieved up to 40% of the ethanol ratio. Hence, the optimum ethanol ratio was established at 35%.

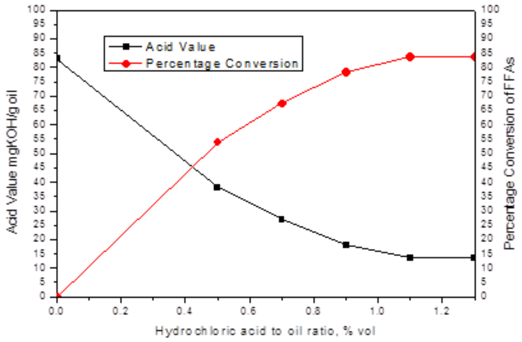


Fig. 1 Effect of the amount of hydrochloric acid

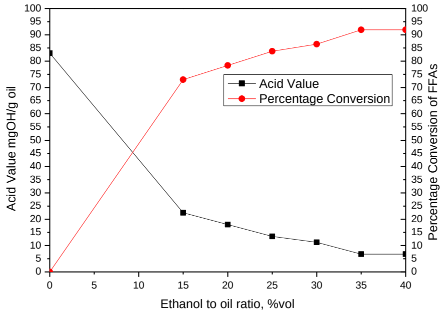


Fig. 2 Effect of the amount of ethanol

3.1.3 Effect of the reaction time on the esterification

The optimum time required for the esterification was also investigated by varying reaction time as: 2, 4, 5. 6 hours, while maintaining other parameters constant as: ethanol ratio of 35% (v/v) to the volume of the oil, hydrochloric acid ratio of 1.1%(v/v) to the volume of the oil, and the temperature of 65^{o}C. Fig. 3 shows a decrease of FFAs of the WVO with increasing reaction time up to 5 hours which resulted in 96.00% FFAs removal to 3.32mg KOH/g oil. Therefore, the ideal reaction time was obtained as 5 hours and further increase in time did not affect free acids reduction.

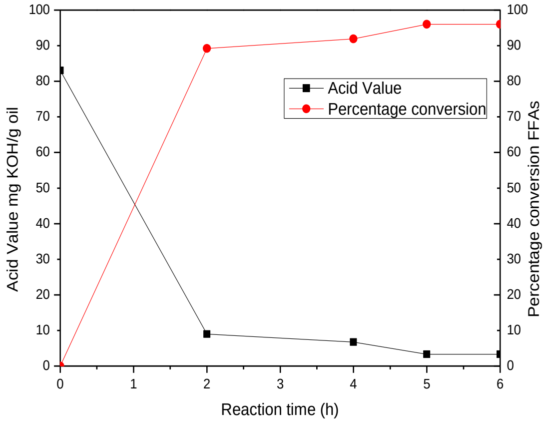


Fig. 3 Effect of the reaction time

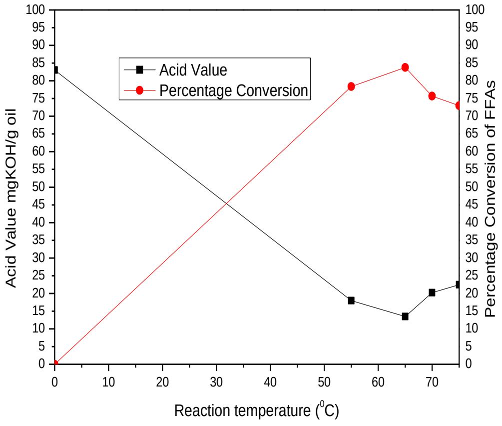


Fig. 4 Effect of the temperature

3.1.4 Effect of the reaction temperature

The reaction temperature was found to be a relevant variable during the esterification process. In Fig.4, the temperature was varied from 55 to 75°C whilst, others parameters were retained constant as follow: 1.1% of hydrochloric acid ratio, 25% of ethanol ratio and the reaction time was 5 hours. As reaction temperature was increased, a maximum acid conversion was 91.89% at 65°C. Further increase of the temperature proved unprofitable since the acidity removal decreased to 72.98% probably due to evaporation of ethanol from the reaction mixture, as the system approached the ethanol boiling point (78.5°C). The product quality decrease as the reaction appeared relatively darker [13] therefore the optimum reaction temperature was established as 65°C.

3.2 Base-catalyzed transesterification

In order to maximize the yield of transesterification reaction the acid value of esterified oil (EO) was favourably reduced through de-acidification, as presented in the early discussion.

3.2.1 Effect of the amount of KOH on the biodiesel yield

The amount of catalyst was varied during the process from 0.5 to 2.5%(w/w) to the DAO ratio as shown in Fig.5. Whilst maintaining a reaction time, ethanol to oil ratio and the temperature of 4 hours, 25%(w/w) and 65°C, respectively. The yield of biodiesel was found to increase from 77.50% at 1% (w/w)KOH to 86.25% at 1.5%KOH to DAO ratio. As presented in Fig.9., further increase of base concentration was noticed to decrease the yield, due to the saponification reaction which interfered with the transesterification process. Therefore, 1.5%*(w/w)* was considered ideal of KOH required.

3.2.2 Effect of the ethanol to oil ratio

The ratio of ethanol to oil was also examined by varying the ethanol concentration from 15 to 45%*(*w/w*)* ethanol to oil ratio. Whilst, using 1.5%*(*w/w) amount of base at 65°C and reaction time of 4 hours. From Fig.6, at 15% ethanol ratio, the biodiesel yield was 75% but increased to 87.5% at as ethanol ratio increased to 35%*(*w/w*)*, whilst further increase of the ethanol ratio produced insignificant change in biodiesel yield. The optimum concentration of ethanol was achieved as 35% ethanol to oil ratio.

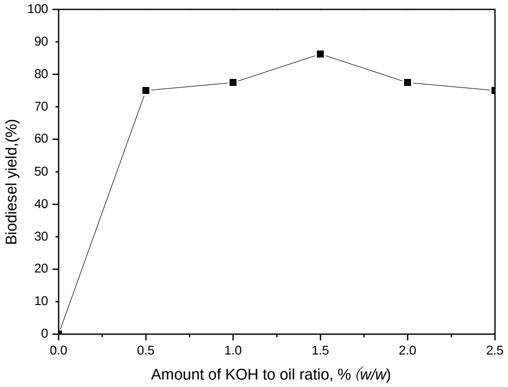


Fig. 5 Effect of KOH on the biodiesel yield

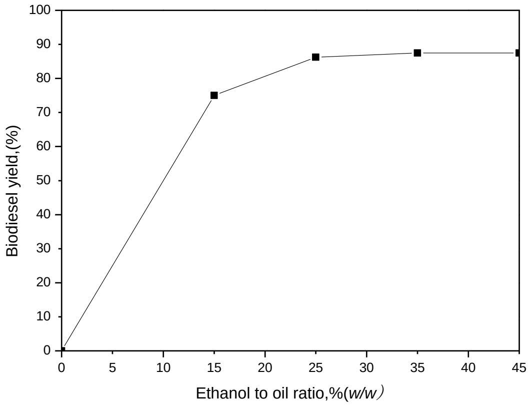


Fig. 6 Effect of ethanol on the biodiesel yield

3.2.3 Effect of the temperature

The temperature was also a relevant parameter during the transesterification process. Fig.7, shows its effect on biodiesel yield as it was varied from 55 to 75°C, at constant 1.5%KOH and 35% ethanol, and reaction time of 4 hours. At 55°C, a biodiesel yield of 73.75% was obtained. As the temperature progressively increased, the yield also increased to 88.75% at

70^{0}C but reduced significantly to 75% at 75^{o}C due to the evaporation of ethanol since its boiling point is about 78.5^{o}C.

3.2.4 Effect of the reaction time

Reaction time was observed to affect the biodiesel yield as shown in fig.8, by varying the time from 2 to 7 hours, whilst maintaining temperature at 70^{o}C, ethanol to DAO ratio of 35% (w/w) and KOH concentration of 1.5% (w/w). As transesterification progressed for reaction time of 4 hours, the yield was 88.75% and increased to 91.25% after 6 hours but subsequent increase of time to 7 hours was inconsequential. Thus, achieving the optimum reaction time of 6 hours.

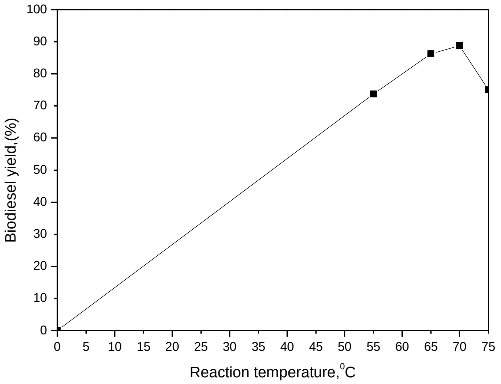


Fig. 7 Effect of temperature on the biodiesel yield

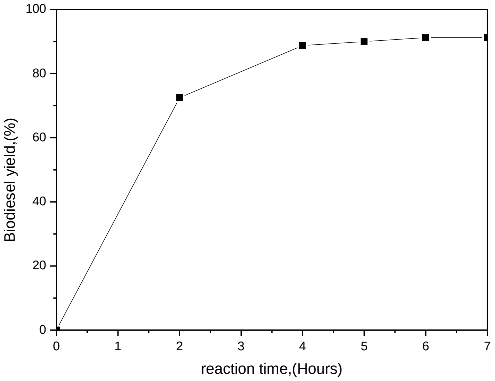


Fig 8 Effect of the time on the biodiesel yield

3.3 Properties of Biodiesel and oil samples

High acidity of biodiesel can cause metal corrosion. The acid value as well as the %FFA of the biodiesel synthesized in this work were determined and compared to standard values. The acid value and %FFA were respectively 0.44 mgKOH/g oil and 0.28 mgKOH/g oil. These values were within the recommended values of EU and US Standard (AV < 0.5mgKOH/g oil) and China Standard(AV < 0.8 mgKOH/g oil). The specific gravity of biodiesel was found to be 0.86, higher than that of tested white oil (0.84) used in some oil based drilling mud. It was however, slightly lower than that of diesel (0.87) used by Odin *et al.* [15] in their work. The spe-cific gravity is an important parameter in the drilling operation, a higher value suggests a greater ability to suspend cuttings and easier emulsification property. Compared to the white oil, the moisture content of the biodiesel was (0.04%) as shown in Fig. 9 thus, satisfied the intentional standards, China/US/UE standard (<0.05max).

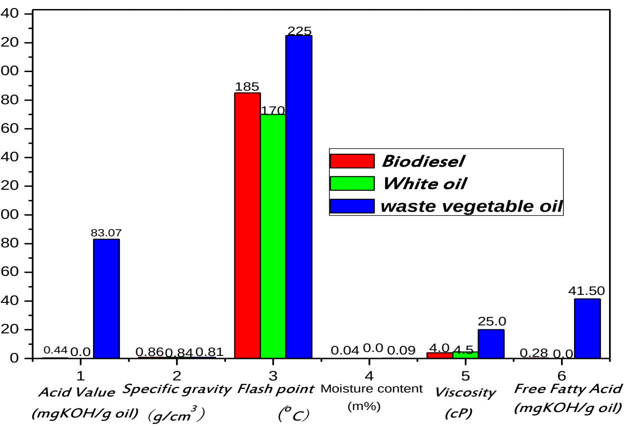


Fig. 9 Comparative study of some relevant parameters of biodiesel, white oil and waste vegetable oil

The flash point of the biodiesel was estimated as 185°C using Pensky-Martens closed cup test (ASTM D93). The value was relatively higher than that of white oil (170°C), however, biodiesel value is within the range of the international standards, EU (>130°C) and China and US (>170°C). The viscosity of the fuel reflects its lubricating effect, the biodiesel fuel viscosity was 4 cP, relatively lower than that of white oil (4.5cP), but also fall within the international standards, China/US (1.9-6 cP) and EU (3.5-5 cP).

3. Conclusion

Biodiesel was successfully synthesized from a low-priced and high acid feedstock. Esterification reaction was first carried out at the optimum condition of: 1.1%(v/v) HCl, 35%v/v ethanol at 65°C for 5 hours, to reduce the acid value from 83.07mg KOH/g oil to 3.36 mg KOH/g of esterified oil. Ethanolic de-acidification was then used to further reduce the acid value to 0.56mg KOH/g DAO. Finally, transesterification reaction was carried out at the optimum condition of:1.5w%KOH, 35w% ethanol at 70°C after 6 hours to obtain biodiesel yield of 91.25%. Its specific gravity was 0.86, the viscosity was measured as 4 cP. The high flash point(185°C) of the fluid was attributed to the water content(0.04%). The properties obtained conformed to China/US/UE international standard. Compared to the white oil, biodiesel synthesized from this feedstock can be a promising alternative.

Acknowledgment

The authors owe a profound gratitude to the staff members of Oil and Gas Materials Research Centre for their support in using laboratory equipments of College of Petroleum of Yangtze University for this research work.

Nomenclature

WVO	*Waste vegetable oil*	W_{FAEES}	*Mass of free acid ethyl ester*
EO	*Esterified oil*	W_{DAO}	*Mass of de-acidified oil*
DAO	*De-acidified oil*	w	*Weight of the oil sample*
φ	*Conversion of free fatty acid, %*	V	*Volume of base used*
AV_{wvo}	*Acid value of the waste vegetable oil*	Na_2SO_4	*Sodium sulfite anhydrous*
AV_{EO}	*Acid value of the esterified oil*	*KOH*	*Potassium hydroxide*
%FFAs	*Free fatty acid percentage*	*HCl*	*Hydrochloric acid*
FAEEs	*Free acid ethyl esters*		

References

[1] Story J, Lee B. The detection of the crude oil contamination in synthetic-based drilling mud. Amoco Corporation, 2001, 338-340.

[2] Adesina F., Abiodun A., Anthony A., Olugbenga F. Modelling the Effect of Temperature on Environmentally Safe Oil Based Drilling Mud Using Artificial Neural Network Algorithm. Petroleum and Coal, 2012, 54, 1.

[3] Adesina F, Anthony A, Gbadegesin A, Esseoghene O, Oyakhire A. Environmental Impact Evaluation of a Safe Drilling Mud, SPE Middle East Health, Safety, Security, and Environment Conference and Exhibition held in Abu Dhabi. UAE, 2–4 April 2012, SPE-152865-PP.

[4] Wang M, Sun M, Shang H, Fan S, Liu M, Liu F. Biodiesel-based Drilling Fluids. Society of Petroleum Engineers, 01 January 2012 doi:10.2118/155578-MS.

[5] Radzlan R, Yusup S, Yusuf NR, Kamil RNM, Chok C. The effect of lime and primary Emulsifier on the Rheological Behaviour of Palm Fatty Acid Distillate(PFAD) Biodiesel-based Drilling Fluid(j) Autralian Journal of Basic and Applied Sciences, 2014, 8(5):267-272.

[6] Fadhil AB, Dheyab MM, Ahmed KM, Yahya M H. Biodiesel Production from Spent Fish Frying Oil Through Acid-Base Catalyzed Transesterification, Pak. J. Anal. Environ. Chem., 2012, 13(1), 09-15.

[7] Gashaw A, Teshita A. Production of biodiesel from waste cooking oil and factors affecting its formation: A review. International Journal of Renewable and Sustainable Energy, 2014, 3(5), 92-98.

[8] Balat M, Balat H. Progress in biodiesel processing. Applied Energy, 2010, 87: 1815-1835, DOI: 10.1016/j.apenergy.2010.01.012.

[9] Encinar JM, Gonzalez JF, Rodriguez-Reinares A. Ethanolysis of used frying oil. Biodiesel preparation and characterization. Fuel Process, 2007, Technol.,88:513-522. DOI: 10.1016/j.fuproc.2007.01.002.

[10] Cetinkaya M, Karaosmanoglu F. Optimization of base - catalyzed transesterification reaction of used cooking oil. Energy&Fuels, 2004, (18):1888-1895.

[11] Alptein E, Canakci M. Fuel, 2010, 89, 4036.

[12] Ghadge SV, Raheman H. Biodiesel production from mahua (Madhuca indica) oil having high free fatty acids. Biomass Bioenergy, 2005, 28, 601-605.

[13] Ding J, Xia Z, Lu J. Esterification and Deacidification of a Waste Cooking Oil (TAN68.81mgKOH/g) for Biodiesel Production. Energies, 2012, 5, 2683-2691; doi:10.3390/en5082683

[14] China Standard-animal and Vegetable and Oils-Determination of Acid Value and Acidity GB/T5530-2005.

[15] Odin EM, Onoja PK, Ochala AU. Effect Of Process Variables On Biodiesel Production Via Transesterification Of Quassia Undulata Seed Oil, Using Homogeneous Catalyst. International Journal of Scientific &Technology Research, 2013, 2(9).

[16] Boakye P. Biodiesel production from selected non-edible feedstocks using unsupported potassium carbonate, Master of science in chemical engineering, Kwame Nkrumah University of Science and Technology.

[17] AOAC (1990). Official Methods of Analysis, 15thedn. Association of Official Analytical Chemists, Virginia, USA.

[18] ASTM D93: Standard Test Method for Flash Point by Pensky-Martens Cup Tester, 40CFR 94, 108(a)(1) Table B-5.