

Acid-Catalyzed Esterification of Waste Cooking Oil with High FFA for Biodiesel Production

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Abstract

In this work, Biodiesel was produced from waste cooking oil (WCO) obtained from Mr. Biggs. Since WCO usually comes with a high content of FFA and thus requires an additional acid pre-treatment process to convert the FFA to ester. Two steps (esterification and transesterification) approach was employed to convert the WCO to biodiesel. In the first step, six experimental run was carried out until the % FFA was constant. Meanwhile, the second step required five experimental runs, and the average WCO biodiesel yield (95.06 % w/w) was computed at the following variable conditions, 0.55% KOH, 5:1 Methanol/oil molar ratio, 60 °C reaction temperature and 30 min reaction time. Meanwhile, the produced WCO biodiesel possess some fuel properties which satisfied both ASTM D6751 and EN 1424 standards. The fatty acid profiles of both the WCO and WCO biodiesel revealed that both profiles contained unsaturated fatty acids. Hence, it can be concluded that WCO is a potential raw material for biodiesel production which are biodegradable, economical, environmental friendly and always available.

Keywords: Waste cooking oil (WCO), esterification, transesterification, biodiesel, fatty acids profile, physicochemical analysis.

1. Introduction

Fossil fuels are non-renewable sources of energy which generate pollutants claimed to be responsible for global warming, climatic change and incurable diseases. The search for an alternative fuel which promises a harmonious correlation with the sustainable development, provide enough energy with impetus to get the engine running, environmental friendly, biodegradable, readily available, energy conservation and management. Legitimate concerns have also been raised about the possible effect of using vegetable oils for fuel on food price (Trostle, 2008). Capacity development may lead to a decrease in availability of land for food crops along with the overall adverse effect on climate change (Knothe, 2001; Fargione et al., 2008).

The huge demand for diesel fuel dwarfs the available supply of vegetable oils. The global production of sunflower, peanut, maize, linseed, sorrel seed, rapeseed, soybean, cottonseed, palm kernel, coconut, Beniseed and olive oil as the top vegetable oils in 2006 was about 125,600,000 metric tonnes (FAOSTAT, 2009). In contrast, the total consumption of diesel fuel by transportation industries in the same year was about 639,000,000 metric tonnes (ESD, 2009). Thus, even if all of the vegetable oils produced in the world in 2006 were converted to biodiesel, this would fill only 18% of the total demand in the same year for the transportation industries alone. It is necessary that feedstock production be increased dramatically if biodiesel is to have any real impact on the energy problem. The issue of alternative feedstock production has been reviewed recently from several different viewpoints (Canakci and Sanli, 2008; Liyama et al., 2008; Moser, 2009; Durrette et al., 2008; Pinzi et al., 2009; Betiku and Adepoju, 2012a; Betiku et al., 2012b). The present paper aims to aid in selection of alternative feedstock for biodiesel production.

Vehicles' being operated with biodiesel from waste or used cooking oils is an ideal that makes sense. Utilization of Waste cooking oil (WCO) is 65% less expensive than the neat vegetable oil, depending on the source and availability, and would also mitigate a waste stream. WCO constitute major waste generated in hotel and other public eateries. This can be recycling for human consumption. Biodiesel produced using WCO had a better rate of returning than a process which used virgin oil, although all of the processes in their papers had negative rate of return. What kept the WCO from being more profitable was a higher capital cost involve in use of acid pretreatment in converting the high FFA content to low FFA content (esterify) before biodiesel production. Nevertheless, the challenges for the full utilization of WCO seem to be purely logistical, operational and economical. Taking into consideration of all conditions, the use of WCO is easily achieved.

In light of this, the main objective of this work is to produce biodiesel from WCO (Mr. Biggs); meanwhile, the characterization of biodiesel produced was also carried out to determine the quality of biodiesel produced.

2. Materials and Methods

2.1 Materials

WCO oil used for this work was collected from Mr. Biggs in Ibadan, Oyo State, Nigeria. The semi-colloidal oil was preheated in a reactor, cooled and then filtered to remove the unwanted impurities. All chemicals used were all of analytical grade.

2.2 Experimental procedure

2.2.1 Acid catalyzed

The purified oil was dark brown in colour. AOAC, 1990 method was used to determine the acid value. The acid value of the oil was evaluated to be 8.52 mg KOH/g oil (%FFA = 4.26 %). The specification for base catalyst transesterification is less than 1.50. Therefore, the oil was first esterified (step 1) with acid catalyst (con. H₂SO₄). This is done by adding 1:10 of concentrated acid to methanol ratio to preheated oil in the reactor. The magnetic stirrer was inserted and the whole set up was heated at 60 °C on hot plate until the two products separated completely. The esterified biodiesel was tapped out, and the acid value was determined. This process was repeated five more times until the constant acid value (1.84 mg KOH/g oil) was obtained. The %FFA was calculated (% FFA = 1.84/2 = 0.92). This product was then used for the alkalis transesterification stage (step 2). Table 1 shows the esterified process by the variable parameters reaction time, concentration of acid (H₂SO₄) and methanol/oil molar ratio used with the acid value and FFAs computed.

Table 1. Acid catalyzed esterification-Esterified process

Variables	Values					
H ₂ SO ₄ conc. (% v/v)	2	2	2	2	2	2
Methanol/oil molar ratio	3	4	5	5	6	6
Reaction time (min)	30	40	50	60	65	70
Acid values of the esterified oil (mg KOH/ g oil)	4.43	3.24	1.85	1.84	1.84	1.84
% FFA of the esterified oil	2.22	1.62	1.43	0.92	0.92	0.92

2.2.2 Alkalis catalyzed step- Transesterification step

Alkalis transesterification step was carried out according to the method cited by Tiwari et al., 2007 and Adepoju et al., 2013. The reaction was carried out with methanol/oil molar ratio of 5:1, with 0.55% KOH added as an alkaline base catalyst. The amount of KOH (5.5 g/l of WCO) was reached based on the amount needed to neutralize the unreacted acids (1.84 mg KOH/g oil) in this stage. The reaction was carried out at 60 °C for 30 min in a reactor. At the completion of the reaction, the product was transferred to a separating funnel for glycerol and biodiesel separation for 24 h. Glycerol was tapped off and the left over was washed with ionized water to remove residual catalyst, glycerol, methanol and soap present. The washed biodiesel was further dried over heated calcium chloride (CaCl₂) powder to remove the residual ionized water. The WCO biodiesel yield was determined gravimetrically as described in Eq.1. The experiment was carried out four more time and the average yield of the WCO biodiesel was evaluated as in Eq. 2. (Table 2.)

$$WCO \text{ biodiesel yield \%}(w/w) = \frac{\text{Weight of WCO oil used}}{\text{Weight of biodiesel produced}} \quad (1)$$

$$\text{Average yield of WCO biodiesel} = \frac{\text{Exp.1} + \text{Exp.2} + \text{Exp.3} + \text{Exp.4} + \text{Exp.5}}{5} \quad (2)$$

2.3 Physicochemical analysis of the WCO oil and WCO biodiesel

The evaluation of physicochemical and other properties of the WCO oil and WCO biodiesel was determined by AOAC, 1990 method, iodine value was determined by Wijs method. Meanwhile, the quality of WCO biodiesel is very important for the performance and it emission reduction characteristics in diesel engine. Thus, the WCO biodiesel produced was subjected to chromatography analysis to determine the fatty acids profile.

3. Results and Discussion

3.1 WCO biodiesel characterization

3.1.1 Acid catalyzed esterification (pre-treatment)

Since WCO usually comes with a high content of FFA and thus requires an additional acid pre-treatment process to convert the FFA to ester, WCO obtained from Mr. Biggs tends to have properties that could influence the repeatability of the tests, the pre-treatment step was repeated five times until the obtained acid value remain constant, % FFA was computed (Table 1). The results showed that the acid value of 1.84 mg KOH/g oil (%FFA = 0.92) at variables conditions of 2.00 (% v/v) H₂SO₄ concentrated, methanol/oil molar ratio of 6 and reaction time, 65 min were found suitable for propagation into second step (alkalis transesterification process).

3.1.2 Alkalis catalyzed transesterification process

Table 2 shows the five experiments carried out. The percentage yield of WCO biodiesel obtained was remarkable. The average percentage yield of WCO biodiesel obtained during the alkalis catalyzed transesterification process after five repeated experiment was 95.06% (w/w) at the following variable conditions, 0.55% KOH, 5:1 Methanol/oil molar ratio, 60 °C reaction temperature and 30 min reaction time.

Table 2. Alkalis catalyzed transesterification process

Experiments	KOH (%)	Methanol/oil molar ratio	Reaction temp. (°C)	Reaction time (min)	WCO biodiesel yield % (w/w)
1	0.55	5:1	60	30	95.75
2	0.55	5: 1	60	30	94.45
3	0.55	5:1	60	30	95.05
4	0.55	5:1	60	30	95.10
5	0.55	5: 1	60	30	94.95

Average yield of WCO biodiesel = 95.06% (w/w)

3.2 Physicochemical analysis and other properties of WCO and WCO biodiesel

3.2.1 Physical properties of the WCO and WCO biodiesel

In order to evaluate the quality of the crude WCO and WCO biodiesel, the content and compositions of the oil and biodiesel was subjected to physicochemical analysis, the results obtained are shown in Table 3. At room temperature, the WCO was dark brown in colour and the WCO biodiesel was brownish in outlook. Observation on refractive index showed that the refractive index increased but the moisture content decreased after conversion of WCO to biodiesel, indicating a good shelf life characteristic of oil (Adepoju et al., 2013). The specific gravity (density of substance relative to the density of water) of WCO was determined as 0.91 which was reduced to 0.83 after conversion. The specific gravity for most vegetable oil are reported to be in a range between 0.874 - 8.2312 (Eze, 2012). The viscosity (resistance of a liquid to shear forces and flow) was determined to be 7.48 mm²/s and 2.56 mm²/s, respectively. The higher value obtained for the WCO shows the oil could be used as lubricant in engine parts in the tropics if left overnight as solidification temperature of the oil is below 10 °C at any season (Oyekunle et al., 2007).

3.2.2 Chemical properties of the WCO and WCO biodiesel

Contained also in Table 3 are the results of chemical properties of WCO and WCO biodiesel. The high acid value of the WCO showed that it is non-edible oil which improves its suitability for biodiesel production. The acid value is expected to range from 0.00 - 3.00 mg KOH/g material, before it can find application in industries but the value is high for oil under study. That was why acid value was made fit by subjecting the WCO to two steps processes and this may also improve its quality for industrial purposes (Adepoju et al., 2013). A high Saponification value was obtained for both WCO and biodiesel, suggesting high concentration of triglycerides. The iodine value of the WCO was high (145.60 g of I₂/100 g of oil), which signified the oil contained a substantial level of unsaturation and could be used to quantify the amount of double bonds present in the oil which reflects the susceptibility of oil to oxidation before conversion to biodiesel (Adepoju et al., 2013).

Peroxide value measures the content of hydro-peroxides in the oil and its low value indicates high resistance to oxidation. The value obtained for the WCO and biodiesel in this work were well within the limit stipulated for vegetable oils and biodiesel. This shows that the oil is not rancid and considered stable (Ajayi et al., 2002; Adepoju et al., 2013). The HHV determined for the WCO was 40.20 MJ/kg, this is within the range earlier reported for most vegetable oils (37.47 – 40.62 MJ/kg) by Demirbas, (1998). The rapid increases in the HHV noticed in conversion of WCO to biodiesel proved that the oil is not only good for biodiesel production, but can be suitably used as fuel in I.C. engine.

Table 3. Properties of WCO and WCO biodiesel as compared with biodiesel specification

Parameters	WCO	WCO biodiesel	ASTM D6751	EN 14214
Physical properties				
Colour	Dark brown	Brownish	-	-
Moisture content %	0.045	0.0104	0.05 max	0.02
Specific gravity	0.91	0.83	0.86-0.90	0.85
Viscosity (mm ² /s) at 40°C	7.48	2.56	1.9-6.0	3.5-5.0
Chemical properties				
Iodine value(g I ₂ /100g)	145.90	116.00	-	120 max
Acid value(mg KOH/g oil)	8.52	3.86	< 0.80	0.5 max
%FFA (as oleic acid)	4.27	1.93	-	-
Saponification value (Mg KOH/g oil)	196.40	182.32	-	-
Peroxide value	3.04	2.48	-	-
Other properties				
Cloud point °C	-	9.00	6	12 max
Flash point °C	-	114.00	100 min	>120
Pour point °C	-	-13.00	- 15	-
HHV (MJ/kg)	34.08	36.15	-	-
Cetane number	41.26	50.14	47 min	51 min

3.2.3 Other properties of the WCO and WCO biodiesel

Additional fuel properties such as cetane number and higher heating value (HHV) of the WCO and WCO biodiesel were determined (Table 3). Cetane number (a measure of the fuel's ignition delay and combustion quality) of the WCO biodiesel showed that it has high fuel potential. The HHV of WCO and WCO biodiesel was determined to be 34.08 and 36.15 MJ/kg, respectively.

3.3 Fatty acid profile of the WCO and WCO biodiesel

Gas chromatography analysis of fatty acids present in both WCO and WCO biodiesel are shown in Table 4. The results indicated that the WCO is highly unsaturated. The dominant fatty acids are linoleic (52.68%), oleic (22.62%), palmitic (17.34%), stearic (4.21%), linolenic acid (2.60%) and others (0.55%). Also, the dominant fatty acids found in WCO biodiesel indicated the presence of unsaturation in the diesel also. The dominant fatty acids are linoleic (59.87%), oleic (19.58%), palmitic (17.80%), stearic (1.86%), linolenic acid (0.85%) and others (0.04%) This indicates that fatty acid composition will play a dominant role in establishing the cetane number (Knothe, 2005; Bamgboye and Hansen, 2008).

Table 4: Fatty acids compositions of the WCO and WCO biodiesel produced

Parameters	Compositions %	
	WCO	WCO biodiesel
Palmitic acid (C16:0)	17.34	17.80
Stearic acids (C18:0)	4.21	1.86
Oleic acids (C18:1)	22.62	19.58
Linoleic acids (C18:2)	52.68	59.87
Linolenic acid (C18:3)	2.60	0.85
Other	0.55	0.04
Total	100	100

4. Conclusion

The results revealed that the average WCO biodiesel yield of 95.06 % w/w was obtained at the following variable conditions, 0.55% KOH, 5:1 Methanol/oil molar ratio, 60 °C reaction temperature and 30 min reaction time. The produced WCO biodiesel have some fuel properties which satisfied both ASTM D6751 and EN 1424 standards. The fatty acid profiles of both the WCO and WCO biodiesel revealed that both are highly unsaturated acids. In conclusion, WCO obtained from Mr. Biggs, is a potential raw material for biodiesel production which are biodegradable, economical, environmental friendly and always available.

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