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CHARACTERIZATION AND ESTERIFICATION OF VARIOUS WASTE FRYING OILS AS FEEDSTOCKS FOR BIODIESEL PRODUCTION

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ABSTRACT

The main objective of the study was to characterize and esterify ten waste frying oil (WFO) samples collected from fried food vendors and analyse their suitability as feedstock for biodiesel production. The parameters of the WFOs analyzed included; colour, odour, pH, specific gravity, kinematic viscosity (Oswald viscometer), moisture content (oven drying method), iodine value, acid value and saponification value. Esterification was carried out to lower the free fatty acid (FFA) contents of the waste frying oils. Mean values for specific gravity varied from 0.892±0.022 to 0.905±0.075 g/cm^3. The mean kinematic viscosity of the WFOs ranged from 43.120 ±1.530 to 97.530 ±6.360 mm^2/s. The mean acid value obtained varied from 2.730 ±0.404 to 16.956 ±3.806 mg/g while the mean free fatty acid concentration in the WFO ranged from 1.95 ±0.17 to 12.09 ±2.11 mg/g. Results indicated that WFOs used for frying fish may not be good feedstocks for biodiesel production since they contained the highest levels of FFA. Both refined and unrefined oils were used for frying in the sampling area. The foodstuffs fried in the oils included Akara (bean cake), yam, potato, plantain and fish. Duration of use of the oils ranged from 5 days to 3 weeks. After, esterification, only the free fatty acid contents of 4 samples were reduced below 0.5% by esterification while others ranged between 0.70% and 2.59%. Optimum conditions for the esterification were methanol: concentrated sulphuric acid ratio of 42:1; reaction temperature of 60^{o}C; reaction time of 30 min with 5 min application of heat.

Keywords: Waste frying oil, feedstock, characterization, esterification

INTRODUCTION

Worldwide petroleum consumption has been increasing as a result of the growth of human population and industrialization. However, combustion of fossil fuels like petroleum contributes to the emission of greenhouse gases and air contaminants such as Carbon dioxide, nitrogen oxides, sulphur oxides, particulate matter and volatile organic compounds which contribute to atmospheric pollution and global warming (Balat, 2010). This scenario has triggered research in the production and use of alternative fuels obtained especially from renewable sources (Kannahi *et al.*, 2013). The global contribution from alternative energy resources to energy supply was 10% in 1993, 11% in 2011 and is expected to increase 16% in 2020 (Filho, 2004; World Energy Council, 2013). Biomass is the main renewable energy resource and biofuels and other forms of energy are obtained from the conversion of these renewable resources (McKendry, 2002). Among biofuels, biodiesel is one of the possible alternatives in the transport sector (Costa Neto, 2000). Many potential raw materials for biodiesel production abound but currently, edible oils are majorly used for world biodiesel production (Ahmia *et al*., 2014). However, their use for biodiesel production is of great concern because it competes with their use as food materials (Arjun, 2008).

Waste frying oil refers to the vegetable oil that has been used for frying food. Waste frying oil is accepted as a suitable material for the production of biodiesel because it is readily available and cost effective. Biodiesel obtained from transesterification of vegetable oil with alcohol is a renewable energy form which has been given adequate attention by many researchers because of the advantages associated with its use in the transport sector (Hossain, 2010). Biodiesel is a biodegradable, non-toxic and renewable fuel that can be produced from a renewable raw material including waste and fresh vegetable oils, oils seed plants and animal fats. The combustion of biodiesel has lower emissions than petroleum based diesel, whether blended with petroleum diesel or used in its pure form. Biodiesel does not increase the level of carbon dioxide in the atmosphere and the use of biodiesel leads to minimization of the intensity of the greenhouse effect (Vincente *et al*., 2004; Antolin, 2002). Also, biodiesel is better than petro-diesel in terms of biodegradability, sulphur content, aromatic content and flash point (Martini, 1997).

The main purpose of this research is to characterize and esterify WFOs collected from roadside food frying vendors as suitable feedstocks for biodiesel production.

MATERIALS AND METHODS

Study Area and Sample collection

Aba metropolis in Abia State was chosen as the study area while Asa Road, Ngwa Road, Uratta Express Junction and its environs were selected as the locations for sample collection. These areas were chosen due to the high rate of oil polluted dumpsites, gutters and walkways corresponding to the high concentration of commercial fried food sellers and fast food joints. The waste frying oil samples were collected from commercial food sellers, restaurants, road side fries and homes. A total of nine 200ml samples were collected with glass bottles from nine different sources and 20ml of each of the samples were mixed to obtain the tenth sample. Plate 1 shows the waste frying oils contained in beakers.

Sample Pre-treatment

The samples were filtered using Buchner funnel with muslin cloth to remove the residual fries from the oil. The samples were then heated to 110^{o}C to remove any water droplet in the oil and were dried with anhydrous sodium sulphate to ensure complete removal of water. The samples were then stored in air-tight plastic containers pending analyses.

Descriptive and organoleptic parameters

Descriptive parameters of the WFOs included the determination of the type of oil, the foodstuff(s) it was used to fry and duration of use. Organoleptic parameters determined were colour and odour. Colour was determined by visual comparison of sample with a colour comparator (Custer Colour Strip). Odour was determined smelling the oil sample using a panel of ten persons.

Physico-chemical Analyses of Waste Frying Oil

Specific Gravity was determined with a Hecht Karl pycnometer by relating the weight of each oil sample with the weight of an equivalent volume of water. Moisture Contents were determined by heating 2 g of each sample, cooling and weighing until constant weight was achieved and calculating the moisture content based on difference in weights. pH of the waste frying oils was determined with a pH meter while viscosity was determined in duplicate using an Thomas Ostwald oil viscometer at the laboratory room temperature of 37^{o}C. Saponification value was determined by the titration of a mixture of oil and ethanolic KOH with 0.5M HCl solution with phenolphthalein as indicator. Acid value was determined by warming and titrating a mixture of the sample and industrial methylated spirit (IMS) previously neutralized to a phenolphthalein end point with 0.1M alcoholic KOH to a pink end-point. Free fatty acid (FFA) determination was done by boiling a mixture of the oil sample and neutral alcohol on a hot plate, stirring with a magnetic stirrer until the oil dissolved and titrating with 0.1M NaOH using phenolphthalein as indicator until a pink colouration appeared (AOCS, 1997). The iodine value which is the number of milligrams of iodine absorbed per gram of oil sample was determined by titrating with 0.1M sodium thiosulphate solution with and without the test substance while peroxide value determination was carried out in terms of milli-equivalents of peroxide per 1000g (1kg) of sample which oxidizes potassium iodide under the conditions of the test.

Esterification Reaction

This was used as a pre-treatment process which was carried out to remove free fatty acid from the oils. The potential reaction conditions were arrived at from a study of the works of several authors (Issariyakul *et al.*, 2007; Wang *et al.*, 2007; Hossain and Boyce, 2009; Prafulla *et al*., 2012). During the esterification process, 150ml of each oil was preheated and maintained at 60^{o}C. Then 31.5ml of methanol and 0.75ml of concentrated sulphuric acid were mixed and stirred for 30 min with heating for 5 min. The methanol-acid mixtures were added to the preheated oils in the beakers and this was immediately covered with aluminium foil (to ensure that the container was air tight to avoid evaporation of the methanol) and stirred continuously with an electric stirrer for 40 min. Stirring was stopped and the mixture was then transferred to a separating funnel. The free fatty acid value of the esterified oil was then determined as described above.

RESULTS AND DISCUSSION

Descriptive and organoleptic parameters of the Waste Frying Oils

Table 1 shows the descriptive and organoleptic parameters of the Waste Frying Oils.

Table 1. Description of the Ten Waste Frying Oils

Sample Number	Type of Oil	Foodstuff fried with the oil	Duration of use	Colour	Odour
B1	Refined and branded oil	Akara (bean cake), fish, potato,	5 days	Dark Brown	Fishy
B2	Unrefined and unbranded oil	Fish	3 weeks	Dark Brown	Fishy
B3	Refined and branded oil	Fish, potato, akara, yam	1 week	Pale brown	Fishy
B4	Unrefined and unbranded oil	Potatoes , akara, yam, plantain	2 weeks	Yellowish	Characteristic
B5	Unrefined and unbranded oil	Akara, yam, potatoes, plantain, fish	1 week and 3 days	Dark brown	Fishy
B6	Refined and branded oil	Akara, potato at home	4 weeks	Yellowish	Characteristic
B7	Refined and branded oil	Akara, yam, potatoes, plantain	2 weeks	Yellowish	Characteristic
B8	Refined and branded oil	Akara, potatoes, yam	2 weeks	Yellowish	Characteristic
B9	Unrefined and unbranded oil	Akara, yam, potatoes	2 weeks	Yellowish	Characteristic
B10	Mixture of (B1-B10)	Fish, akara, potatoes, yam	–	Pale brown	Characteristic

Both refined and unrefined oils were used for frying in the sampling area. While some fried food vendors use refined and branded oils, other use unrefined and unbranded oil. This is the existing scenario despite NAFDAC's regulation which stipulates that vegetable oils for cooking shall be derived from the botanical source, be refined and be branded with the manufacturer's name and the specific name of the particular oil present (NAFDAC Fats and Oils Regulations 2019). Fasogbon (2019) stated that the use of unhealthy and unbranded vegetable oils in Nigeria is a significant cause of death since they may be contaminated and may contain high amounts of bad cholesterol (low-density lipoprotein) which blocks heart vessels and leads to sluggish blood circulation. While the foodstuffs fried in the oils ranged from Akara (bean cake) to fish, duration of use of the oils ranged from 5 days to 3 weeks. Many researchers have warned against the reuse of vegetable oils for frying due to thermal oxidation which degrades the oils and leads to the formation of harmful free radical generation like reactive oxygen species and depletion of natural anti-oxidants in the oils (Leong *et al*., 2015; Falade *et al.*, 2017). Colour ranged from dark brown to yellow while odour was identified as fishy or characteristic odour of fries (Plate 1).

Plate 1. The Waste Frying Oil Samples

Physico-chemical Parameters of Waste Frying Oil (WFO)

The physicochemical properties of the ten different WFO samples are summarized in Table 2. Mean values for specific gravity at 20^{o}C varied from 0.892±0.022 (B1) – 0.905±0.075 (B4) g/cm^{3}. The highest value for specific gravity was slightly less than those recorded by Chhetri *et al*. (2008) and Mahgoulb *et al*., (2015) as 0.9216 and 0.9185g/cm^{3} at 23^{o}C, respectively. This difference may be attributed to the fact that specific gravity is a function of temperature and decreases as temperature increases (Abdullah *et al*., 2013). The mean kinematic viscosity of the WFO was determined at 25^{o}C and the result ranged from 43.120 ±1.530 to 97.530 ±6.360 mm^{2}/s. The mean acid value obtained varied from 2.730 ±0.404 to 16.956 ±3.806 mg/g. Acid value measures the presence of corrosive free fatty acids and oxidation products. The higher the acid value, the lower the potential biodiesel yield of a WFO. Results for mean saponification value showed a range of 6.227 ±1.018 – to 59.887±1.290 mgKOH/g. These values obtained were lower than that of the WFO collected in Malaysia by Tan *et al*., (2015). However, the average molecular weight of oil or fat, usually expressed in g/gmol, is a function of acid and

Table 2. Mean Physico-chemical Parameters of Waste Frying Oil

Analysis	**Samples**									
	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10
Physical state	liquid	Liquid	Liquid	Liquid	Liquid	Liquid	liquid	Liquid	liquid	Liquid
Colour	Dark brown	Dark brown	Pale brown	Yellow	Dark brown	Yellow	yellow	Yellow	yellow	Pale brown
Specific gravity @ 20^{o}C	0.892 ±0.022	0.893 ±0.030	0.895 ±0.018	0.905 ±0.075	0.902 ±0.043	0.903 ±0.016	0.901 ±0.053	0.895 ±0.090	0.894 ±0.011	0.905 ±0.031
K. Viscosity (mm^2/s) @ 25^{o}C	84.310 ±2.370	86.110 ±3.550	94.070 ±2.910	73.010 ±2.840	67.020 ±4.070	63.150 ±5.310	81.420 ±4.950	55.730 ±2.810	97.530 ±6.360	43.120 ±1.530
Moisture content (%)	0.141 ±0.052	1.504 ±0.084	2.810 ±0.247	0.482 ±0.057	0.340 ±0.019	1.931 ±0.420	1.224 ±0.161	2.422 ±0.334	0.391 ±0.088	0.200 ±0.038
pH	5.730 ±0.141	5.620 ±0.288	5.490 ±0.175	4.570 ±0.611	4.750 ±0.091	7.330 ±0.085	7.640 ±0.120	4.870 ±0.358	4.810 ±0.292	5.830 ±0.310
Iodine value (gI$_2$/100g)	3.807 ±0.711	41.877 ±3.850	8.883 ±1.075	152.280 ±10.450	114.210 ±7.214	149.742 ±4.863	143.397 ±8.242	147.204 ±3.916	152.280 ±6.877	35.532 ±5.266
Saponification value (mgKOH/g)	42.636 ±3.270	45.862 ±1.785	47.264 ±6.315	26.227 ±1.018	48.667 ±2.865	50.069 ±4.363	40.252 ±2.331	48.667 ±3.019	31.837 ±1.954	59.887 ±1.290
Free fatty acid value (mg/g)	3.122 ±0.728	12.093 ±2.111	4.291 ±0.517	2.375 ±0.248	8.583 ±1.099	1.952 ±0.240	3.124 ±0.419	1.948 ±0.175	3.117 ±0.433	3.508 ±0.722
Acid value (mg/g)	4.376 ±0.225	16.956 ±3.806	6.017 ±0.935	3.337 ±0.246	12.033 ±1.820	2.730 ±0.404	4.376 ±0.718	2.735 ±0.190	4.376 ±0.511	4.923 ±0.755
Peroxide value (milliequi./kg)	16.202 ±1.854	13.863 ±3.097	15.844 ±1.239	11.875 ±2.644	12.781 ±2.620	15.330 ±3.267	13.676 ±1.150	12.243 ±0.955	9.102 ±0.834	9.900 ±0.877

saponification values of fat and oil (Zhu *et al*., 2006). Saponification value (SV) indicates the presence of high percentage of fatty acids in the oil (Omolara and Dosumu, 2009) and the higher the SV of a WFO, the more the tendency for soap formation, low biodiesel yield and difficulty in separating of products if utilized for biodiesel production. Mean FFA content ranged from 1.952±0.240 to 12.093±2.111 mg/g and WFOs used for frying fish (B2, B3 and B5) contained the highest levels of FFA. The high FFA content (>1% w/w) will cause soap formation during biodiesel production and the separation of the products will be exceedingly difficult which will consequently lead to a low yield of biodiesel product (Crabbe *et al*., 2001). The ranges for physicochemical parameters (FFA, acid and saponification values) indicated that the WFO samples could not be directly converted into biodiesel with appreciable yield via single-step transesterification process but has to be converted via double-step process of esterification and transesterification

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RESULTS OF THE ESTERIFICATION REACTION

The reaction conditions for the esterification reaction of the WFOs and the FFA of the esterified oils are tabulated as shown Table 3.

Table 3. Parameters used for the Esterification Reaction, FFA of Waste Frying Oil and the FFA values of the Esterified Oil

S/N	% FFA values of WFO	Volume of oil (cm^3)	Volume of methanol (cm^3)	Volume of H_2SO_4 (cm^3)	Mixing time (min)	% FFA of esterified oil
B1	3.12	150	31.5	0.75	30 + heat	0.26
B2	12.09	150	31.5	0.75	30	0.96
B3	4.29	150	31.5	0.75	15	2.59
B4	2.38	150	31.5	0.75	30 + heat	0.26
B5	8.58	150	31.5	0.75	30	0.86
B6	1.95	150	31.5	0.75	30 + heat	0.34
B7	3.12	150	31.5	0.75	30 + heat	0.44
B8	1.95	150	31.5	0.75	15	2.34
B9	3.12	150	31.5	0.75	15	2.26
B10	3.51	150	31.5	0.75	30	0.70

The methyl ester-water mixture could not properly separate into two layers for samples B2, B3, B10, B5, B8 and B9 while samples B3, B8 and B9 were very dark before 40 min. However, samples B1, B6, B7 and B4 separated into the upper layer containing the esterified oil and the lower layer containing the un-reacted methanol and water. Waste frying oil contains higher quantity of free fatty acid than the virgin cooking oils (Chhetri *et al*., 2008) and if the amount of free fatty acid in the oil exceeds 3%, then transesterification reaction into biodiesel will not progress even with a homogenous base catalyst (Ahmad, 2010). Hence, esterification is needed as a preliminary step in the process. The results show that the reaction condition of; mixing time 30 min + heat for 5 min was best for reducing the FFA contents of the WFOs since the samples so treated had FFA contents below 0.5% (Table 3). Azhari *et al*., (2013) studied the acid pre-treatment (esterification) steps in which the waste frying oil with the high free fatty acid content was poured into the flask (reactor) and heated. The mixing of methanol with catalyst (sulphuric acid) was also preheated prior to its addition into the reactor. After the reaction was completed, the products were allowed to still for 2 h in a separation funnel and then, the methanol-water fraction at the top layer was removed.

CONCLUSION

Waste frying oil samples were analysed for different parameters and were also esterified to determine their biodiesel feedstock potentials. The oils were used to fry Akara (bean cake), yam, potato, plantain and fish repeatedly for periods ranging from 5 days to 3 weeks. Results indicated that WFOs used for frying fish may not be good feedstocks for biodiesel production since they contained the highest levels of FFA. Only the free fatty acid contents of 4 samples were reduced below 0.5% by esterification while others ranged between 0.70% and 2.59%. Optimum conditions for the esterification reaction was methanol:concentrated sulphuric acid ratio of 42:1; reaction temperature of 60ºC; reaction time of 30 min with 5min application of heat, constant stirring at 200 rpm and methanol:oil ratio of 6:1.

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