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Research Article

Characterization of Condemned Cooking Oil from Refined Palm Olein and Nigerian Beef Tallow and Their Biodiesel Using Gas Chromatography and Physico-Chemical Approach

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Abstract

About 65-80% production costs of biodiesel have been reportedly attributed to the nature of feedstock oils. Fatty acids compositions and physico-chemical parameters of condemned cooking oil (from refined palm olein) and Nigerian beef tallow were studied to ascertain their viabilities as renewable feedstocks for biodiesel production. The Gas Chromatography-Mass Spectrometry (GC-MS) analysis of both feedstock waste oils as performed by GCMS-QP2010 plus, Schimadzu, Japan instrumentrevealedseven different fatty acids components in each samples witha total saturated fatty acid composition of 59.33% in Beef Tallow Oil (BTO) and 71.96% in Condemned Cooking Oil (CCO). The physico-chemical properties of both feedstock oils and their methyl esters as determined by Association of Official Analytical Chemist (AOAC), 1990 standard methods showed1.59 and 0.13 Free Fatty Acid (FFAs) contents in CCO and BTO respectively. Both oils showed improved methyl ester FFAs quality contents of 0.57 in Condemned Cooking Oil Biodiesel(CCOB) and 0.49 in beef tallow biodiesel (BTB) upon transesterification, with viscosity records of 1.30 and 1.48cp in CCOB and BTB respectively.High cetane value records of 71.1 and 68.8 were also obtained from CCOB and BTB respectively.

Keywords: Nigerian beef tallow; Condemned cooking oil; Refined palm olein; Bioenergy; Methyl ester; Transesterification

Abbreviations

CCO: Condemned Cooking Oil; BTO: Beef Tallow Oil; CCOB: Condemned Cooking oil Biodiesel; BTB: Beef Tallow Biodiesel; FFAs: Free Fatty Acids; AOAC: Association of Official Analytical Chemists; GC-MS: Gas Chromatography-Mass Spectrometry

Introduction

Bioenergy generation through biodiesel is among the most viable and safest option of all major emerging industrial research areas of today targeted to address the global increasing energy demand as a result of high population and industrialization growth rate. Fossil fuel has been the sole single source of energy supply to these units due to its easy usability, availability, and cost effectiveness [3]. With the resultant high degrading rate to our ecosystem as well as increased prices of this fossil fuel. Beside many advantages of biodiesel over diesel fuel - renewability, ready availability, portability, lower sulfur and aromatic content, higher efficiency, higher cetane number, better emission profile and safer handling [2]. Its high cost of production remains the obvious reason for its limited commercial application. With the feedstocks cost contribution of about 65% - 80% of the biofuel total cost, several efforts have been carried out in order to reduce biodiesel prices, essentially by altering feedstock sources [4-6].

Condemned Cooking Oil from refined palm olein (CCO) and Beef Tallow Oil (BTO)have been studied as among such materials [3]. Considering their present increasing availability, low sulphur content, ease of storage and good engine performance potentials of their biodiesel products through transesterification processes. With the present world meat, production of about 237.7 million tons in 2010, from which 42.7%, 33.4%, 23.9% corresponds to respectively pork, poultry, and beef [7]. Larger amount of residues from animal processing-plants (tallow inclusive) has been generated with intensive livestock production. Condemned Cooking Vegetable Oil (CCO) on the other hand is a by-product from hotels, fast food restaurants, and shops selling fritter and by-product of an operating vegetable oil refinery [8]. For serving better quality food, these waste oils which has been on increase due to present global change in eating pattern are usually thrown away as wastewithout any treatment [9,12]. Within agroindustrial residues, these waste lipid sources may be used as feedstock to biodiesel supply, helping to solve inappropriate environmental disposal, besides contributing to energy demand.

Biodiesel production using CCO and BTO has not been given much attention it deserved in most of our literatures due to some drawbacks such as increased Free Fatty Acids (FFAs), moisture contents and viscosity value due to the hydrolysis and oxidation as in the case with cooking oil during the frying processes.The slight adjustment in these condemned oils parameters had been the contending challenges during the transesterification processes of their biodiesel production.

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Variousimprovements in the pretreatments techniques of feedstocks characterized with high FFAs and other impurities before the transestrification reaction to overcome these drawbacks had been reported. For instance, use of acidic ion exchange resins in a packed tower for esterification of FFAs in waste cooking oil [10]. Steam distillation [11] sterification by acid catalysis [13] and use of iodine as a catalyst [14]. have been well reported. Of all these methods, the use of acids (mainly H_2SO_4) is widely recommended mostly due to its cost effectiveness and ease of operation processes [15]. As seen in reaction equation 1.

RCOOH + CH_3OH H_2SO_4RCOOH_3+ H_2O (1)

The importance of the above pretreatment reaction for feedstocks characterized with high FFAs is to prevent the unwanted saponification process of the reaction equation 2 with the predominant formation of soap.

R –COOH + CH_3OHNaOHR_1COONa + H_2O (2)

FFA AlcoholSoap Water,

The most common way to produce biodiesel is by transesterification which involves a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol, as can be seen in reaction [3,4].

With these improvements, biodiesel can be available as good alternative to fuel and can be used by blending up to 20% with fossil diesel without any modification of diesel engines. Production of cheaper biodieselusing animal fats (beef tallow) and condemned cooking palm olein with sodium hydroxide (NaOH) base catalyst and short chained methanol as alcohol can be very interesting to be studied and developed further.

Materials and Methods

Material and Biomass Sampling

Materials: All chemicals used were of analytical grade from Merck, Germany with 99.5 % purity.

Biomass and Sampling: Condemned Cooking Oil (CCO) as a result of repeated frying for production of pea nuts using the edible refined palm olein vegetable oil was collected fresh from Nkky Peanuts and Confectionaries Limited Onitsha, Anambra State on their bid for disposal after a long use due to high Free Fatty Acid (FFA) content while the animal fat/Beef Tallow (BTO) were collected from Trans-Amadi beef slaughter house Port Harcourt, Rivers State fresh on the spot from the cow slaughtered and butchered that same day.

The CCO as collected hot from the food industry source was allowed to cool for one day inside the aluminum frying pan used for the frying, and then filtered with filter paper to remove all material particles from the oil. The oil sample was then stored and transported in a black 10 liters plastic container to avoid oxidation by sunlight.

The animal fat was collected from Trans-Amadi beef slaughter house Port Harcourt, Rivers State. The fatty tissue was collected fresh on the spot from the cow slaughtered and butchered that day. A known weight (6kg) fatty tissues and 10% by volume of hot water were boiled in a stainless pot up to a temperature of about 85 ^{0}C for about one hour for the fat to be released by temperature/cell rupture in order to essentially separate its four components, viz. water, protein, bones and fat. The tissue was allowed to cool slightly to a temperature of about 80 ^{0}C and the tallow oil layer on top was carefully decanted and filtered. The oil was further heated alone to release all water contained in the oil and filtered again after further cooling to a temperature of about 50 ^{0}C for further removal of any persistent solid particles. The Beef Tallow (BTO) was then stored in a black 10 liters container.

Physicochemical characterization of CCO and BTO: Prior to the biodiesel production, the properties of the feedstock oils were determined in accordance with Association of Official Analytical Chemists methods: (the acid value by AOAC Ca5a-40, saponification value by AOAC 920:160; iodine value by AOAC 920:158 and peroxide value by AOAC 965.33) while the viscosity was determined by using Oswald viscometer apparatus, the density by using density bottle, moisture content by the Rotary Evaporator Oven (BTOV 1423), the ash content by heating to dryness in Veisfar Muffle furnance and the refractive index by using Abbe Refractometer (Model: WAY-25, Search tech. Instruments).

Sample pre-treatment: Before the base transesterification of CCO and BTO was carried out, acid esterification of CCO was performed to reduce its high FFAs contents as revealed from the physico-chemical analysis. This was done using 200 ml of methanol mixed with 0.5% of sulphuric acid inside a 250 ml conical flask for the acid esterification process. The conical Flask was inserted into a water bath at 50 °C. The mixture was later added to 1000 ml warmed (preheated) CCO inside a 2000 ml conical flask and placed on magnetic stirrer with heater. Heating and stirring is continued for 40-60 min at atmospheric pressure. On completion of this acid esterification reaction, the product is poured into a separating funnel for separation of the excess alcohol with sulphuric acid and impurities on the top surface and the lower layer product taken out for further processing (alkaline esterification).

Methods

Preparation of Sodium Methoxide: This was prepared by adding 5 g of NaOH to 300 ml of methanol (2% weight of the oil) and stirred at 300 rpm until it dissolved completely for about two minutes in the reaction vessel.

Pre heating of feedstock oils: Both BTO and acid esterified CCO were heated fairly to 80 ^{0}C for 30 minutes using Gallenkamp magnetic stirrer thermostat hot plate (WeissTechnik England) to reduce the viscosity of the oils.

Base transesterification: The BTO and acid esterified CCO were subjected to base transesterifiction out in a Sohxlet extractor fitted with thermo-regulator heater and stirrer. Four different runs of experiments of varying molar ratio of methanol to oil (3:1, 4:1, 5:1 and 6:1) were performed using 50 ml of the respective feedstock oils for each run against calculated equivalent ml of the NaOH (catalyst) and methanol (sodium methoxide). Each of the reaction runs was fixed at the temperature of 75°C, reaction time of 50 minutes and steering speed of 400 RPM. 50 ml of the oil was first measured into the flask and was heated to the specified temperature. The Sodium methoxide was then poured into the flask containing the oil and was immediately covered. The temperature was maintained for the specified time at constant agitation.

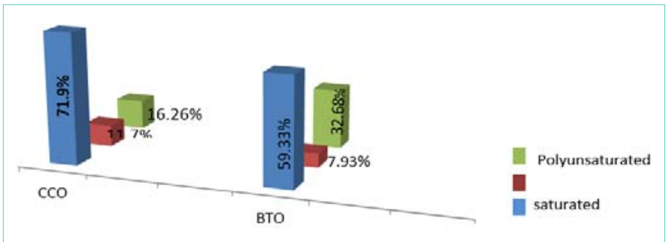

Table 1: Fatty Acid Profile of CCO, BTO.

Separation of biodiesel: The base transesterifiction reaction was stopped at specified time and products allowed to settle for 24hours into two layers inside a separating funnel by gravity. The lower layer containing impurities and glycerol is drawn off while the ester that remained is the biodiesel.

Biodiesel purification: The methyl esters were washed to remove the entrained impurities and glycerol by washing with Warm distilled water at 50°C. The warm water (10% by volume) was sprayed over the surface of the methyl esters and stirred vigorously to allow draining through the bottom of the separating funnel. This was carried out five times until a clear biodiesel was obtained.

To further remove moisture from the biodiesel sample, anhydrous $CaCl_2$ was added to it and heated gently at 50 °C. The anhydrous $CaCl_2$ was later separated from the biodiesel to obtain a clean dry biodiesel. The volumes of the biodiesels (beef tallow biodiesel BTB and Condemned Cooking Oil Biodiesel CCOB) as obtained from each sample were determined and their percentage yield were calculated.

Biodiesel characterization and Physico-chemical analysis: The properties of the synthesized biodiesel were analyzed and determined using ASTM standard,results were shown in Table 2.

Results and Discussions

The chromatographic analysis

The fatty acid compositional analysis of the oil feedstocks (CCO and BTO) are shown in Tables 1 as analyzed by gas chromatography mass-spectrometry (GC-MS) usingGCMS-QP2010 plus, Schimadzu, Japan instrument. It is obvious that the feedstock samples showed most abundant of saturated acid (71.96%), monounsaturated acid (11.75%) and polyunsaturated acid (16.26%), for CCO. The BTO sample had lauric acid (24.51%), oleic acid (7.93%) and osbond acid (22.88%) as the abundant saturated, monounsaturated and polyunsaturated distribution respectively totaling 59.33%, 7.93% and 32.68% as total saturated, monounsaturated and polyunsaturated fatty acids compositions as shown in Figure 1. This indication of higher saturation of fatty acid compositions for both feedstocks oil agrees with 54.6% for beef tallow by [16] hence the biodiesel products of both feedstock samples (and mostly BTB)are expected to have lower thermal efficiency and viscosity, with lower emission of hydrocarbons, carbon monoxide and smoke.However no non-fatty acids were dictated in both oils as against 2.3% by [8] in beef tallow using same GC-MS.

The Physico-chemical analysis

The physico-chemical properties of feedstocks oil (CCO and BTO) and the fuel related properties of CCOB and BTB as obtained at the optimum conditions are shown in Tables 2. Of particular interest is the changes observed in the properties of the feedstocks oil as it went through the transestrification processes. For instance, from the table, there is a sharp reduction in the Free Fatty Acids (FFAs) content of CCO from 1.59 in the oil feedstock to 0.57 in the oil biodiesel most likely due to the esterification reaction that precedes the transestrification, while the slight increase in that of beef tallow from feedstock 0.13 to product 0.49 could be as a result of competing side reactions such as hydrolysis of triglycerides to free fatty acids. However both results are within ASTMD standard limits as higher acid content can cause low conversion of biodiesel products as well as severe corrosion in fuel supply system of an engine.

The cetane number which is an important parameter for the determination of diesel quality that influences engine characteristics

Table 1: Fatty Acid Profile of CCO, BTO.

Fatty Acid	Structure	Formula	Molecular Wt (g/mol)	Composition (%)	
				CCO	BTO
Lauric	C12:0	$C_{12}H_{24}O_2$	200.32	15.019	24.512
Myristic	C14:0	$C_{14}H_{28}O_2$	228.38	38.56	19.343
Palmitic	C16:0	$C_{16}H_{32}O_2$	256.43	-	-
Stearic	C18:0	$C_{18}H_{36}O_2$	284.48	18.395	15.48
Oleic	C18:1	$C_{18}H_{34}O_2$	282.48	11.756	7.93
α-linoleic	C18:2	$C_{18}H_{32}O_2$	280.45	5.95	3.96
γ-linoleic	C18:2	$C_{18}H_{32}O_2$	282.48	-	-
α-linolenic	C18:3	$C_{18}H_{30}O_2$	278.44	-	-
Arachidonic	C20:4	$C_{20}H_{32}O_2$	304.51	6.936	5.843
Eicosapentaenoic	C20:5	$C_{20}H_{32}O_2$	302.5	3.38	-
Osbond	C20:5	$C_{22}H_{34}O_2$	330.5	-	22.883

Table 2: Physico-chemical properties of CCO, BTO, CCOB and BTB as compared to standard ASTM/DIN.

Properties	CCO	BTO	CCOB	BTB	CD	ASTM	ASTM	DIN
						D9751	D6751	**14214**
Acid value (MgKOH/g)	3.18	0.26	1.14	0.97	0	0.062	0.5	0.5
Specific gravity (m/v)	0.91	0.871	0.855		0.84	0.825	850	880
Ash Content (%)	0.08	0.08	0.06	0.1	0.09	0.01	0.02	0.02
Moisture Content (%)	0	0	0.05	0.06	0	-	-	-
Viscosity (cp)	1.14	36.4	1.3	1.48	1.8	2.6	1.9-6.0	3.5-5
Calorific value (kj/kg)	-	-	32.98	33.18	40.8	42-46	-	35
Cloud Point (°C)	25	48	32.98	-4	-12	-20	-3 to 12	0
Pour Point (°C)	-	-	-8	-10	-20	-35	-15 to -16	-
Flash Point (°C)	110	136	-13	82	180	60-80	100-170	120
Saponification Value	258.2	202.6	75	162	-	-	-	
Iodine Value	10.5	48	186.9	34.5	-	42-46	-	120MAX
Cetane Number	61.91	58.64	71.1	68.77	43.7	40-55	47Min	51Min
Free Fatty Acids as Oleic (%)	1.59	0.13	0.57	0.49	0	0.31	0.25	0.25
Smoke Point (°C)	105	130	71	77	180	-	-	-
Sulphur Content (%)	0.07	0.1	0.05	0.09	0.02	-	-	0

such ascombustion, stability, noise, white smoke, carbon monoxide and hydrocarbon emission also recorded appreciable value higher than fossil diesels and both 47 and 51 specified minimum standard limits by ASTMD 6751 and DIN 14214 respectively. This is mostly due to their higher C18 content which placed these biodiesel productsas good alternative biofuels.

There is a lower flash point record of 75 and 82 for CCOB and BTB respectively as against 156.7 by [5] and thestandard limits of 120 byDIN 14214. A good blending can help to improve thetemperature at which it will spontaneously ignite without the presenceof flame orspark thereby aiding their safer handling, transportation and storage with a reduced fire risk.

Both the viscosity and ability for the fuel injection and spray atomization of engine performance particularly at low temperature when the increase in viscosity is expected to affect the fluidity of the fuel showed good record potentials. The high viscosity of 36.4 cp in beef tallow oil when compared to theestablished ASTMD 9751 standard limit was drastically reduced to 1.48cp through the transesterification reaction as the higher viscosity component glycerol is removed and hence the product has a very good improved viscosity close to the 1.8cp result record inconventional fossil fuels and the maximum allowable limit of 2.6 cp according to ASTM D 9751 of which both CCOB and BTB are within the range and totally miscible with mineral diesel in any proportion. Iodine value (grams of iodine per 100 grams of oil) and viscosity are important parametersfor vegetable oils and their biodiesel products, as they indicate the amount of unsaturations in their structure. The higher the number of double bonds, the higher is the Iodine value that also influences fuel oxidation and the type of aging products. The iodine value of CCO is 10.5mgI^2/g as against 48.05mgI^2/g discovered in BTO. This higher iodine value in BTO accounts for the higher unsaturation quality of the latter than the former. According to [2], several samples of biodiesel obtained from waste tallows have iodine number lower than standard limit, just as recorded in this research study of BTB as well as in CCOB.

Other parameters such as cloud point, saponification, iodine and calorific values, moisture and ash contents of the biodiesel compared well with the American standard (ASTMD 6751) and European specification (DIN 14214).

Conclusion

Both condemned cooking oil (from refined palm olein) and beef tallow oil showed higher compositions of unsaturated fatty acids components in their structures. The two-steps transesterification process showed great effectiveness in the conversion of high acid value of CCO to quality biodiesel with lower acid value. The physico-chemical properties of both oils and their biodiesels satisfied both ASTMD 6751 and DIN 14214 limits standards. Both GC-MS and physic-chemical analysis of both biodiesels products from CCO and BTO showed satisfactory evidence supporting both CCOB and BTB of possessing great potential for use as alternative energy generating fuel and good means for waste managements and control.

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