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THE PHYSICOCHEMICAL ANALYSIS OF BIODIESEL PRODUCED FROM AFRICAN SWEET ORANGE (*Citrus Sinensis*) SEEDS OIL

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Abstract:

The research presents experimental study and investigation on the production of biodiesel from African sweet orange seeds oil. The seeds were obtained, sundried, crushed and weighed. Chemical extraction method was used to extract oil from the crushed seeds using soxhlet extractor with n-hexane as a solvent. The physicochemical properties of the oil determined were; flash 1510C, fire point 1730C, acid value 82%, product percentage yield 40% and specific gravity 0.920 at 150C. The production of Biodiesel was carried out through transesterification process from the extracted oil using methanol as catalyst. The results of the physicochemical properties of the produced biodiesel are; Cloud point 60C, Pour point 20C, Flash point 1400C, Density 0.86g/cm and Kinematic viscosity 1.938 mm2/s. The effect of methanol on the yielding of biodiesel at constant ratios of oil and catalyst was determined to be 68% at 10ml, 77% at 9ml and 72% at 7ml. The results obtained are in conformity when compared with ASTM standard D6571 and imply that the African sweet orange seeds oil can be used to produce biodiesel.

Keywords: Physicochemical; Biodiesel; Sweet Orange; Transesterification; Oil; Characterization.

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1. Introduction

The increase in the global energy demand particularly those that are petroleum based, coupled with the depletion of the world's petroleum reserves and increased interest in saving the environment from pollution, geared up interest in the search for alternative sources of petroleum-based fuel, including diesel and gasoline fuels. The search for a viable, sustainable and preferably, renewable energy source led to the renewed interest in biofuels. First generation biofuels where produced primarily from agricultural crops grown for food and animal feed purposes and led to unhealthy competition [1]. The second-generation biofuels addressed the problem of competition with food crops primarily produced for consumption using non edible oil like castor oil and neem oil, as source material for fuel production.

The African sweet orange fruit is a specialized berry known as Citrus Sinensis, which belongs to the race variety sinensis, the fruit size varies base on the plant cultivation that has been produced by selective breeding and crop load, but mostly are measure between 2.5–4 inches in diameter. The shape of the fruit is spherical to oblong (having rectangular shape), with a peel thickness between that of grape fruit and tangerine, and is either smooth or roughly pebbly. It is usually very closely adhered to the flesh of the fruit. Its colour tints from green to light orange, depending on the cultivation variety used in the production of the orange fruit. The presence and amount of seed, depends also on cultivation variety.

Vegetable oils are promising feed stocks for biodiesel production since they are renewable in nature, and can be produced on a large scale. Vegetable oils include edible and non-edible oils. More than 95% of biodiesel production feed stocks come from edible oils, since they are mainly produced in many regions of the world and the properties of biodiesel produced from these oils are very much suitable as substitute for diesel fuel. Some of the oils used in biodiesel production include; soybean oil, palm oil, groundnut oil, palm kernel oil, neem seed oil, castor oil etc. Some of the approaches adopted for processing oils with high moisture and/or free fatty acid contents include; the use of supercritical methanol to convert the oil at high temperature [2], a simultaneous esterification/transesterification of the FFAs and triglyceride contents of the oil using acid catalyst, and a two-step sulfuric acid-catalyzed pre-esterification before base-catalyzed transesterification [3].

Biodiesel is a non-toxic, biodegradable, non-flammable diesel product which has fewer emissions than the conventional petro-diesel [4]. Biodiesel is a renewable fuel consisting of fatty acid methyl esters (FAME) derived through transesterification of vegetable oils, animal fat and also recycled oil from the food industry with methanol, it must meet the special requirements such as the ASTM and the European standards.

Biodiesel is recognized as "green fuel" with several advantages including: safety in operation, non-toxicity and biodegradability compared to petroleum diesel. It is oxygenated and essentially free of Sulphur and aromatics making it a cleaner burning fuel with reduced emission of SOx, CO, un-burnt hydrocarbons and particulate matter [5].
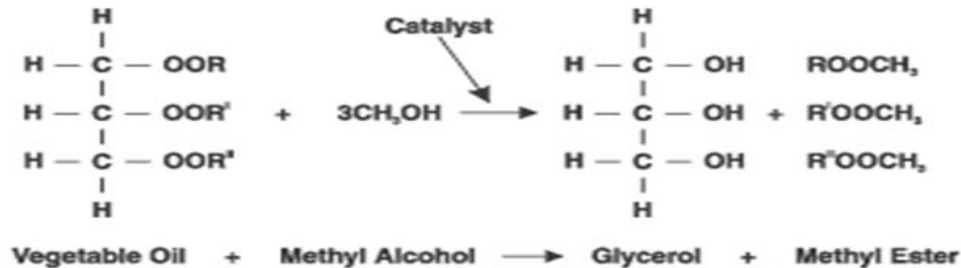
A number of studies have shown that triglycerides hold promise as alternative diesel engine fuel [6]. The high viscosity, carbon deposits, acid composition, free fatty acid content of such oils, gum formation due to oxidation and polymerization during storage and combustion, oil ring sticking, lubricating problems, cooking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices, thickening and gelling of the lubricating oil as a result of contamination by vegetable oils, lower volatilities content which causes formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics are some of the more obvious problems [7].

Consequently, considerable effort has gone into developing vegetable oil derivatives that approximate the properties and performance of hydrocarbon-based diesel fuels. Problems encountered in substituting triglycerides for diesel fuels are mostly associated with high viscosity, low volatility and polyunsaturated character [7]. The following processes have been used in attempts to overcome these drawbacks and allow vegetable oils and oil waste to be utilized as a

viable alternative fuel; Pyrolysis, Microemulsions, Dilution, Transesterification, Acid Catalyzed Process, Base Catalyzed Process and Enzymatic Process.
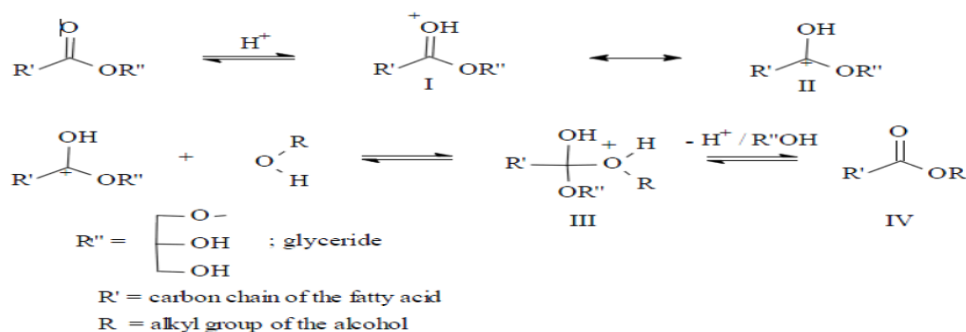
Transesterification

Transesterification also called alcoholysis is the displacement of alcohol from an ester by another alcohol [8]. It is the most used method of conversion and refers to the reaction of a vegetable oil or animal fat with an alcohol in the presence of a catalyst to produce alkyl esters and glycerol. The alkyl esters are what are called biodiesel.

Acid Catalyzed Process

The transesterification process is catalyzed by Bronsted acids, preferably by sulphonic and sulphuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 °C and more than 3 hr to reach complete conversion.
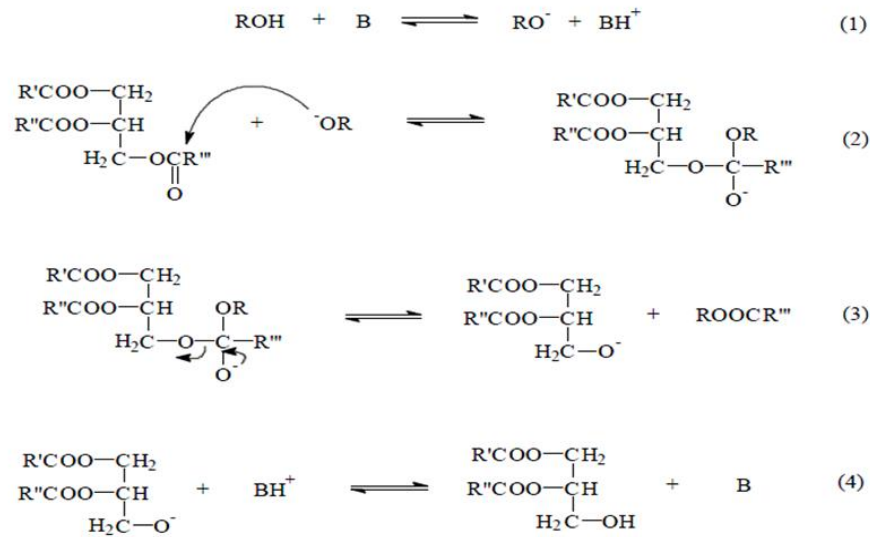
[6] Showed that the methanolysis of soybean oil, in the presence of 1 mol% of H2SO4, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil. The alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification. An excess of the alcohol favours the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process. The mechanism of the acid-catalyzed transesterification of vegetable oils is shown below for a monoglyceride. However, it can be extended to di- and triglycerides [9].

Base Catalyzed Process

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reactions. Due to the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favour base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oils is as shown [9].

$$ROH + B \rightleftharpoons RO^- + BH^+ \qquad (1)$$

Fuel Quality

The primary criterion for biodiesel quality is the adherence to the appropriate standard. The standard utilized in this project is the ASTM D6751-02 standard specification biodiesel fuel (B100) blend for distillate fuels.

The table 1 shows the property values for a mixture of methyl esters to be considered. When these limits are met, the biodiesels can be used in most diesel engines without modifications while maintaining the engine's durability and reliability.

Table 1: ASTM 6751-02 Biodiesel Specification

Property	Method	Limit	Unit
Flash point, closed cup.	D93	130 min	^{0}C
Water and sediment	D2709	0.050 max	%Vol
Kinematic Viscosity	D445	1.9-6.0	mm^2/s
Sulfated Ash	D874	0.020 max	Wt.%
Total sulfur	D5453	0.05 max	Wt.%
Copper Strip Corrosion	D130	No.3 max	
Cetane Number	D613	47 min	
Cloud Point	D2500	Report to customer	^{0}C
Carbon Residue	D4530	0.05 max	Wt.%
Acid Number	D664	0.8 max	Mg KOH/g
Free Glycerine	D6584	0.02 max	Wt.%
Total Glycerine	D6584	0.24 max	Wt.%
Phosphorus	D4951	0.001 max	Ppm
Vacuum Distillation end Point	D1160	360 max	

Specification for Biodiesel (B100) – ASTM D6751-07b, March 2007

2. Materials and Method

2.1. Materials and Equipment

N-hexane, Potassium hydroxide, Methanol, Methanolic potassium hydroxide, Crusher, Beaker, Glass rod, Soxhlet extractor, Conical flask, Rotary evaporator, Heating mantle, Oven, Separating, funnel, Filter paper, Water bath and Weighing Balance.

2.2. Sample Collection and Preparation

The African sweet orange fruit (Citrus Sinensis) seeds were procured from discards of fruits at Muda lawan Market Bauchi, Nigeria. After collection, the seeds were sun dried to remove moisture content, de-coated and were crushed using a crusher in order to be prepared for the extraction. N-Hexane, potassium hydroxide, Methanol, Filter paper were purchased from Department of Chemistry, Abubakar Tafawa Balewa University (ATBU) Bauchi.

2.3. Oil Extraction

The oil was extracted from the seeds using n-hexane as the solvent in a Soxhlet extractor. The crushed African sweet orange seed sample was weighed and placed in the soxhlet extraction chamber. Normal n-hexane was poured into the conical flask; the soxhlet extractor was connected to the power source so as to extract the oil from the seed. The n-hexane in the flask was heated to its boiling point until it starts evaporating. The condensation chamber above the extraction chamber condenses the n-hexane which in turn pours on the sample in the extraction chamber. The final mixture was allowed to stand overnight for proper extraction of the oil. The solvent-oil mixture was poured into round bottom flask and the solvent was dissolved off at 450C using a rotary evaporator.

2.4. Base Catalyzed Transesterification

The transesterification reaction was performed in a lab scale biodiesel reactor consisted of 1 L round-bottomed flask, fitted with mechanical stirrer, thermostat and condensation systems. The African sweet orange seed oil was preheated to 400C on a heating mantle before starting the reaction. Freshly prepared methanolic solution of KOH was separately added to the oil and mixed. In order to ensure complete transformation of the African sweet orange seed oil into fatty acid methyl esters (FAMEs), the experiment was conducted for 45 min. As soon as the reaction was completed, the contents of the reactor were transferred into a separating funnel and allowed to cool and equilibrate for the partitioning of two distinct phases. Of the two separated phases, the upper layer consisted of methyl esters with small amounts of impurities such as residual alcohol, glycerol and partial glycerides, while the lower phase contained glycerol with other materials such as unused methanol, catalyst, soaps derived during the reaction, some suspended methyl esters and partial glycerides. The upper layer consisting of methyl esters was collected and further purified by distilling off residual methanol at 650C (external bath temperature). The traces of the remaining catalyst, methanol and glycerol were removed by repeated washings with distilled water. Any left over water was then removed by drying esters with sodium chloride. The process was repeated 3 times to determine the ratio of oil/methanol which gives the high yield.

2.5. Characterization of the Oil

The physical and chemical properties of the extracted oil and the biodiesel produced were carried out in the chemistry laboratory of Abubakar Tafawa Balewa University, Bauchi.

Physical Properties
The physical properties determined are the kinematic viscosity, density, Flash point, pour point and cloud point using ASTM: D445, D1298, D93, D97 and D2500 standard test procedure respectively.

Determination of the Cloud Point
A portion of the biodiesel was poured into a test tube and the mercury point of the thermometer with calibration below 1 0C was inserted in the test tube. The set up was inserted in a beaker containing ice. The biodiesel was observed closely. After some time, the biodiesel was observed to form a cloud of gel. The temperature was taken as the cloud point was recorded.

Determination of the Pour Point
The same set up as in the cloud point test was immersed in the ice and left to solidify. When the solidification was confirmed, the test tube was removed and tilted and closely observed till it started to flow. The instant temperature taken on observing the flow of solidified biodiesel was recorded as the pour point temperature.

Determination of the Flash Point
Another portion of the biodiesel was poured into a flask with a branch opening and a cork with an opening to allow the entrance of the thermometer was fitted into the flask and the thermometer put in place. The tip of the thermometer was immersed in such a way that it does not touch the bottom of the flask. This was done at every rise in temperature to increase the precision of valve. The flash point temperature was taken to be the temperature at which the fume got ignited by the lighted match stick. The value was recorded.

Kinematic Viscosity Test
The viscosity of biodiesel taken using the old oil glass viscometer, using the mouth the biodiesel in the lower bulb was sucked to a point above the top white ring mark which of the second bulb of the old glass viscometer. The biodiesel meniscus was adjusted by releasing the thumb till it is at the same level with white ring mark on top of viscometer second bulb. The biodiesel was allowed to flow and a stop watch was used to take the time interval of the flow. The time for the biodiesel to pass the second ring mark was recorded. Similar procedure was repeated for water and the time recorded. The viscometer is calculated from the results obtained.

Determination of Density
To determine the density, the mass of an empty container was weighed using an electric weighing balance and the mass of the empty container was recorded. 5 ml of the produced biodiesel was poured into the already weighed container and weighed again with the electric weighing balance. The mass of the empty container was subtracted from the mass of the container plus biodiesel so as to obtain the mass of the biodiesel. The density was then determined by dividing the mass of the biodiesel by the volume.

Chemical Properties
The chemical properties were determined using the standard test procedure as follows:

Determination of Saponification Value (S.V.)
The method that was used for the determination of the saponification value is that of the British standards institute 1995. Two grams of oil was placed in a 250 ml conical flask and 25 ml of 0.5 M methanol potassium hydroxide solution added.

A reflux condenser was attached and the flask content refluxed for 30 minutes on a water bath with continuous swirling until it simmered. The excess potassium hydroxide was titrated with 0.5 M hydrochloric acid using phenolphthalein indicator while still hot. A blank determination was carried out under the same condition and the S.V. calculated.

$$S.V. = \frac{(B - R) \times 28.05}{Weight\ of\ Sample} \qquad (1)$$

Where,
B = Blank titre
R = Real titre value

Peroxide Value (P.V.)
The method used is that of British standards institute No. 684. One gram of oil was placed in a 250 ml conical flask and 30 ml glacial acetic acid/chloroform (3.2 v/v) added. The contents were shaken until they dissolved. Saturated potassium iodide solution (1 ml) was added followed by the addition of 0.5 ml starch indicator solution. This was titrated with 0.1 m Na2S2O3 until the dark blue color just disappeared. A blank determination was carried out under the same condition and the P.V. calculated.

$$P.V. = (R \times B) \times \frac{Molarity\ of\ Na_2S_2O_3}{Weight\ of\ Sample} \qquad (2)$$

Where,
R = Real titre value determined
B = Blank titre value

Determination of Iodine Value (I.V.)
One gram of oil was placed in a 250 ml conical flask flowed by 30 ml of Hanus solution and the flask stopped, and the contents mixed and placed in the drawer for exactly 30 minutes. Potassium iodide solution (10 ml of 15% w/v) was added to the flask washing down any iodide that may be found on the stopper. This was titrated against 0.14 m Na2S2O3 until the solution became light yellow. Starch indicator (1%, 2 ml) was added and the titration continued until the blue colors just disappeared. A blank determination was carried out under the same conditions. The titre value was recorded and used to calculate the I.V.

$$I.V. = \frac{(B - R) \times Molarity\ of\ Na_2S_2O_3 \times 12.69}{Weight\ of\ Sample} \qquad (3)$$

Where,
B = Blank titre value
R = Titre value of real determinants

Cetane Number (CN)

The calculated saponification value (SV) and iodine value (IV) were used to calculate the cetane number (CN) which is the ability of fatty acid methyl esters as a fuel to ignite quickly after being injected. Empirical formula was proposed by [11] and was used in the work. The higher its value, the better is its ignition quality. This is one of the most important parameter which is considered during the selection of fatty acid methyl esters for use as a biodiesel. The cetane number was determined using the relation provided by [12].

$$Cetane\ Number\ (CN) = 46.3 + \frac{5458}{SV - 0.225 \times IV} \tag{4}$$

3. Results and Discussions

3.1. Physicochemical Properties of the Oil

The oil was extracted chemically from the African sweet orange seeds, in which n-hexane was used as solvent because it is the solvent that gives the highest yielding from the literature review. The biodiesel produced was characterized to determine its physicochemical properties which are shown in table 2.

Table 2: Physicochemical Properties of the Biodiesel

Test	Result
Specific Gravity	0.920 at 15^0C
Smoke Point	149^0C
Flash Point	151^0C
Fire Point	173^0C
Product % yield	40%
Acid Value	82%
Saponification Value	292
Iodine Value	108
Peroxide Value	92.84

The biodiesel was produced using methanol and potassium hydroxide as a catalyst as shown in table 3. Three different ratios of oil/methanol/catalyst were used in the production of the biodiesel to check for the effect of methanol that gives the best yielding while the temperature, time and the catalyst are kept constant. The ratios of oil /methanol/catalyst used were 1:10:0.3, 1:7:0.3 and 1:9:0.3. It was discovered that for the three ratios used, 1:9:0.3 has the highest percentage yield.

Table 3: Determination of the Effect of Methanol on the Yielding of Biodiesel at Constant Ratios of Oil and Catalyst

	Oil (ml)	KOH (g)	Methanol (ml)	% Yield (%)	Temp. (^{0}C)	Time (mins)
Ratio	1	0.3	10	68	45	40
Ratio	1	0.3	9	77	45	40
Ratio	1	0.3	7	72	45	40

The physicochemical properties of the oil were determined. These are; flash point, which is 1510C as shown in table 2 and within the range provided by ASTM standard as obtained in table 4. The fire point, smoke point and percentage yield of oil is determined to 1730C, 1490C and 40% respectively. The specific gravity obtained at 150C is 0.92; this is in agreement with the ASTM D6751 values. The flash point, saponification value and iodine value determined was 1510C, 292 and 108 respectively, and is within the range obtained by standard values as shown in table 4. This shows that the oil can be used to produce biodiesel according to ASTM standard which says that oil must have a flash point of 130 0C to 1700C (from table 4), fire point of 140 0C, and yielding of more than 30%.

Table 4: Results for the Physicochemical Properties of biodiesel produced from African Sweet Orange (Citrus Sinensis) Seeds

Fuel property	Diesel	Biodiesel	Units
Fuel Standard	ASTM D975	ASTM D6751	
Lower Heating Value	~129,050	~118,170	Btu/gal
Kinematic Viscosity @ 40^0C	1.3 – 4.1	1.9 – 6.0	mm^2/s
Specific Gravity @ 60^0C	0.85	0.88	kg/l
Density	7.079	0.88	g/cm^3
Water and Sediment	0.05 max	0.05 max	% volume
Carbon	87	77	wt. %
Hydrogen	13	12	wt. %
Oxygen	0	11	
Sulfur	0.0015	0.0 to 0.0024	wt. %
Boiling Point	180 to 340	315 to 350	^{0}C
Flash Point	60 to 80	130 to 170	^{0}C
Cloud Point	-15 to 5	-3 to 12	^{0}C
Pour Point	-35 to -15	-15 to 10	^{0}C
Cetane Number	40 to 55	47 to 65	
Lubricity SLBOCLE	2,000 to 5,000	>7,000	Grams
Lubricity HFRR	300 to 600	<300	Microns

It was shown that the properties determined from the biodiesel were within the range of the properties of biodiesel required according to ASTM standard as shown in the tables 2 and 4.

4. Conclusion

This study has shown that most of the properties evaluated from the biodiesel produced conform to the ASTM standard values. It can be concluded from this study that the biodiesel produced from African sweet orange can be among the potential replacements of fossil fuel while the production and effective usage of biodiesel will help to reduce the cost of protecting the atmosphere from the hazards in using fossil fuels, waste from the environment and hence will boost the economy of the country.

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