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Heterogeneous Transesterification of Extracted Oil from Sweet Orange (*Citrus Sinensis*) Seed using Modified Eggshell as Catalyst

Alam, Nadoo Dorathy[1]; Weor, Torna Timothy[1]; Okopi, Ochaba Stephen[1]; Olawuyi, Oluwashola Ajagbe[2] and *Leke, Luter[1,3]

[1]Department of Chemistry, Benue State University, Makurdi
[2]The Nigeria Defence Academy, Kaduna, Kaduna State
[3]Center for Food Technology & Research, Benue State University, Makurdi
***Correspondence Email:** l.leke@bsum.edu.ng

ABSTRACT

The environmentally sustainable production of biodiesel is important for providing a renewable alternative transportation fuel and a fuel for diesel engines. This research evaluates the use of low-cost catalysts derived from waste materials (eggshell) for converting triglycerides in seeds oil (sweet orange seed oil) into biodiesel composed of fatty acid methyl esters. The oil extracted was first characterised for its physicochemical parameters *viz*; yield (38.88 %), moisture content (6.50 %), relative density (0.89 g/cm^3), specific gravity (0.90), refractive index (1.46), iodine value (55.80 gI_2/100 g), acid value (5.64 mgKOH/g), free fatty acid (2.82 mgKOH/g), saponification value (179.90 mgKOH/g), and viscosity (0.04 Pa. S). The parameters were within the AOAC (1990) standard except for moisture content and saponification values which were slightly below while acid and free fatty acid values were slightly higher than the AOAC (1990) standard. Further treatment of the oil for suitability for transesterification for biodiesel production was carried out. The GC-MS analysis of the oil shows that triglycerides and other organic functional groups were evident. The eggshells were calcined (750°C) and modified with H_2SO_4 (20 %) to improve its surface for catalytic activity. Transesterification conditions were; oil to methanol ratio of 1:9, reaction time of 2 h and temperature of 65°C while the catalyst dosage was 10 %. The physicochemical parameters of the biodiesel were obtained to be; yield (39.03 %), refractive index (1.47), acid value (1.12 mgKOH/g) and free fatty acid (0.56 mgKOH/g) were all within the accepted range specified by American Society for Testing and Materials, (ASTMD6751). The GC-MS result of the separated biodiesel showed different methyl esters implying that, there was conversion of the triglycerides to methyl esters. Thus, orange seeds and eggshells can be harnessed for biodiesel production.

Keywords: Biodiesel, Heterogeneous catalyst, Seed oil, Sweet orange, Transesterification

INTRODUCTION

Energy is one of the most important resources for humanity and its development. The demand for energy has increased due to rise in population and human activities which include agriculture, industrialization and transportation, (Agarwal, 2007). These have resulted to a strong dependence of everyday life and activities on non-renewable energy sources (fossil fuels) as the primary sources of energy. The burning of these non-renewable energy sources (fossil fuels) produces emissions that contribute to air pollution, climate change, acidic rain and global warming (Zhou and Thomson, 2009). To meet this rising energy demand and conserve petroleum reserves, the search for alternative effective, efficient and low-cost energy sources for consistent use is very important. These energy sources ought to be renewable, sustainable, non-toxic, highly degradable, low emission carbon monoxide, widely available and environmentally friendly (Leke *et al*., 2023). Renewable energy sources such as biomass, wind, geothermal solar and hydropower can be supplementary or alternative for energy production to conserve the petroleum reserves and meet the rising energy demand among the numerous possible sources (Huang *et al*., 2012).

Bioenergy is one of the renewable energies and it emphasizes on two aspects which are biofuel and biomass (Scarlat *et al*., 2015). Biomass energy is a sustainable energy source derived from organic matter. Biomass resources can be grown in almost any habitat and come in a variety of forms. A variety of biomass resources are produced by the agricultural, industrial, and residential sectors as waste and byproducts (Barot, 2022). Biofuel is a renewable energy produced from biological materials and is obtained when plants materials are transformed into liquid fuel (Guo *et al.*, 2015). Biofuel is composed mainly of biodiesel and bioethanol. Bioethanol is a liquid biofuel that is obtained from plant sources such as wheat, maize, sugar beet, potatoes and so forth (Sylvia, 2018).

Biodiesel is one of the promising alternatives to fossil fuel for diesel engine and has become rapidly important due to environmental consequences and the decrease in petroleum resources. Many countries are introducing biodiesel blends to enhance the lubricating capacity of low sulphur diesel fuels (Chong *et al*., 2023). The energy density of biodiesel is close to regular diesel because lots of researches on biodiesel have shown that the fuel made by vegetable oil can be used properly by diesel engines. Biodiesel derived from oil seed plants attracts attention as a promising one for substitution or blending with conventional diesel fuel (Huang *et al*., 2012).

Vegetable oils and/or animal fats can be converted to fuel for diesel engines through four major possible ways: direct use or blending of oils, micro-emulsion, thermal cracking or pyrolysis and transesterification reaction (Okoronkwo *et al*., 2012). The most preferred method is the transesterification reaction because it enables the use of diverse feedstock types to produce a fuel that have similar qualities to conventional fossil fuel diesel (Veluru *et al*., 2022). This method converts oils and fats (triglycerides) to their alkyl esters with viscosity similar to diesel fuel (Pandiagan *et al*., 2017). Transesterification is therefore defined as the reaction of a fat or oil with alcohol in the presence of a catalyst to form esters and glycerol (by-product of the reaction) (Marx, 2016). The transesterification reaction breaks down the chemical structure of the triglycerides in oil through the exchange of the alkyl groups between an ester and an alcohol with the alcohol being used as a reactant. Vegetable oil is subjected to transesterification to decrease the viscosity and increase the volatility of biodiesel (Koberg and Gedanken, 2013). The transesterification process has difficulty converting into esters in the presence of free fatty acids (FFA) and water and, therefore, requires high quality raw materials to avoid undesirable side reactions and hydrolysis (saponification) or additional pre-treatment to remove the initial FFAs (Haigh *et al*., 2012).

The reactions involved in biodiesel production can be homogeneously catalyzed to obtain high yields in a relatively short time; however, biodiesel does not compete favorably with fossil fuels because the catalyst cannot be reused and must be neutralized after the reaction (Kibar *et al*., 2023). Solid catalysts which are eco-friendly and effective were brought up as result of environmental concerns. Some solid materials such as eggshell, oyster shell, mussel shell and so forth contain calcium oxide (catalyst) are used as heterogeneous catalysts (Chong *et al*., 2023). These materials can be used either neutrally or can be modified with acids or bases before use in transesterification. The chemical process used to obtain biodiesel is based on the solid in the system catalyzing the reaction to reduce the time and the cost of the process through the reuse of the catalyst, decreasing the level of impurities in the reaction products and carrying out the operation in a continuous fixed bed (Colombo *et al*., 2016).

Catalyst used in the transesterification of triglycerides can be classified as homogeneous, heterogeneous and enzyme catalyst (Mandari and Devarai, 2022). Homogeneous catalysis involves processes in which catalyst and the oil are in the same phase. Basically, in this transesterification process, there are two types of homogeneous catalyst which are acid catalyst (H_2SO_4 or HCl) and alkali catalyst (KOH or NaOH). Homogeneous basic catalyst provides much faster reaction rates than heterogeneous catalyst, but it is difficult to separate homogeneous catalyst from the reaction mixture (Du and Reid, 2005). A heterogeneous catalytic process is a process that involves more than one phase usually the catalyst is solid, and the reactant and product are in liquid or gaseous form. (Hammond 2017). Heterogeneous catalysts are non-corrosive, environmentally friendly, present fewer disposal problems, easier in separation from liquid product and they can also be designed to give higher activity, selectivity and longer catalyst lifetime (Jambhulkar *et al*., 2022). Many types of heterogeneous catalyst such as alkaline earth metal oxides, anion exchange resins, various alkali metal compound supported on alumina and various type of zeolite that can be used in various type of chemical reaction including transesterification process (Supes and Ghio, 2007). Alcohols that can be used in biodiesel production are those with short chains, including methanol, ethanol, butanol, and amylic alcohol. The most widely used alcohols are methanol (CH_3OH) and ethanol (C_2H_5OH) because of their low cost and properties (Demirbas, 2009). Methanol is often preferred to ethanol in spite of its high toxicity because its use in biodiesel production requires simpler technology; excess alcohol may be recovered at a lows cost and higher reaction speeds are reached (Romano and Sorichetti, 2010).

Vegetable oils were thus extracted from sweet orange and was put through the process of transesterification using modified eggshells to confirm the suitability of these readily available catalytic materials for the production of biodiesel as alternatives for the abundant but non friendly fossil fuels.

MATERIALS AND METHODS

Materials

The materials used in this research were sweet orange seeds, eggshells waste, oyster shell, reagents (analytical grade) and laboratory equipment.

Methods

Sample Collection and Preparation

The orange seeds were sampled beside Mount Carmel International College, Amua by-pass Gboko North, Benue State, Nigeria by peeling the orange fruits and removing the seeds into

polyethylene bags, sundried for 7 days, depulped and pulverised using porcelain mortar and pestle.

Extraction of Oil

The powdered sample obtained from the sweet orange seeds, were weighed into a Soxhlet extraction apparatus for extraction using 250 mL of n-hexane. The entire process took about 6 h after which the extraction process was completed. The n-Hexane was recovered through distillation and the oil was obtained (Leke *et al*., 2023).

Determination of Physicochemical Parameters of Oil

The physicochemical parameters of orange seed oil such as acid value, saponification value, iodine value, viscosity, density, specific gravity, refractive index and moisture were determined.

Determination of percentage yield of the extracted oil:

The initial masses of individual samples were weighed and recorded before extraction and after the extraction process. The extracted orange seed oil was kept overnight for evaporation of the solvent and thereafter, the mass of oil extract obtained was also weighed and the percentage yield was calculated as shown in eq. (1) (AbdulRaheem and Okediran, 2015);

$$\text{Percentage yield} = \frac{\text{Weight of oil extracted}}{\text{Weight of saple}} \text{ x } 100\ \% \quad (1)$$

Determination of density

The density of the orange seed oil was determined using a 50 mL density bottle. The empty density bottle was washed, dried and weighed. It was then filled with the oil sample and was weighed. The density of the oil was calculated as eq. (2) (Ishola *et al*., 2020);

$$\text{Density} = \frac{\text{b}-\text{a}}{\text{Volume of density bottle}} \quad (2)$$

Where; a = weight of empty density bottle, b = weight of empty density bottle + weight of oil.

Determination of specific gravity

The specific gravity of the oil is the ratio of the density of the oil to that of the water at same temperature. The specific gravity of the orange seed oil was obtained from eq. (3) as described by Leke *et al*., (2022).

$$\text{Specific gravity} = \frac{\text{Density of oil}}{\text{Density of water}} \quad (3)$$

Determination of moisture content

A crucible was washed, oven-dried and weighed (W_1) after cooling. About 2.0 g of the oil sample was weighed in the crucible and the weight was taken (W_2). The crucible containing the oil sample was placed in an oven at temperature of 105 ^{o}C for 1 h. It was cooled and weighed. The crucible was introduced into the oven again, the process of cooling and weighing continued at intervals until a constant weight was obtained (W_3) The % moisture was calculated through eq. (4) as described by Ibrahim and Yusuf, (2015).

$$\text{Moisture content} = \frac{\text{W2}-\text{W3}}{\text{W2}-\text{W1}} \times 100\ \% \quad (4)$$

Where; W_1 = Initial weight of crucible, W_2 = Weight of crucible + oil, W_3 = Final weight of crucible + oil.

Determination of refractive index of the oil and biodiesel

The prism of the refractometer (Bellingham + Stanley Ltd: Abbe 60/DR :10.99) was cleaned thoroughly and two drops of the sample was placed on it. The temperature of the sample was noted by reading the thermometer on the instrument. The knobs of the instrument were set and the fluid was demarcated by a sharp line dividing the field of view into two equal halves and when the line conceded with the spot mark "X" in the field of the view, the reading was taken (Ibrahim and Yusuf, 2015).

Determination of Acid Value of the Oil and Biodiesel (AV)

The sample was weighed (1 g) into a 250 mL conical flask and warmed. Then 10 mL of methanol was added to the sample flask followed by thorough stirring. Two (2) drops of phenolphthalein indicator were added to the sample flask and titrated against 0.2 M NaOH (Leke *et al*., 2023). The acid value was obtained from eq. (5).

$$\text{Acid value} = \frac{\text{Titre value} \times \text{M} \times 28.2}{\text{W}} \quad (5)$$

Where; M = Molarity of NaOH, 28.2 = Conversion factor, W= Weight of sample.

Determination of Free Fatty Acid of the Oil and Biodiesel (FFA)

Free fatty acid (FFA) is equivalent to half of the acid value; hence the amount of free fatty acid (FFA) was calculated as shown in eq. (6) (Leke *et al*., 2023):

$$\text{FFA} = \frac{\text{Acid value}}{2} \quad (6)$$

Determination of saponification value

Orange seed oil (5.27 g) was introduced into a 250 mL flask and was warmed on a hot plate and 50 mL of 0.5 N ethanolic KOH was added to the sample. The mixture was heated under reflux for 30 min with constant shaking. It was allowed to cool and then titrated with 0.5 M HCl using phenolphthalein as an indicator. The procedure was repeated with a blank solution and the saponification value was calculated as described by AbdulRaheem and Okediran, (2015) in eq. (7);

$$\text{Saponification} = \frac{(B-S)\ 56.1 \times N}{W} \quad (7)$$

Where; B= Volume of HCl used in the blank titration, S= Volume of HCl used in the sample titration, N = Molarity of HCl, W= Weight of sample.

Iodine Value

An amount (0.2 g) of the oil was weighed into a 250 mL conical flask; 25 mL of carbon tetrachloride was introduced into the flask and was stoppered. Wij's solution (25 mL) was added to the sample flask followed by shaking of the flask for proper mixing. Crystals of potassium iodide were added on all round surface of stopper the flask. The flask was kept in a dark cupboard for 30 min. The flask was then removed from the cupboard and 100 mL of distilled water was used to wash the potassium iodide on the surface and stopper of the flask into the flask. The flask was shaken and rotated (2 min) for proper mixing. About 1 mL of starch solution indicator (1 %) was measured and kept for later use and the solution was titrated against 0.1 N $Na_2S_2O_3$. The starch indicator was added during the titration when the color of the solution became lighter. The solution was well shaken and titrated. A color change from dark blue to milky white indicated the end-point of the titration (AOAC, 1990). The same procedure was carried out on a blank solution and the iodine value was calculated from eq. (8) as described by Omotehinse *et al*., (2019):

$$\text{Iodine value} = \frac{(B-S) \times N \times 12.69}{W} \quad (8)$$

Where; B= Volume of 0.1 M $Na_2S_2O_3$ for the blank titration, S= Volume of 0.1 M $Na_2S_2O_3$ for the sample titration, N= Normality of NB volume$a_2S_2O_3$, W= weight of sample and 12.69 = conversion factor.

Determination of viscosity

The viscosity of the oil was determined using the Brookfield viscometer (model: LVDV-11+P). The oil sample (80 mL) was measured into a 100 mL beaker and was kept on the viscometer stand. The spindle (Number: 62, Level: 2) was thoroughly cleaned and fixed on the viscometer. The spindle was then put into the oil to a certain level; the temperature sensor was also put in the oil sample. The spindle determines how viscous oil is, and the temperature sensor determines the temperature of the oil. The viscosity was determined at 5 rpm and % torque of 3.3. The viscometer was set and the values were recorded (Pandurangan, 2014).

Chemical composition of the oil

The chemical composition of the oil was studied using Gas Chromatography-Mass Spectrometry (GC-MS) to determine the fatty acids present in the oil sample.

Catalyst preparation

The eggshells were cleaned, washed crushed and ground using mortar and pestle to achieved a powder form then sieved to pass 100 - 200 mesh (37-75 μm) (Buasri *et al*., 2015). The powder sample were calcined at 750 ^oC for 4 h and kept in a desiccator to avoid contamination with CO_2 and moisture (lrwan *et al*., 2021). H_2SO4 was used to impregnate the catalyst sample 20 % (w/w) by heating under reflux at 100 °C and stirred at 400 rpm for 2 h, the hot mixture of the sample was allow to cool down at room temperature, then filtered using Whatman filter papers, funnels and conical flasks, the residue (impregnated sample) was washed several time with distilled water and allowed to dry at room temperature for several days, the dried impregnated sample was then pounded into powder with porcelain mortar and pestle, heated in an oven for 4 h at 105 °C, then cooled in desiccators (Irwan *et al*., 2021).

Pretreatment of Oil

About 25 mL of the oil sample was transferred into a 250 mL beaker and heated to a temperature of 60 ^oC on a magnetic stirrer. A mixture of concentrated H_2SO_4 (2.5 mL) with methanol (7.5 mL) was added to the heated oil in the reactor. The mixture was heated with continuous stirring for 1 h at 65 ^oC before it was transferred into the separatory funnel and allowed to settle for 24 h. Thereafter, the ethyl esters were separated from the by-product (mixture of methanol, H_2SO_4 and water) (Oguntimehin, 2017).

Transesterification using acid (20 %) modified eggshells (10 % catalyst dosage)

About 10 mL of sweet orange seed oil was heated to a temperature of 60 ^oC for 15 min in a three-neck round bottom flask to remove moisture. Then, 0.89 g (10 % catalyst dosage) of the H_2SO_4 (20 %) modified eggshells was transferred into a beaker followed by 3.02 mL of methanol (1:9, oil to methanol ratio) and stirred continuously. The mixture was then transferred into the heating flask containing the oil. The mixture was heated under reflux for 2 h at 65 ^oC filtered and transferred into a separatory funnel and was kept for 24 h for further reaction. Thereafter, two phases were seen upon completion of the reaction. The biodiesel (upper phase) was separated from the glycerol (lower phase) and kept for further analysis (Leke *et al*., 2023).

Characterization of Biodiesel obtained from Sweet Orange Seed Oil

The percentage yield, acid value, free fatty acid value and refractive index of the biodiesel were determined.

Determination of biodiesel yield

The obtained biodiesel was introduced into a beaker, suspended in a water bath at 65 ^{o}C for 30 min in order to remove moisture and the residual methanol. Thereafter, the weight of biodiesel was taken and recorded. The biodiesel yield was calculated as shown in eq. (9) (Aworanti *et al.*, 2019).

$$\% \text{ Biodiesel yield} = \frac{\text{Weight of biodiesel}}{\text{Weight of oil before transesterification}} \text{X } 100 \% \quad (9)$$

RESULTS AND DISCUSSION

The result of physicochemical properties of the sweet orange seed oil is presented on

Table 1.The result is compared with AOAC standard (1990) and ASTM limits (Castor oil)

Table 1: Physicochemical Properties of Sweet Orange Seed Oil

Properties	Results	AOAC Standard (1990)	ASTM limits (Castor Oil)
Percentage yield (%)	38.38	≥ 32.00	_
Moisture content (%)	6.50	7.00-11.00	_
Relative density (g/cm^3)	0.89	-	_
Specific gravity	0.90	0.89-0.92	0.95-0.96
Refractive index	1.46	1.44-1.47	1.47-1.49
Iodine value (gI_2/100g)	55.80	80.00-100.00	56.00-64.00
Acid value (mg KOH/g)	5.64	≤ 4.00	0.40-4.00
Free fatty acid (%)	2.82	≤ 1.30	_
Saponification value (mg KOH/g)	179.90	≥ 180	175.00-187.00
Viscosity (Pa.s)	0.04	NA	

Key: NA = Not Available

The physicochemical properties of oil

The physicochemical properties of the sweet orange seeds oil were compared with AOAC, 1990 and ASTM limits for castor oil since castor oil is also a non-edible oil as sweet orange seeds oil.

Yield: The mass of orange seed oil used for the extraction was 545.06 g and it yielded 209.21 g of orange seed oil resulting to a percentage yield of 38.38 %. The mass of chaff recovered after the extraction was 318.34 g. The yield of 38.38 % was within the standard range, ≥ 32 % according to AOAC (1990). The percentage of 38.38 % was slightly high as compared to 36 % obtained by Nwobi *et al.* (2006), for sweet orange seed oil and relatively low as compared to a work reported on water melon seed oil (48%) by Ogunwole, (2015). The variation in the percentage yields of the oils can be attributed to geographical and environmental conditions which depend on various regions (Ibrahim and Yusuf, 2015).

Moisture content: The moisture content of sweet orange seed oil was found to be 6.50 % which is slightly below AOAC, (1990) standard limits (7-11 %) but the same as reported on palm kernel oil by Atasie and Akinhanmi, (2009). This is an indication that the oil will not have moisture problems during storage even though the value is slightly higher than a work reported (5.8 %) by Ogunwole *et al*. (2015) on water melon seed oil.

Refractive index: The refractive index value obtained was 1.46 which lies within the AOAC (1990) standard and very close to a work reported by Okechukwu *et al.*, (2015) on castor oil (1.47). The value was higher than a report on palm kernel oil (1.447) by Aladetuyi, *et al.* (2014). The difference can be as a result of the difference in the type of seed. The high refractive index of oils confirms a high number of carbon atoms in their fatty acids (Falade *et al*., 2008). The refractive index of 1.46 was slightly below the ASTM limits for castor oil (1.47-1.49).

Density: The density of the seed oil was 0.89 g/cm^3 which lies within the AOAC, (1990) standard (0.82 - 0.96 g/cm^3) and slightly higher than the value (0.87 g/cm^3) reported by Momoh *et al.*, (2014) on alphonso mango seed oil. Seed oils' densities depend on their fatty acid composition, minor components and temperature (Aremu *et al*., 2015).

Iodine value: The higher the iodine values, the more unsaturated the oil. Oils rich in saturated fatty acids have low iodine values while oils rich in unsaturated fatty acids have high iodine values. Vegetable oils can be classified into four (4) major categories based on their iodine value: saturated oils (Iodine values between 5 and 50), semi-siccative monounsaturated oils (Iodine values between 50 and 100), di-unsaturated oils (Iodine values between 100 and 150) and tri-unsaturated oils called siccative (Iodine values over 150) (Pandurangan *et al*., 2014). The iodine value (55.80 gI_2/100g) obtained was lower than the range of values (80.00 - 100.00 gI_2/ 100g) of AOAC, (1990) but within the ASTM limits for castor oil (56.00 - 64.00 gI_2/100 g). The iodine value implies that the oil is a semi-siccative monounsaturated oil. Monounsaturated oils are the best components for biodiesel because highly saturated biodiesel fuel

produces acetylene and soot precursors than unsaturated biodiesel. The value is lower than the value (75.82) reported by Okechukwu *et al*. (2015) on ricinus communis seeds but lower than the value (39.9 gI_2/100g) reported by Umaru *et al.*, (2014) on mango seeds oil and (41.24 gI_2/100g) reported by Atasie and Akinhanmi, (2009) on palm kernel oil.

Free Fatty Acid (FFA): High quality oils are low in FFAs and in vegetable oils, the lower the FFA, the more acceptable the oil is. From results obtained from sweet orange seed oil, the FFA value was 2.82 mgKOH/g which was lower than the value (5.83 mgKOH/g) reported by Atasie and Akinhanmi, (2009) on palm kernel oil and also Momoh *et al*., (2014) on mongo seed oil (17.95 mgKOH/g) but higher than the AOAC (1990) limits, ≤ 1.32 mgKOH/g. Therefore, esterification was carried out on the oil to reduce the FFA because high values of FFA results to difficulties in separation of the product which gives low yield. After esterification, the FFA reduced from 5.83 mgKOH/g to 1.94 mgKOH/g which was close to the recommended value.

Acid value: In this research, the acid value was obtained to be 5.64 mg KOH/g, which implies that, the oil will not be suitable for consumption but for other uses such as production of biodiesel. The acid value was slightly higher than the limits of AOAC (1990) and ASTM limits for castor oil. The oil might need to undergo further treatment and purification if it is to be consumed. After esterification, the acid value reduced from 5.64 mg KOH/g to 3.94 mg KOH/g which falls within the recommended value ≤ 4.00 mg KOH/g (AOAC, 1990) and 0.40 - 4.00 mgKOH/g for ASTM of castor oil. The acid value is lower than the value (7.84 mg KOH/g) reported by Umaru *et al.*, (2014) on mango seeds oil and (11.60 mg KOH/g) reported by Atasie and Akinhanmi, (2009) on palm kernel oil.

Saponification value: The value obtained to be 179.90 mgKOH/g was almost the same with AOAC, (1990) (≥ 180.00 mgKOH/g) and the value was within the ASTM limits for castor oil (175.00 - 187.00 mgKOH/g). This means that oil will be good for biodiesel production. The result was relatively low as compared to the work done by Umaru *et al*., (2014) on mango seed oil (194.72 mgKOH/g) and 190 mgKOH/g by Enweremadu and Alamu, (2010) on shea nut butter.

Viscosity: Viscosity of the oil was obtained to be 0.04 Pa.s. The value is almost the same as a report on watermelon seed oil (0.0407 Pa.s) by Keke *et al*., (2023). The value shows that sweet orange seed oil is too viscous for use in diesel engines since high viscosity causes excessive engine wear. Hence the oil must be converted to methyl esters before use in diesel engines, the transesterification process reduces the viscosity making the biodiesel to have a lower viscosity.

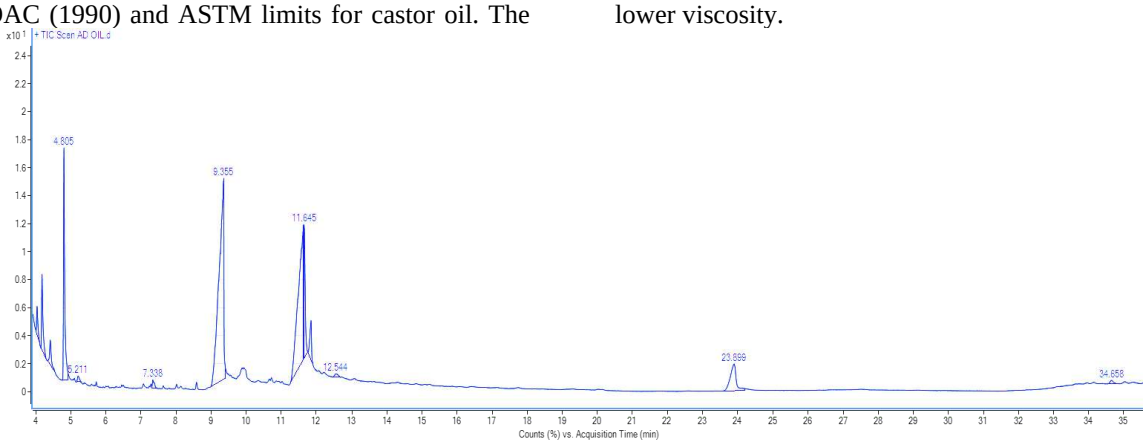

Figure 1: GC-MS Chromatogram of compounds of Sweet Orange Seeds Oil

Table 2: Chemical Composition of Extracted Sweet Orange Seeds Oil

Peak Number	Name	Formula	Retention Time	Molecular Weight	% Area
1	n-Hexane	C_6H_{14}	4.03	86	3.74
2	Propane, 2-methyl-1-nitro-	$C_4H_9NO_2$	4.18	103	10.71
3	Hexane, 2, 5-dimethyl-	C_8H_{18}	4.41	114	4.33
4	Octane, 3-ethyl-	$C_{10}H_{22}$	4.80	142	30.62
5	9-Oxononanoic acid	$C_9H_{16}O_3$	5.21	172	1.06
6	5, 10-pentadecadienoic acid	$C_{15}H_{26}O_2$	7.33	238	1.72
7	Undecanoic acid	$C_{11}H_{22}O_2$	9.35	186	100.00
8	(R)-(-)-4-methylhexanoic acid	$C_7H_{14}O_2$	11.62	130	70.05
9	9, 12-Octadecadienoic acid (Z), Z	$C_{18}H_{32}O_2$	11.63	280	4.46
10	1-Cyclohexylheptene	$C_{13}H_{24}$	11.64	180	17.01
11	Cyclohexane,1-(1,5 dimethylhexyl)-4-(4-methylpentyl)-	$C_{20}H_{40}$	11.84	280	6.79
12	Oleic acid	$C_{18}H_{34}O_2$	12.54	282	1.08

13	1-Hexyl-2-nitrocyclohexane	$C_{12}H_{23}NO_2$	23.89	213	16.58
14	2-Heptaldecenal	$C_{17}H_{32}O$	34.65	252	1.08

GC-MS analyses of Extracted Oil:

Figure 1 and **Table 2** showed the chromatogram of the sweet orange seed oil before transesterification. The chromatogram shows different peaks that correspond to different compounds. The chromatogram has fourteen different peaks, identifying fatty acids and other organic substances with their various peak numbers, retention time, percentage area and molecular weight. From the result, the main fatty acids obtained were, undecanoic, oleic, 5,10-pentadecanoic (z,z)-, 9-oxononanoic and 9,12-Octadecadienoic acids. Even though, the chromatogram has other organic compounds, only the triglycerides were responsible for the transesterification process. Nwobi *et al*., (2006), and Aranha and JoRGe, (2013) also obtained oleic acid in chemical composition analysis for orange seed oil.

Table 3: Physicochemical Properties of Biodiesel Produced from Sweet Orange Seed Oil

Property	Results	ASTM D6751
Percentage yield (%)	39.02	_
Refractive index	1.47	1.47 max
Acid value (mg KOH/g)	1.12	0.80 max
Free fatty acid value (%)	0.56	0.42 max

Nature of biodiesel produced: The acid value of the biodiesel produced was 1.128 mg KOH/g. The acid value indicates the amount of FFA present in the biodiesel at the time of test. The acid value of the biodiesel (1.12 mg KOH/g) produced shows a reduction in the acid value of the original sweet orange seed oil (5.64 mg KOH/g), implying that transesterification occurred. The low acid value in oil indicates that the oil will be stable over a long time and protect against rancidity. The maximum limit of acid value for biodiesel standard is 0.8 max (ASTM D6751), therefore, the acid value in this research was slightly above the ASTM specification and below the values reported by Enweremadu and Alamu, (2010) on share nut butter to be 0.28 mg KOH/g and Eevera *et al*., (2011) on groundnut oil (0.2 mg KOH/g). Furthermore, it was also observed that the FFA content of the product of the reaction shows a reduction from the value obtained from the sweet orange seeds oil used (from 2.82 % for oil to 0.56 % for biodiesel produced). The lower percentage of FFA's in the biodiesel indicates that the biodiesel can be stored for a long time without going rancid. The refractive index was found to increase from 1.46 for oil to 1.47 for biodiesel. The increment is an indication that transesterification took place. The value falls within the standard specified by ASTM D6751.

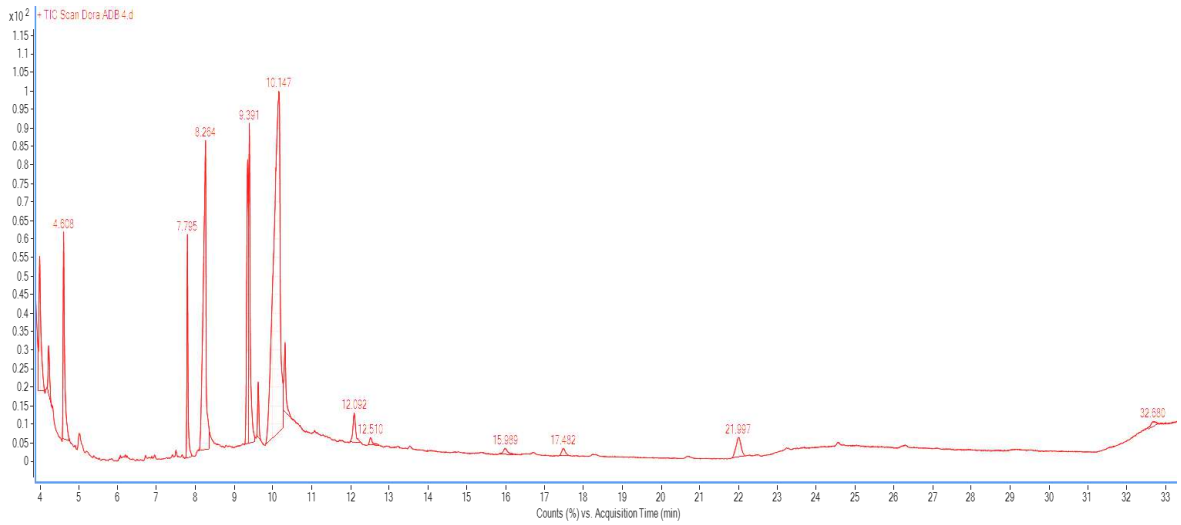

Figure 2: GC-MS Chromatogram of compounds of transesterification of Sweet Orange Seed Oil using 20% H_2SO_4 Eggshells Catalyst

Table 4: Chemical Composition of Sweet Orange Seeds Oil Biodiesel using 20 % H_2S0_4 Modified Eggshells as a Catalyst

Peak Number	Name	Formula	Retention Time	Molecular Weight	% Area
1	n-Hexane	$C_{16}H_{14}$	3.99	86	12.27
2	1-Hexanol, 2-ethyl-	$C_8H_{18}O$	4.21	130	3.27
3	1-Decene, 3,4-dimethyl-	$C_{12}H_{24}$	4.60	168	14.80
4	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	7.79	270	11.45
5	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	8.26	256	39.97
6	9, 12-Octadecadienoic acid (Z, Z)-, methyl ester	$C_{19}H_{34}O_2$	9.34	294	20.33
7	Tetradecanoic acid, 12-methyl-, methyl ester, (S)-	$C_{16}H_{32}O_2$	9.39	256	22.94
8	1-Cyclohexylheptene	$C_{13}H_{24}$	9.62	180	3.25
9	Cyclohexane, 1-(1,5-dimethylhexyl)-4-(4-methylpentyl)-	$C_{20}H_{40}$	10.14	280	100.00
10	6,11-Eicosadienoic acid, methyl ester	$C_{21}H_{38}O_2$	12.09	322	3.65
11	7-Hexadecenal, (Z)-	$C_{16}H_{30}O$	12.51	238	1.10
12	Methyl, 12-Oxo-9-dodecenoate	$C_{13}H_{22}O_3$	15.98	226	1.31
13	9-Octadecenoic acid (Z)-, methyl ester	$C_{19}H_{36}O_2$	17.48	296	1.27
14	3-Methyl-2-(2-oxopropyl) furan	$C_8H_{10}O_2$	21.99	138	4.43
15	Cis-vaccenic acid	$C_{18}H_{34}O_2$	32.68	282	1.12

Biodiesel Produced from 20 % H_2SO_4 Modified Eggshells: The chromatogram in Figure 2 showed different components present in sweet orange seeds oil biodiesel. Fifteen (15) peaks were recorded which showed different fatty acid methyl esters and few non-fatty acid components present **Table 4**. The presence of the fatty acid methyl esters implied that, transesterification (conversion of triglycerides to methyl esters) took place and the product of the reaction was biodiesel (Leke *et al*., 2023).

CONCLUSION

The physicochemical parameters obtained from orange seed oil showed that, the oil possesses qualities suitable for use in the production of biodiesel. From this research, biodiesel was produced from sweet orange seed oil using 20 % H_2SO_4 modified egg shell, oil to methanol ratio (1:9), 10 % catalyst dosage with reaction time of 2 h at 65 ^oC and a biodiesel conversion of 39.03 %. The characterisation results of the seed oil compared favourably to AOAC (1990) standard and ASTM limits for castor oil. The biodiesel produced also compared favourably to ASTM D6751 standard; hence the fatty acid methyl ester (FAME) of sweet orange seeds oil can be used in diesel engine. Therefore, the seeds of sweet orange and eggshells waste can be harnessed for biodiesel production, since they are highly underutilised in Nigeria.

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