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Characteristic and physicochemical properties of some oils

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Abstract
Physicochemical properties of Cucurbita pepo, Brachystegia eurycoma, Cucumis melo, Luffa cylindrica, and Arachis hypogaea oils were studied to determine their potential as viable feedstock for biodiesel production. The nonedible oils were extracted by solvent extraction using n-hexane while the oil of Arachis hypogaea was procured. All the oils were characterized for specific gravity, pH, ash content, iodine value, acid value, saponification value, peroxide value, free fatty acid, flash point, kinematic viscosity, and refractive indices using standard methods. Cucurbita pepo seeds had very high oil content when compared to the others. Specific gravity and flash point of the oils were satisfactory. However, moisture content of some of the oils exceeded the stipulated ASTM standard for biodiesel production. Again, acid values of the nonedible oils were very high and exceeded the ASTM standard. They also exceeded the acid value of Arachis hypogaea oil except for Luffa cylindrica oil. Results indicate that the oils are potential biodiesel feedstocks. However, overall results indicate that the nonedible oils are not suitable for single-stage transesterification process to biodiesel but would be better suited for the two stage esterification and subsequent transesterification in order to obtain reasonable yields of the methyl esters.

Keywords: fatty acid composition, physicochemical properties

Introduction
The rapidly growing global demand for petroleum products and the consequent depletion of the crude oil reserves in addition to adverse environmental concerns and unstable nature of the international market make imperative the need to explore alternative sources of fuel. Biodiesel is one of the promising renewable energy options already exploited by various countries. Categories of feed stocks as source of suitable oil for biodiesel production include seeds, nuts, leaves, wood, and even bark of trees. Nigeria is very well endowed with various edible and nonedible oils.

Currently due to gradual depletion of world petroleum reserves and the impact of environmental pollution of increasing exhaust emissions, there is an urgent need o develop alternative energy resources, such as biodiesel fuel. Vegetable oil is a promising alternative because it has several advantages, it is renewable, environ-friendly and produced easily in rural areas, where there is an acute need for modern forms of energy.

Biodiesel is monoalkyl esters of fatty acids derived from vegetable oils or animal fats, is known as a clean and renewable fuel. Biodiesel is usually produced by the transesterification of vegetable oils or animal fats with methanol or ethanol (Knothe *et al*., 2006). Biodiesel has many advantages include the following: its renewable, safe for use in all conventional diesel engines, offers the same performance and engine durability as petroleum diesel fuel, non-flammable and nontoxic, reduces tailpipe emissions, visible smoke and noxious fumes and odors. The use of biodiesel has grown dramatically during the last few years. Feedstock costs account for a large percent of the direct biodiesel production costs, including capital cost and return (Bozbas, 2005).

One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as inedible oils, animal fats, and waste food oil and by products of the refining vegetables oils (Veljkovic´ *et al*., 2006). The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel to the commercials filling stations. Fortunately, inedible vegetable oils, mostly produced by seed-bearing trees and shrubs can provide an alternative.

With no competing food uses, this characteristic turns attention to Jatropha curcas, which grows in tropical and subtropical climates across the developing world (Openshaw, 2000).

As a result of the extensive demands of oil for consumption and industrial uses, analyses of many oils have been carried out. The extraction and use of vegetable oils has for centuries played an important role in the manufacture of a large number of industrial products and food items and also in biodiesel production. Certain edible oils such as cottonseed and safflower can be used as raw materials for biodiesel production. Some of the nonedible oils such as mahua, castor, neem (Azadirachta indica), rice bran, linseed, Karanja (Pongamia pinnata), andjatropha (Jatropha curcas) have also be used. However availability of these raw materials varies. This requires the search for new sources of novel oils. Several plants are now growing, not only for food and fodder but also for striking range of products with industrial applications.

Brachystegia eurycoma is an economically valuable tree crop mostly grown in the tropical rain forest of West Africa. Its uses range from food to medicine. Sponge-gourds, the fruit of Luffa cylindrica, are widely used throughout the world. It is an annual climbing crop which produces fruit containing fibrous vascular system. It is a summer season vegetable. Melon (Cucumis melo L.) is a commercially important fruit crop that is cultivated worldwide. It is also an important summer vegetable crop especially in the rice fallows of Kerala. Culture and use of cucurbits or squashes (Cucurbita pepo) have been traced to more than 10000 years ago. The oils of Cucurbita Pepo, Brachystegia eurycoma, Cucumis melo, and Luffa cylindrica seeds are generally known as nonedible oils even though some of the seeds are consumed sparingly in some localities, while that of Arachis hypogaea are exported on a large scale as edible oil.

The chemical composition of the oil extract consequently gives a qualitative identification of oils and is a very important area in the selective application guide for the commercialization and utility of oil products. Fats and oils are also very important indigenous raw materials for many edibles and nonedible purposes. The colours of vegetable and animal oils are usually transferred to the biodiesel made from them and so are other properties. Therefore, properties of the biodiesel greatly depend on that of the vegetable oil used for it. This study was therefore undertaken to characterize oils extracted from Cucurbita pepo, Brachystegia eurycoma, Cucumis melo, and Luffa cylidrica seeds and compare their quality with Arachis hypogaea oil, an edible one known to be suitable for biodiesel production.

2. Experimental

The seeds of Cucurbita pepo, Brachystegia eurycoma, Cucumis melo, and Luffa cylidrica were harvested from a farm in Nsukka, Enugu State, and separated from foreign materials and dirt. The seeds were dehulled mechanically to enable separation of seed coat and the testa. They were then sun-dried in the open for up to four days until the seed coat split and then the cotyledon was shredded. The seed coat was separated from the cotyledon by air blowing. A fuel operated grinding machine was used to crush the dried dehulled seed to coarse form.

2.1. Oil Extraction

The coarse meal from the seeds was subjected individually to solvent extraction for 5 h with n-hexane at 55–60◦C using Soxhlet extraction method. The oil solutions were filtered using a Buchner funnel and then subjected to distillation using rotary evaporator. The oils were weighed and put into well-closed containers. At the end of the extractions, the resulting mixtures containing the oils were heated to recover solvent from the oil. However, the peanut oil used for this study was purchased from the market.

The seed kernels were ground, using a mechanical grinder, and defatted in a soxhlet apparatus, using hexane (boiling point of 40–60 ◦C). The extracted lipid was obtained by filtrating the solvent lipid contained to get rid of the solid from solvent before the hexane was removed using rotary evaporator apparatus at 40 ◦C. Extracted seed oil was stored in freezer at−2 ◦C for subsequent physicochemical analysis.

2.2. Physicochemical Analysis

The percentage (%) yields of the nonedible oils were calculated. Odour, colour, and physical state of the oils were estimated by sensory evaluation. They were characterized for specific gravity using specific gravity bottle, pH were determined using a Hanna pH meter model no. 02895, moisture content by the oven dry method, ash content by heating to dryness in furnace, kinematic viscosity using a viscometer, refractive index using Abbe refractometer, and flash point using the semiautomatic Cleveland flash point tester.

Oil Content

The weight of oil extracted from 10 g of seeds powders was measured to determine the lipid content. Result was expressed as the percentage of oil in the dry matter of seed powders.

Acid value, % FFA

Acid value of seed oil was determined according to AOAC Official Method Cd 3a- 63. Percentage free fatty acids (FFAs) were calculated using oleic acid as a factor.

Iodine value

Iodine value of seed oil was determined according to AOAC Official Method 993.20.

Saponification value

The saponification value was determined according to MPOB Official Test Method 2004.

Peroxide value

The peroxide value was determined according to AOAC Official Method 965.33

Viscosity

Viscosity of seed oil was carried out using Brookfield RV-I. Spindle of S03 was used at 10 rpm in room temperature.

Density

The density of the samples was determined at 25 °C by using density meter Anton paar DMA 4500.

3. Results and discussion

As shown in Table 1, the oil contents of Cucumis melo (44.85%) and Cucurbita pepo (92.50%) show that their use for biodiesel production would be highly economical. The oils had agreeably oily smell except for those of Brachystegia eurycoma, Arachis hypogaea, and Cucurbita pepo oils that were odourless. Oils of Luffa cylidrica and Cucumis melo were very dark in colour, but the clarity of Brachystegia eurycoma, Arachis hypogaea, and Cucurbita pepo is an

advantage for their use as biodiesel feedstock. Physical state of all the oils was liquid at room temperature.
Specific gravity of all the oils was in the range of 0.85–0.93, which is close to the standard range of 0.87–0.90 for biodiesel. Density and other gravities are important parameters for diesel fuel injection systems. The values must be maintained within tolerable limits to allow optimal air to fuel ratios for complete combustion. High-density biodiesel or its blend can lead to incomplete combustion and particulate matter emissions. Moisture content of the nonedible oils which were up to 8.27% was very high, far exceeding that of Arachis hypogaea oil (0.089%) and also the stipulated ASTM standard (0.05%). This high moisture content creates problem in transesterification, reduces shelf life, and may also cause corrosion in internal combustion engine.
As shown in Table 2, pH values of all the oils in the range of (5.30 to 6.07) were acidic. The ash content of the nonedible oils were of considerable quantity being up to 2%, higher than the trace amount in Arachis hypogaea oil and exceeding the ASTM standard of 0.02 maximum. Iodine values (g I2/100 g) were higher than the standard iodine value for biodiesel of 120 by Europe's EN 14214 specification except for Luffa cylidrica and Arachis hypogaea oils. Iodine value is a measure of the unsaturation of fats and oils. High iodine value indicates high unsaturation of fats and oils. Oils with iodine value above 125 are classified as drying oils; those with iodine value 110–140 are classified as semidrying oils. Those with iodine value less than 110 are considered as nondrying oil. All the oils are drying oils except Luffa cylidrica and Arachis hypogaea oil which are nondrying oils. Oils that are susceptible to drying are also susceptible to becoming rancid. This implies that the oil cannot be preserved for a long period of time. If used as straight vegetable oil, it is more likely to polymerize in the heat of the engine. The iodine values for the drying oils were close to iodine value of 135 for candlenut oil which can cause the lowering of pour point.

Table 1: Physical properties of Brachystegia eurycoma, Cucurbita pepo, Luffa cylindrica, Cucumis melo, and Arachis hypogea seed oils.

S. No	Properties	Bracystegia eurycoma	Cucurbita pepo	Luffa cylidrica	Cucumis melo	Arachis hypogeal oil	ASTM D6751-02
1	Oil content (%)	14.08	92.50	12.30	44.85	-	-
2	Odour	Odourless	Odourless	Agreeably oily	Agreeably oily	Odourless	-
3	Colour	Yellow	Yellow	Dark brown	Light brown	Yellow	-
4	Specific gravity	0.85	0.84	0.93	0.92	0.93	-
5	Moisture (%)	8.27	4.92	3.50	5.63	0.09	0.05% max
6	Physical state at room temperature	Liquid	Liquid	Liquid	Liquid	Liquid	-

Table 2: Chemical properties of Brachystegia eurycoma, Cucurbita pepo, Luffa cylindrica, Cucumis melo, and Arachis hypogea seed oils.

S. No	Properties	Bracystegia eurycoma	Cucurbita pepo	Luffa cylidrica	Cucumis melo	Arachis hypogeal oil	ASTM D6751-02
1	Ph	5.30	5.65	5.59	6.07	-	-
2	Ash value (g/100g)	2.10	1.86	0.50	2.77	Trace	0.02 max
3	Iodine value (g/100g)	132.61	150.37	66.37	135.36	89.46	-
4	Acid value (mgKOH/g)	27.08	36.47	2.47	5.40	2.61	0.8 max
5	Saponification value (mgKOH/g)	93.27	162.69	65.92	112.19	148.67	-
6	Peroxide value (meq/kg)	4.36	5.66	9.37	9.83	22.25	-
7	Free fatty acid (%)	13.54	18.23	1.23	2.525	1.31	-
8	Flash point (°C)	288.00	312.00	338.00	298.00	178.00	130.00 min
9	Kinematic viscosity (mm^2/s)	0.13	0.70	0.92	0.81	32.66	1.90-6.00
10	Refractive index	0.91	0.73	0.75	0.71	1.46	-

Acid values of the nonedible oils were also very high and exceeded the ASTM standard of 0.8 mgKOH/g. They also exceeded the value for Arachis hypogaea oil except for Luffacylidrica with 2.47 mgKOH/g. Acid value measures the presence of corrosive free fatty acids and oxidation products. This is actually an important variable in considering the quality of oil because the lower the free fatty acid, the better the quality of oil. The acceptable limit for edible oils is ≤10. FFA concentrations of the oils were all higher than the maximum limit of 2.0% reported for high-grade Codex Alimentarius except for Luffa cylidrica and Arachis hypogaea. Vegetable oils containing high free fatty acids have significant effects on the transesterification with methanol using alkaline catalyst. It also interferes with the separation of fatty acid ester and glycerols. This indicates that the oils would be better converted to biodiesel using the two-stage process of esterification and transesterification.

Saponification values (mgKOH/g) of the oils were about >100 except for Luffa cylidrica oil (65.92). Saponification value is used in checking adulteration. The saponification values were close to 148.67 but just a bit lower than 190.34 for Psophocarpus tetragonolobus seed oil, shea-nut oil having 195 and also that of 193.55 for jatropha oil. It indicates the presence of high percentage of fatty acids in the oil and therefore implies the possible tendency to soap formation and difficulties in separation of products if utilized for biodiesel production. This would also suggest that using the oils for biodiesel production would lead to very low yields in the methyl esters. Peroxide values of the nonedible oils were in the range of 4.36–9.82 meq/kg which were far higher than that of jatropha oil seed (1.93 meq/kg) and shea-nut oil (0.28 meq/kg) but lower than that of Arachis hypogaea oil (22.25 meq/kg). The high peroxide value shows that the oil can easily go rancid and therefore has short shelf life. This shows

that shea-nut oil can resist lipolytic hydrolysis and oxidative deterioration and also proves the oxidative stabilities of the jatropha oil relatively and therefore instability of all the oils analyzed in this study. Oils having high percentages of peroxide are unstable and grow rancid easily. This indicates that if the oils are to be used for the purposes of biodiesel production, then they have to be utilized as soon as they are produced or extracted.
Flash point of the nonedible oils was well above 200◦C exceeding 178.00 of the edible oil. They were all above the 130◦C minimum ASTM recommended range and therefore pose no risk of fire outbreaks in case of accidents which also conformed to the >100◦C recommended flash point by SNI 04. The viscosities of the nonedible oils were in the range of 0.13 to 0.92, being far below 32.66 of Arachis hypogaea oil. The refractive index of Arachis hypogaea oil which was 1.4631 is very close to the values reported for other seed oils, that is, 1.48 for Telfairia occidentalis seed oil, 1.47 for soybean oil, and 1.47 for corn oil. Brachystegia eurycoma had the highest refractive index of 0.91 while the others were about 0.73. This indicates that the oil is less viscous compared to most drying oils with refractive indices between 1.48 and 1.49. The refractive index of oils actually depends on their molecular weight, fatty acid chain length, degree of unsaturation, and degree of conjugation. Triacylglycerols have higher refractive indices than do their constituent free acids. Values of refractive index for different oils generally vary between 1.447 and 1.482. Also, when the biodiesel temperature is near to the cloud point, a cloudy state appears and the refractive index changes; hence, it is a significant parameter to evaluate the state of a biodiesel.

4. Conclusion
Cucurbita pepo and Cucumis melo oils had very good yields which show that they are very good and viable food stock for biodiesel production. The other oils though low in yields could be exploited for biodiesel production since they are derived from non common food sources while the byproducts emanating from their processing would be useful in firing boilers for plants or as animal feed if properly processed. The major limitations of all the oils were mostly high acid and FFA values. These high values for those parameters make them more suitable for the two-stage process of biodiesel production in order to obtain reasonable yields of the methyl esters. The conversion of these oils to biodiesel using the two-stage process will constitute a separate report.

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