COMPARATIVE STUDY OF BIODIESEL FROM KERNEL OILS OF*JATROPHA CURCAS* AND *AZADIRACHTA INDICA IN ZARIA NIGERIA*.

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Abstract Comparative study of biodiesel from kernel oils of *jatropha curcas* and *azadiracta indica* were carried out in the production of biodiesel. The seeds of the two plants were collected in August- October of the year for the study. Biodiesel has attracted immense attention in recent time due to its environmental benefits and the fact that it is made from renewable resources such as vegetable oil of plant origin. Evaluated results showed that *Jatropha curcas* seeds contain 52.70±2.91% (dry w/w) crude oil and *Azadirachta indica* seeds 32.50±2.60% (dry w/w) crude oil respectively. The physiochemical properties of the biodiesel produced from these oils showed that jatropha biodiesel has low FFA (0.21±0.02%), acid value (0.41±0.02%), specific gravity (0.8867±0.01g/cm3), viscosity (3.73±0.21mm2/s), saponification value (45.85±0.29mg/g), iodine value (53.33±4.62mg/g) and peroxide value (0.32±0.04meq/l) while *neem* biodiesel has FFA (0.28±0.03%),acid value (0.56±0.05%), specific gravity (0.8831±0.04g/cm3), viscosity (4.40±0.20mm2/s), saponification value (53.54±2.95mg/g), iodine value (47.18±1.17mg/g) andperoxide value (0.43±0.07meq/l). Although when both biodiesels were compared with ASTM and EN standard values, jatropha biodiesel however was of higher quality.

Keywords*: Jatropha curcas,Azadiracta indica,*Transesterification, biodiesel.

INTRODUCTION The energy trend offers a challenge as well as an opportunity to find substitutes for fossil fuels and reap both economic and environmental benefits. Investigation and development of biofuels as an alternative and renewable source of energy for transportation, has become a major target in the effort towards energy self-reliance. Biofuel commands crucial advantages such as technical feasibility of blending, superiority from the environment and emission angle; its capacity to provide energy security to remote and a capacity for rural areas and employment generation[1]. Currently due to gradual depletion of world petroleum reserves and the impact of environmental pollution of increasing exhaust emissions due to incomplete combustion of petroleum fuels, there is an urgent need to develop alternative energy resources such as biodiesel fuels. Vegetable oil is a promising alternative because it has several advantages; it is renewable, environment friendly and produced easily in rural areas, where there is an acute need for modern forms of energy. In recent years, several researches have been conducted to use vegetable oils as fuel in engines, i.e biodiesel[2,3].Biodiesel is mono alkyl ester of fatty acids derived from vegetable oils and animals fats, as a fuel, it is clean and renewable. Biodiesel is usually produced by the transesterification of vegetable oils or animals fats with methanol or ethanol[4]. It is safe for use in all conventional diesel engines, offers the same performance and engine durability as petroleum diesel fuel, nonflammable and nontoxic, reduces tailpipe emissions, visible smoke and noxious fumes and odours. The fact that Jatropha oil cannot be used for nutritional purposes without detoxification makes its use as energy or fuel source very attractive. *J. curcas (Linnaeus)* is a multipurpose bush/small tree belonging to the family of *Euphorbiaceae.* It is a plant with many attributes; multiple uses and considerable potential. The plant can be used to prevent and/or control erosion, to reclaim land, grown as a life fence, especially to contain or exclude farm animals and can be planted as a commercial crop. It is a native of tropical America but now thrives in many parts of the tropic and subtropical Africa and Asia [5,6,7,8,9]. *Neem* oil is another vegetable oil from inedible crop that has been converted to useable items. It belongs to the mahogany family *Maliaceae*[10].

All parts of the tree (sees, leaves, flower and bark) are used for different medicinal preparations. *Neem* oil is useful for skin care such as acne treatment and keeping skin elasticity[11].

MATERIALS AND METHODS

Sample preparation The seeds of Jatropha curcas and Azadiracta indica were obtained in August – October, 2009 from*, Danmagaji, Sabon gari,Tudun* *wada, Kwangila and samara* markets in Zaria, Nigeria for the study. 500g of each of the seeds were used for the study. They were manually separated from the shell and cracked and the shell carefully removed and the kernels thus obtained were used for oil extraction. The oil was prepared by grinding the seed kernel and the crude oil extracted mechanically with hydraulic cool press machine. The oil was collected in a plastic container and stands 24hours, and then carefully decanted.

Sample treatment and analysis The transesterification reaction was carried out in a 500ml round bottom flask as follows. The stoichiometrically defined quantities of reacting products were: for 100ml of jatropha curcas oil, 0.28g NaOH and 13.50ml methanol was used. Similarly, with 100ml of A. indica oil: 0.82g NaOH and 16.5ml methanol was also used. After measuring, the oil was taken into a 500ml round bottom flask. A water condenser system and a thermometer were connected to the flask. The oil was warmed by placing the flask in a 60°C (a much lower temperature than the boiling point) water bath. Then the NaOH pellets were dissolved in methanol obtaining the corresponding methoxide. The sodium methoxide solution was gradually added into the hot crude oil; the mixture was stirred intermittently during two hours in the warm water bath. The resulting product was taken into a separating funnel and allowed to stand for 24 hours. Two phases were distinct: a golden yellow liquid representing the biodiesel on top and the glycerol at the bottom. They were separated and the biodiesel was collected in a flask and then washed with distillated water in order to reduce its pH value. Standard methods were used to determine the physico-chemical properties of both crude oil and the resulting biodiesel.

Characterisation of the desiels Oil Content.

The weight of oil extracted from kernel 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 Ca 5a-40.

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 920:158.

Saponification value

The saponification value was determined according to AOAC method 920:160/AOCS method Cd 3-25.

Peroxide value

The peroxide value was determined according to AOAC Official Method 965.33 V**iscosity**

Viscosity of seed oil was carried out using Brookfield DV-E model, with Spindle code 62s, stirred at 100 rpm at room temperature.

Density

The density of the samples was determined at 25 °C by using Density bottle

Table 1: Tablet properties with Hydrolysed starch, polyvinylpyrrolidone and maize starch as binders

Properties	HS				PVP				MS			
Binder concentration $^{w}/_{v}$(%)	2.5	5.0	7.5	10	2.5	5.0	7.5	10	2.5	5.0	7.5	10
Mean tablet hardess (KgF)	2.0	2.8	4.2	5.2	2.3	4.0	5.1	5.7	3.6	5.0	5.4	6.2
Friability (%)	14	11	3	1.9	12	3.9	2.3	0.3	10	2.3	2.0	0.9
Weight uniformity	612.5	616.5	618.5	617	623.5	613	598.5	611.5	622.5	633	610.5	635
(mg) SD)	(19.97)	(10.14)	(9.10)	(7.14)	(11.08)	(6.40)	(19.82)	(6.54)	(6.98)	(15.50)	(9.21)	(5.92)
Mean disintegration time (min)	0.35	0.38	0.52	1.05	0.83	0.92	1.12	1.13	0.42	0.47	0.58	0.9

* Values shown in bracket represent standard deviation

Peroxide value

The peroxide value was determined using AOAC method 965-33.

Calorific value

The calorific value was determined using the 6100 Bomb Calorimeter.

RESULTS, DISCUSSION AND CONCLUSION

Table 1 shows that the *J. curcas* kernel oil content is relatively higher (52.70±2.91% dry w/w) compared to *A. indica* kernel oil which is 32.50±2.60% dry w/w. The oil content of Jatropha kernel has been found higher than the kernel seed oil of linseed, soybean and palm kernel which are 33.33%, 18.35% and 44.60% respectively[11] , (40-60% is standard range of extracted jatropha oil as stated by Akintayo. The revelation from this study has it that *J. curcas* kernel oil and *A. indica* kernel oil are potential viable vegetable oil feedstock for production of biodiesel. This is as a result of their appreciably high oil content. *J. curcas* kernel is much preferable as it has the higher content of oil compared to *A. indica* (neem). High oil content of *J. curcas* indicates that it is more suitable as non-edible vegetable oil feedstock in oleochemical industries (biodiesel, fatty acid, soap, detergent, e.t.c). The iodine value of *J. curcas* was determined at 99.50±1.44mg/g which is higher than that of *A. indica* (76.86 ± 1.71mg/g). While the iodine value of *J. curcas* falls within the upper reference range of the Satish standard as reported[12], the *A. indica* iodine value investigated was however below the low reference standard value as stated in export-form.com of 1999. The high iodine value is due to its high content of unsaturated fatty acid. This suggests the preference of *J. curcas* kernel oil in production of alkyd, resin, shoe polish[12] . As crude oil, the peroxide value of Jatropha kernel oil and *A. indica* kernel oil showed low values of 1.90± 0.09(meq/kg) and 1.63± 0.34(meq/kg) respectively, proving their relative oxidative stabilities. Saponification values of studied oil samples were 202.60mg/g and 179.91mg/g for *J. curcas* and *A. indica* respectively. Their high saponification value indicates they are normally triglyceride and very useful in production of liquid soap and shampoo. The experimental free fatty acid and acid value content of the *J. curcas* kernel oil were low (2.26%, 4.47mgKOH/g) compared to *A. indica* kernel which is relatively higher (6.07%, 12.08mgKOH/g). Since high FFA have significant effects on transesterification of triglycerides with alcohol using catalyst[13] , *J. curcas* oil stands to produce an increased biodiesel yield over *A. indica* which has higher acid value when transesterification of both oils are done under the same conditions.

Table 2. Physicochemical parameters of Jatropha biodiesel and *Azadirachta indica (neem)* biodiesel in relation with ASTM 6571 and EN14214 standards.

	Parameters	Jatropha Biodiesel	Neem Biodiesel	ASTM 6571 Standard	EN 14214 Standard
1.	Free fatty acid (% as oleic acid)	0.21 ± 0.02	0.28 ± 0.03	-----	-----
2.	Acid value (mg KOH/g)	0.41± 0.02	0.56 ± 0.05	0.80	0.50(max)
3.	Specific gravity (g/cm^3)	0.8867 ± 0.01	0.8831± 0.04	0.87- 0.90	-----
4.	Viscosity (cp)	3.73 ± 0.21	4.40 ± 0.20	------	5.00(max)
5.	Kinematic viscosity (cst)	4.21 ± 0.17	4.98 ± 0.41	1.9- 6.0	-----
6.	Sponification value (mg/g)	45.85 ± 0.29	53.54 ± 2.95	-----	-----
7.	Iodine value (mg/g)	53.33 ± 4.62	47.18 ± 1.17	-----	120.00(max)
8.	Peroxide value (meq/l)	0.32 ± 0.04	0.43 ± 0.07	-----	-----
9.	Colour	Golden yellow	Light brown yellow	Golden yellow	Golden yellow
10.	Calorific value (kcal/kg)	9436.6213	9566.7326	10,170.0000 (this value is for standard petroleum diesel fuel)	-----

American society for testing and material standard (ASTM) and the European standard (EN) were used for biodiesel standard.

Table 3. A relationship between biodiesel production yield and variable temperature using *Jatropha curcas* oil and *Azadirachta indica* oil

	Jatropha curcas oil				*Azadirachta indica* oil			
	1	2	3	4	1	2	3	4
Temp(0^c)	40	50	60	80	40	50	60	80
Quantity of Biodiesel (% v/v)	95	97	98	95	94	95	97	92

Table 4. A relationship between biodiesel production yield and variable quantity of NaOH catalyst, using *Jatropha curcas* oil and *Azadirachta indica* oil.

	Jatropha curcas oil				*Azadirachta indica* oil			
	1	2	3	4	1	2	3	4
Catalyst (NaOH) (g/100cm^3 of oil)	0.10	0.24	0.30	0.40	0.40	0.60	0.82	1.0
Quantity of biodiesel (% v/v)	87	96	90	75	70	85	95	85

Table 5. A relationship between biodiesel production yield and variable molar ratio of methanol to *Jatropha curcas* oil and and *Azadirachta indica* oil.

	Jatropha curcas oil				*Azadrachta indica*			
	1	2	3	4	1	2	3	4
Quantity of methanol (% v/100cm^3 of oil)	10	13.5	16.5	19.5	10	13.5	16.5	19.5
Quantity of biodiesel (% v/v)	90	98	97	98	91	98	98	98

The fluidity of a liquid is described by its viscosity. The viscosity of a liquid tends to increase with molecular weight but decreases with increasing unsaturation and temperature[14]. In this study, the viscosity of *J. curcas* kernel oil was found to be 53.80± 0.25cp less than *A. indica* (72.60± 0.80cp). By these values, *A. indica* kernel oil will however create a more operational problem when used directly in diesel engines than oil of *J. curcas*. High viscosity of both crude vegetable oils makes them unsuitable as fuel in diesel engines. Jatropha kernel oil is however less viscous compared to neem kernel oil. This less viscous nature explains a probable reason why Jatropha oil has been used as blend with conventional diesel, as reported in literatures. The oil energy content is defined by its calorific value. Neem crude oil energy content (9368.2363kcal/kg) is higher than that of jatropha crude oil (9244.7326kcal/kg). Both values were below the standard calorific value for jatropha crude oil (9470.0000kcal/kg). While *J. curcas* kernel oil from cool press is light yellow in colour, the *A. indica* oil is more dark greenish brown in colour. The data on physicochemical parameter of *J. curcas* kernel oil and *A. indica* kernel oil biodiesel from this study are shown in Table 3. The American Society of Testing Material and European standard were used as reference standards in the comparative study.

In Table 2, the viscosity of the crude oil decreases after transesterification to biodiesel in both kernel oil samples used (for *J. curcas* from 53.80± 0.25 cp to 4.21 ± 0.17 cp, and 72.60 ± 0.80 cp to 4.98 ± 0.41cp in the case of *A. indica*). The kinematic of 1.9-6.0 cs. Through this reduction, the flow ability of the crude oil increases greatly. It was found that saponification value of *A. indica* was higher compared to that of *J. curcas*. The observed relationship in terms of saponification value is a reflection of a complete transesterification that has taken viscosities for both biodiesels are all within the ASTM standard place with *J. curcas* oil against the case with *A. indica* oil due to high FFA, in the later.

However, the iodine values of both biodiesels fall below the EN standard maximum of 120 mg/g.

Transesterification of the *J. curcas* crude oil to biodiesel resulted in reduction of acid values from 4.47% to 0.41% and *A. indica* crude oil from 12.08% to 0.56%. Acid value, higher than 0.80 have been found to cause fuel system deposit and reduce life for fuel pump and filter.

Though slight variation still exists in the investigated acid value for both biodiesels, they however fall within the ASTM and EN standard value of 0.80%. Transesterification can occur at different temperatures, depending on the oil used. In this research, the methanolysis of *J. curcas* and *A. indica* oils at 13.5% with an NaOH catalyst of 0.24 g/100cm3 of oil (for *J. curcas)* and 0.82 g/100cm3 of oil (for *A. indica*) at a temperature of 60^{o}C in both cases were found to yield most of the biodiesel. Notably, from Tables 3 and 4, it was observed that marginal decrease in biodiesel yield occurs with increase in temperature above 60^{o}C.The alkali catalyst (NaOH) concentration in the range of 0.1- 1.0g/100cm^{3} of oil was used in the biodiesel production. The effect of catalyst amount on biodiesel yield was shown in Table 4. The maximum yield was achieved at 0.24g (NaOH) for jatropha and 0.82g (NaOH) for *A. indica*. The high amount of NaOH used in *A. indica* was due to the high FFA content which usually interferes with the transesterification reaction. Addition of excess catalyst, gave rise to the formation of an emulsion, which increased the viscosity and lead to formation of gel. Table 5 shows the effect of quantity of methanol used on biodiesel yield. The maximum yield was obtained at 13.5% methanol to 100cm^{3} of oil used. Further increase above this mark had no significant effect on the biodiesel yield. When excess alcohol is used however, it can be removed by either washing or simple distillation. In the case where distillation is used, the recovered alcohol is recycled and used in further transesterification.

CONCLUSION 2.26± 0.25% FFA content of Jatropha kernel oil as against 6.07± 0.05% of FFA in neem kernel oil favors jatropha oil as biodiesel feedstock in a simple base-catalyzed transesterification. The relatively low peroxide value of both oils indicates their oxidative stability at room temperature, hence less storage problem is encountered as such. Though, in relation with corresponding standards, crude oil of *Jatropha curcas* and *Azadirachta indica* from this part of Nigeria are good feedstock for biodiesel industries, *J. curcas* oil is, however, most preferable due to factors discussed above. In this work, biodiesel from *J. curcas* kernel oil with 2.26% FFA was transesterified with 0.24g of NaOH and methanol. *A. indica* kernel oil with 6.07% FFA was equally transesterified with 0.82% of NaOH and methanol also. Both processes were successful. The evaluated physiochemical properties of produced biodiesel were compared with the ASTM and EN standard. The FFA, acid value, specific gravity and viscosity have been found to fall within the reference value of both standards: where applicable. The iodine and saponification values of Jatropha biodiesel were determined at 53.33 ± 4.62mg/g, 45.85 ± 0.29mg/g respectively, in comparison with that of neem which stands at 47.18 ± 1.17mg/g, 53.54 ± 2.95mg/g respectively. The calorific values of the crude oils were a reflection of their energy content, which are not readily released during combustion due to higher viscosity and molecular weight of the triacylglycerol. Thus, in transesterification, the long chain fatty acids are converted to lower molecular weight fatty acid esters (biodiesel) that burn with relative ease. This described the reason for increase in the calorific value from 9368.2363kcal/kg (for crude neem oil) to 9566.7326kcal/kg (for neem biodiesel), and 9244.2321kcal/kg (for crude jatropha oil) to 9436.6213kcal/kg (for jatropha biodiesel).

The effects of temperature, catalyst amount and quantity of methanol on the quantity of biodiesel yield (%v/v) were also investigated in this study. 98% biodiesel yield was obtained at 60oC in the transesterification of jatropha oil (0.24g NaOH) and neem oil (0.82g NaOH). Whereas, 13.5% of methanol was adopted in the transesterification reaction with, biodiesel productions yield of 97% (Jatropha oil) and 96% (Neem oil). Concerning hydrogen peroxide treated neem oil; there was obviously a marked difference in the odour when compared with untreated neem oil. Though the odour was not eliminated completely by the aforementioned treatment, there was however a considerable reduction in the stinking odour.

RECOMMENDATION Feedstock cost is a common problem associated with biodiesel production. Further treatment like decorticating the shell before oil extraction amounts to undue expenditure on the overall production cost. Hence a comparative study can be instituted on the physicochemical parameter of the oil extracted from seed before removal of shell and the oil extracted after removal of shell. Quality of biodiesel can also be investigated from acid transesterified oil and compared with that of base transesterified oil.

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