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PROCESSING OF CASTOR SEED OIL WITH METHANOL TO BIODIESEL OVER CAUSTIC SODA

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ABSTRACT

In this study, the conversion of castor seed oil to biodiesel through transesterification method and determining the physicochemical properties of biodiesel were investigated. The varying molar ratio (1:3, 1:4, 1:5 and 1:6) of oil to methanol was studied for optimum ester content of biodiesel. Gas chromatography-mass spectrometry (GC-MS) was used to determine the ester content of the samples. The ester content of the four samples was, 96.23, 96.53, 98.26 and 93.26%. The physicochemical properties of the biodiesel were determined using Empirical correlation. Kinematic viscosity, saponification value, specific gravity, iodine value, heating value and cetane number were found to be 3.37, 1.36, 4.23 and 3.48 mm^2/s for kinematic viscosity; 192.65, 197.60, 189.94 and 184.25 g/100g for saponification value; 61.84, 90.58, 65.86 and 58.43 mgKoH/100g for iodine value; 69.71, 69.86, 71.16 and 68.55 for cetane number; 1.12, 0.82, 0.82 and 1.07 for specific gravity; 46.31, 46.59, 47.34 and 41.37 mg/kg for upper heating value respectively. Compared to the standard, it proved that castor seed oil was suitable to be used as feedstock for biodiesel production.

Keywords: Biodiesel, castor seed oil, ester content, physiochemical properties.

INTRODUCTION

Petroleum fuels play a very important role in the development of various industries, transportation, agriculture sector and to meet many other basic human needs in modern civilization. These fuels are limited and depleting day by day as the consumption increase very rapidly. The use of petroleum fuel has caused a lot of environmental problems high emission of harmful gases. A global movement towards generation of environmentally friendly yet renewable fuel is therefore under way to help meet the increased energy demands. Bio fuel had become one of the most promising alternatives for petroleum fuels [1].

Biodiesel is potential biofuel that can easily be produced from vegetable oil. Biodiesel has become an interesting alternative fuel over conventional diesel for decades. Biodiesel has

similar properties with conventional diesel in terms of power and torque and none or very minor engine modification is required [2]. Biodiesel is biodegradable which will result in less environmental impact upon accidental release to the environment [3]. It has many important technical advantages over conventional diesel such as inherent lubricity, low toxicity, derivation from a renewable and domestic feedstock, superior flashpoint, negligible sulphur content and lower exhaust emission [3].

Among the common vegetable oils used as feedstock for the production of biodiesel are soybean, rapeseed, castor, jatropha and palm oil. Castor oil is one of the promising feedstock for biodiesel production. Castor oil is produced by means of extraction from castor beans. Castor oil is distinguished by its high content (over 85%) of ricinoleic acid. No other vegetable oil contains so high a proportion of fatty hydroxyacids [3]. Castor oils have high molecular weight (298), low melting point (5 ^{o}C) and very low solidification point (-12 ^{o}C to -18 ^{o}C) that make it industrially useful. It has the highest and most stable viscosity of any vegetable oil [4]. As castor oil is non-edible, there is no issue of competition with the food market and it can be the source of feedstock for biodiesel production [5].

In this study, Biodiesel was produced using acid and based catalyzed esterification and transesterification of castor oil varying methanol molar ratio. Furthermore, the properties of castor oil biodiesel were studied and compared to EN and ASTM standards. Additionally, the ester content of biodiesel samples was investigated using Gas chromatography-mass spectroscopy (GC-MS).

MATERIAL AND METHODS

Crude castor oil was extracted from castor beans by using mechanical press. The castor beans used were obtained from Central market, Kaduna, Nigeria.

The acid value of the crude castor oil was determined by titrimetry. The castor oil was converted into biodiesel by using two-step processes. The first step is acid-catalyzed esterification using sulphuric acid (1% v/v) as catalyst, methanol (2.5% v/v) was used to convert free fatty acids (FFA) in castor oil to methyl ester, followed by base-catalyzed transesterification using sodium hydroxide as catalyst with methanol. In the second step, sodium hydroxide was dissolved in methanol to form methoxide. The pre-treated oil in Step 1 was heated up to$60^{o}C$. The heated oil was mixed with the methoxide and the solution was shaken for 40min using

stirrer. The mass ratio of oil to methanol used was 1:3, 1:4, 1:5 and 1:6 respectively. After completing the process, the mixtures were allowed to settle in separating funnel for 40min. It produced two phases (the lower phase and the upper phase), the lower phase was the glycerol and other byproduct which were removed and the upper layer was the biodiesel.

Biodiesel testing was carried out to compare the properties and performances of castor biodiesel with ASTM and EN standard. The saponification value, iodine value, viscosity, specific gravity, cetane number and upper heating value are determined using correlation developed by researchers [3]. Castor biodiesel was tested for ester content using GC-MS analysis.

The samples physical properties presented in Tables 3-6 were calculated based on the percentage composition of individual fatty acid methyl ester (FAME) in the biodiesel samples. Correlation equations for estimating viscosities of pure FAME [6] are presented in Equations 1,2 and 3 for saturated, mono saturated and poly saturated FAME respectively.

$$\ln v_{sat} = \mathrm{a}NC^{b} + \frac{cNC^{d}}{elnNC+f+t} \qquad (1)$$

$$\ln v_{mono-unsat} = \mathrm{g}NC^{h} + \frac{iNC^{j}}{K+t} \qquad (2)$$

$$\ln v_{poly-unsat} = \mathrm{g}(NC—ND) + \frac{i(NC+ND)^{j}}{K+T} \qquad (3)$$

Where v is kinematic viscosity, NC is the number of carbon atoms in the FAME, ND is the number of double bonds and T is the temperature in Kelvin (313.15K). Others are fitted parameters their values are given in Table 1.

Table 1: Parameter values for equations 1-3 used to calculate the kinematic viscosity of FAMEs

Parameters	A	B	C	D	E	F
Values	-3.02918	-0.138813	186.962	0.400877	-22.9221	-88.9471
Parameters	G	H	I	J	K	L
Values	-0.452351	0.452419	42.9765	0.849646	-158.712	1.14044

Source: Ibrahim et al [6].

Saponification values of pure fatty acid esters were estimated from Eq.4 [6].

$$SV = \frac{56106}{MW} \qquad (4)$$

Where SV is the saponification value of pure individual fatty acid esters and MW is the molecular weight.

The correlation equation [6] was used to estimate the cetane number of fatty acid esters. The correlation is expressed as in Eq 5.

$$CN = 58.1 + 2.8 (\text{No of carbons}/2) - 15.9 \times \text{No of double bonds} \quad (5)$$

Gopinath et al provided expression for specific gravity, SG as in Eq. 6 and it was used to estimate the specific gravity of pure FAME of the samples.

$$SG = 0.8475+0.0003IV+0.00014SV \quad (6)$$

Where SG is the specific gravity of individual fatty acid ester, IV is the iodine value and SV is the saponification value of pure individual esters respectively.

The expression [6] as expressed in Eq. 7 was used to estimate the iodine values of the samples.

$$IV = 100 * \frac{253.82*db}{MW} \quad (7)$$

Where IV is iodine value, db is the number of double bonds and MW is the molecular weight.

Eq. 8 for expression of the Upper heating value of pure FAME of biodiesel sample

$$Q_u = 49.43 - (0.041SV + 0.015IV) \quad (8)$$

Where Q_u is upper heating value, SV is the saponification value and IV is iodine value of individual esters.

RESULTS AND DISCUSSION

From the experiment, the amount of methanol was set as the manipulated variable while the amount of castor oil was set as the constant variable. From Table 2, it is observed that the highest yield of biodiesel was achieved with 1:6 of oil to methanol ratio. The biodiesel yield was affected by the amount of methanol used. The ester content of 1:3 formulation is slightly lower than EN standard as presented in Table 3 and Figure 1. The ester content of 1:4 and 1:5 are higher than EN standard 96.5 as shown in Tables 4 and 5 and also in Figure 1. This implies that the products satisfy the requirement for use in compression ignition engine (CIE). Unfortunately, formulation 1:6 had low ester content as presented in Table 6 and in Figure 1 indicating that it might not be suitable for use in CIE.

The terms from Tables 3-6 are: FM is molecular formula, EC is ester content (%), v is kinematic viscosity (mm^2/s), SV is saponification value (mgKoH/100g), and IV is iodine value (mgKoH/100 g) SG is specific gravity, CN is cetane number and Qu is upper heating value.

Table 2: Biodiesel yield percentage for different amount of methanol

Oil to methanol ratio (g/g)	Biodiesel yield%
1:3	68.40
1:4	67.13
1:5	61.00
1:6	75.38

Table 3: Sample 1 product analyses

S/N	COMPOUND	FM	EC	V	SV	IV	SG	CN	QU
1	Pentanal	$C_5H_{10}O$							
2	Heptane	C_7H_{16}							
3	Methyl octanoate	$C_9H_{18}O_2$	2.13	0.016	7.564		0.018	1.506	1.046
4	Methyl decanoate	$C_{11}H_{22}O_2$	3.32	0.029	10.015		0.028	2.440	1.627
5	Methyl dodecanoate	$C_{13}H_{26}O_2$	1.44	0.0156	3.775		0.122	1.098	0.709
6	Methyl Nonaote	$C_{11}H_{20}O_4$	2.12	0.047	5.507	2.491	0.018	1.221	1.044
7	Methyl tetradecanoate	$C_{15}H_{30}O_2$	1.05	0.0063	2.434		0.009	0.831	0.518
8	Methyl 9, hexadecenoate	$C_{17}H_{32}O_2$	2.64	0.114	5.527	2.500	0.022	1.742	1.300
9	Methyl Octadecanoate	$C_{19}H_{30}O_2$	1.28	0.0096	2.409		0.011	1.084	0.631
10	Methyl tridecanoate	$C_{14}H_{28}O_2$	6	0.0094	14.765		0.125	4.662	2.930
11	methyl 9, octadecenoate	$C_{19}H_{36}O_2$	19.3	1.0141	36.583	16.549	0.166	13.278	9.203
12	Methyl hexadecanoate	$C_{17}H_{34}O_2$	2.54	0.0143	5.963		0.022	2.080	1.249
13	Methyl heptadecanoate	$C_{18}H_{36}O_2$	3.31	0.0114	6.539		0.028	2.757	1.627
14	Methyl ricinoleate	$C_{19}H_{36}O_3$	35.6	1.919	64.019	28.961	0.308	24.493	16.820
15	methyl 9,12-octadecadienoate	$C_{19}H_{36}O_3$	2.28	0.023	4.351	3.937	0.019	1.206	1.123
16	Methyl ,14-methyl hexadecanoate	$C_{18}H_{36}O_2$	2.65	0.023	5.235		0.023	2.207	1.304
17	methyl 9,12,15-octadecatrienoate	$C_{19}H_{32}O_2$	1.15	0.038	2.209	2.999	0.011	0.979	0.567
18	methyl 2-undecyl cyclopentanepentanote	$C_{20}H_{38}O_2$	1.27	0.019	2.299	0.989	0.010	0.892	0.620

19	methyl eicosanoate	$C_{21}H_{42}O_2$	3.76	0.030	6.471		0.032	3.290	1.850
20	Methyl docosanoate	$C_{23}H_{46}O_2$	4.36	0.0025	6.989		0.037	3.937	2.142
	TOTAL		96.23	3.3706	192.647	58.426	1.074	69.708	46.310

Table 4: Sample 2 product analyses

S/N	COMPOUND	FM	ES	V	SV	IV	SG	CN	QU
1	Pentanal	$C_5H_{10}O$							
2	Heptane	C_7H_{16}							
3	Methyl octanoate	$C_9H_{18}O_2$	3.04	0.023	10.795		0.026	2.149	1.490
4	Methyl decanoate	$C_{11}H_{22}O_2$	3.30	0.025	9.954		0.028	2.426	1.618
5	Methyl dodecanoate	$C_{13}H_{26}O_2$	1.13	0.0009	2.963		0.0096	0.862	0.557
6	Methyl Nonaote	$C_{11}H_{20}O_4$	2.03	0.045	5.273	2.385	0.017	1.169	0.998
7	Methyl tetradecanoate	$C_{15}H_{30}O_2$	0.18	0.0002	0.417		0.0015	0.142	0.0889
8	Methyl 9, hexadecenoate	$C_{17}H_{32}O_2$	3.10	0.045	6.489	2.955	0.0263	2.046	1.523
9	Methyl Octadecanoate	$C_{19}H_{30}O_2$	1.92	0.0094	4.728		0.016	1.626	0.945
10	Methyl tridecanoate	$C_{14}H_{28}O_2$	3.56	0.0057	8.760		0.0302	2.766	1.747
11	methyl 9, octadecenoate	$C_{19}H_{36}O_2$	21.4	0.36	40.564	18.351	0.182	14.723	10.282
12	Methyl hexadecanoate	$C_{17}H_{34}O_2$	8.28	0.031	19.437		0.0703	6.781	4.027
13	Methyl heptadecanoate	$C_{18}H_{36}O_2$	2.13	0.009	4.208		0.0181	1.774	1.049
14	Methyl ricinoleate	$C_{19}H_{36}O_3$	32.9	0.554	59.164	26.765	0.280	22.635	15.590
15	methyl 9,12-octadecadienoate	$C_{19}H_{34}O_2$	2.01	0.034	3.835	3.471	0.0171	1.063	0.990
16	Methyl ,14-methyl hexadecanoate	$C_{18}H_{36}O_2$	2.44	0.011	4.819		0.0207	2.033	1.202
17	methyl 9,12,15-octadecatrienoate	$C_{19}H_{32}O_2$	2.12	0.036	4.073	6.363	0.018	1.796	1.046
18	methyl 2-undecyl cyclopentanepentanote	$C_{20}H_{38}O_2$	1.99	0.033	3.837	1.549	0.017	1.397	0.981
19	methyl eicosanoate	$C_{21}H_{42}O_2$	2.03	0.035	3.493		0.0172	1.776	1.00
20	Methyl docosanoate	$C_{23}H_{46}O_2$	2.99	0.007	4.793		0.0254	2.699	1.472
	TOTAL		96.53	1.364	197.602	61.839	0.8203	69.863	46.595

Table 5: Sample 3 product analyses

S/N	COMPOUND	FM	ES	V	SV	IV	SG	CN	QU
1	Pentanal	$C_5H_{10}O$							
2	Heptane	C_7H_{16}							
3	Methyl octanoate	$C_9H_{18}O_2$	1.13	0.0084	4.013		0.0096	0.799	0.558
4	Methyl decanoate	$C_{11}H_{22}O_2$	1.02	0.0093	3.077		0.0088	0.749	0.504
5	Methyl dodecanoate	$C_{13}H_{26}O_2$	2.31	0.0019	6.056		0.0196	1.763	1.140
6	Methyl Nonaote	$C_{11}H_{20}O_2$	1.06	0.0097	2.753	2.385	0.0090	0.661	0.522
7	Methyl tetradecanoate	$C_{15}H_{30}O_2$	1.00	0.0099	2.318		0.0085	0.791	0.494
8	Methyl 9, hexadecenoate	$C_{17}H_{32}O_2$	3.40	0.011	7.118	2.936	0.0289	2.244	1.673
9	Methyl Octadecanoate	$C_{19}H_{30}O_2$	1.03	0.0113	1.939		0.0087	0.872	0.530
10	Methyl tridecanoate	$C_{14}H_{28}O_2$	1.07	0.0120	2.633		0.0091	0.832	0.532
11	Methyl,14-methyl Hexadecanoate	$C_{18}H_{36}O_2$	16.2	0.870	32.004	3.182	0.1380	13.495	7.910
12	methyl9, octadecenoate	$C_{19}H_{36}O_2$	8.61	0.610	16.431	18.475	0.0730	5.924	4.235
13	Methyl hexadecanoate	$C_{17}H_{34}O_2$	1.21	0.014	2.176		0.010	0.991	0.598
14	Methyl ricinoleate	$C_{19}H_{36}O_3$	32.6	1.758	61.584	1.733	0.277	22.439	15.913
15	methyl 9,12-octadecadienoate	$C_{19}H_{34}O_2$	7.03	0.379	13.508	56.807	0.059	3.719	3.300
16	methyl 9,12,15-octadecatrienoate	$C_{19}H_{32}O_2$	7.82	0.422	15.026	5.242	0.0664	6.624	3.848
17	methyl 2-undecyl cyclopentanepentanote	$C_{20}H_{38}O_2$	4.17	0.076	7.547	1.549	0.035	2.927	2.054
18	methyl eicosanoate	$C_{21}H_{42}O_2$	3.00	0.021	5.163		0.025	2.625	1.481
19	Methyl docosanoate	$C_{23}H_{46}O_2$	4.16	0.0097	6.593		0.0353	3.756	2.052
	TOTAL		98.26	4.2323	189.939	90.576	0.8209	71.161	47.344

Table 6: Sample 4 product analyses

S/N	COMPOUND	FM	ES	V	SV	IV	SG	CN	QU
1	Pentanal	$C_5H_{10}O$							
2	Heptane	C_7H_{16}							
3	Methyl octanoate	$C_9H_{18}O_2$	2.01	0.0149	7.138		0.0171	1.421	0.9933

4	Methyl decanoate	$C_{11}H_{22}O_2$	1.04	0.0126	3.137		0.0088	0.764	0.514
5	Methyl dodecanoate	$C_{13}H_{26}O_2$	2.19	0.0029	5.742		0.019	1.671	1.081
6	Methyl Nonaote	$C_{11}H_{20}O_2$	1.08	0.0099	2.805	1.269	0.0092	6.221	0.533
7	Methyl tetradecanoate	$C_{15}H_{30}O_2$	1.10	0.010	2.550		0.0093	0.871	0.543
8	Methyl 9, hexadecenoate	$C_{17}H_{32}O_2$	2.22	0.00121	4.648	2.103	0.0188	1.465	0.671
9	Methyl Octadecanoate	$C_{19}H_{30}O_2$	2.01	0.0123	3.784		0.0171	1.703	0.992
10	Methyl tridecanoate	$C_{14}H_{28}O_2$	2.37	0.0127	5.832		0.0201	1.841	1.169
11	Methyl,14-methyl Hexadecanoate	$C_{18}H_{36}O_2$	4.14	0.310	8.179		0.0351	3.449	2.513
12	methyl9, octadecenoate	$C_{19}H_{36}O_2$	10.7	0.840	20.419	9.238	0.091	9.909	5.256
13	Methyl hexadecanoate	$C_{17}H_{34}O_2$	12.1	0.910	25.144		0.103	21.397	5.935
14	Methyl ricinoleate	$C_{19}H_{36}O_3$	31.1	1.710	55.926	25.301	0.264	2.291	5.867
15	methyl 9,12-octadecadienoate	$C_{19}H_{34}O_2$	4.33	0.312	8.263	7.476	0.0368	6.089	3.913
16	methyl 9,12,15-octadecatrienoate	$C_{19}H_{32}O_2$	7.19	0.381	13.815	18.749	0.0610	1.474	4.531
17	methyl 2-undecyl cyclopentanepentanote	$C_{20}H_{38}O_2$	2.10	0.068	2.801	1.719	0.0178	1.452	2.735
18	methyl eicosanoate	$C_{21}H_{42}O_2$	2.52	0.019	4.337		0.0214	1.969	1.910
19	Methyl docosanoate	$C_{23}H_{46}O_2$	5.05	0.0099	8.004		0.0429	4.560	2.171
	TOTAL		93.26	3.4844	184.524	65.855	1.1236	68.547	41.327

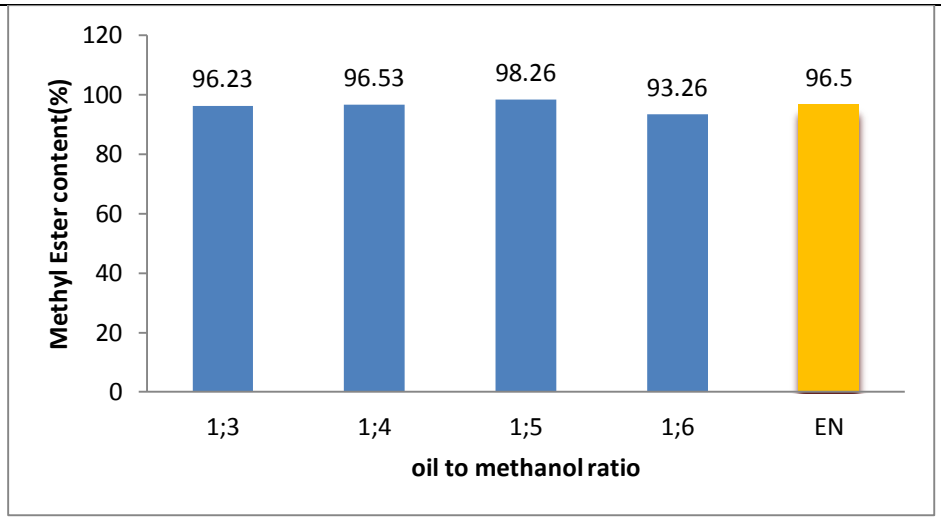

Figure 1: Sample methyl ester content compared to EN standard.

The four samples of biodiesel produced had viscosity within the ASTM set standard of 1.6 – 6.0 mm^2/s and EN standard of 5 as shown in the Fig 2. Iodine value of the samples was generally low. The highest was 90.576 mgKOH/100g of 1:4 (oil to methanol ratio) and the lowest was 65.855 mgKOH/100g of 1:6 which were lower than the ASTM and EN maximum standard of 120 as depicted in Figure 3 indicating the fuels are liable to have long shelf-life. Low iodine values indicate low level of un-saturation of the biodiesel. They have high mono unsaturated esters as presented in Tables 3 to 6 [6].

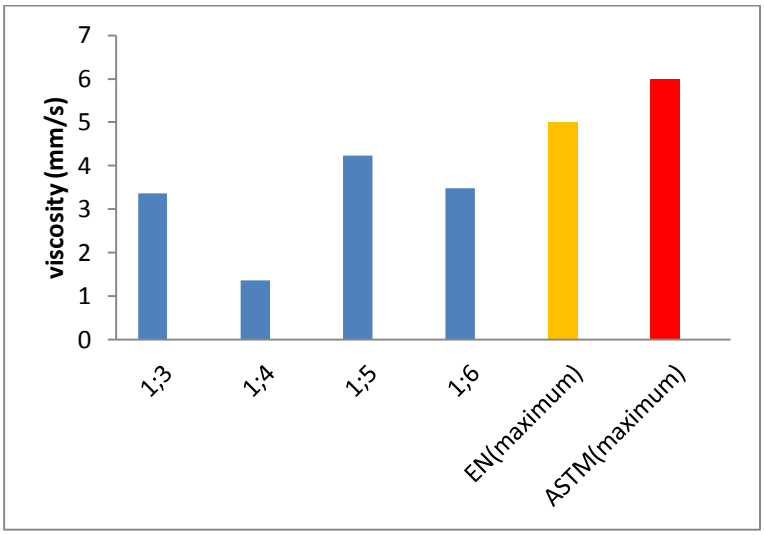

Figure 2: Comparison of samples of viscosities with standard.

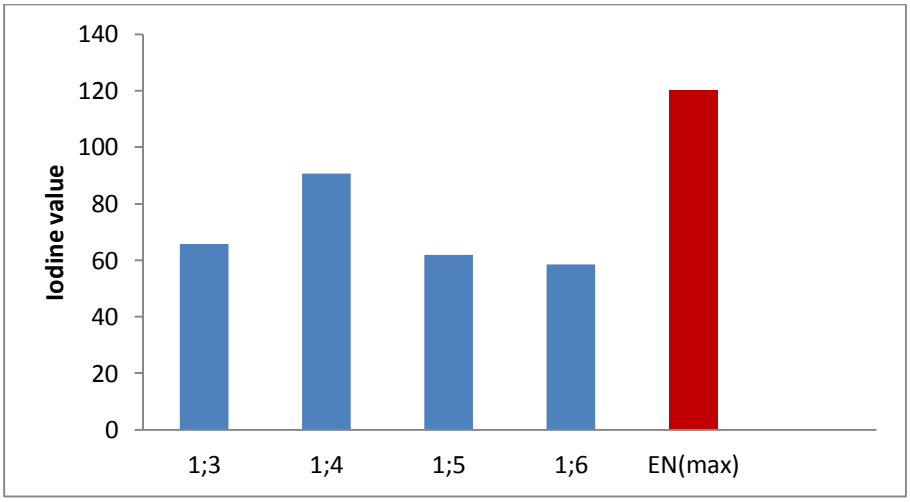

Figure 3: Comparison of samples of iodine values with EN standard.

Their cetane values were higher than the minimum set standard of EN and ASTM of 51 and 47 shown in Figure 4, which specified the ignition quality of a fuel for use in a diesel engine [10] indicating that they have better combustion than fossil diesel.

Two samples have high specific gravity 1.1236 and 1.074 of 1:4 and 1:6 (oil to methanol ratio) and the other two were lower than the EN and ASTM set standard of 0.86 and 0.8203 respectively.

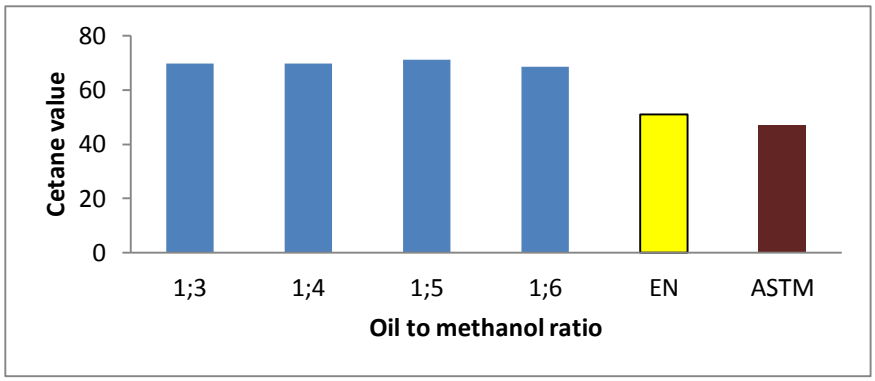

Fig 4: Comparison of samples of cetane values with standards

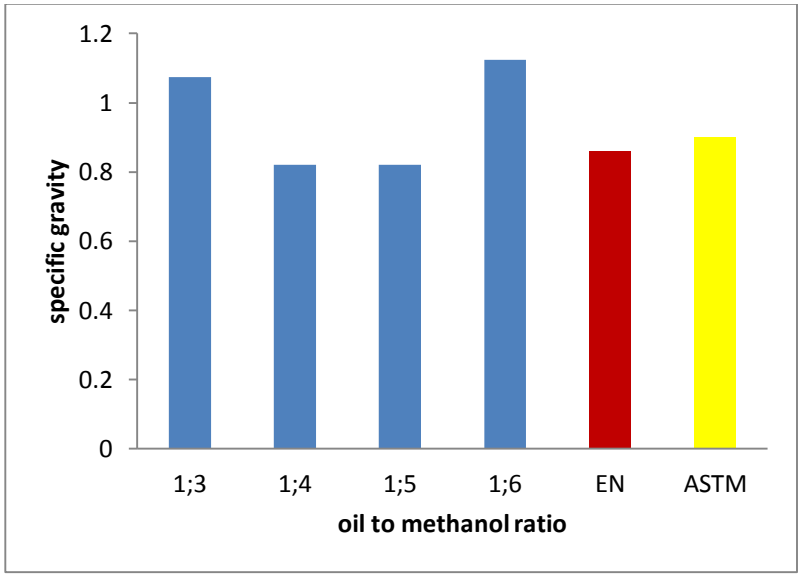

Fig 5: Comparison of samples of specific gravity with standards

All the samples had high saponification values as shown Figure 6. There was no ASTM and EN standard for biodiesel saponification value to compare with our sample values [6].

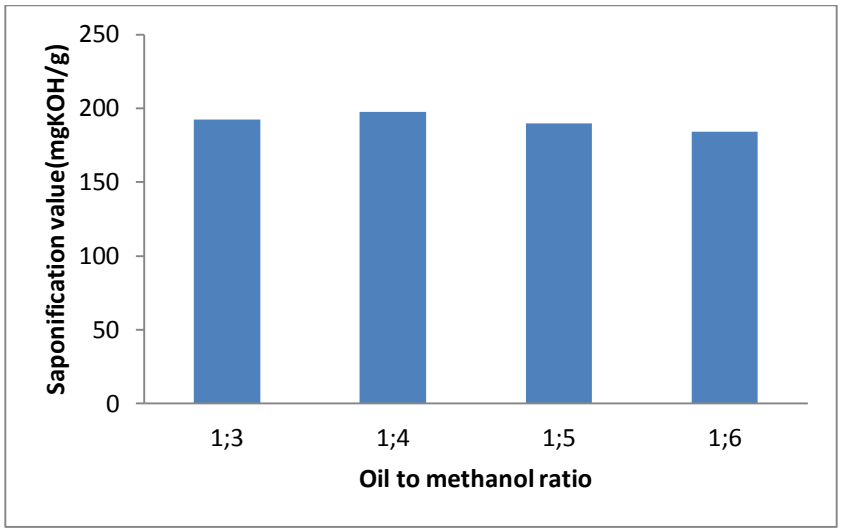

Fig 6: Comparison of saponification values of samples

CONCLUSION

Biodiesel is a good alternative fuel for diesel engines because it is environmentally friendly are renewable in nature. Castor seed is a non-edible seed which has no direct impact on food supply and cheap to purchase. The ester content of the biodiesel produced from 4 sample seeds were 96.23, 96.53, 98.26 and 93.26% respectively. The cetane values, viscosity and iodine values all are in the range of within ASTM and EN standard ranges. The variation of molar ratio between oil and methanol indicated that 1:4 and 1:5 ratios produced the best result. It is recommended that pilot studies of biodiesel production from castor seed oil be considered for commercial production in Nigeria and in other tropical countries.

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