AN EMPIRICAL APPROACH FOR PREDICTING SOME IMPORTANT BIODIESEL PHYSICAL PROPERTIES FROM THEIR FATTY ACID ESTER COMPOSITIONS

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ABSTRACT

Machine analyses of samples are sometimes too tedious and difficult to carry out. The problems may arise from unavailable or faulty machines or lack of power to operate the machines or contamination of samples at the point of analysis. Even, the analyst may not have the skill. Empirical correlations developed by some renowned scientists for biodiesel physical properties have relieved the researchers from some of the bottlenecks. These include: kinematic viscosity, saponification value, iodine value, specific gravity, cetane number and heat of combustion. The aforementioned properties of three biodiesel samples produced from *Jatrophacurcas* seed oil, methanol and solid base catalysts, bulk calcium oxide, super base calcium oxide and calcium oxide/magnesium oxide were empirically calculated based on their fatty acid esters composition obtained from GC-MS. The values obtained were 5.2, 5.2 and 5.3 mm^2/s for kinematic viscosity; 193.2, 193.1 and 192.1 mgKOH/g for saponification values; 62.5, 53.6 and 53.6 $gI_2/100g$ for iodine values; 0.853, 0.848 and 0.854 for specific gravity;73.1, 72.6 and 71.9 for cetane number and 40.82, 40.30 and 40.20 MJ/kg for heat of combustion respectively.

Keywords: biodiesel, empirical approach, fatty acid esters, physical properties,

INTRODUCTION

In recent years, increases in carbon dioxide emissions caused by the use of fossil fuels, have resulted in a rapid advance in global warming [1]. Hence, there is an urgent call for the reduction of carbon dioxide emissions. Efforts are also being made to reduce dependence on fossil products due to rapid decrease in its resource and price instability [2]. This condition has raised interest in the use of bio-based fuels from plant and animal origins, which places a lower burden on the environment as an alternative to fossil fuels. Chiefly in this category are biodiesel and bioethanol. Biodiesel is a reliable, secure, clean, affordable and sustainable energy fuel. Knowing the profile of alkyl esters in biodiesel is of great importance as it controls its main properties [3]

The physical characteristics of fatty acid esters are closer to those of fossil diesel fuels than pure vegetable oils, but its properties depend on the type of feedstock and the alcohol used for the production. Physical properties of biodiesel depend on fatty acid ester compositions of the feedstock [4]. The properties of the various fatty esters that comprise biodiesel determine the overall properties of the biodiesel fuel [5]. Many useful methods have being found by researchers to estimate fuel properties from its fatty acid profile. A simple and reliable calculation method to estimate fuel property is therefore needed to avoid experimental testing which is difficult, costly and time consuming [6].

In this work, three different biodiesel samples produced at different times were analyzed with GCMS machine to determine their fatty acid methyl ester profiles. The most important physical properties of biodiesel for use in compression ignition engine such as viscosity, cetane number, energy content, specific gravity and iodine value and also saponification value were estimated using correlation equations from their Fatty acid methyl ester profile.

MATERIALS AND METHODS

The materials used in this study include *Jatrophacurcas* seed oil, analytical grade methanol, bulk calcium oxide, super base calcium oxide and calcium oxide/magnesium oxide catalysts, conical flask, Gallenkamp hot plate magnetic stirrer, biodiesel process intensify pilot plant and GCMS-QP@) PLUS SHIMADZU/JAPAN in the Quality Control Unit of NARICT, Zaria.

Three transesterifications were carried out at different periods with different catalysts but same feedstock, *Jatrophacurcas* seed oil, from NARICT *Jatropha* farm.

About 200 g of *Jatrophacurcas* seed oil was transesterified with 40 g of methanol and 3.0 g of super base calcium oxide catalyst in a 500 ml conical flask on a Gallenkamp hot plate magnetic stirrer at 60^{o}C for 60 min. The product was filtered and the filtrate was collected for GCMS analysis.

The second transesterification was carried out with 3.0kg of *Jatrophacurcas* seed oil with 324 g of methanol and 45.0 g of bulk calcium oxide catalyst in a biodiesel process intensify pilot plant with a residence time of 68.6 min.

The third transesterification was carried out as in the second but with calcium oxide/magnesium oxide catalyst. The products were filtered and the filtrates were collected for GCMS analysis.

About 2 ml of each sample was diluted with n-hexane filled into samples bottles and inserted into the GC-MS for esters content analysis [7].

The results were interpreted and their esters contents were calculated.

The samples' physical properties estimated in Tables 2-4 were calculated based on the percentage composition of individual fatty acid methyl esters (FAME) in the biodiesel samples.

Chavarria-Hernandez and Pacheco-Catalán, [8] provided correlated equations for estimating viscosities of pure FAME as presented in Eq. 1, 2 and 3 for saturated, mono unsaturated and poly unsaturated FAME respectively.

Eq.1 expresses the viscosities of FAME from C6-C24; Eq. 2 expresses viscosities of mono-unsaturated FAME C14.1 to C22.1 and Eq. 3 expresses those with di and tri double bonds such as C18.2 and C18.3 [8].

$$\ln \nu_{sat} = aNC^{b} + \frac{cNC^{d}}{e\ln NC + f + T} \quad (1)$$

$$\ln \nu_{mono-unsat} = gNC^{h} + \frac{iNC^{j}}{k + T} \quad (2)$$

$$\ln \nu_{poly-unsat} = g(NC - ND^{l})^{h} + \frac{i(NC - ND^{l})^{j}}{k + T} \quad (3)$$

Where ν is kinematic viscosity, NC is the number of carbon atoms in the FAME, ND is the number of double bonds and T is 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: Chavarria-Hernandez and Pacheco-Catalán [8]

Saponification values of pure fatty acid esters were estimated from Eq. 4 as expressed by Gopinath *et al* [9].

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

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

The correlation equation developed by Klopfenstein [9] was used to estimate the cetane number of fatty acid esters. The correlation is expressed as in Eq. 5.

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

Gopinath *et al* [9] 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.

$$SG(15^{o}C) = 0.8475 + 0.0003IV + 0.00014SV \quad (6)$$

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

The expression provided by Gopinath *et al* [9] as expressed in Eq. 7 was used to estimate the iodine values of the samples.

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

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

Eq. 8 for expression of the Upper heating value of pure FAME of biodiesel samples [9].

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

Where Q_U is Upper heating value, SV is saponification and IV is iodine value of individual esters.

The net heat of combustion is related to the upper heat of combustion as expressed in Equ. 9 as reported by Barabás and Todoruţ [10]:

$$Q_n = Q_U - 0.2122H \quad (9)$$

where H is the mass percentage of hydrogen in the fuel

RESULTS AND DISCUSSION

The three samples of biodiesel produced have viscosity within the ASTM set standard of 1.6 - 6.0 [11] as shown in Tables 2-4. Their iodine values were lower than the ASTM maximum standard of 120 [11]. Their low iodine value could be as a result of absence of poly-unsaturated esters. They all have mono-unsaturated esters as presented in Tables 2-4. Their specific gravity were within the EN and ASTM set standards of 0.86 and 0.9 respectively [11]. Their cetane numbers were higher than the minimum set standards of EN and ASTM of 51 and 47 respectively [11]. All their physical properties were in the same range of values. This could be due to the facts that they were all produced from the same source and all yielded 100% esters. They all possess energy value higher than the minimum set standard value for biodiesel of 37.5 MJ/kg [11].

The terms on Tables 2-4 are: FM is molecular formula, EC is ester content (%), v is kinematic viscosity (mm^2/s), SV is saponification value (mgKOH/g), IV iodine value (mgKOH/100g), SG specific gravity, CN is cetane number and Qnis net heating value (MJ/kg).

Table 2: Sample 1 product analyses

Compound	FM	EC	v	SV	IV	SG	CN	Qn
Methyl (caprylate)octanoate	$C_9H_{18}O_2$	0.528	0.0076	1.8751		0.0045	0.3733	0.2404
Methyl (pelargonate)nonanoate	$C_{10}H_{20}O_2$	0.132	0.0023	0.4306		0.0011	0.0933	0.0596
Methyl tridecanoate	$C_{14}H_{28}O_2$	0.114	0.0037	0.2805		0.0010	0.0806	0.0496
Methyl myristate	$C_{15}H_{30}O_2$	0.72	0.0273	1.6694		0.0061	0.5090	0.3096
Methyl (palmitoleate) 9-hexadecenoate	$C_{17}H_{32}O_2$	2.2	0.0910	4.6060	2.0836	0.0187	1.5554	0.9332
Methyl 11-hexadecenoate	$C_{17}H_{32}O_2$	1.1	0.0455	2.3030	1.0418	0.0093	0.726	0.4678
Methyl hexadecanoate	$C_{17}H_{34}O_2$	6.294	0.3152	13.0796		0.0535	5.1548	2.6233
Methyl 14-methylpentadecanoate	$C_{17}H_{34}O_2$	4.196	0.2109	8.7198		0.0356	3.4365	1.7563
methyl heptadecanoate	$C_{18}H_{36}O_2$	0.528	0.0302	1.0359		0.0045	0.4324	0.2204
Methyl oleate	$C_{19}H_{36}O_2$	13.974	0.7187	26.4888	11.9827	0.1195	9.6141	5.6630
Methyl 9-octadecenoate	$C_{19}H_{36}O_2$	12.874	0.6621	24.4036	11.0395	0.1100	8.8573	5.2300
Methyl 7-octadecenoate	$C_{19}H_{36}O_2$	12.874	0.6621	24.4036	11.0395	0.1100	8.8573	5.2300
Methyl 8-octadecenoate	$C_{19}H_{36}O_2$	12.874	0.6621	24.4036	11.0395	0.1100	8.8573	5.2300
Methyl Elaidate	$C_{19}H_{36}O_2$	12.874	0.6621	24.4036	11.0395	0.1100	8.8573	5.2300
Methyl (isosterate) 16-methylheptadecanoate	$C_{19}H_{38}O_2$	3.416	0.2219	6.4318		0.0290	2.8934	1.4041
Methyl (sterate)octadecanoate	$C_{19}H_{38}O_2$	13.664	0.8876	25.7273		0.1163	11.5734	5.5081
Methyl 8-(-2-octylcyclopropyl)octanoate	$C_{20}H_{38}O_2$	1.1	0.0632	1.9910		0.0093	0.7722	0.4541
Methyl (aracidate) eicosanoate	$C_{21}H_{42}O_2$	0.528	0.0439	0.9088		0.0045	0.462	0.2137
Total		**99.99**	**5.3165**	**193.1618**	**59.2659**	**0.8526**	**73.1057**	**40.8234**

Table 3: Sample 2 product analyses

Compound	FM	EC	v	SV	IV	SG	CN	HV
Methyl palmitate (hexadecanoate)	$C_{17}H_{34}O_2$	11.556	0.5788	24.0147		0.0979	9.4644	4.7646
Methyl 14-methylpentadecanoate	$C_{17}H_{34}O_2$	7.704	0.3858	16.0098		0.0653	6.3096	3.2017
Methyl 15-methylhexadecanoate	$C_{18}H_{36}O_2$	1.578	0.0902	3.1176		0.0134	1.3145	0.6574
Methyl Elaidate	$C_{19}H_{36}O_2$	29.14	1.4986	55.2370	24.9876	0.2470	20.0483	11.4087
Methyl oleate	$C_{19}H_{36}O_2$	14.57	0.7493	27.6185	12.4938	0.1235	10.0242	5.8966
Methyl 9-octadecanoate	$C_{19}H_{36}O_2$	14.57	0.7493	27.6185	12.4938	0.1235	10.0242	5.8966
Methyl 8-cotadecanoate	$C_{19}H_{36}O_2$	14.57	0.7493	27.6185	12.4938	0.1235	10.0242	5.8966
Methyl Ooctadecanoate	$C_{19}H_{38}O_2$	6.312	0.4100	11.8846		0.0535	5.3463	2.5803
Total		**100**	**5.2112**	**193.1192**	**62.4689**	**0.8475**	**72.5555**	**40.3026**

Table 4: Sample 3 product analyses

Compound	FM	EC	V	SV	IV	SG	CN	HV
Methyl hexadecanoate	$C_{17}H_{34}O_2$	5.272	0.2640	10.9558		0.0447	4.3178	2.2019
Methyl 14-methyl pentadecanoate	$C_{17}H_{34}O_2$	7.01	0.3510	14.5676		0.0595	5.7412	2.9174
Methyl 15-methylhexadecanoate)	$C_{18}H_{36}O_2$	4.374	0.2499	8.6416		0.0371	3.6435	1.8124
Methyl elaidate	$C_{19}H_{36}O_2$	31.248	1.6070	59.2329	26.7952	0.2685	21.4986	12.1743
Methyl 9-octadecenoate	$C_{19}H_{36}O_2$	15.624	0.8035	29.6165	13.3976	0.1336	10.7493	6.3083
Methyl 8-octadecenoate	$C_{19}H_{36}O_2$	15.624	0.8035	29.6165	13.3976	0.1336	10.7493	6.30823
Methyl 3-octadecenoate	$C_{19}H_{36}O_2$	15.624	0.8035	29.6165		0.1329	10.7493	6.3397
Methyl octadecanoate	$C_{19}H_{38}O_2$	5.214	0.3387	9.8172		0.0444	4.4163	2.1359
Total		**99.99**	**5.2212**	**192.0644**	**53.5903**	**0.8543**	**71.8653**	**40.1982**

The predicted values have the tendency to be different from the experimental values. This is because, the predicted method treats the properties of isomers the same as shown in Tables 2-4. It is reported by Knothe [12] that the viscosity of trans- isomers of fatty acid alkyl esters are higher than that of the corresponding cis-. Knothe and Steidley [13] reported that the kinematic viscosities of the following isomers of FAME, methyl 6-cis –octadecenoate and methyl 6-trans-octadecenoate have 4.51 and 5.86, methyl oleate and methyl Elaidate have 4.64 and 5.51 and methyl 11-cis octadecenoate and methyl 11-trans-octadecenoate have 4.29 and 5.41 respectively. Likewise, the experimental values can also have error due to unnoticed impurity in the sample, inaccuracy of the analytical equipment and the unskillfulness of the analyst as seen in Table 5. The measured values of same physical properties varied from one individual to another probably due to insensitivity of instrument, impurity in the sample or lack of skill of the analysts.

Table 5 shows the records of multiple experimental values (EV) from literatures of the same property of an ester from different analysts which could be due to machine error, contaminations, lack of skill on the part of the operator (analyst). More of these multiple values were recorded for kinematic viscosity which is considered as the most important property for biodiesel. There is much disparity between the experimental values and the predicted values (PV) for kinematic viscosity than other properties. The prediction works much better for other physical properties than kinematic viscosity as the values of predicted method are very close to experimental one as found in Table 5. Cetane number, heating value, and specific gravity of experimental and predicted values are closed, making it safer to use empirical approach to determine the values of these properties if the biodiesel is of highly purity that is about 100% ester content.

Table 5: Comparison of experimental and empirically predicted values of biodiesel properties.

FAME	V		C N		Qn		SG	
	EV	PV	EV	PV	EV	PV	EV	PV
Methyl capylate ($C_9H_{18}O_2$)	0.99[12]	1.436		70.7	34.91	45.53	0.88[9]	0.848
	1.16[12]							
	1.19[12]							
	1.215[8]							
Average	1.139							
Deviation %	15.48				30.42		-3.64	
Methyl mysristate ($C_{15}H_{30}O_2$)	3.23[8]	3.798	66.2[9]	70.7	38.43	43.00	1.004*	0.848
	3.338[8]		72.0[9]		39.5[10]			
	3.30[13]							
Average	3.289		69.1		38.97			
Deviation %	15.48		2.32		10.34		-15.54	
Methyl palmitate ($C_{17}H_{34}O_2$)	4.32[8]	5.00	91.0[9]	81.9	39.5[10]	41.68	0.85[14]	0.849
	3.38[13]		80.0[9]		39.5[13]			
	4.38[13]		74.5[9]					
	4.414[8]		85.6[9]					
Average	4.124		82.78		39.5			
Deviation %	21.29		-1.06		5.52		0.0	
Methyl palmitoleate $C_{17}H_{32}O_2$)	3.67	4.139	51.0[10]	66.0	39.3[10]	42.53	0.87[11]	0.849
Deviation %	12.78		9.8				-2.41	
Methyl stearate ($C_{19}H_{38}O_2$)	5.881	6.496	100[9]	84.7	40.1[10]	41.10	0.85[14]	0.851
	5.61[8]		75.6[9]					
	5.867[8]		81.0[9]					
	5.85[13]		86.9[9]					
Average	5.802		85.88		1.0			
Deviation %	11.96		-1.37		2.49		0.12	
Methyl oleate ($C_{19}H_{36}O_2$)	4.41	5.376	71.0[9]	68.8	40.1[10]	40.48	0.88[9]	0.855
	4.971		52.5[9]		39.3[14]		0.87[14]	
	4.51[13]		55.0[9]					
Average	4.631		59.9		39.7		0.875	
Deviation %	16.09		14.86		1.01		-2.29	

* Extrapolated from the values at -3°C and 24°C

CONCLUSION

The major factor militating commercial viability of biodiesel is its production cost. Empirical analysis saves not only cost, but also time, energy and labour. Once, the GC-MS analysis has identified the biodiesel sample as a high purity fuel from the quality of its fatty acid esters content, most of the important physical properties such as kinematic viscosity, saponification value, iodine value, specific gravity, cetane number and heat of combustion can be determined empirically. This empirical approach is only suitable for high purity biodiesel.

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