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Proposed Model for the Determination of Biodiesel Cetane Number

Ayoola Ayodeji¹, Efeovbokhan Vincent², Ayeni Augustine³, Babalola Rasheed⁴

Abstract: Emphasis on the biodiesel vield from the trans-esterification of waste oils should not only be of interest, but the production of high quality biodiesel should be of greater concern. Factors that determine quality of biodiesel are the production process(es) and biodiesel properties. High quality biodiesel must have cetane number (CN) that falls within the specifications of America Society for Testing and Materials (ASTM) and/or European Committee for Standardisation (EN). CN is a measure of auto ignition quality of a fuel; the higher the cetane number, the shorter the delay interval and the greater is its combustibility. In this research work, conditions for the production of high yields of biodiesel from the trans-esterification of Waste Soyabean Oil (WSO) and proposed model for the determination of biodiesel cetane number were established. The results of biodiesel yields obtained from the WSO trans-esterification showed that biodiesel yield was favoured at methanol/oil mole ratio of 6, NaOH catalyst concentration of 0.7 w/w oil, reaction temperature of 55 ^{0}C and reaction time of 90 minutes. Proposed biodiesel cetane number model obtained was validated. The statistical analysis yielded pearson correlation of 0.824 between the calculated cetane number using the proposed model and the experimentally reported cetane number; p-value of 0.086. Interestingly, percentage average absolute deviation (% AAD) obtained for the calculated cetane numberand cetane number reported by Ramirez-Verduscoet. al. (2012), when compared to experimentally reported cetane number, generated the same result of 3.28 %.

Keywords: Biodiesel, cetane number, proposed model, trans-esterification and waste soyabeanoil.

I. Introduction

Global energy demand is sky-rocketing due to increased world population and more industrialised countries. The world depends heavily on fossil fuels as energy source [1], [2], [3]. The crisis arises from the cost and environmental effects associated with the use of fossil fuels necessitated the need for alternative and/or complimentary sources of energy [4]. There are lesser emissions to the surroundings from high quality biodiesel when compared to petroleum diesel; certain properties of biodiesel make it prefer to petroleum diesel. Of these properties are higher kinematic viscosity, higher flash point, lower ash content, lower sulphur content, lower carbon content, lower volatility and higher cetane number [5].

Performance of biodiesel in diesel engine is a function of its physical properties [6]. Fuel standards and test methods for high efficiency of operation of pure biodiesel is shown in Table 1.Viscosity and density have direct effect on the atomisation process during combustion, biodiesel weather-ability in hot conditions is measured by its flash point, cetane number is used to evaluate the ignition quality of biodiesel [7].

To ascertain the production of high quality biodiesel, cetane number (CN) is one of the properties of biodiesel that must be determined and the value obtained must satisfythespecification[7]. CNis a measure of the auto ignition quality of the fuel. The higher the CN, the shorter the delay interval and the greater is its performance [8]. Lower CN results into higher exhaust gas emissions and particulate matter[9]. Since biodiesel is largely composed of long-chain hydrocarbon groups (with virtually no branching or aromatic structures), it typically has a higher CN than petroleum diesel. The CN of pure Fatty Acid Methyl Ester (FAME) molecules increases with chain length, but this effect is masked when considering complex mixtures of FAME fuels. On the other hand, the CN of FAME fuels clearly vary with average degree of unsaturation, the higher the degree of unsaturation the lower the CN [10].

The CN determination test procedure, using costly and sophisticated equipment, is complex and it is been criticised due to the differences between the cetane test engine configurations and operating conditions of modern engines [11]. Efforts have been made to find alternative methods of estimating biodiesel cetane number[11], [12], [13]; one good way of overcoming the challenge of the CN determination is to formulate simple model that will required easily quantified biodiesel properties.

This work was developed as a result of the need to formulate a simple and reliable model for the prediction of biodiesel cetane number, based on sound scientific principles. This would eliminate experimental work which sometimes could be difficult, costly and time consuming [7]. The aim of the research work is to produce maximum yield of biodiesel (under the specified conditions) from NaOHcatalised trans-esterification

waste soyabean oil and to propose biodiesel cetane number model as a function of density, viscosity, carbon length and the number of double bonds of biodiesel.

Property	ASTM Method	EN Method	ASTM Limits	EN Limits
Water and sediment	ASTM D2709	EN ISO 12937	0.05 max	500 max
			(% vol.)	(mg/kg)
Total glycerol	ASTM	EN 14105	0.24	0.25 max
			(% mass)	(% mol)
Methanol	-	EN 14110	0.2 max	0.2 max
			(% vol.)	(% mol)
Ash content	ASTM D874	ISO 3987	0.02 max	0.02 max
			(% mass)	(% mol)
Sulfur	ASTM D5453	EN ISO 20846		10 max
S15 grade		EN ISO 20884	0.0015 max	(mg/kg)
2			(% mass)	
S500 grade			0.05 max	
e			(% mass)	
Cetane number	ASTM D613	EN ISO 5165	47.0 min	51.0 min
Carbon residue	ASTM D4530	EN ISO 10370	0.05 max	0.3 max
			(% mass)	(% mol)
Flash point	ASTM D93	EN ISO 3679	130 min	120 min
			(°C)	(°C)
Density, 15°C		EN ISO 3675		860 - 900
		EN ISO 12185		(kg/m^3)
Kin. Viscosity 40°C	ASTM D445	EN ISO 3104	1.9 - 6.0	3.5 - 5.0
		ISO 3105	(mm^2/s)	(mm^2/s)

Table 1: Fuel Standards and Test methods for Pure Biodiesel

Source: [14]

The properties of the raw waste soyabean oil (before oil pretreatment) for the trans-esterification process are shown in Table 2.

Oil	Flash Point	Viscosity	Density	Acid Value	Sap. Value	H ₂ O Content
WSO	(°C)	(mm ² /s @ 40°C)	(g/cm ³)	(mg KOH/g)	(mg KOH/g)	(%)
	232	31.67	0.9110	1.843	240.1	0.67

II. Methodology

2.1 Biodiesel Production

Biodiesel was produced from NaOH-catalisedtrans-esterification process. 100g of treated waste soyabeanoil (WSO) was used in each of the experiments carried out. Specified amount of NaOHcatalyst was dissolved completely in the required amount of methanol to form a clear solution of sodium methoxide. The solution was then transferred to warm oil heated to 50° C. The mixture was tightly enclosed, maintained at the specified temperature and continuously stirred at 400 rpm. This allowed reaction to take place at the required reaction time (50 – 90 minutes).

At the end of the specified reaction time, the products obtained were then transferred to separating funnel and left for 24 hours after which two distinct layers were observed; light yellow biodiesel and reddish brown glycerol. Separation of the two products was done by first decanting off the glycerol (bottom layer) from the separating funnel.

Biodiesel obtained was free of impurities (unconverted methanol, catalyst, soap and traces of glycerol) by washing with warm distilled water repeatedly until water removed contained no impurity. Moisture content present in biodiesel was then removed by drying the content at 120° C in an oven for 30 minutes.

2. 2Modeling of Biodiesel Cetane Number

Stavrov*et. al.* (1981) model [15] for the calculation of petroleum diesel cetane number (equation 1) was improved upon to obtain a biodiesel cetane number model that considers other important properties of biodiesel. The important properties of biodiesel include: carbon chain length, number of double bonds and mass fraction of biodiesel.

2.2.1Model of Petroleum diesel Cetane Number - Stavrovet. al., (1981)

According to Stavrovet.al. (1981), petroleum diesel cetane number is expressed as

 $CN_{Petroleum \, diesel} = \left\{ (\upsilon_{20} + 17.8) \left(\frac{1.5879}{\rho_{20}} \right) \right\} (1)$

where

 $CN_{Petroleum diesel} = petroleum diesel cetane number$

 v_{20} = petroleum diesel kinematic viscosity at 20 °C, mm²/sec

 ρ_{20} = petroleum diesel density at 20 °C, g/cm³

2.2.2Proposed Model of Biodiesel Cetane Number

The modification of Stavrovet. al. (1981) model for petroleum diesel cetane number to biodiesel cetane number model was made possible by considering the following findings and assumptions:

Biodiesel has 100 % straight chain structure [1], [16], [17], [18]. 1.

- 2. Petroleum diesel has 75 % straight chain HCs and 25 % aromatic HCs (alkyl benzene, naphthalene) [19].
- 3. Average molecular formula of petroleum diesel is $C_{12}H_{23}$, ranging from $C_{10}H_{20}$ to $C_{15}H_{28}$, [19], [20].
- 4. Cetane number is inversely proportional to the number of double bonds of fatty acids and biodiesel [10], [16], [21].

Based on the above research findings, the predicted model of biodiesel is

$$CN_{Biodiesel} = \frac{C_{100}}{C_{75}} \left\{ (\upsilon_{40} + 17.8) \left(\frac{1.5879}{\rho_{25}} \right) - \Sigma \left(\frac{C_{DB} \cdot x}{C_{D} \cdot N_{DB}} \right)_{i} \right\} (2)$$

where

 $CN_{Biodiesel} = biodiesel cetane number$

 C_{100} = ratio of straight chain carbon of biodiesel to petroleum diesel

$$= \text{conversion factor} = \frac{100}{75}$$

$$\upsilon_{40} = \text{biodiesel kinematic viscosity at 40 }^{0}\text{C}, \text{ mm}^{2}/\text{sec}$$

$$\rho_{25} = \text{biodiesel density at 25 }^{0}\text{C}$$

$$\Sigma \left(\frac{C_{DB} \cdot x}{C_{D} \cdot N_{DB}}\right)_{i} = \text{correction terms}$$

$$C_{DB} = \text{carbon with double bond in biodiesel}$$

$$C_{D} = \text{average number of carbon in petroleum diesel}, C_{12}H_{23}$$

$$N_{DB} = \text{number of double bond in biodiesel}$$

$$x = \text{mass fraction of biodiesel}$$

Findings number 1 and 2 accounted for the introduction of conversion factor in the proposed model while finding number 3 and 4 gave the reason why correction terms were considered in the model.

III. **Results And Discussion**

3.1 Biodiesel Yield Obtained

The results of biodiesel yields obtained from the WSO trans-esterification at varied methanol/oil mole ratio, NaOH catalyst concentration, reaction time and reaction temperature are as shown in Fig. 1. On the average, maximum biodiesel yield was favoured at methanol/oil mole ratio of 6, NaOH catalyst concentration of 0.7 w/w oil, reaction temperature of 55 $^{\circ}$ C and reaction time of 90 minutes.

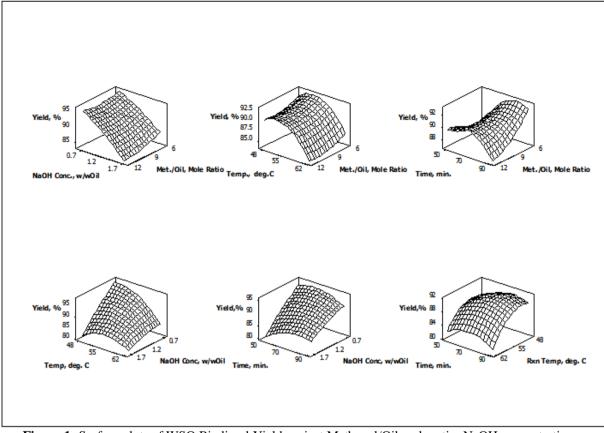


Figure 1: Surface plots of WSO Biodiesel Yield against Methanol/Oil mole ratio, NaOH concentration, Reaction Time and Reaction Temperature.

3.2 Comparison of the reported CN and CN obtained from the proposed model

Comparative analysis of cetane number calculated using the proposed model and the cetanenumber reported in literatures was carried out. Cetane number obtained from Ramirez-Verduscoet. al. (2012) models [7], cetane number determined experimentally (as reported by Ramirez-Verduscoet. al. (2012)) and cetane number calculated using the new proposed model are compared, as shown on Table 3.

Biodiesel	Density	Kinematic	Cetane	Cetane	Cetane
	(g/cm ³)	Viscosity	Number	Number	Number
	@ 25°C	(mm ² /s)	(Experimental)	(Ramirez	(Proposed
		(a) 40 ^o C		et. al., 2012)	Model)
Sunflower oil methyl ester	0.8820	4.05	50.0ª	48.7 ^b	51.4
Soyabean oil methyl ester	0.8810	4.10	51.7 ^b	50.2 ^b	51.6
Corn oil methyl ester	0.8803	4.13	53.0 ^a	51.4 ^b	51.6
Cottonseed oil methyl ester	0.8784	4.12	51.2°	53.8 ^b	51.9
Beef tallow oil methyl ester	0.8774	4.29	57.8 ^d	56.2 ^b	52.2

'[22], "[7], "[23], "[24].

Mass fractions and biodiesel compositions considered for the calculation of biodiesel cetane number in the proposed model are as reported byRamirevz-Verduscoet. al., 2012 (Appendix A). And the calculations of biodiesel cetane number were shown in Appendix B.

With the aid of MINITAB 16 software, both the percentage average absolute deviation (% AAD) and pearson correlation of the CN from the proposed model and CN reported by researchers were determined (Table 4 and Fig.2).

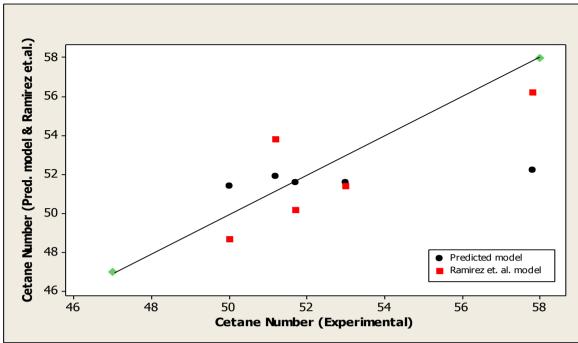


Figure 2: Correlation of Cetane Number using Pred. model and Cetane Number reported by Ramirez et. al. model) with Experimentally determined Cetane Number.

3.3 Validation of the Proposed Model for Biodiesel Cetane Number

Validation of the proposed model for biodiesel cetane number was carried out by comparing the results obtained from the proposed model with several experimental results employed by Ramirez–Verdusco*et. al.* (2012) in their models (Table 3).

Interestingly, percentage average absolute deviation (% AAD) of cetane number for both the proposed model and Ramirez-Verdusco*et. al.* (2012) model from the reported experimental cetane number generated the same result of 3.28 % (Table 4).

Comparatively, the higher pearson correlation value and lower p-value of the predicted model (when compared to Ramirez-Verdusco model) favours the predicted model as a more suitable model. The statistical analysis yielded pearson correlation of 0.824 between the cetane number of the predicted model and experimental cetane number and p-value of 0.086. While a value of 0.812 pearson correlation between the cetane number of Ramirez-Verdusco*et. al.* (2012) model and cetane number of experimental results and p value of 0.095 were obtained.

Using the predicted model, the values of the calculated cetane number of biodiesels produced and the values of the calculated CN of the five biodiesels reported by Ramirez-Verdusco*et. al.* (2012) fall within the ASTM cetane number specification of 47 - 61 [25], [26]. Similarly, the proposed model shows that biodiesel cetane number is directly proportional to viscosity and inversely proportional to density, as reported by some researchers [9], [16], [21], [26].

Table 4: St	tatistical Analy	sis of Absolute Deviati	on of the Results of l	Ramirez <i>et. al.</i> (2012) m	odel and Predicted m	odel from the Experiment	al Results
Biodiesel	CN(Exptal.)	CN (Ramirez et. al.)	CN (Pred. Model)	AD (Ramirez et. al.)	AD(Pred. model)	AAD (Ramirez et. al.)	AAD (Pred model)
SF	50.0	48.7	51.4	1.3	1.4	0.026	0.028
SB	51.7	50.2	51.6	1.5	0.1	0.029	0.001
CO	53.0	51.4	51.6	1.6	1.4	0.030	0.026
CT	51.2	53.8	51.9	2.6	0.7	0.051	0.013
BT	57.8	56.2	52.2	1.6	5.6	0.028	0.096
						$\Sigma = 0.164$	$\Sigma = 0.164$

SF = Sunflower oil methyl ester, SB = Soyabean oil methyl ester, CO = Corn oil methyl ester, CT = Cottonseed oil methyl ester, BT = Beef tallow oil methyl ester.

Percentage Average Absolute Deviation (% AAD)

$$=\frac{100}{n}\sum_{i=1}^{n}\frac{\text{Cetane Number (Experimental)} - \text{Cetane Number (Calculated)}}{\text{Cetane Number (Experimental)}}$$
(3)
% AAD for Ramirez et. al. (2012) model = $\frac{100}{n}\sum_{i=1}^{n=5}\frac{\text{CN (Exptal .)} - \text{CN (Ramirez et.al.)}}{\text{CN (Exptal .)}} = \frac{100(0.164)}{5} = 3.28 \%$
% AAD for Predicted model = $\frac{100}{n}\sum_{i=1}^{n=5}\frac{\text{CN (Exptal .)} - \text{CN (Predicted model)}}{\text{CN (Exptal .)}} = \frac{100(0.164)}{5} = 3.28 \%$

IV. Conclusion

These results reveal the high level of accuracy of the predicted model and also confirm the new approach as a plausible method for the determination of biodiesel cetane number. Since the new approach utilises key indices like density and viscosity, it can be proposed as a reliable method of CN determination for biodiesel. This new and simple model will reduce the cost of biodiesel cetane number determination, for it does not involves the use of complex and costly equipment.

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Carbon Chain	Mass Fraction (x _i)							
	BT	SB	SF	CO	CT			
C14:0	0.005	0.000	0.001	0.000	0.008			
C16:0	0.159	0.101	0.060	0.099	0.229			
C16:1	0.009	0.000	0.000	0.000	0.000			
C18:0	0.085	0.045	0.059	0.031	0.031			
C18:1	0.317	0.243	0.160	0.291	0.185			
C18:2	0.365	0.531	0.714	0.568	0.542			
C18:3	0.046	0.072	0.006	0.011	0.005			
C20:0	0.003	0.004	0.000	0.000	0.000			
C20:1	0.008	0.000	0.000	0.000	0.000			
C22:1	0.003	0.004	0.000	0.000	0.000			

Appendix A: Mass Fractions of Five Biodiesel Samples

Appendix B: Calculation of Cetane Number of the Five Biodiesel using the Proposed Model

$$\begin{aligned} (\text{Cetane Number})_{\text{Sunflower}} &= \frac{c_{100}}{c_{75}} \left\{ (\psi_{40} + 17.8) \left(\frac{1.5879}{\rho_{25}} \right) - \Sigma \left(\frac{c_{DB} \cdot x}{c_{\rho} \cdot N_{DB}} \right)_i \right\} \\ &= \frac{100}{75} \left\{ (4.05 + 17.8) \left(\frac{1.5879}{0.8820} \right) - \left(\frac{18}{12} \times \frac{0.160}{1} \right) - \left(\frac{18}{12} \times \frac{0.714}{2} \right) - \left(\frac{18}{12} \times \frac{0.006}{3} \right) \right\} \\ &= 1.3333 \left\{ 39.337 - 0.24 - 0.536 - 0.003 \right\} \\ &= 51.4 \\ (\text{Cetane Number})_{\text{Soyabean}} = \frac{c_{100}}{c_{75}} \left\{ (\psi_{40} + 17.8) \left(\frac{1.5879}{\rho_{25}} \right) - \Sigma \left(\frac{c_{DB} \cdot x}{c_{\rho} \cdot N_{DB}} \right)_i \right\} \\ &= 1.3333 \left\{ 39.372 - 0.364 - 0.398 - 0.036 - 0.007 \right\} \\ &= 1.3333 \left\{ 39.472 - 0.364 - 0.398 - 0.036 - 0.007 \right\} \\ &= 51.6 \\ (\text{Cetane Number})_{\text{ComOil}} = \frac{c_{100}}{c_{75}} \left\{ (\psi_{40} + 17.8) \left(\frac{1.5879}{\rho_{25}} \right) - \Sigma \left(\frac{c_{DB} \cdot x}{c_{\rho} \cdot N_{DB}} \right)_i \right\} \\ &= \frac{100}{75} \left\{ (4.13 + 17.8) \left(\frac{1.5879}{0.8800} \right) - \left(\frac{18}{12} \times \frac{0.291}{1} \right) - \left(\frac{18}{12} \times \frac{0.563}{2} \right) - \left(\frac{18}{12} \times \frac{0.011}{3} \right) \right\} \\ &= 1.3333 \left\{ 39.558 - 0.436 - 0.426 - 0.005 \right\} \\ &= 51.6 \\ (\text{Cetane Number})_{\text{Contoils}} = \frac{c_{100}}{c_{75}} \left\{ (\psi_{40} + 17.8) \left(\frac{1.5879}{\rho_{25}} \right) - \Sigma \left(\frac{c_{DB} \cdot x}{c_{\rho} \cdot N_{DB}} \right)_i \right\} \\ &= 1.3333 \left\{ 39.625 - 0.277 - 0.406 - 0.005 \right\} \\ &= 51.6 \\ (\text{Cetane Number})_{\text{Cotonseed}} = \frac{c_{100}}{c_{75}} \left\{ (\psi_{40} + 17.8) \left(\frac{1.5879}{\rho_{25}} \right) - \Sigma \left(\frac{c_{DB} \cdot x}{c_{\rho} \cdot N_{DB}} \right)_i \right\} \\ &= 1.3333 \left\{ 39.625 - 0.277 - 0.406 - 0.003 \right\} \\ &= 51.9 \\ (\text{Cetane Number})_{\text{BeefTallow}} = \frac{c_{100}}{c_{75}} \left\{ (\psi_{40} + 17.8) \left(\frac{1.5879}{\rho_{25}} \right) - \Sigma \left(\frac{c_{DB} \cdot x}{c_{\rho} \cdot N_{DB}} \right)_i \right\} \\ &= \frac{100}{75} \left\{ (4.29 + 17.8) \left(\frac{1.5879}{0.8774} \right) - \left(\frac{18}{12} \times \frac{0.031}{1} \right) - \left(\frac{18}{12} \times \frac{0.317}{1} \right) - \left(\frac{18}{12} \times \frac{0.305}{2} \right) \right\} \\ &= 1.3333 \left\{ 39.978 - 0.012 - 0.475 - 0.273 - 0.023 - 0.013 - 0.005 \right\} \\ &= 52.2 \end{aligned}$$

=