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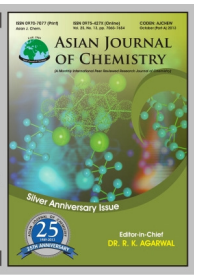

Effect of Double Bond Equivalent of Biodiesels on their Heating Value and Cetane Number

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The mono-alkyl esters of vegetable oils defined as biodiesels are accepted as alternative energy sources for petro-diesel and growing in a stable manner across the globe. The properties of biodiesel depend mainly upon structure of its components and composition. In the present study, the effect of double bond equivalent of biodiesels on their heating value and cetane number was investigated. Double bond equivalents are essentially identical to the iodine value, the major difference being that the molecular weight of iodine is not considered. Hence double bond equivalents can be considered as a numerical index for the total amount of unsaturated fatty acids in given oil. Five different biodiesels were prepared and their properties were measured. The double bond equivalent of each biodiesel was derived from the composition of unsaturated fatty acid methyl esters. A statistical analysis was done to relate the double bond equivalent with heating value and cetane number. From the investigation it is concluded that the heating value and cetane number decrease with increase in double bond equivalent. From the analysis, it was found that a reduction of 22.19 units (kJ/kg) in heating value can be expected for every one unit increase in double bond equivalent. Similarly it was observed that one unit increase in double bond equivalent will result in a decrease of 0.195 units in cetane number.

Key Words: Biodiesel, Cetane number, Double bond equivalent, Heating value, Unsaturated fatty acid esters.

INTRODUCTION

Vegetable oils are considered as viable alternative types of fuels because they are renewable, non-toxic and biodegradable and produce lower emissions[1]. The esters of vegetable oils called as biodiesel are most outstanding choices for diesel alternatives among the many different types of alternative fuels. The basic composition of any vegetable oil is triglyceride, which is of three fatty acids and one glycerol molecule[2]. Biodiesel production generally involves the transesterification of a triglyceride feedstock with methanol or other short-chained alcohols[3,4]. In the process, glycerol is obtained as co-product. Biodiesel fuels are classified as fatty acid methyl esters in general, which are derived from transesterification of vegetable oils with methanol, although other alcohols can be used[5]. The fatty acids vary in their carbon chain length and in number of double bond of carbons[6]. Fatty acids may be saturated or unsaturated. A saturated fat is one that cannot chemically accept additional hydrogen and contains only single carbon-carbon bonds. An unsaturated fat can be hydrogenated and contains one or more double bonds[7].

A complete understanding of physical and chemical properties of fatty acids is necessary to support the development of fuel or fuel extenders using these plant oils[8]. The properties of biodiesel are decided by the structure of the fatty acid methyl esters that constitute biodiesel[9-11]. Generally, cetane number, heating value, melting point, and viscosity increase with increasing chain length and decrease with increasing unsaturation *i.e.*, number of double bonds. Cetane number is influenced by chain length, alcohol moiety, degree of unsaturation and position of double bond.

As the use of biodiesel becomes more prevalent, researchers have shown a strong interest in modeling the combustion processes in the engine in order to understand the fundamental characteristics of biodiesel combustion and hence emissions. The critical properties of biodiesel, which influence the combustion are liquid density, surface tension, viscosity, heat capacity, heating value, heat of vaporization, thermal conductivity and diffusion coefficients[12].

The objective of the present work is to investigate the effect of double bond equivalent of biodiesel fuels on their heating value and cetane number. It appears that "double bond equivalents" are essentially identical to the iodine value, the major difference being that the molecular weight of iodine is not considered. Hence double bond equivalents can be considered as a numerical index for the total amount of unsaturated fatty acids in given oil. One double bond equivalent is defined as arising from a concentration of 1 % methyl oleate (or other monounsaturated compound), which has an allylic position equivalent = 2 (it has two allylic positions in the chain). Thus

1 % methyl linoleate has two double bond equivalents and 1 % methyl linolenate has three double bond equivalents[13].

EXPERIMENTAL

Biodiesel preparation: Five different vegetable oil samples (soybean, rubber seed, jatropha, neem and mahua) were procured and were processed in our laboratory through transesterification. Transesterification is a process of producing a reaction in triglyceride and alcohol in the presence of a catalyst to produce alkyl ester and glycerol. Alkali (sodium hydroxide or potassium hydroxide) and acids (sulphuric acid or hydrochloric acid) catalyze the reaction[14,15]. Alkali-catalyzed transesterification is faster than acid-catalyzed transesterification and is most used commercially[16]. If the free fatty acid content and moisture content are less than 0.5 %, good-quality biodiesel can be produced. Biodiesel was produced from 1000 g of parent oil: 200 g of methanol: 5 g of sodium hydroxide (NaOH) as a catalyst-generally the alcohol and the catalyst quantity are 20 % and 0.3-0.5 % of oil, respectively. The mixture of methanol and NaOH was stirred manually till complete diffusion of NaOH in methanol takes place. The parent vegetable oil was placed in a three necked flask and the oil was heated to a reaction temperature of 50 ºC. At this point of temperature, the methanol and NaOH solution was added and mixture consequently stirred at a speed of 250 m/s (the speed depends upon the mixture quantity) for 2 h. The temperature of the reactant was measured with the help of a thermometer in every 10 min. After the completion of reacion time the mixture was transferred from the flask to a separating funnel. The glycerol settled at the bottom and was removed through the opening of the funnel. To remove the methanol and catalyst present in the ester, the ester was washed with 120 g of distilled water at 40 ºC. The ester and the water were allowed to remain in the funnel for 8 h. The water with milky-white colour settled at the bottom and removed through funnel opening. The ester (biodiesel) was heated again and maintained at 100 ºC for 1 h to remove the moisture content. Thus the required biodiesel was obtained.

Fuel properties: The fatty acid composition of biodiesel products was determined using gas chromatography analysis. The cetane number and heating value were determined following the methods specified in ASTM standard[17] as given in Table-1 for different biodiesel fuels.

TABLE-1
ASTM METHODS FOR DETERMINATION OF BIODIESEL PROPERTIES

Property	Units	ASTM standard[17]
Cetane number	–	D 613
Heating value	kJ/kg	D 240
Moisture content	wt (%)	D 2709

RESULTS AND DISCUSSION

The results of fuel tests are summarized in Tables 2-4. One double bond equivalent is defined as arising from a concentration of 1 % methyl oleate (or other monounsaturated compound), which has an allylic position equivalent = 2 (it has two allylic positions in the chain). Thus 1 % methyl linoleate has two double bond equivalents and 1 % methyl linolenate has three double bond equivalents[13].

TABLE-3
MEASURED PROPERTIES OF DIFFERENT BIODIESELS

Biodiesel	Cetane number	Heating value (kJ/kg)	Moisture content (wt %)
Soybean	48.1	39100	0.05
Rubber seed	51.3	39400	0.03
Jatropha	57.6	39600	0.03
Neem	63.9	39900	0.06
Mahua	65.7	40500	0.08

Heating value: Heating value or energy content or heat of combustion is a measure of the energy available in a fuel. It is a critical property of fuel intended for use in weight-limited vehicles. The effect of double bond equivalent on heating value is illustrated in Fig. 1. It can be observed from the figure that the heating value decreases with increase in double bond equivalent of biodiesels. This is believed due to the fact that the heating value decreases with increase in unsaturation *i.e.*, number of double bonds. The increase in double bond equivalent (greater unsaturation) due to deficiency in hydrogen atoms lowers heating value. It can also be seen from the figure that the slope between heating value and double bond equivalent is different for different set of fuels. The slope was found using eqn. 1 and listed in Table-5.

$$\text{Slope (m)} = \frac{\text{Difference in heating value } (\Delta Y)}{\text{Difference in double bond equivalent } (\Delta X)} \quad (1)$$

The slope between mahua and neem is slightly higher than that between rubber seed and soybean biodiesels. This is because of the difference in heating value between rubber seed and soybean is twice that of mahua and neem, whereas the double bond equivalent difference between rubber seed and soybean is only half of the same between mahua and neem biodiesels. Though the difference in heating value between jatropha and rubber seed is 2.5 times that of rubber seed and soybean, the magnitude of slope between jatropha and rubber seed is lower as compared to slope between rubber seed and soybean biodiesels. This is because of the significant increase in difference in double bond equivalent between jatropha and rubber seed as compared to that of rubber seed and soybean (almost 3 times) biodiesels. While comparing the slope

TABLE-2
FATTY ACID METHYL ESTER COMPOSITION OF DIFFERENT BIODIESELS

Biodiesel	Lauric acid (C12:0)	Myristic acid (C14:0)	Palmitic acid (C16:0)	Stearic acid (C18:0)	Oleic acid (C18:1)	Linoleic acid (C18:2)	Linolenic acid (C18:3)
Soybean	0.1	0.3	10.8	3.7	22.8	53.7	8.6
Rubber seed	0.0	0.2	12.6	8.3	27.8	37.6	13.5
Jatropha	0.2	0.4	15.6	10.5	42.1	30.9	0.3
Neem	0.8	0.5	18.4	22.1	41.3	16.7	0.2
Mahua	0.0	0.2	20.9	26.2	36.5	15.9	0.3

TABLE-4
DOUBLE BOND EQUIVALENT OF DIFFERENT BIODIESELS

Biodiesel	Ester	Amount (%)	No. of double bond equivalent	Total number of double bond equivalent
Soybean	18:1	22.8	22.8	156.0
	18:2	53.7	107.4	
	18:3	8.6	25.8	
Rubber seed	18:1	27.8	27.8	143.5
	18:2	37.6	75.2	
	18:3	13.5	40.5	
Jatropha	18:1	42.1	42.1	104.8
	18:2	30.9	61.8	
	18:3	0.3	0.9	
Neem	18:1	41.3	41.3	75.3
	18:2	16.7	33.4	
	18:3	0.2	0.6	
Mahua	18:1	36.5	36.5	69.2
	18:2	15.9	31.8	
	18:3	0.3	0.9	

One double bond equivalent is defined as arising from a concentration of 1 % methyl oleate (or other monounsaturated compound), which has an allylic position equivalent = 2 (it has two allylic positions in the chain). Thus 1 % methyl linoleate has two double bond equivalents and 1 % methyl linolenate has three double bond equivalents[13].

TABLE-5
SLOPE BETWEEN HEATING VALUE AND DOUBLE BOND EQUIVALENT

Slope between	Difference in double bond equivalent (ΔX)	Difference in heating value (ΔY)	Slope = (ΔY) ± (ΔX)
Mahua and neem	(75.3 – 69.2) = 6.1	(40800 – 40600) = 200	32.8
Rubber seed and soybean	(156.0 – 143.5) = 12.5	(39200 – 38800) = 400	32.0
Jatropha and rubber seed	(143.5 – 104.8) = 38.7	(40100 – 39200) = 900	23.3
Neem and jatropha	(104.8 – 75.3) = 29.5	(40600 – 40100) = 500	16.9

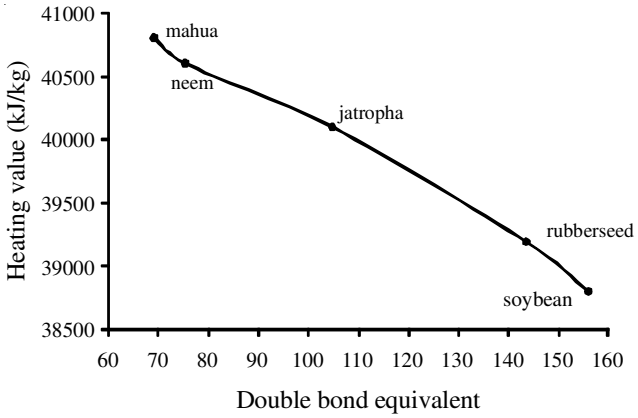

Fig. 1. Effect of double bond equivalent on heating value

between jatropha and rubber seed with the slope between neem and jatropha, it can be observed that the slope of the former is higher than that of the later one. A correlation analysis was done using eqn. 2 to find out the linear relationship between double bond equivalents and heating value.

$$r = \frac{\Sigma(X-\overline{X})(Y-\overline{Y})}{\sqrt{(X-\overline{X})^2(X-\overline{Y})^2}} \quad (2)$$

where, r = correlation coefficient, X = independent variable (double bond equivalent) and Y = dependent variables (heating value/cetane number). Using eqn. 2, it was found that a high degree of negative correlation exists between double bond equivalent and heating value. The correlation coefficient was found to be (–) 0.997. A simple fitted line was plotted between double bond equivalent and heating value and illustrated in Fig. 2.

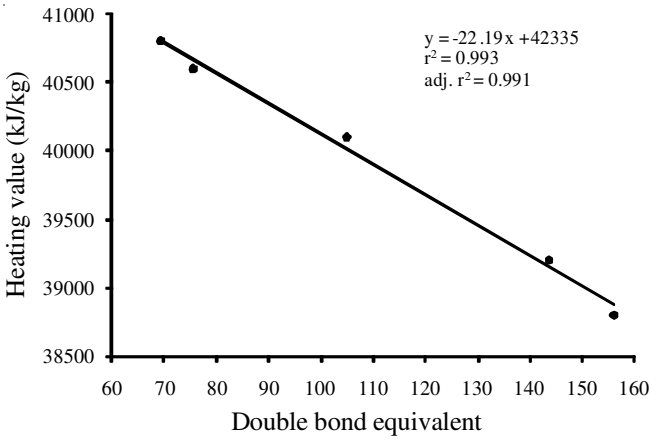

Fig. 2. Fitted line plot of heating value *versus* double bond equivalent

The fitted line equation shown in Fig. 2 is rewritten as eqn. 3.

$$\text{Heating value} = [(-22.19) \times \text{double bond equivalent}] + 42335 \quad (3)$$

where, slope = (–) 22.19, intercept = 42335, r^2 = 0.993 and adj. r^2 = 0.991. From the first order differentiation of eqn. 3 with respect to double equivalent, it can be observed that increase of one unit in double bond equivalent can result in a decrease of 22.19 units (kJ/kg) in heating value. Hence by knowing the double equivalent, heating value can be estimated.

Cetane number: The cetane number is one of the most significant properties to specify the ignition quality of a fuel. As an indicator of ignition quality, the cetane number is a prime

indicator of fuel quality in the realm of diesel engines. Fig. 3 depicts the cetane number of biodiesels as a function of double bond equivalent.

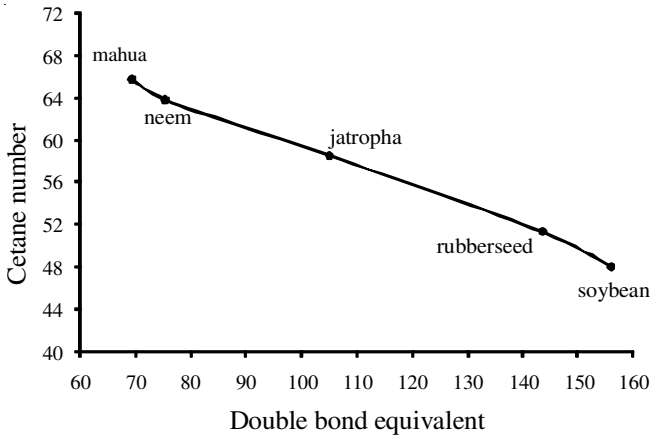

Fig. 3. Effect of double bond equivalent on cetane number

It is obvious from the figure that the cetane number decreases with increase in double bond equivalent. This is due to the fact that the cetane number increases with chain length, decreases with number of double bonds or unsaturation. In addition cetane number is influenced by alcohol moiety, degree of unsaturation and position of double bond. The slope between cetane number and double bond equivalent was found using eqn. 4 and listed in Table-6.

$$\text{Slope (m)} = \frac{\text{Difference in cetane number } (\Delta Y)}{\text{Difference in double bond equivalent } (\Delta X)} \quad (4)$$

From Table-6, the following points are observed. The slope between mahua and neem is higher than the same between rubber seed and soybean biodiesels. This is because of the difference in double bond equivalent between rubber seed and soybean is 1.8 times of the same between mahua and neem whereas the difference in cetane number between rubber seed and soybean is around 0.5 times of that between mahua and neem biodiesels. When compared to the slope between jatropha and rubber seed, the slope between rubber seed and soybean biodiesels is on the higher side. This is due to the reason that the difference in cetane number between jatropha and rubber seed is 2.2 times of that between rubber seed and soybean, but the difference in double bond equivalent between jatropha and rubber seed is 3.1 times of the same between rubber seed and soybean biodiesels. No significant variation was found in magnitude of slope between jatropha and rubber seed when compared to the slope between neem and jatropha. This is because of the difference in cetane number between jatropha and rubber seed is 1.36 time of that between neem and jatropha. And the difference in double bond equivalent between jatropha and rubber seed is 1.31 times the same between neem and jatropha which is not so significant. Using eqn. 2, it was found that the cetane number and double bond equivalent were highly negative correlated with each other and the correlation coefficient was found to be (–) 0.999. A fitted line plot of cetane number *versus* double bond equivalent is illustrated in Fig. 4.

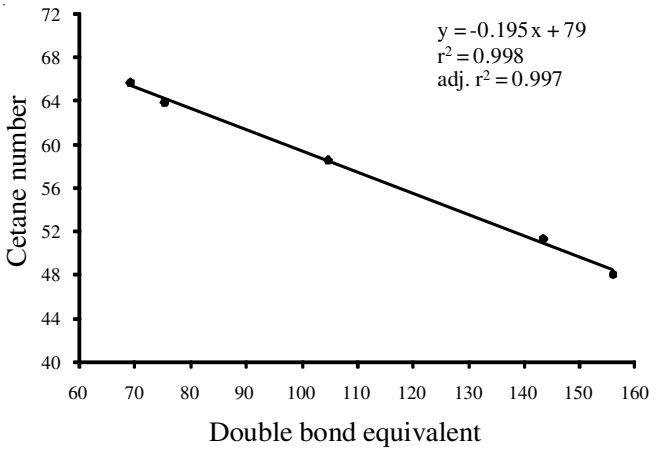

Fig. 4. Fitted line plot of cetane number *versus* double bond equivalent

The fitted line equation shown in Fig. 4 can be rewritten as eqn. 5.

Cetane number

$$= [(-0.195) \times \text{double bond equivalent}] + 79 \quad (5)$$

where, slope = (–) 0.195, intercept = 79, $r^2 = 0.998$ and adj. $r^2 = 0.997$. Differentiating the eqn. 5 with respect to double bond equivalent, it can be observed that every one unit increase in double bond equivalent results in a decrease of 0.195 units in cetane number.

Therefore by knowing the double equivalent, cetane number can be estimated. The eqns. 3 and 5 are developed to mathematically relate the double bond equivalent with heating value and with cetane number of biodiesels. However, if a large number of sample sizes are considered for calculations, then the magnitude of the slope may vary.

Conclusion

Double bond equivalent derived from the composition of unsaturated fatty acid methyl esters can have a significant influence in heating value and cetane number of biodiesels. The heating value decreases with increase in double bond equivalent. It was found that the heating value was highly negatively correlated with double bond equivalent with a correlation coefficient of (–) 0.997. A reduction of 22.19 units (kJ/kg) in heating value could be predicted for every one unit increase in double bond equivalent. Like the heating value, the cetane number decreases with increase in double bond equivalent.

TABLE-6
SLOPE BETWEEN CETANE NUMBER AND DOUBLE BOND EQUIVALENT

Slope between	Difference in double bond equivalent (ΔX)	Difference in cetane number (ΔY)	Slope = (ΔY) ÷ (ΔX)
Mahua and neem	(75.3 – 69.2) = 6.1	(65.7 – 63.9) = 1.8	0.30
Rubber seed and soybean	(156.0 – 143.5) = 12.5	(51.4 – 48.1) = 3.3	0.26
Jatropha and rubber seed	(143.5 – 104.8) = 38.7	(58.6 – 51.4) = 7.2	0.19
Neem and jatropha	(104.8 – 75.3) = 29.5	(63.9 – 58.6) = 5.3	0.18

The correlation coefficient between cetane number and double bond equivalent was found as (–) 0.999. It was found that every one unit increase in double bond equivalent can result in a decrease of 0.195 units in cetane number.

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