DETERMINATION OF HIGHER HEATING VALUE OF BIODIESELS

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ABSTRACT

Biodiesel, an alternative fuel can be used in diesel engine as neat or blended with diesel. The physio-chemical properties of fuel are important in design of fuel system for compression ignition engine run on diesel, biodiesel or biodiesel blend. The HHV is an important property which characterizes the energy content of a fuel such as solid, liquid and gaseous fuels. The biodiesels were characterized for their physical and main fuel properties including viscosity, density, flash point and higher heating value. The viscosities of biodiesels were much less than those of pure oils and their HHV's of approximately 42 MJ/kg were 10% less than those of petro diesel fuels. The HHVs of vegetable oils and their biodiesels were measured and correlated using linear least square regression analysis. An equation was developed relating HHV and thermal properties. The predicted higher heating values compare well with the measured Higher Heating Values. This work establishes the general dependence of higher heating value on thermal properties of biodiesel.

Keywords: Biodiesel, Higher heating Value (HHV), Fuel Properties.

1. INTRODUCTION

Biodiesel as an alternative fuel of diesel is described as fatty acid methyl or ethyl esters from vegetable oils or animal fats. One of the most important properties to characterize a fuel is its energy content. [1]
The standard measure of the energy content of a fuel is its heating value (HHV) sometimes called the calorific value or heat of combustion. The heating value is obtained by the complete combustion of a unit quantity of solid fuel in oxygen – bomb calorimeter under carefully defined conditions. The Gross Heat of Combustion or Higher Heating Value (GHC or HHV) is obtained by oxygen – bomb calorimeter method as the latent heat of moisture in the combustion products is recovered. The higher heating value is one of the most important properties of a fuel. [2] Some researchers have attempted to estimate the HHV of the vegetable oils by using their physical properties such as: saponification and iodine data [3,4]Some researchers have attempted to estimate the HHV of the vegetable oils by using their Fatty acids composition [5]Fuel properties of vegetable oils were characterized by determining its viscosity, density, Cetane number, cloud and Pour points, distillation range, flash point, ash content, sulfur content, carbon residue, acid value, copper corrosion and HHV [6].
The flash point of biodiesel is higher than that of biodiesel fuel. Although flash point does not directly affect combustion, it makes biodiesel safer regarding the storage and transport [7, 8]
Kinematic viscosity and density are the parameters required by biodiesel and diesel fuel standards because of being key fuel properties for diesel engines [9].The objective of this study was to estimate mathematical relationships between higher heating value (HHV) and viscosity, density or flash point measurement of various bio diesel fuels from various vegetable oils by transestrification method.

2. EXPERIMENTAL PROCEDURE

The vegetable oils were obtained from commercial sources and used without further purification. The samples were converted to methyl esters by alkali catalytic and non catalytic super critical methanol transestrification methods.

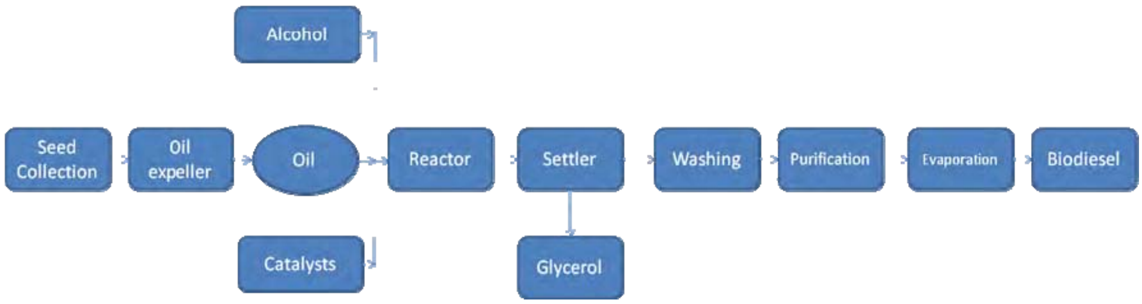


Fig.1 Preparation of Laboratory Samples of Biodiesel

3. MATERIALS AND METHODS

3.1. *Measurement of Different Fuels Properties*

Untreated oil is mixed with a mixture of anhydrous methanol and a catalyst (Methoxide) in proper proportion. The mixture is maintained at a temperature little below 65°C (being the B.P. of methanol) and continuously stirred the mixture for around three hours. After completion of stirring, the mixture is allowed to settle down for 24 hours. The layer of glycerol settled at the bottom is carefully taken out and the upper layer is the ester of karanja oil which is tapped separately.

The important physical and chemical properties of oil and biodiesel were determined by standard methods. In order to measure the properties of the oil diesel fuels, the test methods were used as follows.

Density (ASTM D941), Viscosity (ASTM D445), Flash point (ASTM D93), higher heating value (ASTM D2015). The details about the apparatus is given in table1

Table 1. Measurement Methods

S.No	Parameters	Method of Analysis	Instruments Used
1	Viscosity @ 40ºC	IS:1448:(P:25):1976	Redwood Viscometer
2	Density @ 27ºC	IS:1448:(P:32):1992	Pycnometer
3	Flash Point	IS:1448:(P:21):1992	Pensky Martens Apparatus [Closed Cup]
4	Calorific value	IS:1448:(P:33):1991	Bomb Calorimeter

3.1.1. *Density*

Relative density otherwise known as the specific gravity refers to the ratio of the density of a fuel to the density of water at same temperature with its other properties could be judged. Density measurements were carried out using a pycnometer at a temperature of 311.5 $\pm$ 0.05 k: the pycnometer of capacity about 25 ml being calibrated with water.

3.1.2. *Flash Point*

Flash point is the lowest temperature corrected to a standard atmospheric condition at which application of a test flame Cause the vapour specimen to ignite under specific conditions of test, flash point of the samples were measured by Pensky martens apparatus.

3.1.3. *Viscosity*

The resistance to flow exhibited by fuel blends is expressed in various units of viscosity. It is a major factor of consequence in exhibiting their suitability for the mass transfer and metering requirements of engine operation. Higher the viscosity results low volatility and poor atomization of oil during injection in CI engine, that results in complete combustion and ultimately carbon deposit on injector nozzle as well as in the combustion chamber. The viscosities of oil as well as derived bio diesel are measured by red wood viscometer at 313 k.

3.1.4. *Higher Heating Value*

Heating Value of a fuel is the thermal energy released per unit quantity of fuel when the fuel is burned completely and the products of combustion are cooled back to the initial temperature of the combustible mixtures. It measures the energy content in a fuel. The HHV, of the vegetable oils and their methyl esters were measured in a bomb calorimeter according to ASTM D2015 standard method. An oxygen – bomb was pressurized to 3 Mpa with an oxygen container. The bomb was fired automatically after the jacket and a bucket temperature equilibrates to within acceptable accuracy of each other.

4. RESULTS AND DISCUSSION

The viscosity density, flash point, and higher heating value (HHV) measurements of fourteen methyl esters of various vegetable oils are tabulated in Table 2, taken from the literature [1.]

Table 2Viscosity Density, Flash Point, and Higher Heating Value (HHV) Measurements of Fourteen biodiesel

Vegetable Oils	Viscosity (cst)	Density (g/L)	Flash Point (k)	HHV (MJ/kg)
Cotton seeds	3.75	871	455	41.18
Corn	3.62	873	427	41.14
Crambe	5.12	848	463	41.98
Hazelnut	3.59	875	425	41.12
Linseed	2.83	885	415	40.84
Mustard	4.10	866	442	41.30
Olive	4.18	860	447	41.35
Palm	3.94	867	434	41.24
Rapeseed	4.60	857	453	41.55
Safflower	4.03	866	440	41.26
Sesame	3.04	880	418	40.90
Soybean	4.08	865	441	41.28
Sunflower	4.16	863	439	41.33
Walnut	4.11	864	443	41.32

Viscosity is a measure of the internal friction or resistance of an oil to flow. As the temperature of oil is increased, its viscosity decreases and it is therefore able to flow more readily. Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray to poorer atomization of the fuel spray and less accurate operation of the fuel injectors.

The viscosity values of vegetables oils are between 27.2 and 53.6 mm^2/s where as those of vegetable oils methyl esters are between 2.83 and 5.12 mm^2/s. The viscosity values of vegetable oil methyl esters highly decreases sharply after transesterification process. The viscosity of Diesel fuel is 2.76 mm^2/s at @40ºC. Compared to diesel fuels, all of the vegetable oil methyl esters are slightly viscous.

Density is another important property of biodiesel. It is the weight of a unit volume of fluid. Specific gravity is the ratio of the density of a liquid to the density of water. Specific gravity of biodiesels ranges between 848 and 901 g/L. Fuel injection equipment operates on a volume metering system; hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel. An increase in density from 848 to 901 g/L for biodiesels for increases the viscosity from 3.6 and 5.1 mm^2/s. and the increases are highly regular.

The higher heating values (HHVs) of biodiesels are relatively high. The HHVs of biodiesel (39 to 43.33 MJ/kg) is slightly lower than that of diesel (49.65 MJ/kg). The oxygen content of biodiesel improves the combustion process and decreases its oxidation potential. The structural oxygen content of a fuel improves its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. Because of this the combustion efficiency of biodiesel is higher than that of petrodiesel and the combustion efficiency of methanol and ethanol is higher than that of diesel.

The HHV is an important property defining the energy content and thereby efficiency of fuels. Fuel properties for the combustion analysis of biodiesel blends can be grouped conveniently into physical, chemical and thermal properties. Physical properties include viscosity, density, cloud point, pour point, flash point, boiling range, freezing point and refractive index. These exists a number of correlations for estimating the HHV of vegetables oils based upon its physical properties.

The experimental data were correlated as a function of viscosity, density, flash point by empirical linear equation. These equations, obtained from regression analysis by using the measured values, were used for estimating the calorific value. The measured HHVs for each fuel are shows in table 3.

Table-3.The calculated and measured values of HHV – biodiesel

Biodiesel	**Measured**	**K_4**	**K_3**	**K_2**	**K_1**	**R^2**	**Calculated**	**Absolute Error**	**Error (%)**
Cotton seeds	41.18	40.3667	0.4527	-0.0008	-0.0003	0.949	41.14	0.04	0.09
Corn	41.14						41.09	0.05	0.12
Crambe	41.98						41.78	0.20	0.47
Hazelnut	41.12						41.07	0.05	0.12
Linseed	40.84						40.72	0.12	0.29
Mustard	41.30						41.31	0.01	0.02
Olive	41.35						41.36	0.01	0.02
Palm	41.24						41.23	0.01	0.02
Rapeseed	41.55						41.54	0.01	0.02
Safflower	41.26						41.27	0.01	0.02
Sesame	40.90						40.82	0.08	0.19
Soybean	41.28						41.30	0.02	0.04
Sunflower	41.33						41.34	0.01	0.02
Walnut	41.32						41.31	0.01	0.02

Formula (1) is obtained from physical properties of biodiesel

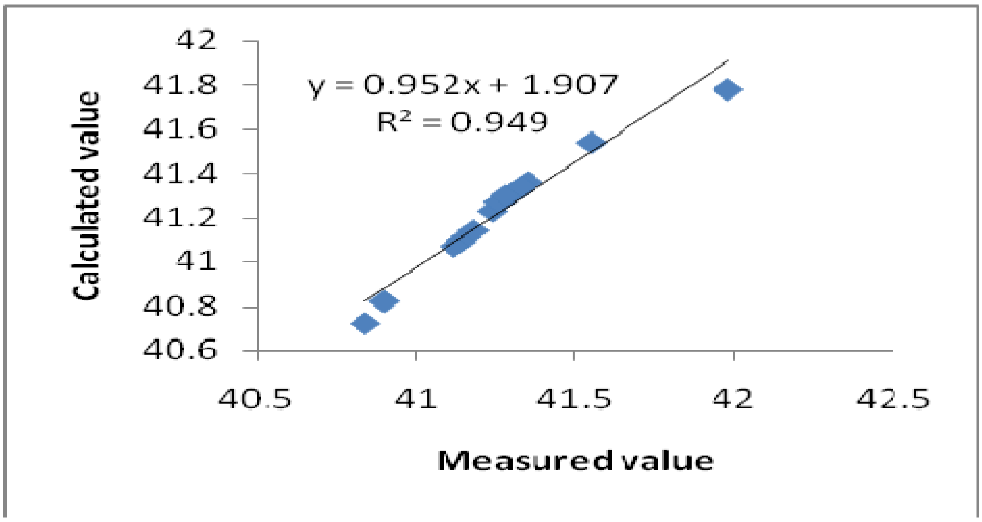
$$D = K_4 + K_3\nu + K_2\rho + K_1FP \qquad \text{----- (1)}$$

Where D is HHV (MJ/kg), ν is viscosity (CST), ρ is density (g/L), FP is flash point (K), K_1, K_2, K_3, and K4 are co-efficient.

Table 3 shows the co-efficient R^2 and the calculated HHVs from regression analysis, the measured HHV, the absolute and % error between the measured and calculated HHVs.

$$HHV = 0.4527\,\nu - 0.0008\rho - 0.0003FP + 40.3667 \qquad (2)$$

The calculated HHVs from equation are validated by using the measured HHVs for all biodiesels. There is an excellent agreement between the measured and estimated values which is shown in fig2



To check whether the equation is applicable for biodiesel and bioethanol blends, Karanja oil, ethanol is taken and properties were studied in the laboratory. The properties are given in table 4.

Table-4 . The properties of diesel, biodiesel (Karanja), ethanol and their blends

Fuel	Viscosity @40ºC (cSt)	Density @ 20ºC (g/l)	Flash Point (k)	HHV (MJ/kg)
Diesel	2.76	828	321	49.65
Biodiesel (Karanja)	5.58	901	467	43.33
Ethanol	1.17	783	291	34.50
B10	2.32	833	322	49.08
B20	2.76	835	325	45.81
B30	3.19	850	329	43.13
BE10	4.00	886	349	37.68
BE20	3.61	876	294	36.12
BE30	2.76	869	293	33.33

Table-5.The calculated and measured values of HHV – diesel, biodiesel (Karanja), ethanol and their blends

Fuel	Measured	Calculated	Absolute Error	Error (%)
Diesel	49.65	44.98	4.67	9.4
Karanja	43.33	38.36	4.97	11.47
B10	49.08	42.36	6.72	13.69
B20	45.81	43.05	2.76	6.02
B30	43.13	39.74	3.39	7.85
BE10	37.68	31.87	5.81	15.42
BE20	36.12	30.66	5.46	15.11
BE30	33.33	30.59	2.74	8.22

Equation 2 was able to predict the HHV value with 0.94 accuracy. The calculated HHVs from equation are validated by using the measured HHVs for all biodiesels. There is an excellent agreement between the measured and estimated values which is shown in fig 3

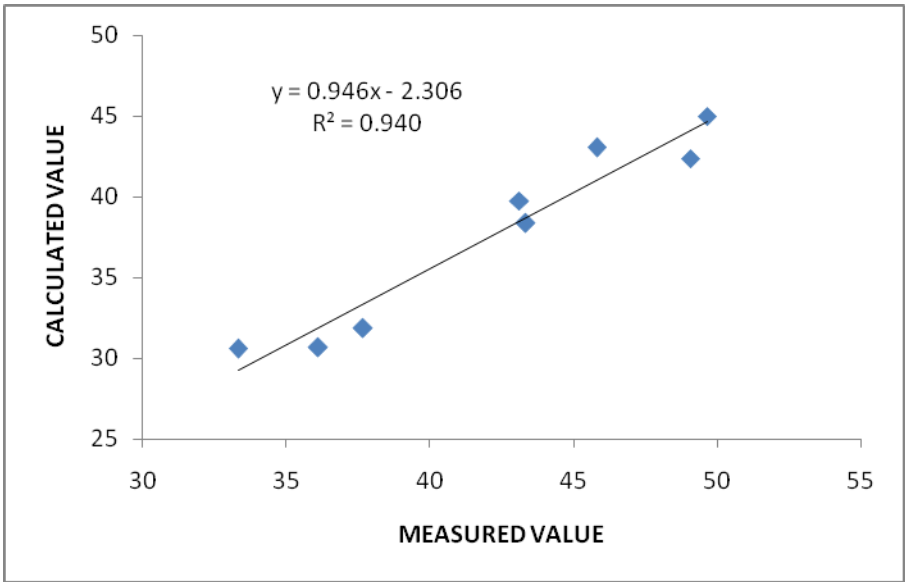


Fig 3. Calculated and measured values of HHV

5. CONCLUSION .

A new method of HHV estimation of vegetable oils, biodiesel is presented. The aim of this work is to show that it is possible to estimate the HHV of vegetable oils and biodiesel from viscosity, density and flash point. It is established that the physical properties of the bio-fuels has a predominate effect on the HHV of the bio diesel. From the results obtained it is found the HHV as affected by the physical properties. An equation was developed to predict the HHV based on physical properties and it was able to predict with 0.949 accuracy. The developed equation can effectively predict the HHV of the biodiesel based on its physical properties.

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