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Relationships among the physical properties of biodiesel and engine fuel system design requirement

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Abstract
Biodiesel, an alternative fuel can be used in diesel engines as neat or blended with diesel. The physio-chemical properties of fuel are important in design of fuel system for compression ignition engines run on diesel, biodiesel or biodiesel blends. Biodiesel (B100) standards specify the limit values of these properties for blending with diesel. However, there are variations in the properties of biodiesel. The properties of biodiesel vary depending on the feedstock, vegetable oil processing, production methods and degree of purification. The objective of this study is to estimate the mathematical relationships between viscosity, density, heating values and flash point among various biodiesel samples. There is a high regression between various properties of biodiesel and the relationships between them are observed to be considerably regular.

Keywords: Biodiesel, Fuel properties, Diesel engine.

1. Introduction
Petroleum product consumption is increasing day-by-day as the number of vehicles on road increases. Consumption of hydrocarbon fuel increases the environmental pollution also. There is a need to solve these twin problems–fuel supply and environmental pollution. Non-renewable fuel emits more hydrocarbon emissions, oxides of nitrogen, sulphur and carbon monoxides as compared to renewable biofuels. Various alternative fuels are considered as substitute fuels for petroleum products and efforts were made to analyze the suitability of the fuel and its demonstration. Renewable fuels have received more attention as it reduces the environmental pollution (by completing carbon cycle) and reduces the import of petroleum. Hence, researchers and scientific community worldwide have focused on the development of biodiesel and the optimization of the processes to meet the standards and specifications needed for the fuel to be used commercially.

2. Vegetable oil characterisation
Vegetable oil molecules are triglycerides with unbranched chains of different lengths and different degree of saturation. Diesel is a complex mixture of thousands of individual compounds, most with carbon numbers between 10 and 22 and mostly of saturates. The natural organic compounds in the vegetable oils and animal fats are made up of various combinations of fatty acids (in sets of three) connected to a glycerol molecule, making them triglycerides [1].

Straight vegetable oil (neat vegetable oil) can be used as fuel for I.C. engines with some minor modifications in the fuel system. Results of short-term tests conducted by various researchers were found to be successful. However, some problems were experienced during engine operation include,

i. High viscosity, low cetane number and high flash point cause cold staring problems
ii. Vegetable oils are of low oxidation stability and hence form injector plugging and gum formation. Filtering of vegetable oils before injection would reduce the injector plugging
iii. Poor atomisation of vegetable oils causes incomplete combustion and dilution of crankcase due to blow by cause excessive engine wear, coking of injectors, ring sticking, lube oil dilution and increase in combustion chamber deposits.

3. Biodiesel production and characterisation

To tackle these problems the vegetable oils are modified as emulsions, blended with diesel and methyl esters. Among the various conversion methodologies, transesterification process i.e. conversion to esters has become commercial success. Transesterification is a chemical process of transforming large, branched, triglyceride molecules of the vegetable oils and fats into smaller, straight chain molecules, almost similar in size to the molecules of the species present in the diesel fuel (Figure 1).

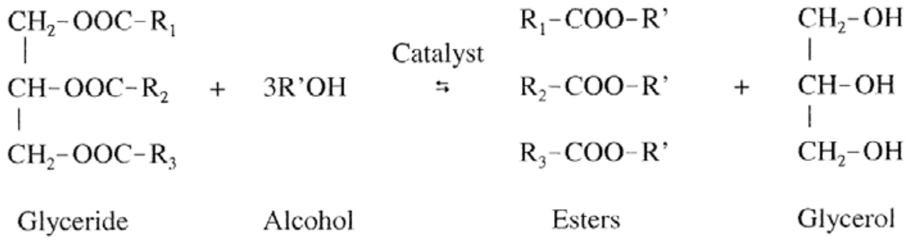

Figure 1. Transesterification of vegetable oils

By-product of transesterification process, glycerol has commercial value also. Stoichiometrically, three moles of alcohol are required for each mole of triglyceride, but in general, a higher molar ratio is often employed for maximum ester production and moves the reaction towards forward direction. The yield of the process also depends upon the type of feedstock, amount of catalyst, temperature, etc. Commonly used alcohols include methanol, ethanol and butanol. The esters have reduced the viscosity and increased volatility relative to the triglycerides present in vegetable oils. Biodiesel production methods include acid, alkaline, two-step, supercritical methanol and ultrasonic methods [2, 3].

Many countries started biodiesel production industries and biodiesel is blended with diesel commercially as per their national policy. Based on the positive results obtained by them and automotive manufacturers extended the warranty of biodiesel operated vehicles. European Union has become the leader of biodiesel production in the world.

Fuel properties can be grouped conveniently into physical, chemical and thermal properties. The important properties of vegetable oils are classified into three groups, viz.

i. Physical properties - viscosity, cloud point, pour point, flash point etc.
ii. Chemical properties - chemical structure, acid value, saponification value, sulphur content, copper corrosion, oxidation resistance and thermal degradation etc.
iii. Thermal properties - distillation temperature, thermal conductivity, carbon residue and calorific value etc.

The objective of this study is to establish the mathematical relationships between viscosity and other fuel properties of biodiesel that used in the design of fuel system.

4. Testing of biodiesel

Biodiesel fuel quality depends upon composition of feedstock, production process, storage and handling. Biodiesel quality is evaluated through the determination of chemical composition and physical properties of the fuel. Contaminants and other minor components due to incomplete reaction are the major issues in the quality of biodiesel i.e., glycerol, mono, di, triglycerides, alcohol, catalysts and free fatty acid present in the biodiesel. Moreover, biodiesel composition could be changed during storage and handling. Biodiesel can absorb water or undergoes oxidation during storage. Therefore, significance of these parameters and their analytical or engine test methods are addressed in standards. Each country has its

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own fuel quality testing methods and standards to specify the properties of the fuel. Here the standard methods and limits are described with reference to ASTM / EN/ IS standards. In India, IS 15607 specifies the properties of biodiesel, B100 is given in Table 1[4].

Table 1. Biodiesel specification - IS 15607

S.No	Characteristics	Unit	Requirement	Test method ISO,ASTM,EN / IS 1448
1	Density at 15ºC	kg/m^3	860-900	ISO 3675 /P 32
2	Kinematic viscosity at 40ºC	cSt	2.5-6.0	ISO 3104 / P25
3	Flash point (closed cup), min	ºC	120	P21
4	Sulphur, max	mg/kg	50	D5443/P83
5	Carbon resiue (Ramsbottom),max	%m	0.05	D4530
6	Sulfated ash, max	%m	0.02	ISO 6245/P4
7	Water content, max	mg/kg	500	D2709 / P40
8	Total contamination, max	mg/kg	24	EN12662
9	Copper corrosion 3 hr @50ºC, max	-	1	ISO 2160 / P15
10	Cetane number, min	-	51	ISO 5156/ P9
11	Acid value, max	mg KOH/g	0.50	P1
12	Methanol, max	%m	0.20	EN 14110
13	Ethanol, ax	%m	0.20	-
14	Ester content, min	%m	96.5	EN 14103
15	Free glycerol, max	%m	0.02	D6584
16	Total glycerol, max	%m	0.25	D6584
17	Phosphorous, max	mg/kg	10.0	D 4951
18	Sodium and potassium, max	mg/kg	To report	EN 14108
19	Calcium and magnesium, max	mg/kg	To report	-
20	Iodine value	-	To report	EN 14104
21	Oxidation stability at 110ºC, min	Hr	6	EN 14112

5. Mathematical relationships

5.1 Density vs kinematic viscosity

There exists a number of correlations for estimating the properties of fuel upon its physical properties. The important properties of various biodiesel are given in Table 2 [5,6]. Kinematic viscosity is the resistance to flow of a fluid under gravity. It is the time taken for a fixed volume of fuel to flow under gravity through the capillary tube viscometer immersed in a thermostatically controlled bath at 40ºC. It is the product of measured time flow and calibration constant of viscometer. The viscosity of vegetable oils reduces drastically when blending with diesel or transesterification. However, as compared to diesel, biodiesel has slightly higher viscosity. From Table 2, measured values of kinematic viscosity of biodiesel are in the range of 2.83 and 5.78 cSt. The kinematic viscosity is a basic design parameter for the fuel injectors used in diesel engines. Fuel viscosity has influence on fuel droplet size and spray characteristics. Viscosity is inversely proportional to temperature. Viscosity increases with chain length and degree of saturation. Fuel specification viscosity upper limit ensure that fuel will flow readily during cold starting. Higher viscosity leads to poor atomization incomplete combustion and increases carbon deposits. More, higher viscosity fuel needs higher pumping power also. Fuels with lower viscosity leaks past plunger through the clearance between plunger and barrel during fuel compression.

Table 2. Properties of biodiesel [5, 6]

Biodiesel	Kinematic viscosity (cSt)	Density (kg/m^3)	Flash point (ºC)	Calorific Value (MJ/kg)
Linseed oil methyl esters	2.83	885	117	40.2
Seasame oil methyl esters	3.04	880	170	40.7
Hazelnut oil methyl esters	3.59	874	183	-
Corn oil methyl esters	3.62	873	174	41.35
Cotton seed oil methyl esters	3.75	871	170	41.32
Palm oil methyl esters	3.94	867	169	41.3
Safflower oil methyl esters	4.03	866	167	41.26
Soybean oil methyl esters	4.08	865	161	41.24
Soybean oil methyl esters	4.08	885	124	40.5
Walnut oil methyl esters	4.11	864	-	41.18
Sunflower oil methyl esters	4.16	863	154	41.14
Olive oil methyl esters	4.18	860	-	-
Soybean ethyl esters	4.41	-	-	40
Rapeseed oil methyl esters	4.6	857	145	40.9
Tallow methyl esters	4.8	876	131	40.4
Rapeseed oil methyl esters	4.83	883	185	40.5
Crambe oil methyl esters	5.12	848	142	40.84
Soy butyl esters	5.24	-	-	40.7
Frying oil ethyl esters	5.78	872	166	41.33
Rapeseed ethyl esters	6.17	876	190	-

Density is mass of the substances occupying unit volume at 15ºC. Density of fuel is evaluated as per ASTM D4052. Hydrometers are used to evaluate the density of liquids. Biodiesel is slightly higher than conventional diesel. Diesel engine injectors normally operate on volume metering system. If the fuel is of higher density large mass of fuel is injected and hence more power and emissions.
Fuel injectors operate on a volume based metering system, Hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel. Increase in viscosity of biodiesel increases its density. The relationship between viscosity and density is shown in Figure 2. From that, we can understand that viscosity of biodiesel decreases with increase in density. The correlation between viscosity and density is: Density= -15.77 * viscosity +929.59 with coefficient of regression value of 0.9724. There is considerably high regression between viscosity and density for biodiesel samples.

5.2 Flash point vs. Kinematic viscosity

Flash point is defined as the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test. Flash point of the fuel is evaluated as per ASTM D93 test method. Flash point of biodiesel is higher than that of diesel (>130 ºC) which makes biodiesel safer than diesel in handling and storage point of view. A minimum flash point for biodiesel is specified in restricting the alcohol content. Flash point of biodiesel will reduce drastically if the alcohol used in production of biodiesel is not completely removed from it. Moreover, it reduces the combustion quality of fuel. Excess methanol in the fuel may also affect engine seals and elastomers and corrode metal components. Hence, alcohol content in biodiesel is given in biodiesel specification to a limit value of 0.24 mg/kg.
Figure 3 depicts the correlation between viscosity and flashpoint of biodiesel. Higher the viscosity increases the flash point of biodiesel however it affects the burning quality of biodiesel and affects its atomization. The correlation between viscosity and flash point can be written as Flash point = 12.36 * viscosity + 176.3 with the coefficient of regression 0.964.

5.3 Density vs. Flash point

Figure 4 shows the correlation between density and flash point of biodiesel samples. The flash point of biodiesel increases with density also. Higher density fuel increases its heat carrying capacity also. The equation between density and flash point can be written as Flash point = 1.46 * density – 1099.9 with the coefficient of regression 0.91.

5.4 Density vs. Calorific value

Calorific value is an important property that defines the energy content in the biodiesel and hence thermal efficiency and specific fuel consumption. The relation between density and higher heating value of biodiesel is shown in Figure 5. The equation between density and HHV can be written as HHV = 0.0207 * density + 23.28 with the coefficient of regression value of 0.9568.

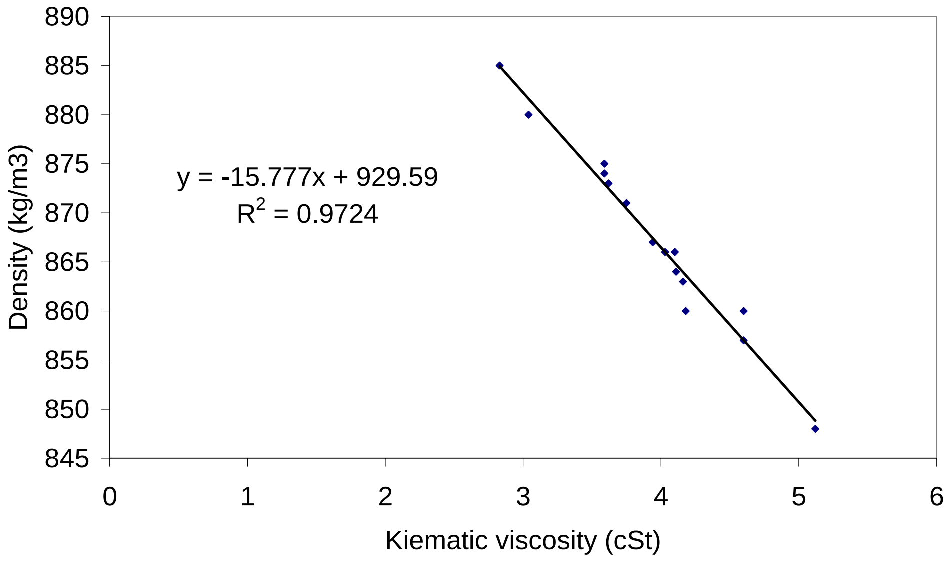

Figure 2. Correlation between viscosity and density of biodiesel samples

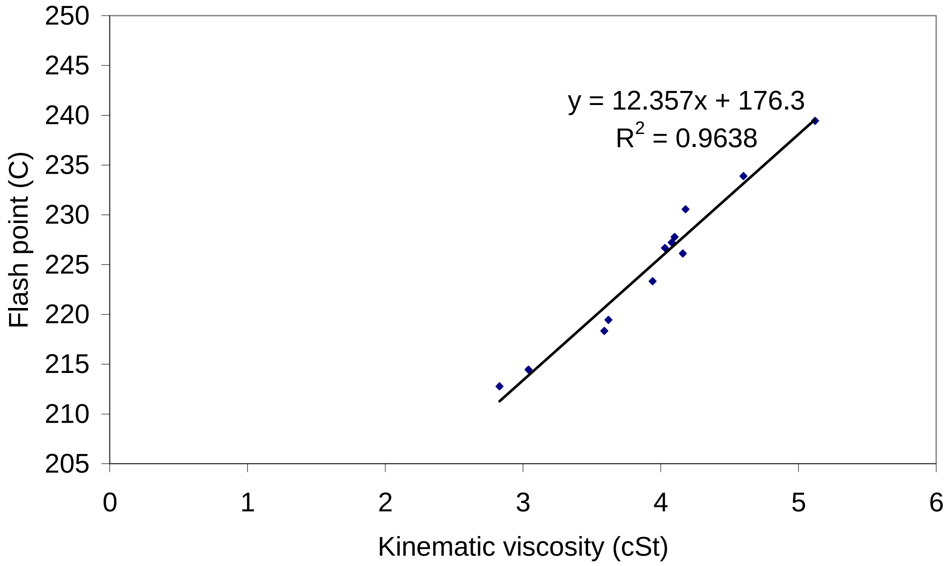

Figure 3. Correlation between viscosity and flashpoint

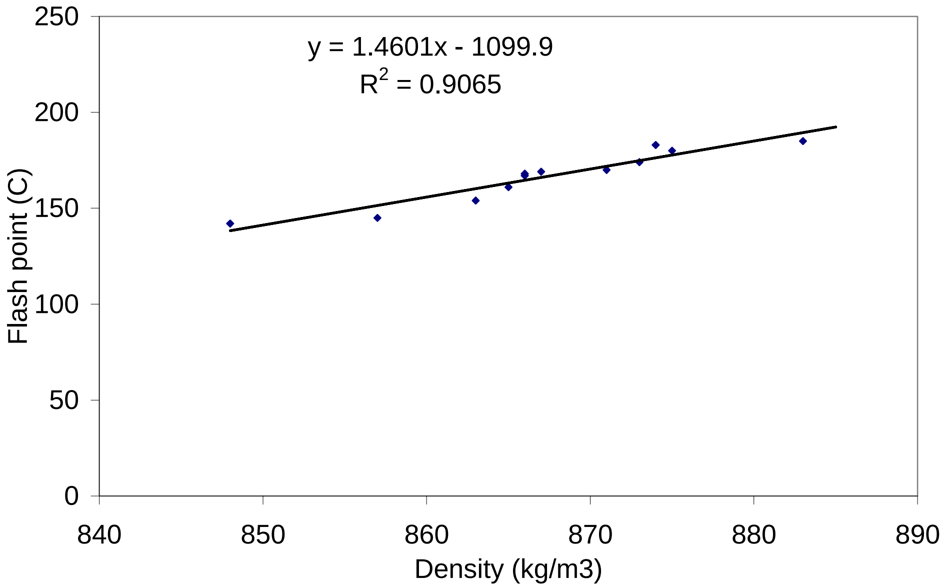

Figure 4. Correlation between density and flash point

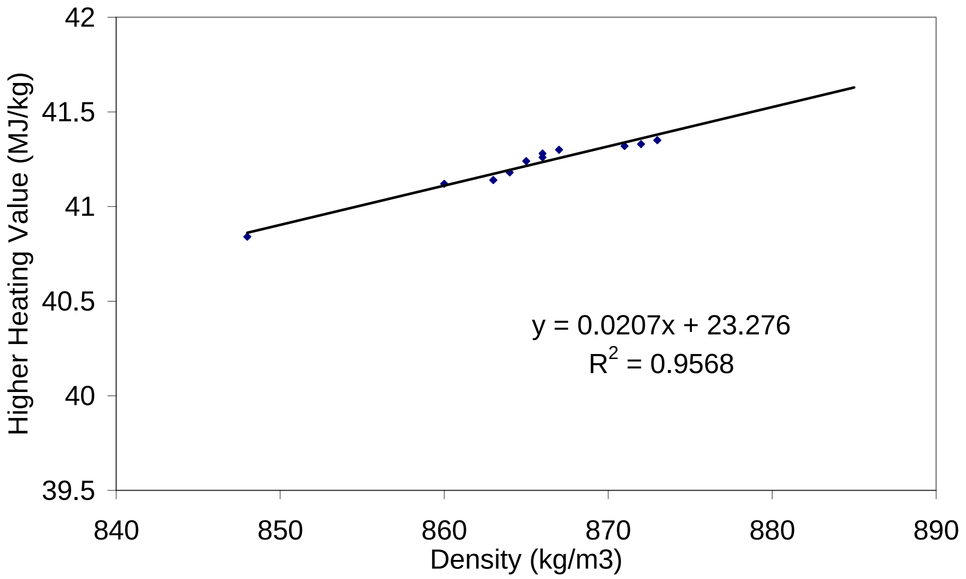

Figure 5. Correlation between density and heating value

6. Conclusion

The transesterification of vegetable oil decreases its viscosity and the properties of biodiesel depend on feed stock i.e. vegetable oils and process technologies employed. However, there is a correlation among the properties of biodiesel. Correlations have been established between flash point, density, viscosity and heating value. Viscosity is one of the most important parameters required in the design of combustion process. Viscosity must be closely correlated with structural parameters of fuel flow systems. Hence, the neat biodiesel or biodiesel blends should meet the desired viscosity in order to avoid damage of fuel injectors and fuel pump. A correlation developed between heating value and density of biodiesel with viscosity of fuel. These correlations between these properties follow the linear regression with high coefficient of regression. These physical properties of fuel are the significant parameters in the design of fuel system for biodiesel engine.

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