Prediction of cold flow properties of Biodiesel

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Abstract— **Biodiesel being environmentally friendly is fast gaining acceptance in the market as an alternate diesel fuel. But compared to petroleum diesel it has certain limitations and thus it requires further development on economic viability and improvement in its properties to use it as a commercial fuel. The cold flow properties play a major role in the usage of biodiesel commercially as it freezes at cold climatic conditions. In the present study, cold flow properties of various types of biodiesel were estimated by using correlations available in literature. The correlations were evaluated based on the deviation between the predicted value and experimental values of cold flow properties.**

***Index Terms*— Biodiesel, cold flow properties, cloud point, pour point, cold filter plugging point**

I. Introduction

Biodiesel is a clean burning, renewable replacement for the petroleum diesel, it could reduce the dependence on the petroleum diesel. Biodiesel is made from various feedstock's including vegetable oils, animal fats, recycled cooking oil. Biodiesel is made through a chemical process called transesterification whereby the glycerin is separated from the fat or vegetable oil. The process leaves behind two products, methyl esters and glycerin which can be sold to be used in soap production. Biodiesel is said to be good for diesel engines, as it has better lubricating properties than petroleum diesel. Biodiesel is safe to handle and transport because it has higher flash point than the petroleum diesel. Biodiesel actually degrades about four times faster than petroleum diesel when released into the environment. Because biodiesel is physically similar to petroleum diesel fuel, it can be blended with diesel fuel in any proportion. Many federal and state vehicles are now using biodiesel blends in their diesel engines. The most common blend is a mixture consisting of 20% biodiesel and 80% petroleum diesel, called B20. The motive for blending the fuels is to gain some of the advantages of biodiesel while avoiding higher costs. The major concern over using biodiesel as a fuel commercially is its cold flow properties [1]. Biodiesel is less suitable for use in low temperatures, than petroleum diesel. At lower temperatures, the fuel becomes a gel that cannot be pumped, and as fuel forms wax crystals, which can clog fuel lines and filters in a vehicle's fuel system.

For the low temperature application of biodiesel, the cold flow properties like cloud point, pour point and cold filter plugging point are of concern and the same are discussed below.

A. Cloud point

The cloud point (CP) is the temperature at which a cloud of wax crystals first appears in a fuel sample that is cooled under conditions described by ASTM D2500. The cloud point is determined by visually inspecting for a haze in the normally clear fuel [2]. The cloud point of biodiesel depends on level of saturation and unsaturation of fatty acid methyl ester (FAME). For different saturated FAME, cloud point depends on chain length and for unsaturated FAME, it depends on degree of unsaturation, orientation of double bonds.

B. Pour point

As the temperature gets colder, crystal growth continues and a lattice is obtained leading to solidification at the pour point. The pour point (PP) is the temperature at which the biodiesel fuel becomes so thick that it will no longer be pumped to the engine. Pour point is measured using ASTM D-97 test method. Fuel suppliers typically set pour point specification seasonally [2]. Pour point is typically well below the temperature at which the fuel will plug a fuel filter. Therefore, pour point is a useful measure of fuel handling properties, but not a good indicator of vehicle operability.

C. Cold filter plugging point

Cloud point and pour point cannot be directly correlated to the phenomenon leading to the plugging of diesel vehicle filters by n-alkane crystals, so a third parameter is used, the cold filter plugging point, which corresponds to the plugging of a 45 μm filter under 200 mm H_2O (0.019 atm) vacuum within 60 s [3]. Cold filter plugging point (CFPP) is accepted nearly worldwide and listed among the limiting fuel parameters in the aforementioned European biodiesel fuel standard EN 14214.

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III. PREDICTION OF COLD FLOW PROPERTIES

Some studies have focussed on developing empirical correlations to predict the low-temperature flow properties of biodiesels. Dunn et al. [4] and Tang et al. [4] had proposed relationship between CP and PP. Lopez et al. [5] proposed that for determining CP the main factor affecting its prediction is saturated esters, as they have higher melting points. As a result of this the predicted values showed large errors for biodiesel containing unsaturated fatty acid esters. Sarin et al. [5] proposed a series of linear correlations for CP, PP, and CFPP of blends of biodiesel (Jatrpoha, Palm and Pongmia). Two set of correlations were developed, first one based on the palmitic acid methyl ester (P_{FAME}) and the second one based on the total unsaturated fatty acid methyl esterôs (U_{FAME}). Yung et al. [6] proposed correlations for CP, PP, and CFPP based on the chain length and degree of unsaturation. Researchers have proposed various correlations for the prediction of cold flow properties of biodiesel, but their study was limited to particular type of biodiesels and hence they were not generalized.

The objective of this study is to carryout comparative evaluation of various types of correlations available in literature for the prediction of cold flow properties for a different set of biodiesels. Hence for this study six biodiesel sunflower, rapeseed, soybean, olive, palm and beef tallow were selected. The experimental values of cold flow properties and composition analysis (fatty acid ester content) of biodiesel were obtained from the literature [7,8]. For these biodiesels, cloud point, pour point and cold filter plugging point was predicted using the correlations proposed by Sarin et al. and Yung et al.

A. Method of Sarin

Sarin et al. proposed various correlations for cold flow properties of biodiesel based on palmatic acid methyl ester (P_{FAME}) content and on total content of unsaturated FAMEôs (U_{FAME}).

$$CP = 0.526 (P_{FAME}) - 4.992 \quad (0 < P_{FAME} < 45)$$

$$PP = 0.571 (P_{FAME}) - 12.24 \quad (0 < P_{FAME} < 45)$$

$$CFPP = 0.511 (P_{FAME}) - 7.823 \quad (0 < P_{FAME} < 45)$$

$CP = - 0.576 (U_{FAME}) + 48.255 \quad (0 < U_{FAME}$ Ò $84)$

$PP = - 0.626 (U_{FAME}) + 45.594 \quad (0 < U_{FAME}$ Ò $84)$

$CFPP = - 0.561 (U_{FAME}) + 43.967 \quad (0< U_{FAME}$ Ò $84)$

B. Method of Yung

Sarinôs method is mainly dependent on either the palmitic acid methyl ester or the unsaturated methyl ester, and thus is not accurate enough for the prediction of the cold flow properties of the biodiesel. A more precise method was developed by Yung et al., where chain length and degree of unsaturation is used for the prediction of cold flow properties. He proposed various correlations based on the weighted average number of carbon atoms in FAME (Nc) and the total unsaturated FAME content (UFAME, wt %).

CP = 18.134 (Nc) ï 0.790 (UFAME)

PP = 18.880 (Nc) ï 1.000 (UFAME)

CFPP = 18.019 (Nc) ï 0.804 (UFAME)

IV. RESULTS AND DISCUSSIONS

The predicted values of cold flow properties were compared with their experimental values and absolute deviation was calculated. Table 1, Table 2 and Table 3 shows the predicted values and experimental values of CP, PP and CFPP respectively.

Table 1

PREDICTED AND EXPERIMENTAL VALUES OF CP FOR VARIOUS BIODIESEL

Biodiesel	Predicted values of CP (°C)			Experimental values of CP(°C)
	Sarin (P_{FAME})	Sarin (U_{FAME})	Yung	
Sunflower	-1.53	-2.79	-0.33	4
Rapeseed	-2.57	-4.95	-1.95	-3
Soybean	0.70	-0.33	1.20	2
Olive	0.65	-1.68	-2.74	-2
Palm	16.20	16.23	10.35	12
Beef tallow	7.15	19.86	22.24	17

Table 2

PREDICTED AND EXPERIMENTAL VALUES OF PP FOR VARIOUS BIODIESELS

Biodiesel	Predicted values of PP (°C)			Experimental values of PP(°C)
	Sarin (P_{FAME})	Sarin (U_{FAME})	Yung	
Sunflower	-8.48	10.78	-4.84	-6
Rapeseed	-9.61	-12.23	-7.20	-9
Soybean	-6.05	-9.88	-2.48	1
Olive	-6.12	-8.68	-7.16	-3
Palm	10.77	10.79	11.57	12
Beef tallow	0.95	14.73	25.64	15

Table 3
Predicted and experimental values of CFPP for various biodiesels

Biodiesel	Predicted values of CFPP (°C)			Experimental values of CFPP(°C)
	Sarin (P_{FAME})	Sarin (U_{FAME})	Yung	
Sunflower	-4.46	12.77	-3.74	-7
Rapeseed	-5.47	-7.85	-5.42	-14
Soybean	-2.28	-3.33	-2.13	-4
Olive	-1.59	-4.67	-6.12	-6
Palm	12.77	12.77	7.44	9
Beef tallow	3.98	16.31	19.43	9

The deviation of CP, PP and CFPP for these methods are represented in Figure 1, Figure and Figure 3 respectively.

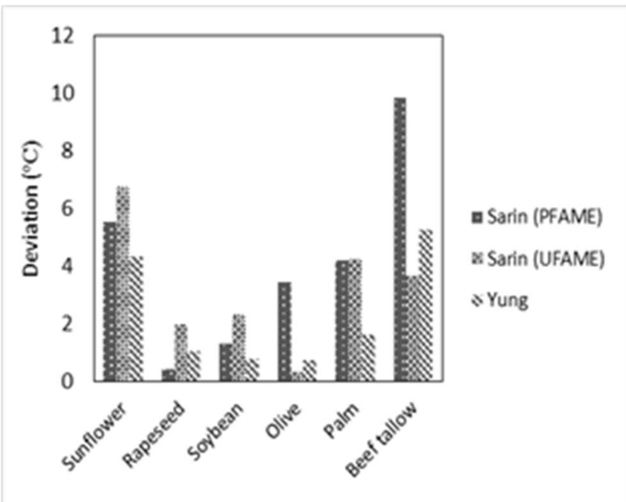

Fig 1 Deviation in the prediction of CP

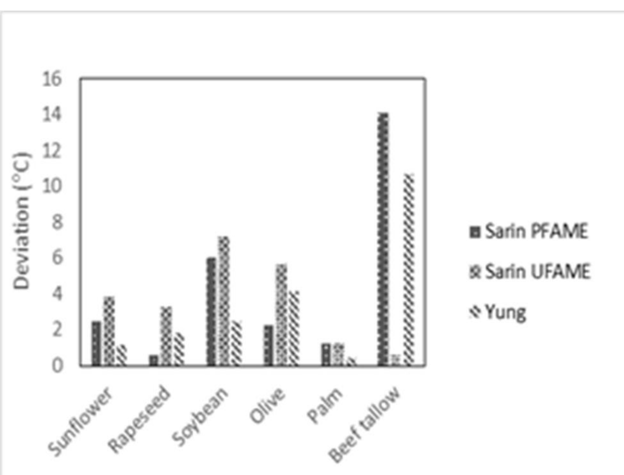

Fig 2 Deviation in the prediction of PP

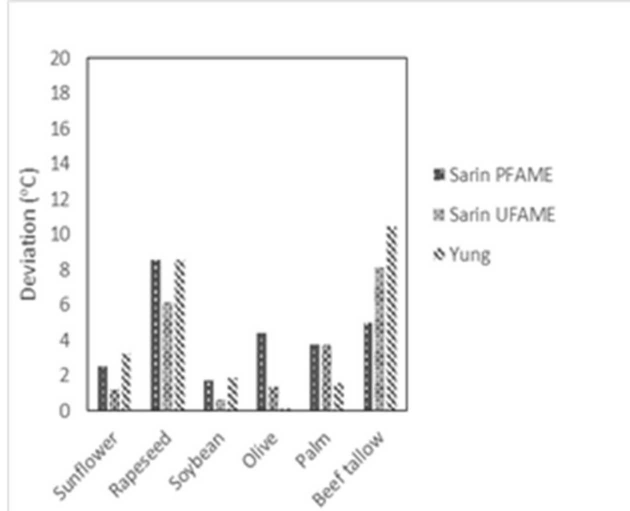

Fig 3 Deviation in the prediction of CFPP

It can be observed not a single method gave good prediction of cold flow property for all biodiesels. For sunflower, rapeseed and soybean, Sarin P_{FAME} gave lesser deviation for CP and PP in comparison to Sarin U_{FAME}, but the same trend is not observed for CFPP. Similarly method of Yung performs better in comparison to method of Sarin, but for beef tallow it gives very high deviation. Hence the method proposed by Sarin and Yung cannot be generalized for the prediction of cold flow properties of biodiesels.

V. Conclusions

In this study, cold flow properties of biodiesel were predicted using method of Sarin et al. and Yung et al. Method of Sarin is based on the content of Palmatic methyl ester and unsaturated FAME in the biodiesel, while method of Yung is based on the weighted average number of carbon atoms and unsaturated FAME. Both the methods could not predict the cold flow properties of all the biodiesels accurately. As these methods couldnot be generalized for predicting the cold flow properties of biodiesels, hence there is a scope for the development of generalized models for the prediction of cold flow properties of biodiesels.

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