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Prediction of cold flow properties of various biodiesels

Sauvir V. Mevada[a], Parag A. Saxena[b,*], Milind H. Joshipura[b]

[a] Student, Chemical Engineering Department, Institute of Technology, Nirma University, Ahmedabad 382481, Gujarat, India
[b]Assistant Professor, Chemical Engineering Department, Institute of Technology, Nirma University, Ahmedabad 382481, Gujarat, India
[c]Associate Professor, Chemical Engineering Department, Institute of Technology, Nirma University, Ahmedabad 382481, Gujarat, India

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 work various types of biodiesels have been studied and its cold flow properties have been predicted using correlations available in the literature to evaluate as to which correlation gives the least deviation compared to the experimental values.

Keywords: Biodiesel; Cloud point; Pour point; Cold filter plugging point, FAME

1. 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 feedstockôs 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.

*Corresponding author. Tel.: +91-9924159006
E-mail address: parag.saxena@nirmauni.ac.in

The major concern over using biodiesel as a fuel commercially is its cold flow properties. 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 vehicleôs fuel system.

Nomenclature

FAME	Fatty acid methyl esters
CP	Cloud point
PP	Pour point
CFPP	Cold filter plugging point
Deviation	$\|X_{exp} - X_{cal}\|$

2. Various Cold flow properties of Biodiesel

Biodiesel fuels derived from vegetable oils or animal fats, which are used as substitutes for conventional petroleum fuel in diesel engines, have recently received increased attention. This interest is based on a number of properties of biodiesel including its biodegradability and the fact that it is produced from a renewable resource. While the high density and viscosity of vegetable oils and animal fats tend to cause problems when used directly in diesel engines, if oils and fats are transesterified using short chain alcohols, the resulting methyl esters (biodiesel) have viscosities that are closer to petroleum based diesel fuel [1]. So the knowledge of their physical properties as a function of temperature and reliable predictive models is of great practical interest for process engineering, considering the demand of computational tools for process design, evaluation, simulation, optimization and control.

2.1. Cloud point

The cloud point 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 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.

2.2. 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 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.

2.3. 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 45ε m filter under 200 mm H_2O (0.019 atm) vacuum within 60 s [3]. CFPP is accepted nearly worldwide and listed among the limiting fuel parameters in the aforementioned European biodiesel fuel standard EN 14214.

3. Predicting cold flow properties of biodiesel

3.1. Cold flow properties

Some studies have focused on developing empirical equations to predict the low-temperature flow properties of biodiesels. Dunn et al. and Tang et al. had proposed relationship between CP and PP. However, these equations are applicable to the selected biodiesels and cannot be generalized [4].

Lopez et al. 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 [5].

Sarin et al. proposed a series of liner equations between CP, PP, and CFPP. Two set of equations 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}) [5]. Yung et al. proposed the prediction of CP, PP, and CFPP based on the chain length and degree of unsaturation [6].

Method of Sarin et al [5].

Correlation based on palmatic acid methyl ester (P_{FAME}) content,

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

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

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

Correlation based on the total content of unsaturated FAMEôs (U_{FAME}),

$CP = -\ 0.576\ (U_{FAME}) + 48.255) \qquad (0 < U_{FAME}$ Ò84)

$PP = -\ 0.626\ (U_{FAME}) + 45.594 \qquad (0 < U_{FAME}$ Ò84)

$CFPP = -\ 0.561\ (U_{FAME}) + 43.967 \qquad (0 < U_{FAME}$ Ò84)

Method of Yung et al [6].

Correlation based on the weighted average number of carbon atoms in FAME (N_c) and the total unsaturated FAME content (U_{FAME}, wt %) are,

$CP = 18.134\ (N_c)$ ï $0.790\ (U_{FAME})$

$PP = 18.880\ (N_c)$ ï $1.000\ (U_{FAME})$

$CFPP = 18.019\ (N_c)$ ï $0.804\ (U_{FAME})$

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 is

developed by Yung et al. where chain length and degree of unsaturation is used for the prediction of cold flow properties.

Table 1.Deviation of Cold flow properties predicted by Sarinôs P_{FAME}. correlations of various biodiesel fuels.

Biodiesel	Sarin et al. by P_{FAME}			Experimental values from literature [7]			Deviation		
	CP	PP	CFPP	CP	PP	CFPP	CP	PP	CFPP
Sunflower	-1.53	-8.48	-4.46	4	-6	-7	5.53	2.48	2.53
Rapeseed	-2.57	-9.61	-5.47	-3	-9	-14	0.42	0.61	8.52
Soybean	0.70	-6.05	-2.28	2	1	-4	1.29	7.05	1.71
Olive	1.42	-5.27	-1.59	-2	-3	-6	3.42	2.27	4.41
Palm	16.20	10.77	12.77	12	12	9	4.20	1.22	3.77
Beef tallow	7.15	0.95	3.98	17	15	9	9.84	14.05	5.019

Table 2. Deviation of Cold flow properties predicted by Sarinôs U_{FAME}. correlations of various biodiesel fuels.

Biodiesel	Sarin et al. by P_{FAME}			Experimental values from literature [7]			Deviation		
	CP	PP	CFPP	CP	PP	CFPP	CP	PP	CFPP
Sunflower	16.22	10.78	12.77	4	-6	-7	12.22	16.79	19.77
Rapeseed	-4.95	-12.23	-7.85	-3	-9	-14	1.95	3.23	6.14
Soybean	-2.79	-9.88	-5.75	2	1	-4	4.79	10.88	1.74
Olive	-2.20	-9.24	-5.17	-2	-3	-6	0.20	6.24	0.82
Palm	16.23	10.79	12.77	12	12	9	4.22	1.21	3.77
Beef tallow	19.86	14.73	16.31	17	15	9	2.85	0.26	7.31

Comparison of the methods suggested by Sarin et al. can be done by predicting various cold flow properties of different biodiesel fuels. In table 1, based on the data available in the literature [7] cold flow properties of various biodiesel fuels was predicted and deviation is calculated using the experimental values [8]. It can be seen that the results obtained for U_{FAME} for rapeseed, soybean, olive are not good enough as it has higher U_{FAME} content in the biodiesel fuels. Sarin et al. method can be used effectively and accurately.

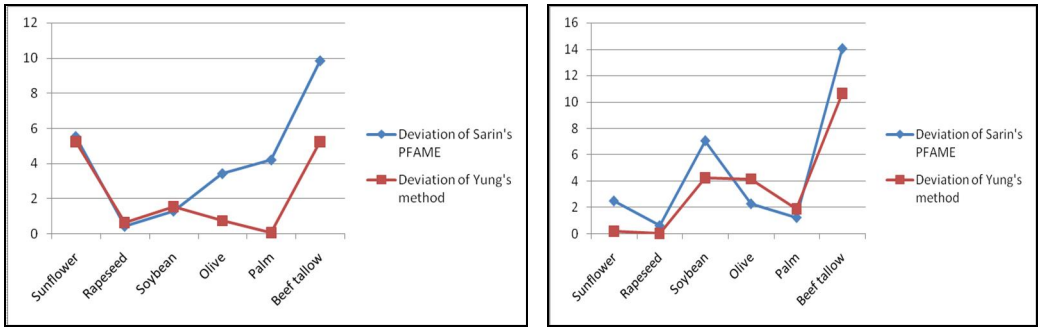

Fig. 1. (a)Deviation of Cloud point of Sarin P_{FAME} and Yungôs method; (b) Deviation of Pour point of Sarin P_{FAME} and Yungôs method.

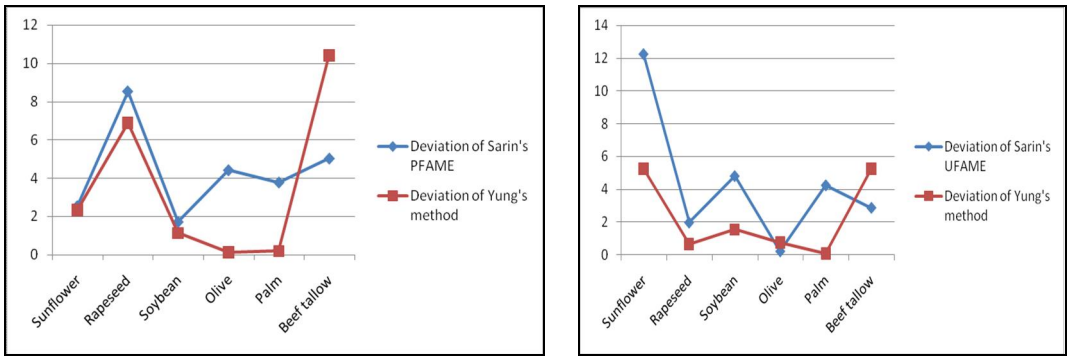

Fig. 2. (a) Deviation of CFPP of Sarin P_{FAME} and Yungôs method; (b) Deviation of Cloud point of Sarin U_{FAME} and Yungôs method.

Yungôs method is based on the contribution of chain length and degree of unsaturation and it describes biodiesel more precisely. Thus Yung et al. have proposed that for the prediction of the three cold flow properties of biodiesel the usage of chain length and degree of unsaturation was proposed [3].

Table 3. Deviation of Cold flow properties predicted by Yung et al. correlation of various biodiesel fuels.

Biodiesel	Yung et al.			Experimental values from literature [7]			Deviation		
	CP	PP	CFPP	CP	PP	CFPP	CP	PP	CFPP
Sunflower	-1.25	-5.79	-4.66	4	-6	-7	5.25	0.21	2.34
Rapeseed	-3.65	-8.96	-7.11	-3	-9	-14	0.65	0.04	6.89
Soybean	0.46	-3.25	-2.87	2	1	-4	1.54	4.25	1.13
Olive	-2.74	-7.16	-6.12	-2	-3	-6	0.74	4.16	0.12
Palm	12.06	13.92	9.19	12	12	9	0.06	1.92	0.19
Beef tallow	22.24	25.64	19.43	17	15	9	5.24	10.64	10.43

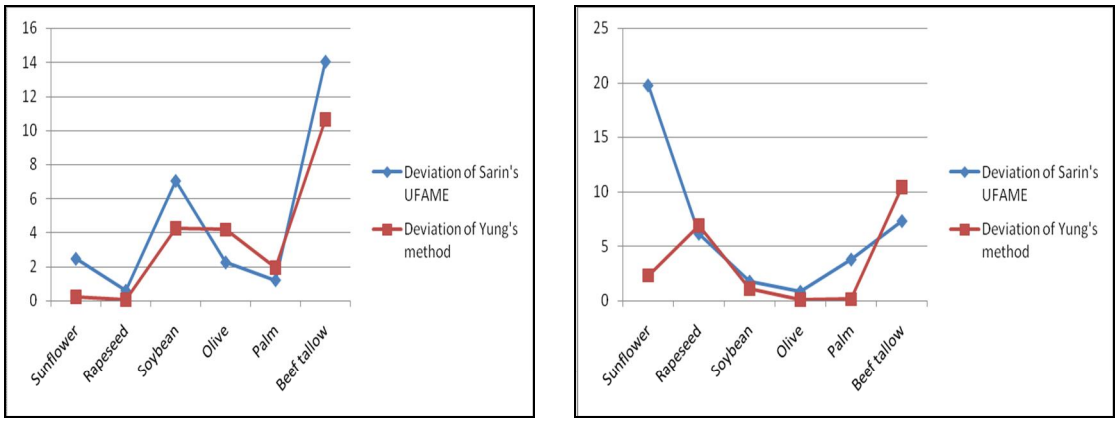

Fig. 3. (a) Deviation of Pour point of Sarin P_{FAME} and Yungôs method; (b) Deviation of CFPP of Sarin P_{FAME} and Yungôs method.

Comparison of Sarinôs method and Yungôs method is seen in the Fig 3., and Table.2, it can been observed the variation in the deviation obtained from the comparison of the predicted values and the experimental values shows less deviation for Yung et alôs method compared to the Sarin et alôs method. Yung et alôs method seems to be more accurate of the two methods and can be used for precise calculations.

Result and Conclusion

In this paper cold flow properties of various biodiesel fuels is studied by using the correlations available in the literature. The predicted values where compared with the experimental values available in the literature and their comparison was done using the deviation to determine the accuracy of the methods available in the literature. The methods that are used are highly accurate for predicting all three cold flow properties. Sarin et al. method gives good accuracy but it mainly depends upon P_{FAME} and U_{FAME}. However Yung et alôs method is more precise as it is not solely dependent on any particular type of methyl esters and is rather based on the chain length and the degree of unsaturation.

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