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Impact of Oil and Biodiesel on Engine operation in Cold Climatic condition

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Abstract

Due to excessive utilisation of fossil fuels and rise in price of crude oil, the concern for alternate sources of fuels is growing in a serious manner. Rising demand of petroleum-diesel for vehicles, power generation and agricultural sector, industrial sector, the biofuel is being viewed as an alternative to diesel. Biodiesel is an engine fuel that is produced by transesterification of fatty acids with alcohol. But major issue associated with biodiesel is its cold flow property and performance in colder climatic regions. This paper focuses on cold flow property of biodiesel and its effect on engine operation. Some of the cold flow properties (CFPs) like Cloud Point (CP), Pour Point (PP)& cold filter plugging point (CFPP) are responsible for solidification of fuel causing blockage in fuel lines filters which further leads to fuel starvation in engine operation during starting operation. This paper involves the studies in the area of CFP, problems and remedial measures using oil and biodiesel.

Keywords: Alcohol; Biodiesel; Cloud Point; Pour Point; Cold Filter Plugging Point

1. Introduction

Inclining demand of energy due to rise in population has led to over use of conventional fuel sources. To eradicate this problem, need of hour is to develop next generation resources of energy. Among several emerging alternatives to petroleum diesel, biodiesel is one of the promising options as its fuel properties are quite similar to diesel [1-6]. Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable sources. It is a potential next generation fuel because has lesser harmful impact on atmosphere due to minimal emissions in comparison to conventional diesel. In earlier times, biodiesel was being prepared from several edible oils but due to concerns of negative impact on food crops, focus has shifted tom develop biodiesel from non-edible oils, animal fats and waste materials [7-18]. The characteristics of biodiesel rely on several factors, like raw material used, technique used for production and free fatty acid (FFA) content. Key properties like viscosity, FFA, being substantially different in comparison to diesel, thus properties of biodiesel must be evaluated before its operation in engine. Fuel properties of biofuels, like viscosity, iodine value, saponification value, PP, CP, flash point, fire point and density, have major role in the combustion, transportation and storage processes. The fatty acid proportion has an important role on the physical characteristics of fats & oils, and eventually on biodiesel. Variations in physical properties of different biodiesel fuels are responsible for the problems in engine performance tests. High CP biodiesel in contrast to conventional diesel raises complications while its engine operation [19-25]. Biodiesel can affect the performance of engine at low temperatures in colder climatic conditions due to its fatty acid component. Fuel properties of biofuel such as viscosity, density, CP and PP tend to grow the % saturated fatty acid component of the lipid material increase in biodiesel. The biodiesel from Beef tallow has high Saturated Fatty Acids (SFAs) content, is not favoured for biodiesel production. The study shows that lowering down the SFAs content of biodiesel prepared from non-edibles by process including fractional crystallization is known as winterization. The FAME component of the filtrates obtained by crystallization were calculated. Further, CP, PPand CFPP, viscosity and density of winterized biodiesel winterized were checked. It was noted that percent saturated fatty acid of winterized biodiesel from beef tallow declined from to 73.38% from its initial value of 86.91% while unsaturated ones attained 19.95% from 12.00% till the lowest crystallization temperature reached 16.3 °C. It was found out that density, viscosity and low temperature properties of biodiesel substantially enhanced by the removing SFAs [26].

The 12 different set types of biodiesel fuels from various oil sources, CP, PP, and CFPP illustrate a uniform sequence. Every results shows that due to increase in temperature of Palm Oil Biodiesel & tallow biodiesel exhibited bad results, whereas rapeseed biodiesel provided best results at lowest temperature. As because of the wide alterations of environmental temperature, any international biodiesel standards have not met the low temperature properties that is the most important property for a biodiesel to be considered for practical usage. Inferior cold flow properties are due to existence of longer chain saturated fatty acids in feedstock. Saturated fatty acid having chain longer than C12 have significant impact CP & PP which tends to increase. Non-edible oils having complex saturated fatty acid contents like Palm oil & tallow which provide biodiesel the subordinate cold flow properties. In contrast, biodiesel from raw materials containing far most of unsaturated fatty acid represent having fuel properties [27].

The various investigations on Palm biodiesel show that it had better oxidation stability, but have inferior cold flow properties (CFPs), whereas soybean biofuel has better CFPs. Among the techniques used to solve complications linked to the biodiesel composition, are the mixing biodiesel with petroleum diesel in various percentages to get that is blending best mixture, CFPs of a fuel represent its behaviour in specific climatic conditions. Partial solidification of the fuel in colder temperature condition can result choking of fuel supply pipes and filters that will lead to improper ignition [28].

Mainly the process of biodiesel formation is from transesterification reaction of the non-edible oil with a short-chain alcohols in presence of catalyst. This process may result in some traces of saturated monoacylglycerols (MAGs) or free sterylglucosides (FStGs). These components might have higher melting points and lower solubility, leading to the formation of solid residues when stored under low temperature conditions. When mixed with petroleum diesel the problem worsens. Settling solid residues clogged the fuel filters resulting in improper flow of fuel. One disadvantage of biodiesel is also related with its properties & performance when exposed to lower temperature conditions. In colder climatic regions, higher-melting point (MP) of fuel cause nucleates to merge into bigger crystals. The temperatures at which crystals get perceptible & look like a cloudy suspension is known as the CP. Extended exposure of the fuel to temperatures at or lower than CP results in crystallisation and form interlocking nodes. PP of the fuel may be defined as the lowest temperature at which flow ability of fuel is significant. None of CP and PP could represent the performance of diesel in during cold weather. Due to this, low-temperature filterability tests were induced to predict limiting fuel temperatures in a better way where start-up or operability complications may be expected after enhanced exposure. The first test, CFPP, was accepted worldwide and maximum temperature ranges for this parameter were mentioned in European fuel standard EN 14214 [29].

The paper focuses on is to review the cold flow properties of various biodiesel prepared from various vegetable oils and studied the effect of ethanol, kerosene and other commercial additives on cold flow properties of this biodiesel. The study also reveals about the various methods used to improve the cold flow properties of biodiesel. The literature review divided into following section: Cold flow properties; Factor affecting CFP; method and measure to improve the CFP.

2. Cold flow properties

The main CFPs are CP, PP and CFPP. The literature review shows that due to change in dynamic viscosities of biofuel with declining temperature below the PP or CFPP, the reason being poor cold flow properties for biodiesel blends. For temperatures above PP and CFPP, Newtonian behaviour of fluid is observed, whereas for temperatures below PP and CFPP non-Newtonian behaviour is identified. At temperatures under PP and CFPP, there is formation of wax crystals which form clusters with declining temperatures [30]. Three types of fatty acids can be found in any oil or fat, these are: [30].

1. Saturated fatty acids
2. Mono-unsaturated fatty acids
3. Poly-unsaturated fatty acid

Saturated fatty acids, crystallise at higher temperature and have higher melting point reason being higher degree of saturation. In comparison to other fatty acids, they form crystals easier in cold temperature. Vegetable oils having more saturation will result in biodiesel which has poor cold flow properties. Fatty acids that include long carbon chains also affect cold flow properties. These fatty acids also crystallise at higher temperature and exhibit poor properties. For instance biodiesel from peanut oil has inferior characteristics which is mainly due to higher carbon atoms namely acid lingoceric and behenic acids. Branched chain fatty acids need a thermodynamic force to form crystals therefore lowering down the temperature required to crystallise. This leads to good effect on cold flow properties of biodiesel. Moreover use of higher linear and branched chain alcohols result in improvement of properties.

The linear correlation have been developed between CFPs of raw materials and CFPs of products. CFPP of the biodiesel obtained from vegetable feedstock is equivalent to the sum of the product of portion of particular vegetable in the mixture and CFPP products from the feedstock [31].

Correlations for Used Vegetable Oil (UVO):

$$CP = 0.0534\%\text{ of UVO} - 2.5369 \quad R^2 = 0.9674 \quad (1)$$
$$CFPP = 0.1405\%\text{ of UVO} - 14.916 \quad R^2 = 0.9789 \quad (2)$$
$$PP = 0.1176\%\text{ of UVO} - 20.115 \quad R^2 = 0.794 \quad (3)$$

The relation between PP of feedstock & biodiesel:

$$PP\text{ (of biodiesel)} = 0.8958 * PP\text{ (oil)} + 4.0541 \quad R^2 = 0.9991 \quad (4)$$

The relation among PP of feedstock used and CFPP of biodiesel:

$$CFPP\text{ (of Biodiesel)} = 1.0753 * PP\text{ (oil)} + 15.405 \quad R^2 = 0{:}9949 \quad (5)$$

Higher R^2 values show that the relation has high accuracy. The CFPP is mostly observed cold property because it mainly has effects on adoption of fuel in lower range of temperatures. Values for the CFPP of biofuel from every feedstock can be supposed on basis of past experiments or may be calculated with help of developed correlations and knowledge to relate CFPs of feedstock used with biodiesel prepared [32].

Biodiesel from Jatrophacurcas oil have high percent unsaturated fatty acids, mainly oleic and linoleic acids, containing one and two double bonds, respectively. Oleic acid have carbon–carbon double bond present in it which results in strong intermolecular relation among the p electrons of double bonds, which favours the packing of molecules of this type of ester. In contrast to it, the existence of two double bonds in linoleic forms a cis–cis conformation, which reduces the intermolecular attraction & blocks the packing of the molecules. In addition to it, heavy functional groups (esters) also confine the lamellar spacing among individual molecules. This consequences a rotational disorder which forms crystalline nuclei and eventually a less stable packing of the chains is formed, which in turn improves the cold flow properties of Jatropha biodiesel [33].

Structure of the alkyl esters also play an important role on cold flow properties of biodiesel. The melting point rises with chain length and drops on increasing the number of double bonds. Saturated fatty acids with 10 or higher number of carbons are in solid form at room temperature and their melting point rises with chain length, on the other hand, unsaturated fatty acids are liquid. In saturated acids, odd-chain acids have low melting points than even-chain acids. The cis configurations or the presence of —OH groups in the chain substantially trims down the melting point. Biodiesel prepared from oils having high unsaturated fatty acids sunflower oil (73.73% linoleic acid, methyl ester melting point of −35 °C) will be having low CP (1 °C). A biodiesel prepared with non-edible oil of large proportions of fatty acids with high melting points, like palm oil (43.9% palmitic acid, methyl ester melting point of 30.5 °C), will be having a higher CP (16 °C) [34].

The figure 1 shows that CFP of various biodiesel obtained from fats with high concentration of saturated fatty compounds will exhibit higher CPs and PPs

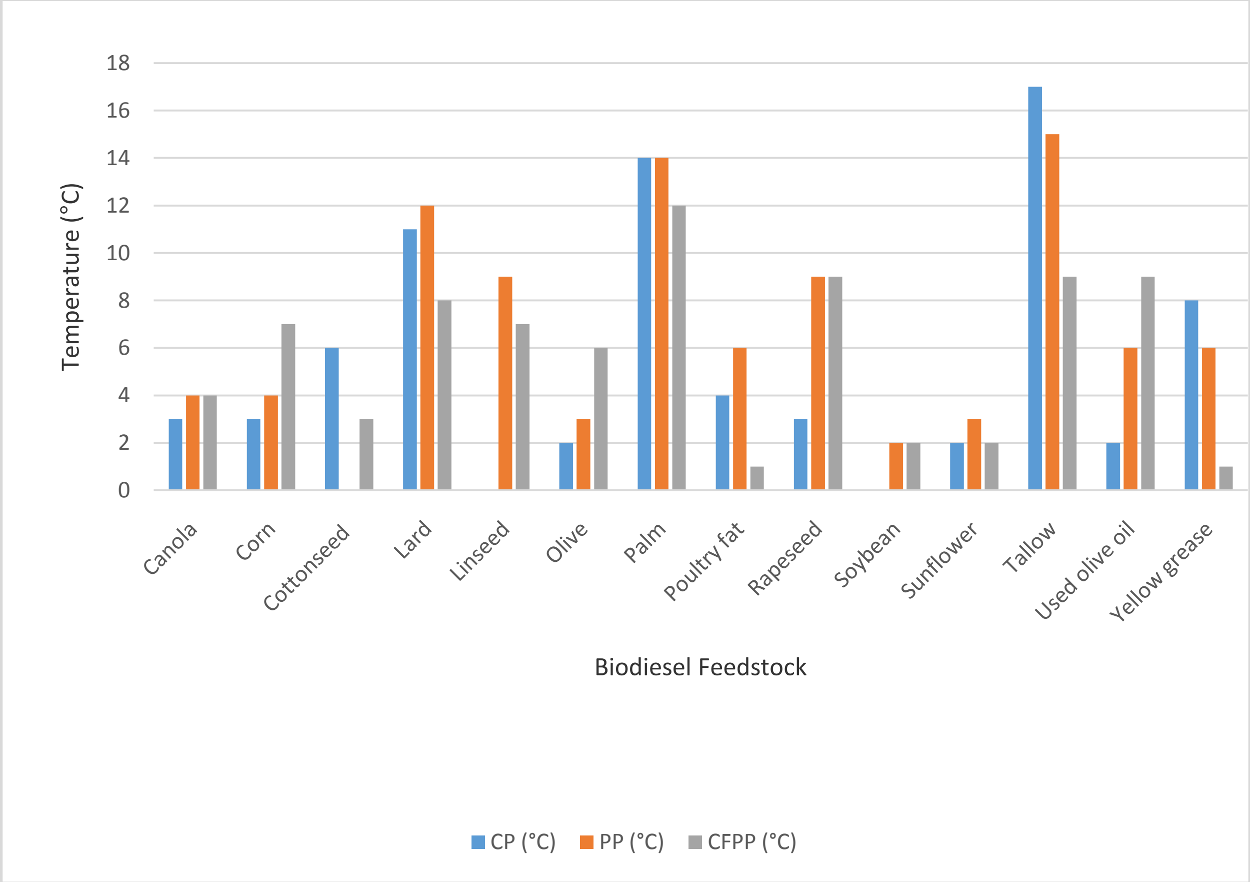

Figure 1: CFPs of biodiesel (FAME) made from various feedstocks [4]

The figure 1 shows that oils like Lard, Palm, Rapeseed and Tallow have high CP, PP and CFPP which have in poor CFP so these are not recommended as fuel for cold climatic conditions. On the other hand oils like Canola, Soybean and Sunflower have better CFPs as compared to other oils so these can be recommended for cold flow operations.

Table 1 shows that fatty acid proportions of different blending ratios among Palm, Rapeseed and Soybean oils.

CFPs of diesel are obtained by the monitoring these three temperatures; CP at which crystal formation starts, CFPP at which fuel initiates to clog a fuel filter, and PP at which fuel is not able to pour in or move. In any case, if cold flow properties could be predicted, complications could be avoided and the vegetable oils can be appropriately chosen to prepare a biodiesel that can meet standard requirements. Since CP is the trigger for negative effect on fuel injection, its prediction is extremely meaningful [34]. The saturated vegetable oils, like coconut oil, are more stable but these get frozen without any trouble.

Table 1: Fatty acid composition of the blended biodiesel [32]

Blending Ratio (PB:RB:SB)	Palmitic Acid	Oleic acid	Linoleic acid	Linolenic acid
100:00:00	40.1	43	11	0.2
80:20:00	33	46.9	12.8	2.1
80:00:20	34.3	39	19.5	1.5
60:40:00	25.8	50.8	14.5	3.9
60:20:20	27.1	42.9	21.2	3.4
60:00:40	28.4	35.1	27.9	2.8
40:60:0	18.7	54.6	16.3	5.8
40:40:20	20	46.8	23	5.2
40:20:40	21.3	38.9	29.7	4.7
40:0:60	22.6	31.1	36.4	4.1
20:80:0	11.6	58.5	18	7.6
20:60:20	12.9	50.7	24.7	7.1
20:40:40	14.2	42.8	31.4	6.5
20:20:60	15.5	35	38.1	6
20:0:80	16.8	27.1	44.8	5.5
0:10:0	4.4	62.4	19.7	9.5
0:80:20	5.7	54.5	26.4	8.9
0:60:40	7	46.7	33.1	8.4
0:40:60	8.3	38.8	39.9	7.8
0:20:80	9.6	31	46.6	7.3
0:0:100	11	23.1	53.3	6.8

Better cold flow properties have been observed in oils having more polyunsaturated oils like rapeseed but inferior stability. Cold flow is only one of the several performance parameters of biodiesel which demands introduction of additives to improve the fuel quality. Unless cold flow improvers are added, fuel filter may get clogged. To enhance the cold flow properties, kerosene or diesel may also be blended. Even then, there is inclining cost on using additives to improve properties and using kerosene drops down the engine power. It is necessary to match the composition and properties of additives with petroleum diesel for better results. For instance, an additive that yields good results with rapeseed biodiesel may not work well with soybean biodiesel or cotton seed biodiesel due to difference in composition. As for the thumb rule the treat rates for additives used with biodiesel are greater in comparison to the treat rates used with petroleum biodiesel [35].

Ethylene vinyl acetate copolymer (EVAC) is a Cold Flow Improver (CFI) adopted for conventional diesel. EVAC is generally bio-based as it is obtained from ethylene and vinyl acetate. Ethylene can be prepared through ethanol dehydration, and ethanol is derived from sugar fermentation. Vinyl acetate is obtained from ethylene and acetic acid, which can be derived from biomass fermentation [36]. Ethylene vinyl acetate copolymer (EVAC) was used to improve CFPs of waste cooking biodiesel and

its blends with diesel, the effect of was studied. The CP, CFPP and PP of B20 blend declined by 8 °C, 11 °C and 10 °C, respectively, with addition 0.04 wt.% EVAC. The effect of EVAC on other fuel properties of B_{20} were also determined. The B20 samples treated with EVAC satisfied ASTM D6751. Differential scanning calorimetry was adopted to study the crystallization behaviour of the blends. The crystallization rate and crystal content of B20 went down. EVAC thus has substantial effect on biodiesel to improve its CFPs. The effect of several proportions of rapeseed and used frying oil on the most important physio-chemical properties of biodiesel, viscosity and CFPs were studied. It shows that percentage of used frying oil (UFO) in raw material mixtures does not have any substantial effect on viscosity of biodiesel, but on only cold flow properties. Relations among CFPs of biodiesel from mixtures of raw materials & CFPs of the biodiesel from pure raw materials were developed [37]
$CP = 0.0527\%UFO - 2.345 \quad R^2=0.9319 \quad (6)$
$CFPP = 0.184\%UFO - 15.273 \quad R^2=0.9948 \quad (7)$
$PP = 0.1458\%UFO - 18.936 \quad R^2=0.8551 \quad (8)$

3. Factors affecting cold flow behaviour

The biggest problem faced with biodiesel is the inferior flow with lower temperature. Various researchers have observed that as the temperature drops down, biodiesel gets crystallised or thickens. As a consequence of that, there is improper engine operation due to choking in fuel pipes. This might be due to presence of more saturated FAME components. Suitability of diesel or biodiesel in lower temperature operation depends mainly on (PP) & CFPP [30].

Degree of unsaturation has a substantial impact on CFPs, with higher percentage of unsaturation resulting into significantly enhanced colder regions performance of fuel. Therefore, the impact of unsaturation masks the effect of chain length in these FAME materials. Molecular structure of PP ataractics for petroleum diesel is contains polymeric hydrocarbons with polar groups. Unsaturation content mainly caused inferior PP & CP. CFPs are majorly deteriorated by the strong intermolecular forces of attraction, which becomes even stronger if chain length is increased [38]. Saturated mono-acylglycerols (MAG) are lesser soluble and suffer from gel formation while stored in colder regions [39]. CP is the temperature at which a sample of the fuel starts to appear cloudy whereas PP is the temperature below which the fuel will not flow.

Higher CP & PP of alkyl esters are related to higher proportion of the saturated fatty acid alkyl esters as the unsaturated components generally have lower melting points. Correlation between the proportions of unsaturated fatty acid with cold flow properties is as follows:
$CP = -0{:}576 * A + 48.255 \quad (9)$
$PP = -0{:}626 * A + 45.594 \quad (10)$
where A is % unsaturated fatty acid. PPs of Jatropha and Pongamia methyl ester were found to vary between -6 to 21°C and -3 to -1 °C [40].

CFPP rises with amount & carbon chain length of Saturated Fatty Acid Methyl Ester (SFAME). CFPP for blends of biodiesel & diesel generally depends upon chemical compositions and ratio of biodiesel. The biodiesel ratio for the lowest CFPP rang increases with decreasing SFAME. Such as SFAME contents in biodiesel from Palm, Cottonseed, Soybean and Rapeseed are 35.86, 32.12, 18.29 and 14.69 w% respectively. The temperature at which biodiesel starts crystallising is normally greater in comparison to diesel. Therefore, crystallisation at higher temperature can result in clogging of fuel pipes thus complicating the pumping ability of fuel and affects engine operation in winters [41]. Smith et al. [42] observed that use of higher alcohols improved the CFPs of biodiesel as for beef tallow biodiesel, CP and PP for biodiesel prepared with n-butanol was better alcohols having lower carbon atoms.It is observed that for most of samples, biodiesel prepared with higher alcohols better cold flow properties are obtained. With short, unsaturated and branched carbon chains tend to have possess better cold flow but substandard ignition quality and oxidation stability. The aim is to prepare better biodiesel with supreme characteristics. Although this is tough to achieve and creates major complications in ongoing research.

On studying CFPs and oxidation stability (OS) Ural biodiesel, it has been identified that the blends of biodiesel, prepared from rape seed oil and soybean oil in 70:30 proportion or in 50:50 ratio, with conventional diesel lowers down the CFPP. The lowering of CFPP of fuel relies on physiochemical properties. The Honeywell software RPMS model was proficient of predicting CP of several fuels having blends of biodiesel and diesel in different. The highest class 4 of arctic diesel according to EN 590 can be produced by blending petroleum diesel with the 100% rape seed FAME treated with cold flow improver in concentration up to 10%. The introduction of the synthetic anti-oxidant ionol (BHT) to conventional diesel is capable in hampering secondary reactions of peroxides decomposition to acids to a substantial extent than the oxidative polymerization [43]. Mainly there are two steps which include the process of formation of crystals. Initially there is nucleation which is followed by crystal growth. Molecules of liquid, merge to become solid embryos viz. crystal lattice. In a similar way, exiting lattices get convert to bigger ones lattices on nucleation. This process goes on till a network forms.

Homogenous mixture containing different constituents of unlike melting point, have crystallisation affected by solubility of constituents. Those having lower melting point proceed as solvent whereas solutes tend to have higher melting point. For crystallisation to occur, solute must be in super-saturated state that is a condition where solvent has more dissolved than its ability. There, super-saturation is controlled by:

1. The temperature of the solution
2. The accumulation of the solute in the solution

4. Parameter for CFP

The main factors to evaluate the CFPs are CP, PP, CFPP& LTFT. Formation of small solid like structure of certain size at some temperature make operation of engine difficult reason being blockage of fuel lines when CFPP is achieved. CFPP depends upon climate and some seasonal standards are given by EN 14214. Some correlations do support CFPP research for oils having long chain saturated acids. Biodiesel containing higher properties of saturation exhibit inferior CFPP. Contaminants also degrade the low temperature properties even in small proportion. These may arise during conversion of oils or fats into biodiesel. These may be water, monoglycerides, FFA, alcohol, sodium or potassium salts of fatty acids (soaps), antioxidants, sterols and other unsaponifiable matter. Some of the minor components have higher melting points whereas some solid residues arise in low temperature regions. In addition to it, crystallisation also occurs due to low solubility [44].

Saturated fatty acids play key role in CP of biodiesel. Formation of gel structures initiates by close packing of molecules. Therefore conditions that harm tight packing of molecules will lower down CP.

Ethanol usage for biodiesel production yielded good cold flow properties because of difference of 5 to 10 °C in melting points of ethyl and methyl esters. Higher bonds mainly double bonds also disturb packing of molecules [27]. To identify the basic characteristics of cold flow nature of fuel, CP & PP have been used as a reference for longer time. These are helpful in determining the class of fuel, usage conditions in regions of lower temperature. Some standards are given by ASTM like D-97, D-4539 and D-2500 to identify cold flow properties. Increasing size of crystals up to the range of 50 to 250 mm in diameter and thus blocking the filterability is called low temperature filterability (LTFT). Kerosene is used in past to improve the CFPs but it has negative impact on calorific value and lubrication properties. Blending diesel with soybean biodiesel is also reported to have god CFPs [45].Table 2 shows the melting point of various fatty acid alkyl esters.

The Table 2 shows that MP variation lies between -35 to 79 ˚C. Lowering the temperature of a heterogeneous mixture from liquid condition to cloud like appearance, constituents having highest freezing point from crystals and start nucleating which are visible with naked eye. On further decreasing the temperature, crystals grow bigger and bigger. Saturated acids start forming crystals initially. Higher proportions of saturated acids results in inferior CP. Appearance of turbidity also confirms the CP of fuel. Fuel becomes thicker due to turbidity and movement starts slowing down. Increased viscosity due to these causes issues in engine operation.

Table 2: Melting point of fatty acid alkyl esters and impurities [46]

Chemical Name	**Melting Point (°C)**
$C_{17}H_{34}O_2$	30.5
$C_{19}H_{38}O_2$	39.10
$C_{19}H_{36}O_2$	-20
$C_{19}H_{34}O_2$	-35
$C_{21}H_{42}O_2$	54.5
$C_3H_8O_3$	18
$C_{19}H_{38}O_4$	74
$C_{21}H_{42}O_4$	79
$C_{21}H_{40}O_4$	32

The CP can be calculated by:

$$CP = 1.44 * Y - 24.8 \qquad (11)$$

where Y is the amount of % saturated fatty acid present in the oil.

It is least temperature at which fuel has semi-solid state and forms gel. CP is always higher than PP.

$$CFPP = 0.8537 * CP - 4.72 \qquad (12)$$

After CFPP is achieved fuel is unable to flow in fuel filters and cold regions are more vulnerable to it [21].

Formation of cloudy and wax like structures result in improper engine operation as solidified substance blocks the fuel pipes. Inferior PP may cause flow inability. To improve the CP, saturation content needs to be lowered down and imparting more saturation will give good cold flow properties [47].

Engines being operated in colder regions come across complications of blockage in fuel filters or fuel injector. These can be eliminated by improving low temperature properties with use of certain additives. Biodiesel is suitable up to 5 °C but additives may be helpful to lower down the usability at about -3 to -4 °C, whereas certain winter blends my lower operating temperature by 15 °C further [48]. Table 3 shows the fuel properties of biodiesel from different vegetable oils sources.

Table 3: Biodiesel properties of different vegetable oil sources [49]

Biodiesel	**Flash Point (^{0}C)**	**Specific Gravity**	**High Heating Value (MJ/Kg)**	**CP (^{0}C)**	**PP (^{0}C)**
Soybean	131	0.885	40.4	-0.5	-3.8
Rapeseed Ethyl Ester	185	0.876	40.5	-2.0	-15.0
Tallow Methyl Ester	117	0.876	40.2	13.9	9
Canola Methyl Ester	163	0.88	39.9	1	-9

It has been observed from the above table that for rapeseed oil, ethyl ester has better cold flow properties than its methyl ester. As the proportion of biodiesel increase in blends, CP and PP drop down [49]. Research has provided suitable results showing the longer length of carbon chain has substantial effect of cold flow properties e.g. C16-C24 saturation leads to poor CFPP [50].

5. Methods to improve CFP

Literature review shows that there are various methods to enhance the CFPs of biodiesel which are shown in Figure 2. Blending biodiesel with petroleum diesel is the most widely employed method for the application of biodiesel, and the European committee for standardization has a limit of a maximum of 5% (by volume) of biodiesel blended in petroleum diesel and when blended with petroleum diesel in small quantities, the cold flow of the biodiesel is improved significantly. At low blend levels, petroleum diesel fuel, being miscible with biodiesels, dominates the effect of the high melting point of saturated esters.

Transesterification of fatty acids with branched chain alcohols, as opposed to the commonly used methanol, was proposed to improve the cold flow of biodiesel. These branched chain alcohols increase the branching in the fatty ester structure and thereby reduce the temperature of crystallization and its CP the biodiesel. Biodiesel is cooled to a temperature between its CP & PP & any crystals formed are fractionated; it is repeated till formation of is stopped completely when the sample is held at that temperature for more than three hours. The crystals formed are usually crystals of the high melting point saturated fatty esters and the resultant biodiesel has a lower percentage composition of saturated fatty acids [51].

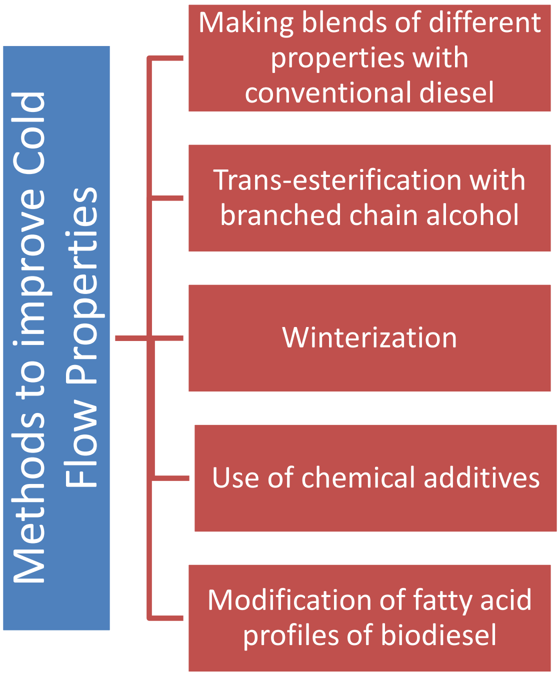

Figure 2: Methods to improve Cold Flow Properties

Fractionation of the crystals formed during winterization with a solvent has been employed in a bid to increase the yield from the winterization process.

The use of CFIs is the conventional technique adopted to enhance the CFPs of fuels. This method seems to be the most economically and technically favoured means of enhancing the CFPs biodiesel. Cold flow improvers improve cold flow either by reducing the PP of the diesel fuel or by reducing its CFPP. Conventional additives used for petroleum diesel fuel are mainly polymeric materials like polyacrylate, polymethacrylate of poly ethylene-co-vinyl acetate (EVA). These additives have chemical structures consisting of a hydrocarbon chain that is able to co-crystallize with the hydrocarbon chain of the fuel and thereby affecting the growth and nucleation of the wax crystals.

To get better CFPs, certain methods have been reported, like use of depressants to lower down the freezing point e.g. methyl stearate and methyl palmitate. Toluene also yielded good results. Homo-polymer have given best effects among several polymers to decrease freezing point. Even use of 1% by weight, PP drops by 30 °C and LTFT by 28 °C [52].

One more crucial point of these depressants is their transportation in colder regions. B80 to B100 biodiesel was blended with kerosene and some depressants to get best results in colder regions. Using 0.2% of additive in blend of 79.2% biodiesel and 20% kerosene resulted in dropping PP by 27 °C.

Variation in CP of blends of low sulphur diesel and soybean biodiesel with varying additive percentage (0 to 2%) is shown in figure 3. Biodiesel has inferior CP due to presence of unsaturation. On 2% additive in B100 blend CP dropped to 12 °C from 18 °C.

Variation of PP is explained in figure 4 for different blends of biodiesel and low sulphur diesel with use of additive.

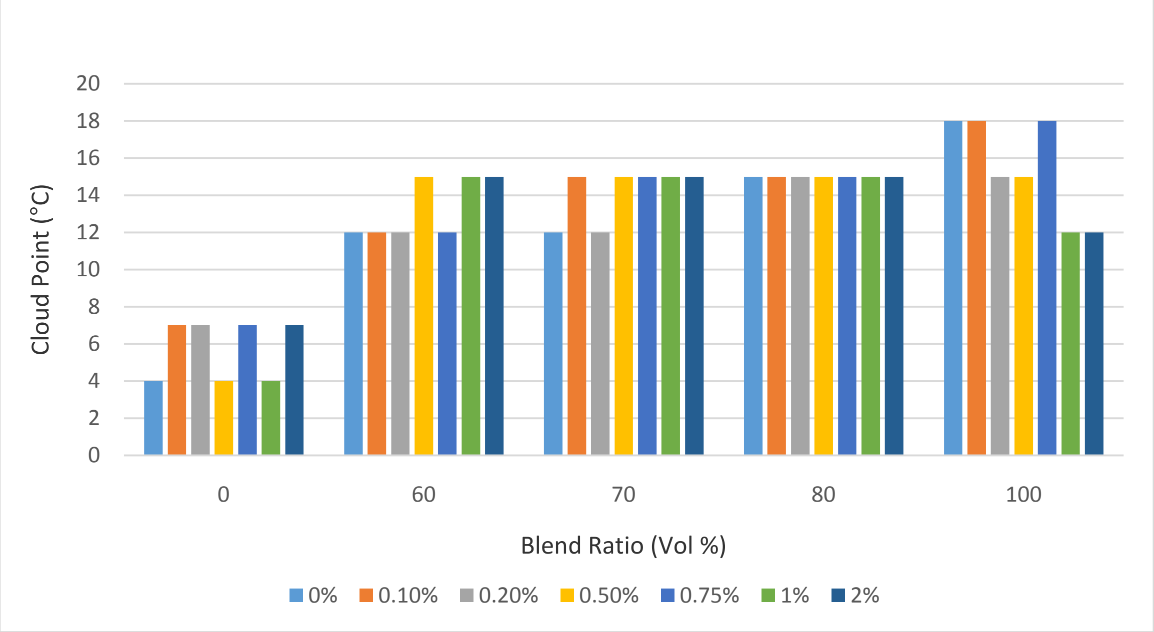

Figure 3: CP of low sulphur diesel blended with soybean biodiesel [45]

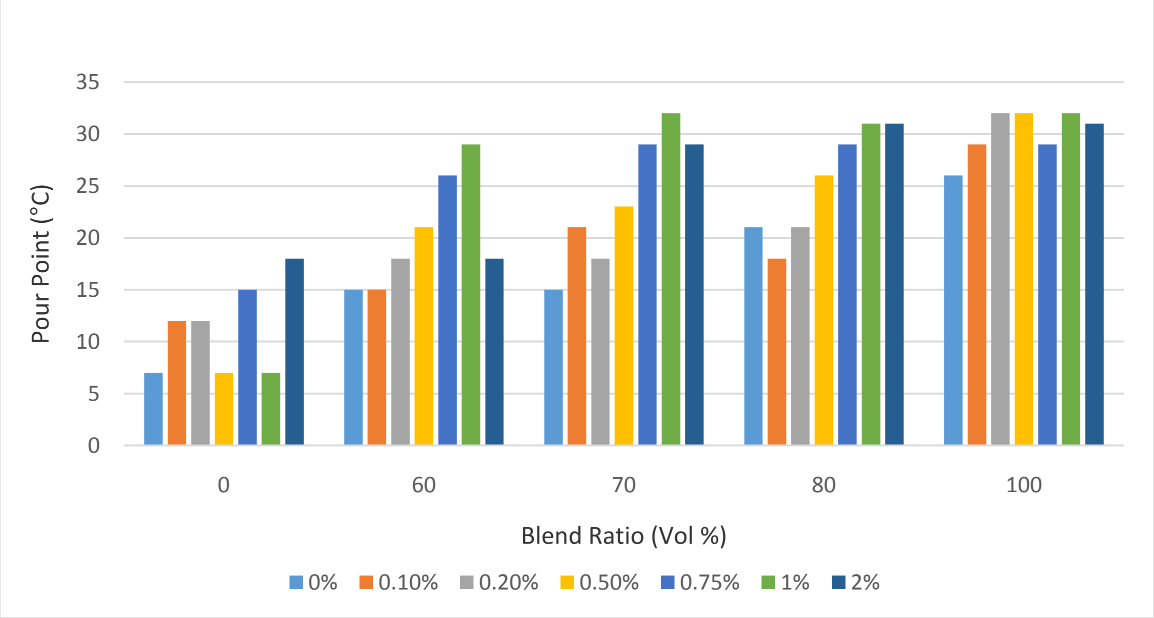

Figure 4: PP of low sulphur diesel blended with soybean biodiesel [45]

It is observed from figure 4 that using 0.10% of additive in most of blends was found to be useful. Mainly, additives disturb the crystal structure and size. These also prevent the growth of wax thus lower down PP. CP was lowered only when 5% additive was used. It was not feasible to lower down freezing point of fuel by just 1% of additive. Additives that contains longer carbon chain prevent crystallisation even when diesel is stored at lower temperature. Mainly additives effect surface crystals but do not inhibit the growth But these techniques are difficult to use on biodiesel because of more uniform chemical structure as compared to diesel. On the other hand, conventional diesel has bigger bridge between CP and PP to cover so is more diverse nature [45].

Efforts have been made to change FFA composition of vegetable oil or biodiesel by winterisation to lower down the proportion of saturated fatty acids. Excessive reduction of saturated acid will harm ignition ability whereas growth of unsaturation will lead to unstable fuel. Specifically, branched chain additives like alkyl esters have been used to lower down CP. Moreover shifting double bonds of esters and adding side chain will improve cold flow properties and also enhance oxidation stability.

Number of double bonds play important role in cold flow characteristics. CP of normal biodiesel lies around 0°C whereas fuels having 50% composition in saturation terms will have CP in range of 8 to 17 °C.

Reason behind using PP depressant was to enhance flow ability. These depressants prevent crystal formation. Winterisation was used to differentiate these oils with different solidification temperature. Refrigerating the oils for certain time at definite temperature and then draining out the liquid part is helpful. This can be done more precisely by placing oil tanks in atmosphere of colder regions to save energy. Once solid part is removed remaining oil will have superior PP. Dunn et al. conducted phased winterisation approach on soybean biodiesel till oil remained at -10 °C for 3 hours without cloud formation. Conventionally 5-6 iterations were used in a week. PP for soybean biodiesel had cut off value of -16 °C. It was also concluded that small proportions of saturated esters in soybean biodiesel had significant impact on low temperature properties [42].

Use of additives or depressants is encouraged to get superior CFPP because diesel engine experiences problems while starting on use of pure biodiesel. Various results suggest that below 0 °C, behaviour of engine is not acceptable due to greater viscosity of fuels which complicates the fuel injection and causes improper combustion. Therefore using blends like B10 or B20 are encouraged so that there is less harm on viscosity. There is pressure difference on both sides of fuel filter which depends upon viscosity rather than CFPP. Thus using blends of biodiesel are recommended rather than B100 so that there is minimal pressure loss and acceptable viscosity [53].

It was observed that reaction time did not have much effect on low temperature properties whereas molar ratio between 3.15:1 and 4.15:1 improved the properties. Keeping 20 °C and catalyst concentration 0.75% were useful [53].

Ethyl acetoacetate was experimented as an additive for better cold flow properties of waste cooking biodiesel. It is seen that waste cooking oil has higher proportion of saturated acids and viscosity therefore biodiesel has poor cold flow properties. Ethyl acetoacetate was used in range of 0-20% by volume. For 20% additive, PP & CP declined by 4 °C. 5% blend was having properties in acceptable range according to ASTM D6751. Oxidative stability also improved. Effect on PP was visible as soon as additive was added and finally got reduced by 4 °C on 20% addition. There was some significant impact on CP also. This might be due to reason that freezing point of Ethyl acetoacetate is -45 °C. Due to this, it tends to be in liquid state [54].

Four different additives polymethyl acrylate (PMA), ethylene vinyl acetate copolymer (EVAC), poly-a-olefin (PAO), and polymaleic anhydride (HPMA) were used to improve low temperature properties of waste cooking biodiesel. Out of all, PMA gave best results in terms of cold flow properties and viscosity. Even use of 0.04% PMA, PP and CFPP got decreased by 8 and 6 °C. It lowered down crystal formation rapidly. Stopping the growth of crystals yielded good properties [55].

Comparison was done among glycerol ketals, glycerol acetates and branched alcohol-derived fatty esters as cold flow enhancers for Palm biodiesel. These improvers were added in range of 1-10%. Size of crystals was measured. 2-butyl esters on 5% addition, decreased PP & CP by 5 °C. There is negligible impact on fuel properties of Palm biodiesel [56].

The CFPP reducing additives, which are otherwise called "CFPP depressants", act during nucleation by altering the structure of the crystals formed from an orthorhombic shape to a needle-like shape so that fuel filters are not blocked, and then, they inhibit the growth of the crystals formed to make sure that they remain in a fine suspension rather than gelling up. The "PP depressants", however, do not alter the shape of the crystals formed; instead, they collect on the surface of the crystals formed to hinder their growth and prevent gel network formation. Polyunsaturated fatty acids are healthier and more desirable for food purposes, and hence, the oil should contain both the monounsaturated and poly unsaturated fatty acids.

Meanwhile, conventional cold flow improvers (CFI) for petroleum diesel are co-polymeric substances that have a paraffin backbone similar to the paraffin components of the diesel fuel with polar moieties attached to the backbone to give comb-like structures; the paraffin backbone provides for an interaction between the diesel and the additive, while the polar moieties actively alter the shape of crystals that are formed during the nucleation process. The idea behind these CFIs can be a basis of the design of a similar compound which would work well with biodiesel. In addition, renewable chemical substances that can be blended with biodiesel to act as freezing point depressants for the esters in biodiesel may also be sought [51]. It has been found in literature that using bio-butanol to produce biodiesel is helpful in improving cold flow properties [57].

The higher surface tension and viscosity of biodiesel results in substantial effect on injection of fuel resulting in improper combustion. For having better CFPs and more viability additives can be used to improve properties. Such research has been reported in literature to find out suitable additives [58].

Reactions having polymerisation nature strongly effect physiochemical properties. Results showed that the cis–trans isomerization reactions had least impact on viscosity and CFPs of biodiesel, but polymerization and pyrolysis reactions had significant effect on both properties. Polymerization reactions resulted in increases in both viscosity and the crystallization onset temperature, while pyrolysis reactions showed the opposite effect [57].

Fractionation of crystals is also used to improve CP and PP which has similar characteristics to winterisation. Dry fractionation includes crystal formation without any additional solvent. This is easier and cheaper technique. Lee et al. used bench-scale dry fractionation to methyl soyate in a ten phased method in 84 hours to get biodiesel having 5.5 wt% saturated content and crystallisation temperature 10.8 K lower than the equivalent non-fractionated product. Final product obtained had yield of 25.5% lower than of initial material. It is observed that there is decline in separated composition equally covered by rise in unsaturated proportion. This leaves substantial impact on physiochemical characteristics of biodiesel, more importantly oxidation stability. It also effects cost thus price related to biodiesel is higher. Fractionation also includes some extra technique like introduction of solvent, formation of crystals and recovering the solvents. Moreover, yield gets reduced. Generally, it is about 75% loss of yield which is strictly intolerable [68].

6. Literature Review

Application of various additives to enhance low temperature properties of biodiesel has been reported in literature. It has been noticed that if two or more feedstocks are used to make blends, the additive used must be compatible with all feedstock, which is difficult task to achieve. Mainly additives available work out with single feedstock. There has been continuous research going on to enlarge the compatibility. Main emphasis should be to lower down CP instead of PP. It has been perceived that LTFT and CFPP depend directly on CP. But mainly, available improvers act on PP only. Improvers like secondary alkyl esters, poly-alkyl methacrylate. Cold Flow Improvers (CFIs) nucleate and co-crystallise saturated fatty acids and lower down size to acceptable range. Smaller sized crystals then can pass through fuel filter thus blockage is prevented [44].

CFPP of biodiesel rises as saturated proportion rises up and drops down with increases of unsaturated content. Methyl palmitate has major impact on CFPP [28].

Surfactants and detergents have also been used to enhance the low temperature properties of waste cooking biodiesel. Sugar esters (S270 and S1570), silicone oil (TSA 750S), polyglycerol ester (LOP-120DP) and diesel conditioner (DDA) were introduced to diminish CFPP. Polyglycerol ester had major effect reducing CFPP to -16 °C from -10 °C with marginal addition of 0.02%. Using detergent fractionation, yield obtained was 73.1% & CFPP dropped to -17 °C [60].

Biodiesel standards give filtration time 360 seconds & good reproducibility to be helpful for the calibration of a downscaled method. Biodiesel sample of varying purity were examined and filtration time thus ranged between 62 to 104 seconds [61].

Ethanol is also used as a CFI for biodiesel. Piezoelectric quartz crystal is used to cool down biodiesel. PP of biodiesel fuel is calculated by minimum frequency of piezoelectric quartz. Results were compared with ASTM technique. PP ranged between -2.3 °C from B100 to -15 °C for diesel [62].

FFA composition was monitored to improve low temperature properties. CFPP dropped as unsaturated acids proportion grew. The correlation was obtained as

$$Y = -0.4880 * X + 36.0548 \ (0 < X < 88) \qquad (13)$$

$$Y = -2.7043 * X + 232.0036 \ (88 < X < 100) \qquad (14)$$

where X is the content of the unsaturated fatty acid (wt%) and Y is the CFPP (°C).

Palm biodiesel acted oxidation stability improver to soybean biodiesel. Having blends of palm, soybean and rapeseed biodiesel showed several results for CFPP and oxidation stability. CFPP for rapeseed biodiesel was minimum. Therefore blends of both rapeseed and soybean improved the CFPP of Palm biodiesel which originally had poor low temperature properties [63].

Most critical demerit of using biodiesel is its poor performance in colder areas. The production of fatty acid derivatives by esterification of FFAs with various alcohols is done. Crystallisation patterns have been studied. PP dropped down & viscosity increased by fair amount. Altering main carbon chain can also change structure of fatty esters [64].

Productive way to lower the PP is ozonising the raw feedstocks. In this process, CP did not change. For palm biodiesel, CP declined drastically but no effect of PP. Other properties like viscosity and density remained unaffected but Flash Point faced increment. Winterisation has been adopted but that lowers down the yield to 25-26% [65].

CP & PP for biodiesel can be directly linked with its CFPP which gives it viability in colder regions. Additives are there which can reduce the PP. It was seen that ethyl esters gave better response to additives than methyl esters as CP and PP for ethyl esters dropped by 3 °C and 19.4 °C whereas as same for methyl esters was 0.3 °C and 7.2 °C respectively. Mustard biodiesel showed good results in comparison to others. PP dropped down to less than -36 °C with introduction of all additives at optimum concentration. This was observed because of the reason that additives generally stop the crystallisation completely. The impact of additives was more profound in diesel as compared to biodiesel to improve PP, & there more the % of diesel is there in blend, the superior will be the impact of additive [38].

Several methods have been adopted to improve the CP & PP for fatty esters for colder regions. Winterization is the process of removing components having saturation by introduction of crystals by lowering temperature and thus filtering the constituents having high melting point. CP for modified biodiesel from Soybean biodiesel fractionation by urea and methanol was as low as -45°C [46].

Figure 5 compares the PP of different biodiesel blends with different additives at recommended loading and it is observed that mustard methyl ester has best PP among different samples. Palm biodiesel was mixed with diethyl ether in range of 2 to 8 % to check effect on different characteristics. As the percentage of DEE rose, there was refinement in properties. Due to lower freezing point i.e. -117.4 °C of DEE, cold flow properties of biodiesel improved significantly especially PP [65].

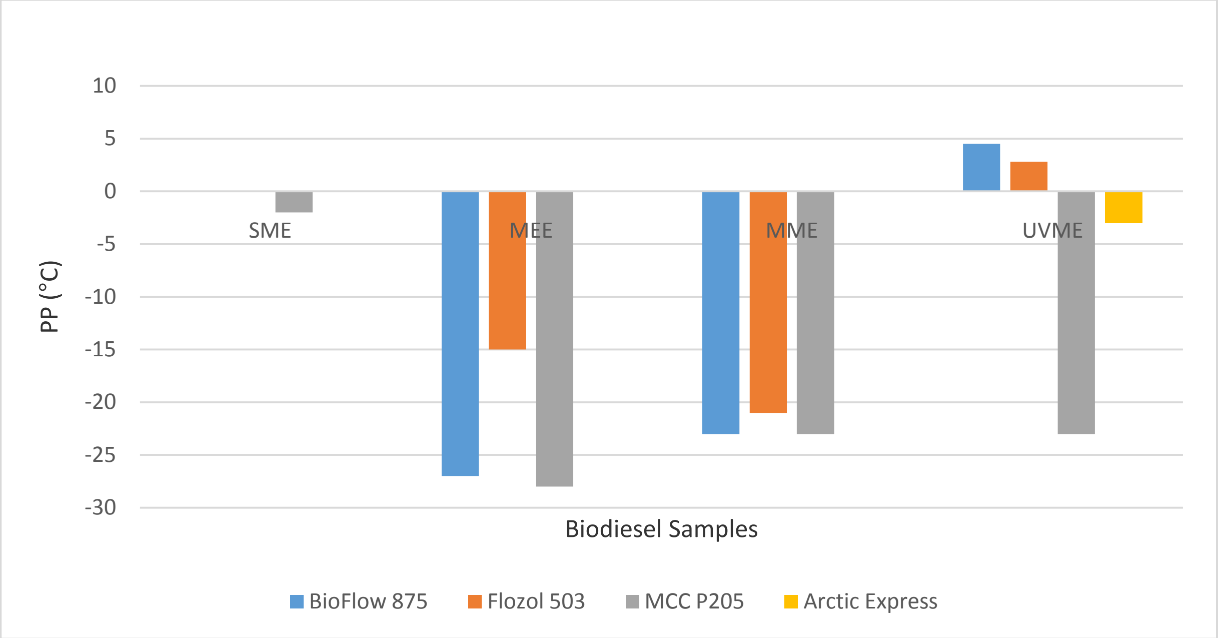

Figure 5: PP (°C) for biodiesel blends treated with different additives at recommended loading [46]
SME = Soybean Methyl Ester, MEE = Mustard Ethyl Ester, MME = Mustard Methyl Ester

In a different study, additives like commercial DEP & poly-glycerol ester (PGE) were investigated with Palm biodiesel. Significant effects on CFPP were noticed only when improvers used were more than 1% by weight. Maximum drop is CFPP was found by 7 °C [66].

Using ethanol to decrease he viscosity is quite popular. Blends of ethanol and palm with petroleum diesel in range of 0-30% enhanced the cold flow properties with much negative effect on oxidative stability. But Flash point &Cetane number dropped due to ethanol [67].

Modulated Temperature Differential Scanning Calorimetry (MT-DSC) was implemented to comprehend the fundamentals of low temperature properties of biodiesel. It was distinguished that crystallization peak temperature had values comparable to CFPP & CP. This way CP was found to be associated with the first solidified material and not with the early formation of the first nuclei, as normally reported. On the other hand, these crystals already lead to the flow decrease, as indicate by the CFPP. PP values were near to the second crystallization peak temperature, not being related to the complete solidification of the fuel [68]. Lanjekar and Deshmukh [69] found that feedstock having polyunsaturated fatty acids show excellent low temperature properties that is CFPP in range of 0 to -10 °C. Monirul et al. [70] recommended B30 blend of biodiesel (up to 30% biodiesel in pure diesel) for better cold flow properties. However, addition of cold flow improver yields best results for CFPs.

Conclusion

The study shows that there are several problems associated with biodiesel, while we are using it as fuel in engine. The CFPs of biodiesel is the major problem, associated with engine operation during cold climates. In this study, from work of several researchers it has been found out that the inferior CFPs of biofuel is the major cause for the deterioration of fuel quality and it will not be in condition to be used in cold climatic regions. Due to ignition problem there will be an incomplete combustion of fuel, which will further lead to starting problem in the engine. To overcome these issues, various researchers have suggested several remedial measures to enhance the CFPs of biofuel using different methods like winterisation, blending with petroleum diesel and solvents, use of additives. The literature review reveals that biodiesel prepared with higher alcohols better cold flow properties are obtained. Out of various methods, use of alcohols like blending of fuel with ethanol is recommended.

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