Cold Flow Behaviour of Biodiesel-A Review

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Abstract- The rapid rise in energy consumption in the country results in shortage of fossil fuels such as oil, coal and petroleum products. The devaluation of rupee against dollar in world market leads to concern about the availability of energy requirement for sustaining our economic growth in India. Increased use of fossil fuels and petroleum product in recent years leads to environmental problems both locally and globally. So looking at huge demand of diesel for all sectors of economy, the biodiesel is being viewed a substitute of diesel. The vegetable oils, animal fats and grease are the main feed stocks for the biodiesel production. Biodiesel fuel properties are quite comparable to diesel. From the various research analysis it has been identified that biodiesel have two major problems: fuel stability and its performance under cold conditions. Various researchers have worked extensively on improving the biodiesel stability but very less work has been reported on cold flow properties of biodiesel. The poor cold flow properties create problem in engine operation by choking the fuel lines and filters. This paper provides the various aspects of cold flow behaviour of biodiesel.

Keywords- Biodiesel, Jatropha, Pongamia, Cloud point, Pour point.

1. Introduction

The world is facing with the two major crises these are fossil fuel depletion and environmental degradation. The indiscriminate extraction and consumption of fossil fuels have led to depletion in petroleum reserves. Therefore, those countries not having these resources are facing a foreign exchange crisis, mainly due to the import of crude petroleum oil. Hence it is necessary to look for alternative fuels, which can be produced from materials available within the country. [1] Biodiesel is defined as the mono alkyl esters of vegetable oils or animal fats. Biodiesel is the best candidate for diesel fuels in diesel engines. The biggest advantage that biodiesel has over gasoline and petroleum diesel is its environmental friendliness. Biodiesel is now mainly being produced from soybean, jatropha, pongamia, rapeseed and palm oils. [2, 3] There are two major problems of using biodiesel as fuel are its oxidation stability and other is its performance under cold condition. Oxidation of fatty acid chains is a complex process that proceeds by a variety of mechanisms. Besides the presence of air, various other factors influence the oxidation process of biodiesel including presence of light, elevated temperature, extraneous materials such as metals which may be even present in the container material, peroxides, and antioxidants, as well as the size of the surface area between biodiesel and air. This susceptibility is due to its content of unsaturated fatty acid chains, especially those with bis-allylic methylene. [4, 5] However, other than stability the poor cold flow characteristics of vegetable oils are other problems which lead to injector coking, severe engine deposits, filter gumming, and piston ring sticking and thickening of lubrication oil from long-term use in diesel engines. This paper focuses on behaviour of biodiesel under cold flow condition.

2. Straight Vegetable Oil

There are more than 300 oil-bearing crops identified, among which some only considered as potential alternative fuels for diesel engines. Like in case of India Jatropha and Pongamia are the main non edible sources for biodiesel production. [6] The scientists and researchers conducted tests by using different oils and their blends with diesel. The various researchers reported that vegetable oil and its biodiesel give same efficiency as compared to diesel but slightly more fuel consumption. They concluded that vegetable oils, either chemically altered or blended with diesel to prevent the engine failure. It was reported that due to high viscosity of vegetable oil creates problem in engine operation so the direct use of vegetable oil is avoided and by the process of transesterification it is converted into biodiesel. [7, 8]

From Table 1 we can conclude that out of these non edible sources the Neem and Sal have other uses like they are used in production of various types of medicines. So we have to back the other remaining source that is Pongamia and Jatropha. The production of Pongamia oil is three times of Jatropha oil. So Pongamia can be a major source of fuel for replacement of diesel in India.

Table 2 shows the various properties of different oil sources from which it is quite clear that there is major variation in cloud point and pour point of oil as compare to diesel. From table 2 it is evidenced that oil cannot be directly replace diesel as fuel there have to improvement in the cold flow properties of these oil to be used as fuel.

Table 1. Production of Non-Edible oils in India [6, 9]

S. No.	Botanical Name	Local Name	Annual Productivity (Tons)
1.	Jatropha curcas	Ratanjyot	45,000
2.	PongamiaPinnata	Karanja	135,000
3.	Schleicheraoleosa	Kusum	25,000
4.	Azadirachtaindica	Neem	1,00,000
5.	Shorearobusta	Sal	1,80,000
6.	Modhucaindica	Mahua	1,80,000

Table 2. Various Properties of Oil [1]

Vegetable Oil	Cetane Number	Heating Value (MJ/kg)	Cloud Point (°C)	Pour Point (°C)	Flash Point (°C)	Density (kg/ltr)
Corn	37.6	39.5	-1.1	-40	277	0.909
Cotton Seed	41.8	39.5	1.7	-15	234	0.914
Crambe	44.6	40.5	10.0	-12.2	274	0.904
Linseed	34.6	39.3	1.7	-15.0	241	0.923
Peanut	41.8	39.8	12.8	-6.7	271	0.902
Rapeseed	37.6	39.7	-3.9	-31.7	246	0.911
Safflower	41.3	39.5	18.3	-6.7	260	0.911
Sesame	40.2	39.3	-3.9	-9.4	260	0.913
Soya bean	37.9	39.6	-3.9	-12.2	254	0.913
Sunflower	37.1	39.6	7.2	--15.0	274	0.916
Jatropha	45	40	16	-	240	0.912
Pongamia	51	46	23	-	160	0.882
Diesel	50	43.8	-5	-16	76	0.855

3. Biodiesel

Biodiesel is defined as the mono-alkyl esters of vegetable oils or animal fats. Biodiesel is produced by transesterification of the oil or fat with an alcohol such as methanol under mild conditions in the presence of a base catalyst. [10] Biodiesel is dependent upon the length and degree of unsaturation of the fatty acid alkyl chains. The carboxylic (fatty) acids are all straight-chain compounds ranging in size from 8 to 20 carbons. [11] Biodiesel has many important technical advantages compared to petro diesel including superior inherent lubricity, low toxicity, high (non-flammable) flash point and biodegradability, very low or negligible sulphur content and lower exhaust emissions.

Table 3. Biodiesel Properties as Fuel in Different Standards [6]

S.No.	Parameter	Austria ONC-1191	India BIS-15607	France EU-15412	Germany DIN-EN-590	Italy UNI-10946	USA ASTM-424720
1.	Density at 150C (g/cm3)	0.85-.89	0.87-0.89	0.87-0.89	0.875-0.89	0.86-0.90	0.88
2.	Viscosity at 400C (mm2/s)	3.5-5	1.9-6	3.5-5	3.5-5	3.5-5	1.96
3.	Flash point (°C)	100	130	100	110	100	130
4.	CFPP (°C)	0-5	0-5	N.A	0-10/-20	N.A	N.A
5.	Pourpoint (°C)	N.A	N.A	10	N.A	1-5	15-18
6.	Cetane number	>=49	>=40	>=49	>=49	N.A	>=47
7.	Neutralization number (mgKOH/g)	<=0.8	<=0.5	<=0.5	<=0.5	<=0.5	<=0.8
8.	Carbon residue (%)	<=0.05	<=0.05	N.A	<=0.05	N.A	<=0.05

Table 3 shows the various standard followed by different countries for their biodiesel. But the values of cloud point and CFPP has been not been given in various standards. It shows that irrespective of similarity in other values of different property there is no common ground for determining the cold flow properties of biodiesel.

4. Fatty Acid in Biodiesel

The Differences in chemical and physical properties among biodiesel fuels can be explained largely by the fuels' FA profiles. Two features that are especially influential are the size distribution and the degree of unsaturation within the FA structures. The finding is that several fuel properties – including viscosity, specific gravity, cetane number, iodine value, and low temperature performance metrics – are highly correlated with the average un saturation of the FAME profiles. Due to opposing effects of certain FAME structural features, it is not possible to define a single composition that is optimum with respect to all important fuel properties. However, to ensure satisfactory in-use performance with respect to low temperature operability and oxidative stability, biodiesel should contain relatively low concentrations of both long-chain saturated FAME and poly-unsaturated FAME. [12]

The relative oxidation rate of the unsaturated esters are **linolenic > linoleic > oleic**. This is attributed to the fact that these unsaturated fatty acid Chains contain the most reactive sites which are particularly susceptible to the free-radical attack. The biodiesel that has higher level of saturated FAME has higher cetane number and higher oxidation stability.

Table 4. Typical fatty acid (FA) groups in biodiesel [12]

Common Name	Formal Name	Abbreviation	Molecular Formula	Molecular Weight
Lauric acid	Dodecanoic acid	12:0	$C_{12}H_{24}O_2$	200.32
Myristic acid	Tetradecanoic acid	14:0	$C_{14}H_{28}O_2$	228.38
Myristoleic acid	cis-9-Tetradecenoic acid	14:1	$C_{14}H_{26}O_2$	226.26
Palmitic acid	Hexadecanoic acid	16:0	$C_{16}H_{32}O_2$	256.43
Palmitoleic acid	cis-9-Hexadecanoic acid	16:1	$C_{16}H_{30}O_2$	254.42
Stearic acid	Octadecanoic acid	18:0	$C_{18}H_{36}O_2$	284.48
Oleic acid	cis-9-Octadecenoic acid	18:1	$C_{18}H_{34}O_2$	282.47
Linoleic acid	cis-9,12-Octadecadienoic acid	18:2	$C_{18}H_{32}O_2$	280.46
Linolenic acid	cis-9,12,15-Octadecatrienoic acid	18:3	$C_{18}H_{30}O_2$	278.44
Arachidic acid	Eicosanoic acid	20:0	$C_{20}H_{40}O_2$	312.54
Gondoic acid	cis-11-Eicosenoic acid	20:1	$C_{20}H_{38}O_2$	310.53
Behenic acid	Docosanoic acid	22:0	$C_{22}H_{44}O_2$	340.60
Erucic acid	cis-13-Docosenoic acid	22:1	$C_{22}H_{42}O_2$	338.58

5. Problem of using Biodiesel as Fuel

There are two major problem related to use of biodiesel as fuel are its oxidation stability and cold flow performance. The various researchers have done lot of work in this area to find out the exact cause and solution of these problems. Jain and Sharma [13] states that biodiesel consists of long chain fatty acid esters derived from feed stocks such as vegetable oils, animal fats and used frying oil, etc. which may contain more or less unsaturated fatty acids which are prone to oxidation accelerated by exposure to air during storage and at high temperature may yield polymerized compounds. Auto oxidation of biodiesel can cause degradation of fuel quality by affecting the stability parameters. Biodiesel stability includes oxidation, storage and thermal stability. Oxidation instability can led to the formation of oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, in solubles, gum and sediment in the biodiesel. Thermal instability is concerned with the increased rate of oxidation at higher temperature which in turn, increases the weight of oil and fat due to the formation of insoluble. Storage stability is the ability of liquid fuel to resist change in its physical and chemical characteristics brought about by its interaction with its environment and may be affected by interaction with contaminants, light, factors causing sediment formation, changes in colour and other changes that reduce the clarity of the fuel. These fuel instabilities give rise to formation of undesirable substances in biodiesel and its blends beyond acceptable quantities as per specifications and when such fuel is used in engine, it impairs the engine performance due to fuel filter plugging, injector fouling, deposit formation in engine combustion chamber and various components of the fuel system. Dunn [14] states that blending with petro diesel exacerbates the problem. Settling solid residues were found to clog fuel filters in fuel dispensers and vehicles. In response to documented problems the biodiesel industry in the United States collaborated with the American Society of Testing and Materials (ASTM) to develop a cold soak filterability performance test that will help identify fuels that may have a propensity to clog filters if exposed to long-term storage in cold weather. The ambient temperatures cool towards their crystallization temperature, high-molecular weight paraffins (C18–C30 n-alkanes) in petro diesel nucleate and form wax crystals suspended in a liquid phase composed of shorter-chain n-alkanes and aromatics. Left unattended for a long period of time (such as overnight) the solid wax crystals may plug or restrict flow through filters causing start-up and operability problems. One of the major problems associated with the use of biodiesel is its poor low temperature properties, as happens in cold weather with methyl esters of stearic and palmitic acid of palm biodiesel.

The longer and unsaturated the carbon chains in the biodiesel, the worse the low-temperature properties.

6. Mechanism of Cold Flow Operation

At low temperatures, higher-melting point (MP) components in the fuel due to high amount of saturated fatty acid in the fuel leads to nucleation and growth of solid crystals. Prolonged exposure of the fuel to temperatures at or below CP causes crystals to grow and form interlocking networks. These solid crystals will cease the flow and lead to starvation of fuel in the engine and engine will not operate in that condition.

7. Cold Flow Properties

Poor cold flow properties may result in fuel line and pump blockage, ultimately leading to fuel starvation. There are no European or US specifications for low temperature properties (each country is free to determine its own limits according to local weather conditions), but it is well known that biodiesel fuels suffer from cold flow properties way more (i.e. they are higher) than mineral diesel fuel. The cold flow properties are expressed in terms of Cloud Point (CP), Pour Point (PP), and Cold filter plugging Point (CFPP).

7.1. Cloud Point (CP)

CP is the temperature at which crystallization begins when small, solid crystals become visible the fuel cools. [15].

7.2. Pour Point (PP)

Pour point (PP) is the lowest temperature at which the fuel becomes semi solid and loses its flow characteristics being no longer pump able; hence it is a measure of the fuel gelling point. The pour point is always lower than the cloud point.

7.3. Cold Filter Plugging Point (CFPP)

Cold filter plugging point (CFPP) is the lowest temperature, expressed in 1°C, at which a given volume of diesel type of fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. This gives an estimate for the lowest temperature that a fuel will give trouble free flow in certain fuel systems. This is important as in cold temperate countries; a high cold filter plugging point will clog up vehicle engines more easily. [11]

8. Impact of Cold Flow Properties on Biodiesel

The various researchers have done lot of work to study the impact of cold flow property on biodiesel and its performance which shows that poor cold flow property will lead to crystallization of fuel particles. In cold climate it will difficult to operate the vehicle because fuel will lose its flowablility and there will be fuel starvation in the engine. [16]

Knothe [10] states that for low-temperature applications of biodiesel the cloud point (CP) is a decisive parameter. It is the temperature at which the first visible crystals form upon cooling a fuel and at which therefore problems such as fuel filter plugging could result.

For biodiesel derived from soybean oil the CP is around 0°C and for biodiesel derived from rapeseed (canola) oil it is only slightly lowers. Biodiesel fuels derived from palm oil or animal exhibit significantly higher CP, around 15 °C, due to their content of saturated fatty esters. Hoekman et al. [17] reported that for variation in cold flow properties is due to large seasonal and geographic temperature variability, neither the U.S. nor European biodiesel standards have firm specifications for these low temperature properties, though they are among the most important properties in determining the suitability of biodiesel fuels in-use Poor low temperature performance may be exhibited in several ways, but principally by filter plugging due to wax formation, and engine starving due to reduced fuel flow. There is no single best way to assess low temperature performance, and the existing fuel standards (both U.S. and European) do not include explicit specifications for cold flow properties – for either conventional diesel or biodiesel. Zuleta et al. [18] evaluated the Oxidative stability and cold-filter plugging points (CFPP) of blends of biodiesel from palm, sacha-inchi, jatropha and castor oils The properties of biodiesel depend on the type of methyl-ester constituents and they are generally opposed, i.e., a biodiesel with good oxidative stability exhibits bad CFPP. Cold flow properties of a fuel define its behaviour in a given climate conditions. Partial solidification that a fuel may have in cold weather can cause clogged fuel supply lines and filters, which creates problems for engine ignition.

The liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturate. This causes fuel starvation and operational problems as solidified material clog fuel lines and filters. With decreasing temperature more solids form and material approaches the pour point. The poor pour point temperature will deteriorate the flow ability of the fuel which will lead to failure in the engine operation. [12, 16]

Smith et al. [20] provides the method for the reduction of the cloud point of biodiesel that reduce the proportion of saturated esters, thereby increasing the proportion of unsaturated esters, impact directly on the oxidative stability and cetane number of the fuel.

Bhale et al. [21] States that most of the properties of biodiesel fuels are comparable with that of diesel fuel but cloud point and pour point which indicate the cold flow behaviour of a fuel are very poor. A cloud point of 291 K (18°C) and pour point of 280 K (7°C) was observed for Mahua Methyl Ester. The reduction in cloud point of MME was from 291 K (18°C) to 281 K (8°C) when blended with 20% of ethanol and up to 278 K (5°C) when blended with

20% of kerosene. Similarly the reduction in pour point was from 280 K (7°C) to 269 K (-4°C) when blended with 20% ethanol and up to 265 K (-8°C) when blended with 20% kerosene. MME with 10% ethanol and 10% diesel reduces the pour point from 291 K (18°C) up to 268 K (-5°C). Thus ethanol and kerosene improve the cold flow properties MME when blended up to 20%.

Table 5. Literature Review on Cold Flow Property of Biodiesel

S.No.	Name of Author	OIL Used	Parameter Measured	Result
1-	Verissimo et al. [12]	Biodiesel Blended fuels	Pour Point	1-Impedance and phase of impedance vs. frequency of the piezoelectric quartz crystal change significantly during cooling of biodiesel and biodiesel blended fuels and allows confirming the role of ethanol as a cold flow improver for biodiesel.
2-	Mejia et al. [15]	Castor oil biodiesel, palm oil bio diesel, diesel	Viscosity , cloud point, pour point	1-Diesel and castor oil biodiesel blends showed appropriate and approximately the same cloud point temperatures when the biodiesel concentration in those mixtures was fewer than 40% in volume. 2-The use of palm oil biodiesel–castor oil biodiesel (POB COB) blends to obtain a type of pure biodiesel with both low cloud point and viscosity was not a practical option.
3-	Hoekman et al.[17]	Biodiesel Diesel	Specific gravity Viscosity Cetane Number Low Temperature operability (CFPP) Oxidation Stability	1- That because of its considerable oxygen content (typically 11%), biodiesel has lower carbon and hydrogen contents compared to diesel fuel, resulting in about a 10% lower mass energy content. 2-Due to biodiesel's higher fuel density, its volumetric energy content is only about 5–6% lower than petroleum diesel. 3-Biodiesel has somewhat higher molecular weight than petroleum diesel, which is reflected in slightly higher distillation temperatures. 4-The viscosity of most biodiesel fuels is significantly higher than petroleum diesel, often by a factor of 2.
4-	Zuleta et al. [18]	biodiesel from palm, sacha-inchi, jatropha and castor oils	Cold filter plugging point (CFPP) Oxidation Stability	1- Biodiesel with good oxidative stability exhibits bad CFPP 2- Partial solidification that a fuel may have in cold weather can cause clogged fuel supply lines and filters, which creates problems for engine ignition. 3- Cold flow properties of biodiesel also depend on the structure of the alkyl esters. The melting point increases with chain length and decreases with the increase of double bonds.
5-	Yoon et al. [24]	Diesel Biodiesel	Specific gravity Density Viscosity	1-The specific gravity of biodiesel fuel increased with the increase of the blending ratio of biodiesel and gradually decreased as the fuel temperature increased linearly. 2- The density value measurement was correlated as a function of fuel temperature and blending ratio by an empirical equation. 3- The viscosity of the test fuels was found to decrease linearly with increasing temperature and decreasing blending ratio.
6-	Echim et al. [35]	biodiesel from vegetable and animal origin containing highly saturated methyl esters.	Cold filter plugging point (CFPP)	1-The CFPP of the biodiesel samples with poor cold flow properties was improved by formulation with biodiesel samples exhibiting better cold flow properties and/or additivation. 2-The use of biodiesel from these feed stocks in moderate-temperate climates during cold seasons is associated with their crystallization temperature due to high concentrations of high-melting point saturated

S.No.	Name of Author	OIL Used	Parameter Measured	Result
				long chain fatty acids.
7-	Wang et al. [36]	sugar esters (S270 and S1570), silicone oil (TSA 750S), polyglycerol ester (LOP-120DP) and diesel conditioner (DDA)	Cold filter plugging point (CFPP)	1-The greatest reduction to the CFPP of the BWCO (from -10 °C to -16 °C) being was achieved by the addition of 0.02 wt% of polyglycerol ester (LOP-120P). 2-Detergent fractionation of the BWCO was performed by first mixing partially crystallized biodiesel with a chilled detergent (sodium dodecylsulfate) solution accompanied by an electrolyte (magnesium sulphate), and then separating the mixture by centrifugation to obtain the BWCO liquid.
8-	Sharafutdinov et al. [37]	zero sulphur diesels from Ural crude oil fatty acid methyl esters (FAME) from rape seed oil, palm oil, sunflower oil	Cold flow properties oxidation stability	1-. It was found that undercutting the petroleum diesel to obtain arctic diesel deteriorates its oxidation stability and anti-oxidant addition is required to keep the oxidation stability within acceptable limits. 2- The addition of commercially available FAMEs, produced from 100% rape seed oil; 70% soya and 30% palm oil; 50% rape seed oil and 50% sunflower oil, to the petroleum diesel depresses the cold filter plugging point (CFPP). 3- The depressing effect on the conventional diesel CFPP of the FAME depends on the petroleum diesel and the FAME properties. 4- The relative oxidation rate of the unsaturated esters are linolenic > linoleic > oleic. This is attributed to the fact that these unsaturated fatty acid Chains contain the most reactive sites which are particularly susceptible to the free-radical attack. 5- The biodiesel that has higher level of saturated FAME has higher cetane number and higher oxidation stability.
9-	Joshi et al. [38]	Ethyl Levulinate (ethyl 4-oxopentanoate) (cold flow improver) Biodiesel from cotton seed oil and poultry fat	Cloud point (CP), Pour point (PP), and Cold filter plugging points (CFPP)	1-The cloud (CP), pour (PP), and cold filter plugging points (CFPP) of biodiesel fuels prepared from cottonseed oil and poultry fat were improved upon addition of ethyl levulinate at 2.5, 5.0, 10.0, and 20.0% (vol). 2- Reductions of 4-5 °C in CP, 3-4 °C in PP and 3 °C in CFPP were observed at 20 volume % ethyl levulinate. 3- The Approaches for improving the low temperature operability of biodiesel include blending with petro diesel, transesterification with long- or branched-chain alcohols, crystallization fractionation, and treatment with commercial petro diesel cold flow improver (CFI) additives.
10-	Jain and Sharma [39]	Biodiesel Petro-diesel	Thermal Stability	1-The thermal stability of biodiesel and their blends with diesel under different conditions. The work revealed that biodiesel is more prone to oxidation when exposed to higher temperature due to the formation of oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, insolubles, gum and sediment in the biodiesel, which may often be responsible for fuel filter plugging, injector fouling, deposits formation in engine combustion chamber and various components of the fuel system.

Imahara et al. [22] states that cloud point of biodiesel could be determined only by the amount of saturated fatty acid methyl esters regardless of composition of unsaturated esters. Tang et. al. [23] studied the cold-flow properties of diesel fuel. The cloud point of biodiesel fuels is generally higher than that of petro diesel fuel, and biodiesel has a 15–40°C higher pour point than that of diesel fuel. Thus, biodiesel begins to gel at crystallization temperatures, and it can clog filters or eventually become so thick that it cannot be pumped from the fuel tank to the engine. The cold properties of biodiesel have determined that the length of the hydrocarbon chains and the presence of un saturation greatly affect low temperature flow properties. Biodiesel from vegetable oils such as soybean oil (SBO-) has better fluidity in cold climates than that from animal fat because SBO-biodiesel had more unsaturated components. However, the effects of biodiesel on cold-flow fuel properties when blended with ultra-low sulphur diesel (ULSD) have not been fully elucidated.

9. Advantage and Disadvantage of Biodiesel

Biodiesel is widely accepted as an additive for fossil derived diesel in compression ignition engines. It offers many advantages including: higher cetane number; reduced emissions of particulates, NOx, SOx, CO, and hydrocarbons; reduced toxicity; improved safety; and lower lifecycle CO2 emissions. [20] A characteristic of biodiesel limiting its application is its relatively poor low-temperature flow properties, which are primarily a consequence of the fatty acid make-up of the oil feedstock. Attempts to influence the fatty acid profile of either the oil feedstock or the biodiesel product include winterisation and fractionation which reduce the fraction of saturated fatty acids and result in large reductions in yield. A reduction in saturated fatty acids reduces ignition quality of the fuel, while an increase in unsaturation reduces oxidation stability. The removal of the double bonds on the ester group and the addition of a side-chain may provide a benefit in terms of low-temperature properties and offer improved oxidation stability. Biodiesel currently limiting its application to blends of 20% or less is its relatively poor low-temperature properties. Petroleum diesel fuels are plagued by the growth and agglomeration of paraffin wax crystals when ambient temperatures fall below the fuel’s cloud point (CP). These solid crystals may cause start-up problems such as filter clogging when ambient temperatures drop to around -10 to -15 °C. Whilst the CP of petroleum diesel is reported as -16 °C, biodiesel typically has a CP of around 0°C, thereby limiting its use to ambient temperatures above Freezing. The nature of the alcoholic head-group of the ester produces an equally clear effect on the low-temperature properties of biodiesel. The use of long (3–8 carbon) normal alcohols or branched alcohols to manufacture biodiesel reduces the CP compared to those for conventional methyl esters.

Hasimoglu et. al. [5] states the important advantages of biodiesel are lower exhaust gas emissions and its biodegradability and renewability compared with petroleum-based diesel fuel. Although the transesterification improves the fuel properties of vegetable oil, the viscosity and volatility of biodiesel are still worse than that of petroleum diesel fuel.

Yoon et al [24] establish that biodiesel does have numerous advantages; it has different properties compared with diesel fuel. It has a higher viscosity, specific gravity, density, cloud point, and pour point than petroleum diesel fuel, and these specificities have a significant influence on the fuel spray atomization and evaporation characteristics, resulting in changes in the combustion process.

Mishra and Murthy [25] state that biodiesel offers many advantages including: higher cetane number; reduced emissions of particulates, NOx, SOx, CO, and hydrocarbons; reduced toxicity; improved safety; and lower lifecycle CO2 emissions. A characteristic of biodiesel limiting its application is its relatively poor low-temperature flow properties. Improvement of its low temperature flow characteristic still remains one of the major challenges when using biodiesel as an alternative fuel for diesel engines. The biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds display higher cloud points and pour points thus limiting their applications.

Torres et al. [26] report the main drawback of the use of biodiesel is its bad behaviour at low temperatures. In this study he shows that it is possible to take profit of the presence of free fatty acids in the starting materials used for biodiesel production (i.e. reused oils) by synthesizing additives able to improve cold flow properties. The synthesis of fatty acid derivatives have been successfully carried out by esterification of stearic, oleic and linoleic acids with bulky linear and cyclic alcohols and by epoxidation of methyl oleate and subsequent ring-opening reaction with the same alcohols. The study of crystallization patterns of pure derivatives by DSC and optical microscopy revealed the improvement of cold properties of biodiesel. Blends of biodiesel with up to 5% of some of these compounds allowed a decrease of CFPP. The presence of unsaturated esters improves cold properties of biodiesel but worsens oxidation properties. Another way of improving cold properties of biodiesel consists in shortening hydrocarbon chains by ozonolysis of the starting oils. The addition of these products to biodiesel improved cold filter plugging point (CFPP).

Smith et al. [20] states that disadvantages of biodiesel are its relatively poor low-temperature flow properties. Pure biodiesel can solidify in fuel lines or clog filters when utilised in cold ambient conditions.

Singh et al. [1] reported the various disadvantage of biodiesel these are

1-Constraints on the availability of agricultural feedstock impose limits on the possible contribution of Biodiesels to transport.

2-The kinematic viscosity is higher than diesel fuel. This affects fuel atomization during injection and requires modified fuel injection systems.

3-Due to the high oxygen content, it produces relatively high NOx levels during combustion.

4-Oxidation stability is lower than that of diesel so that under extended storage conditions it is possible to produce oxidation products that may be harmful to the vehicle components.

5-Biodiesel is hygroscopic. Contact with humid air must be avoided.

6-Production of Biodiesel is not sufficiently standardised. Biodiesel that is outside European or US standards can cause corrosion, fuel system blockage, seal failures, filter clogging and deposits at injection pumps.

7-The lower volumetric energy density of Biodiesel means that more fuel needs to be transported for the same distance travelled.

8-It can cause dilution of engine lubricant oil, requiring more frequent oil change than in standard diesel-fuelled engines.

9-A modified refuelling infrastructure is needed to handle Biodiesels, which adds to their total cost.

10. Impact of Cold Flow Properties On Engine Performance

The various researchers have worked in this area to study the impact of cold flow properties on engine performance. Their research shows that poor cold flow properties result in crystallization of fuel particles which result in obstruction in fuel flow and due to that engine cannot operate in cold climate. Kim et al. [27] examines the cold performance of biodiesel blends in a passenger car and a light duty truck at -16°C and -20°C. Six different types of biodiesels derived from soybean oil, waste cooking oil, rapeseed oil, cottonseed oil, palm oil and jatropha oil were blended with different volume ratios (B5 (5 vol. % biodiesel - 95 vol. % diesel), B10 and B20). The cold filter plugging point (CFPP) and the cloud point had an effect on the start ability and driveability of both the passenger car and the light duty truck. The start ability and driveability of the passenger car with all biodiesel blends (B5) were generally good at -20°C. In the light duty truck, biodiesel blends (B10 and B20) of soybean, waste cooking, rapeseed and jatropha ended to be good at -20°C in the start ability and driveability tests than the biodiesel blends (B10 and B20) of cottonseed and palm. In particular, the palm biodiesel blend (B10) failed at -20°C, and the palm biodiesel blend (B20) also failed at -16 °C in the start ability test. The cold flow properties of biodiesel dictate that the length of the hydrocarbon chains and the presence of unsaturated structures significantly affect the low temperature properties of biodiesel.

Lin et al. [28] evaluate the impact of saturated monoglycerides, glycerin, and soap on cold soak filterability. When operated under winter conditions in the Northern Plains of the USA, biodiesel may impede engine performance through fuel line and fuel filter plugging. The cold soak filterability was measured according to ASTM D 7501-09b. Biodiesel (300 mL) was stored at 4°C for 16 h, and then transferred to a water bath at 25 °C for 2 h, or for 4 h if precipitate was present. The incubated biodiesel was then filtered through a 0.7 lm glass microfiber filter (Grade No. 151, Ahlstrom, Mt. Holly Springs, PA) under 16–31 kPa. The time required for the biodiesel to pass through the filter was recorded as the filtration time.

Kegl [29] investigated the fuel flow through the whole injection system (all six injection assemblies) to all six cylinders with respect to fuel temperature. The pressure drop through the fuel filter and fuelling through each of six injection assemblies are analyzed.

Haseeb et al. [30] reported that biodiesel, having different chemical characteristics from diesel, can interact with materials in a different way. It can cause corrosive and tribological attack on metallic components and degrade elastomeric parts. Biodiesel has chemical characteristics that are distinct from that of petroleum diesel. It is therefore expected that they will interact with materials differently. Compositional differences of biodiesel derived from different feed stocks complicate the situation. In automobile fuel systems, numerous materials come in contact with fuel. These can be mainly grouped into ferrous alloys, non-ferrous alloys and elastomers. Among these groups of materials, elastomers undergo degradation to a greater extent in biodiesel. Common elastomers like natural rubber, nitrile, chloroprene/neoprene etc. are not suitable for use in biodiesel. Fluorocarbons have shown good resistance and are recommended for used in biodiesel. Corrosion studies done so far suggest that biodiesel is more corrosive than diesel.

Perez et al. [31] studied about biodiesel that it has susceptible to start-up and performance problems, consistent with its chemical composition, when vehicles and fuel systems are subjected to cold temperatures. In this work, a comprehensive evaluation of the crystallization behaviour of different biodiesels was performed by measuring the cold filter plugging point (CFPP), cloud point (CP) and pour point (PP). Results were related to differential scanning calorimetric (DSC) thermograms. Peanut methyl esters in particular led to the most unfavourable properties due to the presence of long-chain saturated compounds approaching 6 wt.%. The cold flow properties may be improved with different winterization techniques to eliminate some of these compounds. In this work, various techniques are tested, and the best technique is found to be crystallization filtration using methanol, which reduces the CFPP from 17 °C to -8°C with a biodiesel loss of 8.93 wt.%. Moreover, the cake from filtration, enriched with long-chain saturated methyl esters, can be used as phase change material (PCM) for thermo-regulated materials. Cold flow properties of diesel fuel are usually characterized by the following three temperature measures: cloud point (CP), cold filter plugging point (CFPP) and pour point (PP). Initially, cooling temperatures cause the formation of solid wax crystal nuclei that are submicron in scale and invisible to the human eye. Further decreases in temperature cause the crystal nuclei to grow. The temperature at which crystals become visible is defined as the cloud point (CP) because the crystals usually form a cloudy or hazy suspension. The temperature at which crystal agglomeration is sufficiently extensive to prevent free pouring of fluid is defined as pour point (PP). The cold filter plugging point (CFPP) is then defined as the lowest temperature at which 40 mL of oil safely passes through the filter within 60 s. The crystallization of these compounds may lead to plugged filters and tubes.

Bhale et al. [21] investigate the performance and emission with ethanol blended Mahua biodiesel fuel and ethanol–diesel blended Mahua biodiesel fuels. A considerable reduction in emission was obtained. Ethanol blended biodiesel is totally a renewable, viable alternative fuel for improved cold flow behaviour and better emission characteristics without affecting the engine performance. The cloud point, which usually occurs at a higher temperature than the pour point, is the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturates. Crystallization of the saturated fatty acid methyl ester components of biodiesel during cold seasons causes fuel starvation and operability problems as solidified material clog fuel lines and filters. With decreasing temperature more solids form and material approaches the pour point, the lowest temperature at which it will cease to flow. Tang et al. [23] states that the formation of precipitates in biodiesel blends may have serious implications for diesel engine fuel delivery systems. Precipitates were observed in Soybean oil (SBO-), cottonseed oil (CSO-), and poultry fat (PF-) based biodiesel blends after storage at 4°C. CSO- and PF-based biodiesel had a lower mass of precipitates observed than the SBO-based. Moreover, different rates of precipitate formation were observed for the B20 versus the B100.

Panoutsou et al. [32] analyse the resources available for biodiesel production and identify the most realistic options under technical, economic and environmental perspectives. Sahid and Jamal [33] reviewed the test conducted using different types of raw and refined oils. These experiments with raw biodiesel as fuel did not show the satisfactory results, when they used the raw biodiesel. The fuel showed injector coking and piston ring sticking. Dwivedi et al. [34] states that diesel engines operated in cold weather experience the problems of clogging of the filters and/or choking of the injectors. The use of flow improving additives and "winter blends" of biodiesel and kerosene has proved effective in the operating range of climate temperatures B100 tends to operate well at temperatures down to about 5°C.

Biodiesel is On Farm Fuel" where farmer can grow his own resource, convert to biodiesel and use in agricultural sets itself without the need of any diesel for blending.

11. Main Findings

The main findings from the literature review are:

1-Cold flow operation is major problem associated with the use of Biodiesel as fuel.

2-The Cold flow problem arises due to higher number of saturated fatty acid present in the biodiesel.

3-Cold flow is characterized by Cloud point; Pour Point and Cold filter Plugging Point.

4-The poor cold flow properties result in crystallization of fuel particles which result in obstruction in fuel flow which results in failure of engine operation.

5-Cold flow properties of biodiesel are improved by winterization and antioxidants.

12. Conclusion

In this literature review the various researchers establishes that the poor cold flow property of biodiesel will cause the plugging of fuel lines, filters and creates the fuel starvation in engine which leads to ignition problem. Due to ignition problem there will be an incomplete combustion of fuel and which will lead to starting and operational problem in the engine. The fatty acid composition of biodiesel is the main factor that affects its cloud point, pour point and cold filter plugging point. The poor cold flow properties can be improved by use of antioxidants and winterization. That will lead to development of biodiesel as an alternative source of energy to diesel.

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