A review on cold flow properties of biodiesel and their improvement

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Abstract. The depletion of petroleum derivatives and expanded contamination caused by the consuming of fossil fuel is a driving component to consider the renewable source. Biodiesel is considered as most promising fuel to use in diesel engines. Biodiesel obtains from animal fats, Straight vegetable oils and waste by transesterification and esterification process. The properties of biodiesel oil meet the requirement of fuels and it can build a huge positive impact on pollution and make the fuel eco-friendly. Biodiesel with its points of interest undergoes a notable downside in the low-temperature properties. Due to inferior low-temperature properties of biodiesel, fuel crystallization and gum formation occur at low-temperature which leads to stopping of channels and tubes. It indicated higher pour point and cloud point, higher nitrogen oxide (NOx) which cuts down engine speed and power, injector coking. The present study review is done on low-temperature properties and Impact of different actions taken to improve these properties.

Keywords: Biodiesel, cold flow properties, additives.

Introduction

In many countries including India, researchers are focusing on an alternative fuel that is eco-friendly and renewable in nature. It is needed for the position of conserving the global environment and concern about long-term supplies of orthodox hydrocarbon based mineral diesel fuels. Biodiesel is derived from triglycerides using different sources vegetables and animal fats. With the help of transesterification chemical reaction biodiesel can be obtained, based on chemical reaction of fatty acid and alcohol catalyst and this biodiesel is known as methyl ester of fatty acid [1]. The main advantages of using this fuel these renewable properties such as good superiority exhaust gas emission and bio-degradability. The utilization of biodiesel gives significant decrease in emission of carbon monoxides, unburned hydrocarbon and particulates in conventional diesel engines [2]. Diesel fuel is essential in our country for transportation and agriculture. The chemical reaction to obtain fuel is transesterification. The lubricity effects of biodiesel are also better for engine then mineral diesel and prolong the engine life. [3] All vegetable oils have their own properties. Biofuel is enormously significant to preserve the engine from malfunction. With huge amount of mono, di, and triglycerides fuels are susceptible to coking and lead to the development of deposits in engine pistons, and other parts[4]. India imports 46% of edible oilseed and got fourth largest oil-producing country. India produces 9.3% of total world oilseed. Total world consumption is 3.1% while crude oil production in India is only 1%. [5].

Potential sources of production of biodiesel are Sal, Mahua, Pongamia, Jatropha and Neem. Bio-fuels not only help in stopping indiscriminate fossil fuel consumption but also are proven to be
environmentally safe and very much capable of solving the energy related problems. Ethanol is a renewable fuel produced using plant materials for example. Corn, sugar cane, agricultural feedstocks, crops, etc. Ethanol has capability to substitute the non-renewable limited fossil fuel resources and their environmental consequences. [7]. Renewable energy is energy from a source that is not depleted when used. The govt. of India is working on the development and effective use of bio-based fuel. The country stands fourth in the world in the consumption (973,000 GWh/yr.) and third in the world in production (1,208,400 GWh/yr.) [8]. An advantage of bioethanol is that it has advanced octane rating than ethanol-free gasoline available at roadside gas (petrol) places, Increased thermal efficiency is found for increase in compression ratio. In some states of cold climate areas a mix of gasoline and ethanol is mandatory (as winter oxidizer) to reduce atmospheric pollution emissions [9]. The cultivation process of Jatropha is able to do under the very easy condition and the oil of these species having various characteristics as stability and power [10]. Bio-ethanol is normally got from the conversion of carbon-based compound feedstocks, Ethanol may be produced from a variety of feedstocks such as sugar- cane, grain, peanut, fruits, corn, wheat, cotton, biomass-carbon compound etc. Biodiesel is produced from refined oil which is defined on the number of impurities [11]. With the rise in population, the need for the individual has also raised day by day. The fossil fuel consumption has also gone to a very large extent, in the result of which people are looking for fuel which is not only economical but also officially feasible, competitive, environmentally acceptable & easily available [12]. Biodiesel fuel has shown many of the above qualities. It is being extracted from many different sources & some of them are biodiesel from triglycerides, biodiesel from Mahua oil (madhuca indica oil) etc. The utmost commonly utilized oils for the making of biodiesel are sunflower, soybean, rapeseed, cottonseed & Jatropha. As the cost of consumable vegetable oil is higher than the diesel fuel, therefore left-over vegetable oil & non-edible crude vegetable fat is taken as a direct source of biofuel. In India only, those plants are considered for biofuel which is non-edible & grown a large scale on a non-crop. Some of the foundations of biofuel in the form of vegetable fats, animal fats, non-edible oils etc. are listed in the given table [13].

**Biodiesel**

Biodiesel produced by chemical process known as transesterification. Straight Vegetable oils and animal fats converted into FAME (Fatty Acid Methyl Esters). Vegetable oils (cottonseed, sunflower, coconut, peanut, soybean, canola/rapeseed, and corn oil) and animal fats (Pork lard, beef tallow) considered as edible feedstocks of 1st generation for production of biodiesel. 2nd generation nonedible feedstocks are waste biomass and agricultural waste (Pongamia oil, Jatropha oil, Mahua oil, Rubber seed, Caster oil, neem, sal etc.)[6].Biofuel impact on exhaust varies with the type of biofuel used. There are lesser pollutant emissions on the combustion of biodiesel. The engine dissipates emission mainly contains sulfur oxide and shows decreasing emission of carbon monoxide, hydrocarbon& aromatic compounds. The economic biofuel drastically decreases particulate matter emission compared to petrol diesel. NOx emission has slightly risen with economic biofuel in comparison to diesel fuel. Although on changing chain length concentration nitrogen oxides and particulate matter remained unchanged that of carbon dioxide and hydrocarbon were changed to great extent, which was later decreased by reducing the chain length. [14].

To use biodiesel in a diesel engine, biodiesel should have similar combustion properties to diesel. Physico-chemical properties of biodiesel are flash point, fire point, specific gravity, viscosity, cloud point, calorific value, pour point, and cetane number considered to meet ASTM standard.
shown in Table-1.
Table-1, Comparison of fuel properties of Diesel and Biodiesel and Their Testing methods [14]

| S.No. | Fuel Properties                  | Units   | Testing Methods | Diesel | Biodiesel |
|-------|----------------------------------|---------|----------------|--------|-----------|
| 1.    | Fuel Standard                    |         | ASTM D975      | 1.3-4.1| 1.9-6.0   |
| 2.    | Kinematic Viscosity @40˚C         | mm²/s   | D445           | 1.9    | 6.0       |
| 3.    | Density @15 °C                   | Kg/m³   | D4052          | 848    | 878 min   |
| 4.    | Flash Point                      | °C      | D 93           | 60 to 80| 93.0 min  |
| 5.    | Cloud Point                      | °C      | D2500          | -15 to 5| -3 to 12  |
| 6.    | Pour Point                       | °C      | D97            | -35 to -15| -15 to 10 |
| 7.    | Cetane Number                    |         | D613           | 40 to 55| 48-60     |
| 8.    | Free glycerine                   | % m/m   | D6584          | -      | 0.020     |
| 9.    | Total glycerine                  | % m/m   | D6584          | -      | 0.240     |
| 10.   | Water & sediment                 | % Vol   | D2709          | 0.05 max| 0.050 max |
| 11.   | Carbon residue                   | % m/m   | D4530          | 0.15   | 0.050 max |
| 12.   | Specific gravity @60 °C          | Kg/l    | D1250          | 0.85   | 0.88      |
| 13.   | Acid number                      | mgKOH/g | D664           | -      | 0.50 max  |
| 14.   | Oxidation stability              | Hours   | EN14112        | -      | 3 min     |

**Cold flow properties**

Cold flow properties of fuel specify low-temperature operation of the engine in cold climate. It may categorize as different points in operation like Pour point, Cloud point and cold filter plugging point (CFPP).
Cloud point (CP)
The temperature at which wax kind of structural starts forming when fuel goes to lower temperature. The existence of solidified wax increases thickness the oil and it stops the gasoline injectors, filters and valves. The wax gathers superficially and structures a blend with water. At the lower temptation solidification increases which creates problem to engine [15,16].

Pour point (PP)
Pour point is that the temperature to which fuel do not able to move toward or becoming semi-strong and loses its flow attributes. It is the temperature at which the fuel gelling point can measure. Pour point is comes lesser than that of cloud point [15,16].

Cold filter plugging point (CFPP)
Cold filter plugging point is the most minimal temperature at which fuel has ability to pass through fuel standardized filtration machine without any trouble in fuel system. This process performs at specific temperature under specific conditions. Cold filter plugging point requires finding out for cold regions to check the fuel ability to flow at lower temperatures [15,16].

Cold flow property Mechanism of Biodiesel
When an engine operates at lower temperature the fuel particles gather and their gelling formation occurs. At this temperature fluid particle comes closer and crystallization of molecules of fluid particles starts inside liquid to form crystal structure. In cold regions temperature of liquid goes below its melting point then thermodynamic force created. An adequate amount of thermodynamic force required for crystallization of liquid particles. Crystal growth and nucleation are two steps to formation of crystallization. When particles of fluid come closer to make fetus called crystalline in the process of nucleation. Crystal growth and nucleation layer by layer to form a new lattice. By combination of these two processes, first nucleation and crystal growth, large solid crystal form which disturb in fuel flow and ultimately incomplete combustion found at the end of combustion. Incomplete combustion is responsible to start of the vehicle in cold weather [16,17].

Impact of different actions on cold flow property of biodiesel
Many researchers have been worked to overcome problem related in engine operation due to cold weather conditions. Biodiesel consist of saturated fatty acid profile (SFA) and unsaturated fatty acid profile (USFA). A higher degree of unsaturated fatty acids is more susceptible to oxidation deterioration. In other way presence of saturated fatty acid leads to low-temperature properties [18]. Highly unsaturated fatty acid methyl esters show good cold flow properties and low oxidation stability while saturated fatty acid leads to high oxidation stability and inferior cold flow property. High quality of fuel can obtain by optimizing fatty acid profile of biodiesel by blending of biodiesel from different feedstocks. Poor low-temperature execution of biodiesel limits its utilization in chilly atmosphere [19]. Table 2 Effect on cold flow properties of biodiesel by different action taken by researches is given.

| Biodiesel                              | Action (Blends/Additive) | Effect on cold flow property                                                                 | Ref  |
|---------------------------------------|--------------------------|------------------------------------------------------------------------------------------------|------|
| Beef tallow, soybean oil, palm oil,   | Binary blends            | • Cold flow properties of heavier biodiesel decreased by blending.                              | [20] |
| palm kernel, olein and macauba,       |                          | • macauba kernel and Soybean oils found best blends with a CFPP lower than −20 °C             |      |
| stearin and macauba kernel oils       |                          | • Soybean oil and tallow biodiesels blend found satisfactory.                                   |      |
| Trait                  | Description                                      | Notes                                                                 |
|-----------------------|--------------------------------------------------|----------------------------------------------------------------------|
| Palm Biodiesel        | Blended with diesel and kerosene Ethanol (Additive) | - B20 blend increases CP and PP                                      |
|                       |                                                  | - 20% additive addition gives significant increases in CP and PP     |
| Soybean and Palm      | Ethanol and n-butanol additive                   | - n-butanol blend shows better cold flow property than Ethanol       |
| Biodiesel             |                                                  | - No significant difference in CFPP was found                        |
| Waste cooking oil     | MgO Nanoparticles                                | - 30 ppm MgO nanoparticles gives a significant improvement in CP, PP, CFPP. |
| Canola Biodiesel      | Copolymer additive                               | - 1% addition of poly (lauryl methacrylate) gives best result        |
| Dairy washed milk scum| Di-ethyl ether (DEE) and Acetone (ACE) additive   | - 20% Addition of DEE and ACE improves low-temperature properties.   |
| oil (DWMS)            |                                                  |                                                                      |
| Palm Biodiesel        | Commercial DEP, Polyglycerol ester (PGE) and PA additive | - Crystallization temperature found close to CFPP.                   |
|                       |                                                  | - More than 1% additives show considerable effect on measured parameter. |
| Soybean Biodiesel     | Olefin-ester copolymers (OECP), Polymethyl acrylate (PMA) and Ethylene vinyl acetate copolymer (EACP), additive | - OECP found the best additive among these.                          |
|                       |                                                  | - It significantly reduces the value of CP, PP, CFPP.                |
| Rapeseed Biodiesel    | Blends of RME, Rapeseed butyl ester and butanol  | - Butanol shows a positive effect on low-temperature properties.     |
| (RME)                 |                                                  |                                                                      |
| Fatty Acid Glycerol   | Acetals (GF, Glycerol Formal and GFO MOM, Methoxy-methyl glycerol formal) | - Acetals improve up to 2 degrees of cold flow properties            |
| Esters                |                                                  |                                                                      |

**Conclusion**
Biodiesel is considered promising fuel to be utilized in the internal combustion engine. Problems associated with biodiesel like low-temperature properties and oxidation stability which depends on saturated fatty acid profile and unsaturated fatty acid profile of biodiesel can improve by blending of biodiesels and by adding cold flow improver additives. Both these methods are found to give good results. Cold flow improvers also provide adequate improvement in low-temperature flow properties of biodiesel.
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