ISSN: 0128-7680
Pertanika J. Sci. & Technol. **20 (1)**: 1 – 14 (2012)

Review Article

Factors Affecting the Cold Flow Behaviour of Biodiesel and Methods for Improvement – A Review

Odeigah Edith*, Rimfiel B. Janius and Robiah Yunus
[1]Department of Biological and Agricultural Engineering,
[2]Department of Chemical and Environmental Engineering,
Faculty of Engineering, Universiti Putra Malaysia,
43400 Serdang, Selangor, Malaysia
**E-mail: edith_odeigah@yahoo.com*

ABSTRACT

Biodiesel is an attractive renewable energy source, which is suitable as a substitute to the non-renewable petroleum diesel. However, it is plagued by its relatively bad cold flow behaviour. In this review, the factors affecting the cold flow of biodiesel, vis-à-vis the contradicting requirement of good cold flow and good ignition properties, are discussed. Fuel filter plugging, and crystallization of biodiesel are considered, together with the cold flow properties such as Pour Point (PP), Cloud Point (CP), Cold Filter Plugging Point (CFPP) and Low Temperature Filterability Test (LTFT). In addition, various methods used to improve the cold flow of biodiesel are also presented, with a special emphasis laid on the effects of these methods in reducing the Cloud Point. Strategies to improve cold flow, and yet maintaining the good ignition quality of biodiesel, are also proposed. As far as the cold flow of biodiesel is concerned, desirable attributes of its esters are short, unsaturated and branched carbon chains. However, these desirable attributes present opposing properties in terms of ignition quality and oxidation stability. This is because esters with short, unsaturated and branched carbon chains possess very good cold flow but poor ignition quality and oxidation stability. The target is therefore to produce biodiesel with good cold flow, sufficient ignition quality, and good oxidation stability. This target proves to be quite difficult and is a major problem in biodiesel research. New frontiers in this research might be the design of the new cold flow improvers that is similar to those used in the petroleum diesel but is tailored for biodiesel. Genetic modifications of the existing feedstock are also desirable but the food uses of this particular feedstock should always be taken into consideration.

Keywords: Biodiesel, cold flow properties, pour point, cloud point, cold filter plugging point and low temperature filterability test

ABBREVIATIONS

PP : Pour Point
Cp : Cloud Point
CFPP : Cold Filter Plugging Point
LTFT : Low Temperature Filterability Test
CI : Compression Ignition Engine

Received: 22 June 2010
Accepted: 8 Feb 2011
*Corresponding Author

WAI	:	Wax Appearance Index
DSC	:	Digital Scanning Calorimetry
ASTM	:	American Standard Testing Methods
TCO	:	Crystallization Onset Temperature
CFI	:	Cold Flow Improvers
EVA	:	Ethylene-co-Vinyl Acetate
WASA	:	Wax Anti Settling Agents
ULSD	:	Ultra Low Sulfur Diesel
MME	:	Madhuca Indica Biodiesel
E20	:	20% Ethanol blend with bidioesel

INTRODUCTION

Biodiesel consists of complex mixtures of esters obtained by the trans-esterification of triglycerides (fatty acids) from agricultural fats and oils with lower alcohol. Methanol is mostly employed for the trans-esterification because of its low cost; hence, methyl esters are mostly produced (de Oliveira *et al*., 2009; Joelianingsih *et al*., 2008; Ma & Hanna, 1999; Wang, 2007; Xu & Hanna, 2009). There are various types of biodiesel fuels, depending on the feedstock oil. In particular, biodiesel exhibits fuel properties that are similar to those of petroleum diesel and as such, it can be used in an unmodified diesel engine.

At 40°C, biodiesel exhibits viscosities ranging from 3.88mm^2/s to 5.3mm^2/s (Benjumea *et al*., 2009; de Oliveira *et al*., 2009; Sharma *et al*., 2008). This is much lower than that of the feedstock oil and close to that of petroleum diesel #2, which ranges from 1.9mm^2/s to 4.1mm^2/s, and is also an advantage over their feedstock oils (Demirbas, 2005). Biodiesel has densities between 0.860g/cm3 and 0.897g/cm^3 at 15°C which is higher than that of petroleum diesel (Bhale *et al*., 2009). This high density can be said to make up for their lower volumetric energy content. On the basis of ignition quality, biodiesel is said to be better than the petroleum diesel. The ignition quality of a diesel fuel is a measure of the relative ease by which the fuel will ignite in an internal combustion compression ignition engine. The ignition quality of diesel fuels is measured by their cetane number, i.e. a high cetane number indicates a good ignition quality and vice visa. Biodiesel exhibits higher cetane numbers than petroleum diesel and hence burns smoother in a diesel engine than petroleum diesel. This high cetane number is as a result of the presence of greater quantities of straight hydrocarbon chains in the esters than in petroleum diesel. More so, biodiesel has higher flash and fire points than the petroleum diesel. The flash point of a fuel is the lowest temperature at which the fuel can form an ignitable mixture with air and the fire point of the fuel is the lowest temperature at which the fuel will continue to burn even after the source of ignition has been removed. The fire point is usually slightly higher than the flash point. A higher flash and fire point indicates that biodiesel is less flammable than petroleum diesel; hence, biodiesel is safer to handle. In fact, biodiesel has better lubricant than the petroleum diesel, and this indicates that an engine running on biodiesel will last longer and less prone to wear out.

However, biodiesel exhibits worse oxidation stability than petroleum diesel and will deteriorate under prolonged storage due to oxidation in the presence of air. Furthermore, biodiesel exhibits worse cold flow behaviour as compared to its fossil cousin. This bad clod flow behaviour is otherwise known as the low temperature flow property which is a major property of biodiesel that hampers its usage as a neat fuel (B100), especially in temperate regions. Knothe *et al*. (2005) discusses at length the properties of biodiesel. The cold flow behaviour of biodiesel is determined by two major factors, namely:

1. The fatty acid composition of its constituent esters and
2. The presence of minor components such as monoglycerides and steryl glycosides.

This paper discusses at length the relation between the cold flow behaviour of biodiesel fuels and the fatty acid composition of its constituent esters. The effect of the minor components on the cold flow of biodiesel has been discussed in detail by Dunn (2009).

COMPRESSION IGNITION (C.I) ENGINE AND FUEL FILTER PLUGGING

In cold weather, diesel fuels tend to crystallize and become gel-like. The temperature at which fuel filter plugging occurs varies from fuel to fuel depending on the composition of the fuel. However, this temperature is higher for biodiesel than petroleum diesel, for example: palm oil biodiesel will start to crystallize at about 16°C and will form a gel at about 12°C. this makes biodiesel not favourable in cold weather.

The fuel injection pump and the fuel injectors of the compression ignition (CI) engine are precision equipment with very close tolerances. It is thus very important that clean fuel gets into the system because impurities may block the fuel injector and also cause wear within the engine. Engine wear reduces output torque and increases brake's specific fuel consumption of the engine. Meanwhile, large particles cause fuel filter plugging and reduce fuel supply to the injector and the combustion chamber, resulting in a loss of power and probable engine shut down. A plugged engine will have intermittent starting problem or may not start at all.

THE BASIC CONCEPT OF CRYSTALLIZATION AND GEL FORMATION

Gelling involves crystallization of the molecules of a liquid forming a continuous network of crystals within the bulk of the liquid. For crystallization to occur, the molecules of the liquid must generate sufficient thermodynamic force by strong intermolecular interaction. This thermodynamic force is generated when the temperature of the liquid is reduced to below its melting point.

Crystallization occurs in two major and interrelated steps known as nucleation and crystal growth. Nucleation is the first stage of crystallization and it occurs when the molecules of the liquid come together to form solid embryos called crystal lattices or crystallites. Crystal growth is subsequent to nucleation. It involves the growth of the crystal lattices formed. Meanwhile, the lattices grow by the nucleation of the layers of new lattices on the existing ones to form large crystals. This growth continues until a continuous network of crystals is formed (Gunstone *et al*., 2007).

In a homogenous mixture of many components with different melting points, crystallization is governed by the solubility of the components in the mixture. The low melting point components act as the solvent, while the high melting point components act as the solute (Marangoni & Narine, 2002). At any temperature below the melting point of the solute, crystallization will only occur if the solute is supersaturated in the solvent at that temperature. A solute is said to be supersaturated in a solvent when the solvent has dissolved more of the solute that it can hold at that particular temperature. Thus, super-saturation depends on:

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

In general, solubility decreases and super-saturation increases with the decrease in the temperature. In addition, super-saturation increases with the increase in the concentration of the solute in the solution. Thus, as temperature reduces and the concentration of the solute increases, the rate of crystallization will increase as well.

FACTORS AFFECTING THE COLD FLOW BEHAVIOUR OF BIODIESEL

The cold flow properties of biodiesel like every other of its fuel properties are influenced by the composition of its esters. Trans-esterification of triglycerides is a chemical process that does not involve any change in the inherent properties of the fatty acids present in the triglyceride, thus the composition of fatty acids in feedstock oils plays a vital role in determining the properties of the biodiesel.

Three types of fatty acids can be found in any oil or fat (Xu & Hanna, 2009), these are:

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

Biodiesel from various feedstock oils exhibit closely related properties; however, these properties vary with the varying compositions of the types of fatty acids that are present in the feedstock oil. Saturated fatty acids have no double bonds in their carbon chain; some examples of these are palmitic acid and stearic acid with 16 and 18 carbon atoms, respectively. Mono-unsaturated fatty acids have only one double bond in their carbon chain, such as palmitoleic acid and oleic acid which are also with 16 and 18 carbon atoms, respectively. Meanwhile, poly-unsaturated fatty acids have either two or three double bonds in their carbon chain, such as linoleic acid and linolenic acid each with 18 carbon atoms and two and three double bonds, respectively. Various studies on these fatty acids and the resulting esters show that saturated fatty acids result in esters with higher cetane number, lower NO_x emissions, higher oxidation stability and higher lubricity, whereas unsaturated fatty acids result in esters with better cold flow. Singh *et al*. (2009) reported a comprehensive fatty acid composition of various vegetable oils that had been used as biodiesel feedstock.

Meanwhile, saturated fatty acids, due to their high degree of saturation, have higher melting points and temperatures of crystallization and in cold temperature they will crystallize before the mono-unsaturated and poly-unsaturated fatty acids. The melting points of the commonly encountered fatty acids and their corresponding methyl esters are given in Table 1. Due to the high temperature of crystallization exhibited by the saturated fatty acids, biodiesel with high composition of saturated fatty acid esters exhibits worse cold flow and has higher cloud points indicating the crystallization of the esters of these saturated fatty acids.

Studies on the Differential Scanning Calorimetry (DSC) of palm oil biodiesel indicated that two crystallization peaks were observed, with the first peak corresponding to the crystallization of methyl palmitate and methyl stearate at the onset of crystallization and the second peak corresponding to the crystallization of methyl oleate (Foon *et al*., 2006; Narváez *et al*., 2008). Dunn (1999) reported a DSC cooling thermogram for soybean methyl esters, which showed split peaks between -30˚C to 10˚C, indicating a fusion event during the melting process as expected for the mixtures of saturated and unsaturated fatty esters. The high peak is due to the saturated fatty esters and the low peak is due to the unsaturated fatty esters. This explains the really poor cold flow exhibited by palm oil biodiesel which has a high composition of esters of palmitic and stearic acids (Dunn, 1999; Ramos *et al*., 2009) and the relatively good cold flow exhibited by soybean biodiesel which is richer in esters of oleic acid (Wang, 2007). Imahara *et al*. (2006) reported that saturated acid esters have a very significant effect on the cold flow of biodiesel; in particular, biodiesel with higher percentages of saturated fatty esters has higher cloud points.

TABLE 1
The melting points of fatty acids and their corresponding methyl esters

Fatty acid	Melting point (°C)	Methyl ester	Melting point (°C)
Lauric acid (C12;0)	44	Methyl laurate (C12;0)	5
Myristic acid (C14:0)	54	Methyl myristate (C14:0)	18.5
Palmitic acid (C16:0)	63	Methyl palmitate (C16:0)	30.5
Stearic acid (C18:0)	70	Methyl stearate (C18:0)	39.1
Oleic acid(C18:1)	16	Methyl oleate (C18:1)	–20
Linoleic acid (C18:2)	–5	Methyl linoleate (C18:2)	–35
Linolenic acid (C18:3)	–11	Methyl linolenate (C18:3)	–52

N.B: The first number before the colon in the parenthesis stands for the number of carbon atoms, while the second number stands for the number of double bonds in the molecule.
Adapted from Foon *et al*. (2006) & Gunstone (1996).

Long carbon chain fatty acids also have a negative effect on the cold flow of biodiesel. Long carbon chain fatty acids have a higher temperature of crystallization as compared to the shorter carbon chain fatty acids and a high composition of esters of these fatty acids will worsen the cold flow of the biodiesel. Ramos *et al*. (2009) explained that the poor cold flow exhibited by peanut oil biodiesel is due to the presence of lingoceric and behenic acids, which have 22 and 24 carbon atoms without any double bond.

The presence of branches in the carbon chain of fatty acids gives the fatty acid a structure, which requires an increase in the thermodynamic force required for crystallization, and thus, decreasing the temperature of crystallization of the fatty acid. This in turn has a positive impact on the cold flow of the resultant biodiesel. In fact, the increase in the branching of resultant fatty acids by trans-esterification with branched chain alcohols has been employed as a means of improving the cold flow of biodiesel (Wang, 2007).

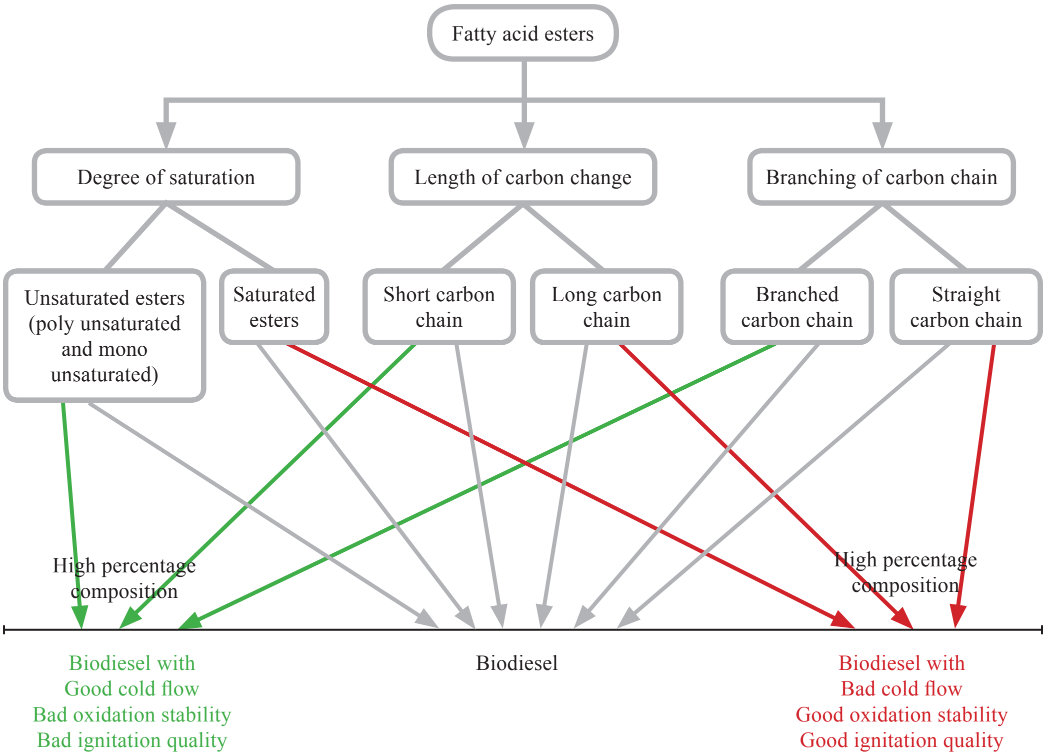
Meanwhile, the presence of carry-overs from the trans-esterification process has also been reported to increase the cloud point of the biodiesel, and thus, having a negative effect on the cold flow of the biodiesel (Fernando *et al*., 2007; Ma & Hanna, 1999b). These carry-overs are triglycerides, diglycerides and monglycerides. *Fig. 1* summarizes the effects of fatty esters on the cold flow of biodiesels. As indicated earlier on, the biodiesel with high percentage composition of unsaturated, branched and short chain fatty esters exhibits improved cold flow properties.

CHARACTERIZATION OF THE COLD FLOW OF BIODIESEL

Four parameters are usually used to characterize the cold flow of biodiesel, namely;

1. Pour point (PP)
2. Cloud point (CP)
3. Cold filter plugging point (CFPP), and
4. Low temperature filterability test (LTFT)

Meanwhile, pour points (PP) and cloud points (CP) have been widely used to estimate the behaviour of diesel fuels in cold weather, but these parameters cannot accurately predict the performance of the diesel fuels in the fuel system of compression ignition engines. According to



Green arrows indicates a higher composition of short, unsaturated and branched fatty acids ester which produces biodiesel with good cold flow but poor oxidation stability and poor ignition quality; the red arrows indicate a higher composition of the long, saturated and straight fatty esters which produce biodiesel with poor cold flow but good oxidation stability and good ignition quality. In between is a balanced in the attributes of the fatty esters.

Fig. 1: The effects of fatty esters compositions on the cold flow properties of biodiesel

the ASTM standard, the pour point (PP) is the "lowest temperature at which movement of the oil is observed", whereas the cloud point (CP) is the highest temperature at which crystals formed within the oil become visible (in form of cloudiness). However, the pour point (PP) approach is too optimistic because diesel fuels will exhibit fuel filter plugging problems at temperatures higher than their pour point. Moreover, since fuel filter plugging does not necessarily occur at the cloud point of the diesel fuel, the cloud point is really not sufficient to estimate the cold flow of biodiesel. However, the cloud point is a good parameter for quality control in the operation of diesel engines in low temperatures and the pour point is a good indicator of the behaviour of diesel fuels in wide storage and pipeline distribution (Gerpen *et al*., 2004).

The Cold Filter Plugging Point (CFPP) and the Low Temperature Filterability Test (LTFT) can better predict the operation of diesel fuels within the fuel system of compression ignition engines; these parameters estimate the filterability of diesel fuels in the fuel filter system at low temperatures. The LTFT reports the lowest temperature at which 180mL of a sample can pass through the filter in 60 seconds or less, while the CFPP reports the lowest temperature at which 20mL of sample can pass through the filter in 60 seconds or less. Although both the tests are identical, the LTFT is a better approach because it takes into account the rigorous conditions within the engine. In more specific, even though the LTFT involves a larger quantity of the sample, smaller filter wire mesh size and slower cooling rates, the CFPP is more user-friendly. LTFT is more accepted in North America but both are equally accepted in other parts of the world. The ASTM standard test methods for obtaining the four said parameters are given in Table 2.

CFPP and LTFT are proportional to CP; LTFT has been reported to have a 1:1 correlation with CP, while CFPP values are a bit lower than the LTFT values, i.e. about 3.3°C ± 2.1°C below LTFT (Dunn *et al*., 1996). Thus, a reduction in CP is translated into a significant reduction in CFPP and LTFT, and when working on improving the cold flow of biodiesel, a reduction in CP is more effective than a reduction in PP. Other parameters that are also indicative of the cold flow behaviours of biodiesel include the wax appearance index (WAI) and freezing point. The differential scanning calorimetry has been proved to be an effective, accurate, fast and easy method of obtaining the cloud points and pour points of biodiesel (Dunn, 1999; Foon *et al*., 2006; Narváez *et al*., 2008). The DSC crystallization onset temperature (Tco) is reported as the cloud point and the melting point temperature is reported as the pour point.

TABLE 2
Standard test methods

Parameters	Standard test methods
Cloud point	ASTM D-2500
Pour point	ASTM D-97
Cold filter plugging point	ASTM D-6371
Low temperature filterability test	ASTM D-4539

Adapted from ASTM (2003)

IMPROVING THE COLD FLOW OF BIODIESEL

Improving the cold flow of biodiesel has been proven to be quite a heavy task because in most cases, it has had adverse effects on other fuel properties of the biodiesel, especially ignition quality and oxidation stability. This is because the saturated esters, which give rise to bad cold flow of biodiesel, have very good ignition qualities and oxidation stability, and thus, removing the saturated esters will result in biodiesel having lower ignition quality and oxidation stability. Furthermore, the economic viability of the process is an important parameter as biodiesel is already more expensive than the petroleum diesel and any method which will result in a very high increase in the production cost of biodiesel may not be economically feasible. The following methods have been employed to improve the cold flow of biodiesel:

1. Blending with petroleum diesel
2. Trans-esterification with branched chain alcohol
3. Winterization
4. Use of chemical additives
5. Modification of fatty acid profiles of biodiesel

Blending with Petroleum Diesel

In the present times, 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 (Schnopf, 2006). A number of work, which has been done on blending biodiesel with petroleum diesel, show that 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.

However with increasing levels of biodiesel in the blend the cold flow of the resulting blend is worsen. It has been reported that to achieve the best result, a 20% by volume, biodiesel in diesel fuel #2 and 35% by volume, biodiesel in diesel fuel #1 is required (Dunn & Bagby, 1995). Diesel fuel #1 can accommodate a higher volume of biodiesel because it exhibits a better cold flow than diesel fuel #2 [National Research Council (U.S.). 1982]. Choo *et al*. (2006) were able to produce a patent on a palm-oil based biodiesel formulation with enhanced cold flow properties comprising a blend with not more than 40 percent volume of biodiesel in petroleum diesel blended with a cold flow improver.

Trans-esterification with Branched Chain Alcohol

Trans-esterification of fatty acids with branched chain alcohols, as opposed to the commonly used methanol, was proposed by Lee *et al*. (1995) 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 cloud point. Lee *et al*. (1995) reported that isopropyl soyate had a T_{co} 5.5°C less than that of propyl soyate, but that the use of highly branched alcohols resulted in lower yields and incomplete trans-esterification reaction. Wu *et al*. (1998) reported that isopropyl tallowate had a cloud point of 9°C, which was lower than that of methyl tallowate whose value was 15°C; similarly, isopropyl tallowate was reported to be more viscous than methyl tallowate, and this was probably due its higher molecular weight.

Kleinova *et al*. (2007) studied the effect of the branching on the CFPP of sunflower oil and castor oil biodiesel and reported that the increase in the branching of the fatty ester did not significantly reduce the CFPP in comparison to methyl ester. Moreover, the branched chain alcohols are more expensive than methanol and utilizing them will translate into an increased production cost. To mitigate this high production cost, as a result of trans-esterification with branched chain alcohols, Dunn (2009) studied the effects of blending the more expensive propyl and butyl esters with the cheaper methyl and ethyl esters on the cold flow of the resulting biodiesel. The study reported a 65% by volume requirement of isopropyl soyate in an admixture with methyl soyate to reduce the CP of methyl soyate by 5.1°C to -3.7°C. This, however, still has an adverse effect on the production cost of biodiesel. Yori *et al*. (2006) sought to increase the branching in the methyl ester structure without incurring any extra cost associated with the use of branched alcohol by isomerizing the methyl esters in the liquid phase over solid catalysts. Thus, to achieve the best result, the biodiesel was first fractionated into a saturated ester fraction and an unsaturated ester fraction, after which the unsaturated esters were isomerized at 150°C over SO_4-ZrO_2 catalyst and the saturated esters were isomerized at 200°C over H-Mordenite catalyst. However, the authors concluded that this method might not be favourable because the decrease in the cloud point was accompanied by a relative decrease in cetane number and viscosity.

Winterization

Winterization is a process which was employed in old times to improve the quality of oils and fats, especially salad oils, so that they do not become cloudy at low temperatures. It is a physical process which involves fractionating the oil to remove its high melting components. Extending this approach to biodiesel has been found to significantly reduce the cloud points and pour points of the biodiesel (Fernando *et al*., 2007). Biodiesel is cooled to a temperature between its cloud point and pour point and any crystals formed are fractionated; this process is repeated until the crystals are no longer formed 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.

A study on winterization of soybean biodiesel by Dunn *et al*. (1996) shows that the cloud point of soybean biodiesel can be reduced to -16°C by winterization. The percentage composition of methyl palmitate was reduced by a factor of three and thereby translating to an increased composition of oleate and linoleate. However, five to six steps were required, and the yield was low (about 25%) and there was a 20% loss of starting materials. From the study, it was suggested that in order to increase the yield and reduce the loss of starting materials, a pre-treatment of the biodiesel with cold flow is needed to improve additives before the winterization process and more advanced fractionating techniques for the removal of the crystals after the winterization process could be used.

Fractionation of the crystals formed during winterization with a solvent has been employed in a bid to increase the yield from the winterization process. This particular method is very effective but it increases the production cost (Knothe *et al*., 2005). Common solvents employed are hexane, isopropanol, and ethanol. Fractionation with hexane as a solvent presented a relatively interesting result as compared to the other solvents. There was appreciable decrease in the cloud point; however, the decrease in the percentage composition of saturated esters was relatively small. This decrease in the cloud point might have been due to the small quantities of hexane in the biodiesel, which were carried over from the fractionation process.

The reduction of the saturated fatty esters by winterization has been reported to have an adverse effect on the cetane number of the biodiesel because these saturated fatty esters have better ignition qualities and higher cetane numbers than the unsaturated fatty esters. Moreover, the various steps required to achieve a significant reduction in cloud point and the low yield translate into a higher production cost which impedes the widespread use of this particular method.

The Use of Chemical Additives

The use of cold flow improvers (CFI) is the conventional method employed to improve the cold flow of petroleum diesel. This method seems to be the most economically and technically favoured means of improving the cold flow of biodiesel. Cold flow improvers improve cold flow either by reducing the pour point (PP) of the diesel fuel or by reducing its cold filter plugging point (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 (Yu-hui & Ben-xian, 2006). The modes of action of these additives are very similar. 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. Furthermore, they are usually used with wax anti settling agents (WASA). 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 (Soni *et al*., 2008).

Dunn *et al*. (1996) studied 12 commercial CFI additives for diesel fuels on soybean biodiesel and reported that the additives effectively reduced the PP of neat soybean biodiesel by 3°C to 6°C; thereby, suggesting that the mechanism of nucleation and crystal growth in biodiesel is similar to that in petroleum diesel. However, these additives did not have any significant effect on the CP of both the neat biodiesel and its blend with petroleum diesel; this could be due to the fact that these additives started to take effect after the onset of crystal nucleation. In addition, these additives were also observed to be more effective at lower biodiesel blend ratios. Four additives on soybean biodiesel blends with petroleum diesel#1 were also not effective in reducing the cloud point of the fuel although they had a significant effect on the pour point (Chiu *et al*., 2004).

Studies carried out an investigation on the effect of ozonized vegetable oils and found no significant CP depression for soybean, sunflower, and rapeseed; however, the cloud point of the palm oil biodiesel was reduced by about 5°C to about 12°C, which is still on the high side (Soriano *et al*., 2006). The ozonized oil was prepared by passing a mixture of ozone and oxygen into the vegetable oil. Ozonized oil is a more effective pour point depressant when it is prepared from the same vegetable oil as the biodiesels. This is because there is a better interaction between ozonized oil and biodiesel from the same feedstock. It was also noted that the addition of ozonized oil greatly increased the flash point of the biodiesels.

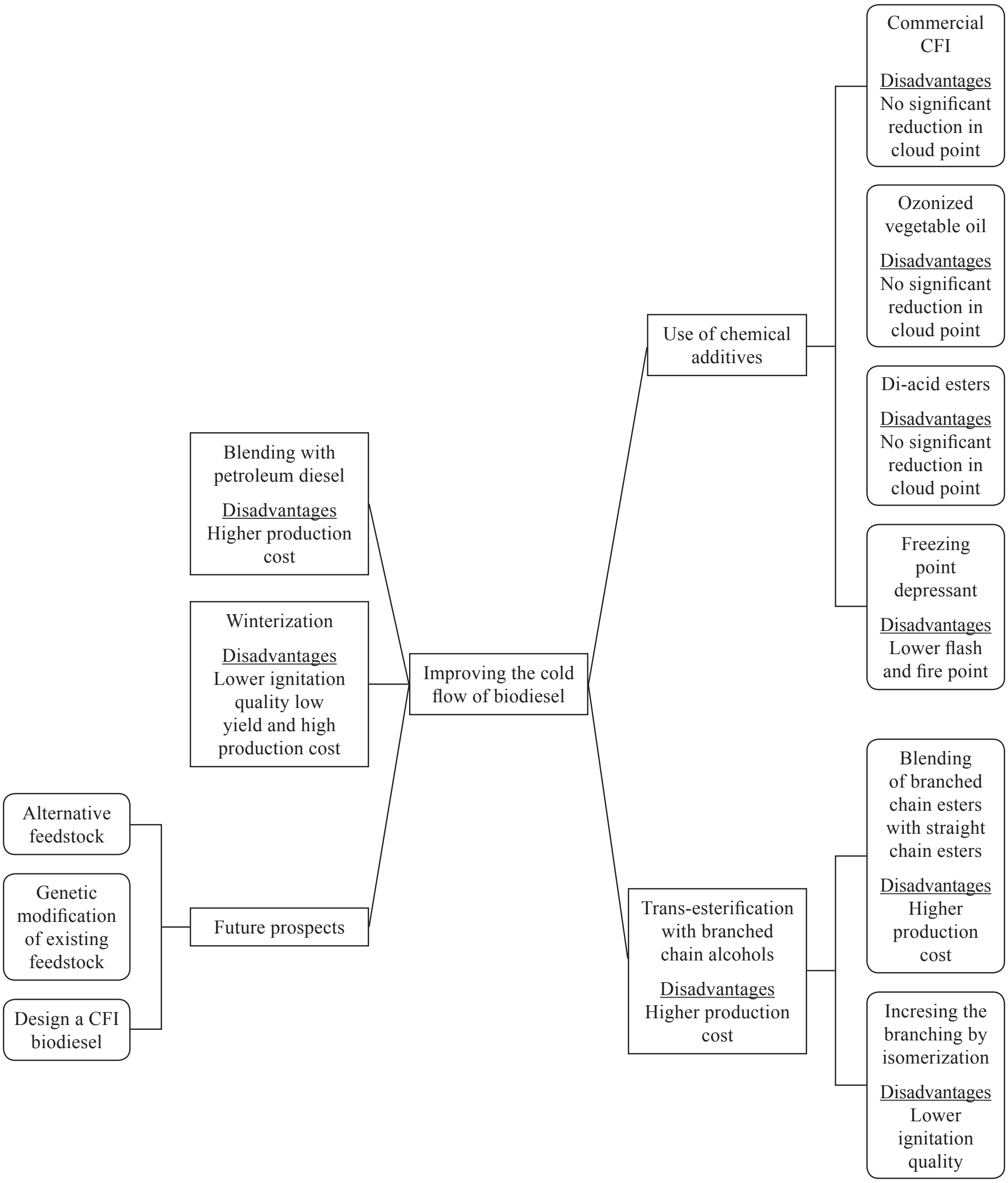
Estolides and ethylhexyl esters of castor oil and lesquerella oil were also studied for their effects on the cold flow of biodiesel and its blend with ultra low sulphur diesel fuels (ULSD) (Moser *et al*., 2008). From the study, it was observed that these additives did not have any significant effect on the CP and PP of soybean biodiesel, but all four were able to reduce the pour point of palm oil biodiesel by about 3°C. In particular, the estolides and ethylhexyl esters of castor oil and lesquerella oil were attractive to the authors because of their very good cold flow characteristics, oxidation stabilities and lubricities. Serdari *et al*. (1999) used diacid esters and Knothe *et al*. (2000) Synthesized diols of diacids; however, no significant reductions of CP and PP were reported in both studies.

Bhale *et al*. (2009) studied the effect of ethanol, Lubrizol 7671 and kerosene on the cold flow properties of neat madhuca indica biodiesel (MME); Lubrizol 7671 is a pour point depressant developed by an American company named Lubrizol. From this study, it was observed that the cloud point was reduced by 10°C with 20% ethanol and 13°C with 20% kerosene, but there was no effect on the cloud point when blended with Lubrizol. Meanwhile, ethanol and kerosene reduced the flash and fire point of MME, and hence, higher blends should be discouraged. The ethanol-blended biodiesel also showed low NO_x emissions and was in fact the lowest for the E20 blend.

Modification of the Fatty Acid Profiles of Biodiesel

More recently, Knothe (2009) proposed that modification of the fatty ester composition of biodiesel could improve its fuel properties, especially its cold flow properties. This modification could be by either genetic modification of the feedstock or the use of alternative feedstock. The production of biodiesels rich in short chain monounsaturated fatty acids, especially methyl oleate by genetic modifications of agricultural fats and oils, is highly desired (Krishna *et al*., 2007). However, these genetic modifications should take into account the fact that these fats and oils are utilized not only for fuel production but also for food purposes and thus, a balance should be reached between the two purposes. 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. Among other, a combination of 71% oleic acid and 21% lenoleic acid was suggested. For alternative feedstock, oleaginous algae and non-lipid sources like carbohydrates were suggested.

Further research into designing new chemical additives that would be effective with biodiesel should also be encouraged. 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. *Fig. 2* shows a summary of the various methods employed to improve the cold flow of biodiesel and their disadvantages.



This is a summary of all the methods that have been employed to improve the cold flow of biodiesel.

Fig. 2: The methods employed to improve the cold flow of biodiesel and their disadvantages

CONCLUSION

Biodiesel is a renewable alternative to petroleum diesel fuel; however, biodiesel crystallizes to form gel in cold weather, which causes fuel filter plugging in the compression ignition engine. Saturated, long and straight carbon chain esters have high melting points and when their composition in the biodiesel is high, crystallization tends to occur at a higher temperature. Reducing the composition of these saturated, long and straight carbon chain esters in the biodiesel will result in a better cold flow but will also cause a decrease in the ignition quality of the fuel of which the saturated fatty esters are responsible for. It is imperative that any improvement to the cold flow of the fuel does not sacrifice its good ignition quality. Towards this end, a desirable strategy would be to address the long and straight carbon chain issues and improve or retain the saturated carbon chain - the target being to significantly reduce the cloud point.

Blending with petroleum diesel reduces the impact of the high melting point and is a good immediate strategy, but it limits the amount of biodiesel in the blend. Meanwhile, winterization removes the saturated esters and reduces the ignition quality of the fuel. Trans-esterification with branched chain alcohol increases branched carbon chain and hence improves cold flow; however, it also increases the production cost of the fuel. So far, employing the existing chemical additives has only been able to reduce the pour point, not the cloud point. Further exploration into a more cost effective method of increasing the branching and the design of a new cold flow improver tailored for biodiesel is therefore desirable. Genetic modification of the existing feedstock should be parallel with the accompanying legalities of handling and processing of the products in order to avoid contamination of food stuff.

REFERENCES

ASTM Committee D-2 on Petroleum Products and Lubricants. (2003). *Analytical Chemistry, 24*(12), 2010-2013.

Benjumea, P., Agudelo, J., & Agudelo, A. (2009). Effect of altitude and palm oil biodiesel fuelling on the performance and combustion characteristics of a HSDI diesel engine. *Fuel*, *88*(4), 725–731.

Bhale, P. V., Deshpande, N. V., & Thombre, S. B. (2009). Improving the low temperature flow properties of biodiesel fuel. *Renewable Energy, 34*(3), 6.

Chiu, C. W., Schumacher, L. G., & Suppes, G. J. (2004). Impact of cold flow improvers on soybean biodiesel blend. *Biomass and Bioenergy*, *27*(5), 485–491.

Choo, Y. M., Ma, A. N., Basiron, Y., Yung, C. L., & Cheng, S. F. (2006). United States patent No. 20060288637.

de Oliveira, J. S., Leite, P. M., de Souza, L. B., Mello, V. M., Silva, E. C., & Rubim, J. C. (2009). Characteristics and composition of Jatropha gossypiifolia and Jatropha curcas L. oils and application for biodiesel production. *Biomass and Bioenergy*, *33*(3), 449–453.

Demirbas, A. (2005). Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science, 31*(5–6), 466–487.

Dunn, R. O. (2009a). Effects of minor components on cold flow properties and performance of biodiesel. *Progress in Energy and Combustion Science*, *35*(6), 481–489.

Dunn, R. O. (2009b). Cold-flow properties of soybean oil fatty acid monoalkyl ester admixtures†. *Energy & Fuels*, *23*(8), 4082–4091.

Dunn, R. (1999). Thermal analysis of alternative diesel fuels from vegetable oils. *Journal of the American Oil Chemists' Society*, *76*(1), 109–115.

Dunn, R., Shockley, M., & Bagby, M. (1996). Improving the low-temperature properties of alternative diesel fuels: Vegetable oil-derived methyl esters. *Journal of the American Oil Chemists' Society*, *73*(12), 1719–1728.

Dunn, R., & Bagby, M. (1995). Low-temperature properties of triglyceride-based diesel fuels: Transesterified methyl esters and petroleum middle distillate/ester blends. *Journal of the American Oil Chemists' Society, 72*(8), 895–904.

Fernando, S., Karra, P., Hernandez, R., & Jha, S. K. (2007). Effect of incompletely converted soybean oil on biodiesel quality. *Energy*, *32*(5), 844–851.

Foon, C. S., Liang, Y. C., Dian, N. L. H. M., May, C. Y., Hock, C. C., & Ngan, M. A. (2006). Crystallisation and melting behaviour of methyl esters of palm oil. *American Journal of Applied Sciences, 5*(3), 1859–1863.

Gunstone, F. D. (Ed.). (1996). *Fatty Acid and Lipid Chemistry.* Weinheim: Blackie Academic & Professional.

Gunstone, F. D., Harwood, J. L., & Dijkstra, A. J. (Ed.). (2007). *The lipid handbook* (3rd ed.). New York: Tailor & Francis.

Imahara, H., Minami, E., & Saka, S. (2006). Thermodynamic study on cloud point of biodiesel with its fatty acids composition. *Fuel*.

Joelianingsih, Maeda, H., Hagiwara, S., Nabetani, H., Sagara, Y., & Soerawidjaya, T. H. (2008). Biodiesel fuels from palm oil via the non-catalytic transesterification in a bubble column reactor at atmospheric pressure: A kinetic study. *Renewable Energy, 33*(7), 1629–1636.

Kleinová, A., Paligová, J., Vrbová, M., Mikulec, J., & Cvengros, J. (2007). Cold Flow Properties of Fatty Esters. *Process Safety and Environmental Protection, 85*(5), 390–395.

Knothe, G. (2009). Improving biodiesel fuel properties by modifying fatty ester composition. *Energy and Environmental Science*, *2*(7), 759–766.

Knothe, G., Dunn, R., Shockley, M., & Bagby, M. (2000). Synthesis and characterization of some long-chain diesters with branched or bulky moieties. *Journal of the American Oil Chemists' Society*, *77*(8), 865–871.

Knothe, G., Van Gerpen, J., & Krahl, J. (Ed.). (2005). *The Biodiesel Handbook*. AOCS Press.

Krishna, C. R., Thomassen, K., Brown, C., Butcher, T. A., Anjom, M., & Mahajan, D. (2007). Cold flow behaviour of biodiesels derived from biomass sources. *Industrial & Engineering Chemistry Research*, *46*(26), 8846–8851.

Lee, I., Johnson, L., & Hammond, E. (1995). Use of branched-chain esters to reduce the crystallization temperature of biodiesel. *Journal of the American Oil Chemists' Society*, *72*(10), 1155–1160.

Ma, F., & Hanna, M. A. (1999). Biodiesel production: A review. *Bioresource Technology, 70*(1), 1–15.

Marangoni, A. G., & Narine, S. S. (Ed.). (2002). *Physical properties of lipids*. New York: Marcel Dekker, Inc.

Moser, B. R., Cermak, S. C., & Isbell, T. A. (2008). Evaluation of castor and lesquerella oil derivatives as additives in biodiesel and ultralow sulfur diesel fuels. *Energy and Fuels*, *22,* 1349–1352.

Narváez, P. C., Rincón, S. M., Castañeda, L. Z., & Sánchez, F. J. (2008). Determination of some physical and transport properties of palm oil and of its methyl esters. *Latin American Applied Research, 38*, 1–6.

Ramos, M. J., Fernández, C. M., Casas, A., Rodríguez, L., & Pérez, Á. (2009*).* Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology*, *100*(1), 261–268.

Schnopf, R. (2006). *European union Biofuels policy and Agriculture: An Overview.*

Serdari, A., Lois, E., & Stournas, S. (1999). Impact of esters of mono- and dicarboxylic acids on diesel fuel quality. *Industrial & Engineering Chemistry Research*, *38*(9), 3543–3548.

Sharma, Y. C., Singh, B. & Upadhyay, S. N. (2008). Advancements in development and characterization of biodiesel: A review. *Fuel*, *87*(12), 2355–2373.

Singh, S. P. & Singh, D. (2009). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel; A review. *Renewable and Sustainable Energy reviews*. In Press, Corrected Proof.

Soni, H. P., Kiranbala, & Bharambe, D. P. (2008). Performance-Based Designing of Wax Crystal Growth Inhibitors*.* *Energy & Fuels*, *22*(6), 3930-3938.

Soriano, N. U., Migo, V. P. & Matsumura, M. (2006). Ozonized vegetable oil as pour point depressant for neat biodiesel. *Fuel, 85*(1), 25–31.

Van Gerpen, J., Shanks, B., Pruszko, R., Clements, D., & Knothe, G. (2004). *Biodiesel Analytical Methods.* Colorado: National Renewable Energy Laboratory.

Wang, P. S. (2007). *Isopropyl esters as solution to biodiesel challenges*. Unpublished Dissertation. University of Idaho: Idaho.

Wu, W. H., Foglia, T., Marmer, W., Dunn, R., Goering, C., & Briggs, T. (1998). Low-temperature property and engine performance evaluation of ethyl and isopropyl esters of tallow and grease*. Journal of the American Oil Chemists' Society, 75*(9), 1173-1178.

Xu, Y. X. & Hanna, M. A. (2009). Synthesis and characterisation of hazelnut oil-based biodiesel*. Industrial Crops and Products, 29*, 473-479.

Yori, J. C., D'Amato, M. A., Grau, J. M., Pieck, C. L., & Vera, C. R. (2006). Depression of the Cloud Point of Biodiesel by Reaction over Solid Acids. *Energy & Fuels*, *20*(6), 2721-2726.

Yu-hui, G. & Ben-xian, S. (2006). QSAR Research of the Activity of Span Surfactants as Wax Antisettling Additives for Diesel*. Energy & Fuels, 20*(4), 1579-1583.