



## Improving the Low-temperature Properties and Filterability of Biodiesel

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In the last few years, biodiesel has emerged as a promising alternative to the traditional petrodiesel. Two features have been limited its more widespread use: its relative poor low-temperature properties (LTP) and recently the excessive sedimentation above its cloud point (CP). In the first part of this work, factors affecting LTP along with the main aspects of the most commonly techniques performed to influence the fatty acid composition of the biodiesel are reviewed, as well as their consequences on the fuel properties. The use of additives to enhance LTP is also summarized. Attempts to identify the nature of the sediments formed in the biodiesel are reviewed in the second part of this work. Efforts to examine the influence of feedstock, temperature, biodiesel blend level and concentration of minor components on precipitate formation and filterability of biodiesel are also summarized, along with some techniques to improve filterability and perspectives about their feasible implementation.

### 1. Factors affecting the low-temperature properties of biodiesel

#### 1.1 Fatty acid profile

At low temperatures, higher-melting point components in biodiesel nucleate and grow to form solid crystals. This growth may continue until a continuous network is formed. CP is defined as the temperature at which the smallest observable cluster of crystals first occurs. Pour point (PP) refers to the lowest temperature at which a fuel flows or can be pumped. Once these temperatures are achieved, solid crystals may plug or restrict flow through filters causing start-up and operability problems (Dunn, 2009). The CP and PP of biodiesel are generally higher than those of petrodiesel and depend on its composition. The dominant factor influencing these properties is the number of double bonds in the alkyl chain of its fatty acid ester. The higher the saturation degree of a fatty acid is, the higher the melting point of the fatty acid and of its corresponding fatty acid esters are. Thus, saturated methyl palmitate and methyl stearate have melting points 48.5 and 57.7 °C higher than that of unsaturated methyl oleate (-20.7 °C). As a result, CP and PP of palm biodiesel are around 14 °C higher than those of soybean biodiesel (Dunn, 2009).

Another factor influencing LTP is the length of the alkyl chain of the fatty acid esters. The lower the length of the alkyl chain, the lower the melting point of the fatty acid and of its corresponding fatty acid esters are. Methyl octanoate, methyl decanoate, methyl laureate and methyl miristate have melting points 65.1, 40.9, 22.8 y 9.5 °C lower than that of methyl palmitate (27.8 °C) (Knothe, 2008).

## 2. Low-temperature properties improvements

### 2.1 Physical and chemical modification of biodiesel

Fractionation of biodiesel to remove its high melting components through cooling to a temperature below CP and above PP significantly reduces these properties. Traditional fractionation process includes two stages. The first one consists of selective nucleation and crystal growth under a strictly controlled cooling rate combined with gentle agitation. The second one consists of separation into solid and liquid fractions once crystals with a distribution of specific sizes are formed (Odeigah et al. 2012). Dunn et al. (1996) reported that CP of soybean biodiesel may be reduced to -16 °C by this approach. Fractionation with solvents reduces the loss of the original material. Perez et al. (2010) encountered that crystallization of peanut biodiesel using methanol reduced the CP from 20 °C to 0 °C and the PP from 15 to -6 with a biodiesel loss of 8.93 wt.%. Nevertheless, fractionation consumes large amounts of energy and result in unacceptably high reductions in yield (Smith et al. 2010).

Synthesis of palm oil polyol esters from fractionated palm biodiesel and trimethylolpropane was proved by Yunus et al. (2005) to improved LTP. Concentration of methyl palmitate in liquid fraction below 10% by weight ensured that the PP of the product was below -30 °C. Moser et al. (2006) demonstrated that  $\alpha$ -hydroxy ethers derived from isopropyl oleate previously epoxidised and a variety of alcohols in the presence of H<sub>2</sub>SO<sub>4</sub> had better CP and PP than those of methyl and isopropyl esters of soybean oil. However, a potential negative impact of alkoxylation onto viscosity is expected since hydroxyl groups are generally associated with higher viscosities (Smith et al. 2010).

### 2.2 Use of additives

Cold flow improvers used for petrodiesel, mainly copolymers of ethylene vinyl ester, have been employed for biodiesel. However, improvements of a few degrees in PP and no effect on CP were achieved (Smith et al. 2010). Thus, several novel fatty diesters with bulky moieties were synthesized by esterification of mono- or bifunctional fatty acids with mono- or bifunctional alcohols using *p*-toluene sulfonic acid as catalyst. These diesters had only minor effects (no more than 1°C), if any, on CP or PP (Knothe et al. 2000). Furthermore, treatment of biodiesel with small amounts of ozonized vegetable oil (1-1.5 wt.%) was also proved. This approach was effective in reducing the PP of biodiesel prepared from sunflower oil, soybean oil and rapeseed oil to -24, -12 and -30 °C, respectively, but CP remained unaffected. In the case of palm biodiesel, significant reduction was observed in CP but not in PP (Soriano et al. 2006).

### 2.3 Blending of different biodiesels

Some authors have been blend biodiesels in order to enhance the LTP of the most saturated biodiesels. Park et al. (2008) quantified cold filter plugging point (CFPP) and induction time of binary blends of palm biodiesel with rapeseed biodiesel and with soybean biodiesel. They founded that CFPP diminished below 0 °C if rapeseed and soybean biodiesel content was higher than 50 and 65 wt.%, respectively. These results were similar to those of Sarin et al. (2007), who blended palm biodiesel with *Jatropha curcas* biodiesel. They encountered that content of palm biodiesel in the blend did not have to be higher than 35 wt.% to CFPP be lower than 0 °C. However, blending at these proportions caused low oxidation stabilities, i.e. induction time of all the blends were lower than 6 h. Not only oxidation stability but also other properties like cetane number are reduced as unsaturation degree is increased. Due to this antagonistic effect, Pinzi et al. (2011c) performed multiple response optimization to set the most suitable fatty acid composition (expressed in terms of chain length and unsaturation degree) that simultaneously optimizes fuel properties and provides a biodiesel that fits the European standard EN 14214. Based on these results, blending of palm oil with a type of hybrid palm oil can be expected as a promising approach to improve the LTP of biodiesel in Colombia. This hybrid palm oil is obtained from a cultivar obtained by transferring of genes from the species *Elaeis oleifera* to the species *Elaeis guineensis* using backcrosses. The cultivar has higher fruit and oil production per unit of area, better tolerance to four deadly diseases, and slower rate of growth, and produce oil which has higher unsaturation degree (Bastidas et al. 2007). The approach of blending palm oil with hybrid palm oil requires the optimization of parameters that affect the production of fatty acid esters, i.e. molar ratio of alcohol to oil, amount of catalyst, reaction temperature, since main and interaction effects of these parameters are markedly dependent upon the fatty acid composition of feedstock, main effect of

catalyst concentration being the most sensitive to variations in fatty acid composition (Pinzi et al., 2011b). Chemical composition also influences rate of biodiesel conversion, so that oils with longer fatty-acid chains need half of the reaction time requested by oils comprising shorter fatty-acid chains to achieve maximum yield (Pinzi et al., 2011a).

### **3. Sedimentation of insolubles in biodiesel**

The sedimentation of some substances that appear to be soluble in pure biodiesel at temperatures well above its cloud point or standing at room temperature for extended periods has become an important concern in recent years. These substances come out of solution and form deposits on the bottom of biodiesel storage tanks, which affect the process equipment upstream of the tank farm. They also cause clogging of fuel filters in engine fuel delivery systems and form deposits on injectors, causing operability problems (Van Hoed et al. 2008).

Attempts to identify the nature of the sediments have been revealed that they can be a mixture of several compounds. Pfalzgraf et al. (2007) encountered a preponderance of saturated monoglycerides in the paste collected from clogged fuel filters of vehicles that used B20 or lower soybean biodiesel/petrodiesel blends during the 2,005-2,006 winter in Minnesota. Several researchers have been recently identified free sterol glucosides (FSG) in the insolubles isolated from biodiesel and linked the problem of excessive sedimentation to the presence of these compounds, even at very small concentrations. Sterol glucosides are glycosides derived from a phytosterol and glucose. In acylated form, the 6-position of the sugar is esterified with a long chain fatty acid. Under alkaline conditions, this ester bond is broken and acylated sterol glucosides are converted into their free form, which has high melting points and very low solubilities in biodiesel, so that it may drop out of solution precipitate. FSG aggregates form complexes with residual monoglycerides, exacerbating precipitation and settling of solid residues in biodiesel (Van Hoed et al. 2008).

Other compounds like free and esterified sterols (Tang et al 2008a), carboxylic acids, alcohols, aldehydes and ketones (McGinnis and Peyton, 2010) and soaps and glycerin (Lin et al. 2011) were also found in the sediments isolated from cottonseed biodiesel, soybean biodiesel after 12 weeks stored at 43 °C and canola biodiesel, respectively. Moreover, Tang et al. (2008b) reported that the precipitates formed in palm oil biodiesel were a mixture of monoglycerides whereas Bondioli et al. (2008) reported that those precipitates were a mixture of sterol glucosides. This discrepancy was attributed to the fact that the technologies used to produce both biodiesels (feedstock refining and transesterification) were different. In other words, the nature of the precipitates may be determined not only by the kind of feedstock but also by the technologies used to produce it.

### **4. Factors affecting insolubles formation and filterability of biodiesel**

#### **4.1 Temperature and blending with petrodiesel**

Blending with petrodiesel may increase the mass of insolubles isolated from biodiesel as a consequence of the lower polarity of petrodiesel. It is known that the precipitates can be formed mainly by polar compounds which aggregate due to their low solubility in biodiesel and their chemical affinity. When their solubility barrier is exceeded, they may sediment. As the level of biodiesel decreases in the blend, the bulk polarity of the solution decreases as well and the precipitates can be formed more easily and overcome the solubility barrier imposed by the bulk polarity of the solution more easily too. This effect is called "solvent effect" (McGinnis and Peyton, 2010).

Tang et al. (2008a) investigated this phenomenon and founded that at room temperature the mass of precipitates formed in blends of soybean biodiesel with ultra low sulfur diesel (ULSD) diminished as the proportion of biodiesel did. At -15 °C, it was showed the same tendency but the mass of precipitates is higher for any proportion than at room temperature. Interestingly, at 4 °C, "new precipitates" were formed in the blends and the mass of precipitates became higher for some blends than for pure biodiesel. The same was observed by Haupt et al. (2009), who encountered that filter blocking tendency according IP 387 for rapeseed-based biodiesel increased from 1.02 to 4.40 when blended with petrodiesel to form a B7 blend. Sedimentation can be accelerated by blending with petrodiesel as well. Tang et al. (2008a) found that the amount of precipitates formed in pure biodiesel refrigerated at 4 °C increased only after 24 h of refrigeration and further after 3 days whereas the mass of precipitates

formed in B20 blend increased within the first 24 h and remained constant thereafter. From these results, they suggested that there were two different mechanisms for the formation of precipitates in B20 and B100 blends. Moreover, at this temperature, the mass of insolubles retained in B70 blend was higher than that in B50 blend, while the filtration time after cold soaking (FTACS) for B70 blend was lower than for B50 blend. This was attributed to the smaller and more uniform precipitates formed from B70, maintaining the fluid flow properties.

#### **4.2 Minor components concentration**

Trace concentrations of minor components may compromise filterability of biodiesel. Pfalzgraf et al. (2007) investigated the effect of trace concentrations of monoglycerides, FSG, soaps and water on FTACS of soybean biodiesel and concluded that FSG were among the most influential components. 10,000 ppm of monoglycerides caused a FTACS of 97 s whereas similar values were produced by only 20 ppm of FSG. On the other hand, 40 ppm of soaps rose FTACS to 488 s and interaction with similar amounts of FSG originated filtration times after cold soaking as high as 1,400 s. Lin et al. (2011) evaluated the effect of saturated monoglycerides content on FTACS of canola biodiesel and founded that FTACS met the ASTM specification of maximum 360 s if concentration was below 26 wt.%. Above this value, not only FTACS increased markedly, but also repeatability diminished. This result was consistent with that reported by Chupka et al. (2011), who encountered that FTACS of soybean biodiesel spiked with monostearin increased from 93 to 291 s as monostearin concentration did from 0 to 0,075 wt.%, but above 0.1 wt.% FTACS reached to 720 s.

Interaction among minor components may be complex. Lin et al. (2011) founded that an increment in the concentration of monoglycerides at low concentrations of soaps and glycerin caused an increase in FTACS whereas an increment in the concentration of monoglycerides at high concentrations of soaps and glycerin improved the filterability. In a similar way, Pfalzgraf et al. (2007) predicted a decrease of FTACS of soybean biodiesel from 237 to 221 s as a result of incrementing the concentration of monoglycerides from 3,000 to 9,000 ppm.

Some researchers have made some efforts on developing empirical models which relate FTACS to minor components concentration; however those models either did not produce satisfactory results when more than one component were present at their maximum or minimum values (Pfalzgraf et al. 2007), or did not take into account FSG (Lin et al. 2011). Regarding to the mass of precipitates formed in biodiesel, to the best of our knowledge no model has been developed for relating this variable to minor components concentration. A model of this type would contribute to establish limits for the influential components, providing additional protection for prevention of filter plugging issues.

### **5. Biodiesel filterability improvements**

Several strategies to remove FSG have been developed during the last years. Room temperature and cold soak filtration, adsorbent treatment with commercial adsorbents, centrifuge and vacuum distillation were examined by Tang et al. (2010). They reported that the four formers could all significantly remove precipitation by reducing FSG content in biodiesel; however, they had no impact on the soluble FSG content in biodiesel (about 20 ppm) below which the FSG content could not be reduced further, except by vacuum distillation. Vacuum distillation was the most effective method for reducing the FSG content in biodiesel in their study; however, it resulted in a significant decrease in the natural antioxidant content, reducing the oxidative stability of the biodiesel. More recently, Sohling et al. (2011) patented a method for purifying biodiesel, wherein a crude biodiesel is reacted with an adsorbent which contains at least one smectite-silica gel mixed phase. The smectite-silica gel mixed phase has a specific surface area of more than 120 m<sup>2</sup>/g, a total pore volume of more than 0.35 ml/g and a silicon content, calculated as SiO<sub>2</sub>, of at least 60 wt.%. Using this invention it can be obtained a biodiesel with FSG levels well below 20 ppm. Another invention recently patented relates to a process which comprises a step contacting of the biodiesel with an enzyme being capable of acylating FSG in the presence of an acyl donor (Brask and Nielsen, 2012). The enzyme is claimed to be preferably a lipase. The FSG levels obtained using this invention also drop to levels below 20 ppm. An additional application patented by Kass et al. (2011) provides a method to remove precipitates in biodiesel that comprises subjecting the biodiesel to ultrasonic energy at levels between 2,000 and 7,000 Joules. The ultrasonic energy is pulsed for intervals of around forty seconds to prevent excessive heating of the biodiesel. It appears

that precipitates are dissociated as a consequence of the sonication and their structure permanently alters so that the precipitates can no longer form upon cooling. By this way, filtration time can be reduced by 19 % from the original condition.

In spite of the efficiency showed by any of the aforementioned approaches, the introduction of extra steps in the transesterification chain adds cost and complexity to the process. Thus, efforts on removing acylated sterol glucosides (ASG) during the refining of feedstock should be performed. It should place special emphasis on the enhancement of degumming and bleaching steps, which have been showed to diminish both FSG and ASG content. Verleyen et al (2002) reported an increase in the free sterol content without any reduction in esterified sterols after degumming of crude soybean oil. This increment might be explained by the fact that presence of mineral acid, moisture and temperature at which degumming is typically carried out are ideal for the cleavage of the glucosidic bond between glucose and sterols in sterol glucosides. For their part, Murui and Siew (1997) stated that around 90 % of FSG and 50 % of ASG were removed after bleaching of crude palm oil and showed that FSG were preferentially adsorbed onto bleaching earth whereas ASG seemed to undergo dehydration on the acid-activated bleaching earth to form non-polar sterols.

## 6. Conclusions

Poor low-temperature properties and sedimentation above the cloud point are issues of current concern to most biodiesel producers. Transesterification of oil mixtures is seemed to be the most promising approach to improve low-temperature properties since it is not required the addition of an extra step and it is feasible to find a set of conditions that simultaneously optimize the most critical properties of biodiesel. Hybrid palm oil obtained from a cultivar currently cultivated in Colombia and obtained by transferring of genes from the species *Elaeis oleifera* to the species *Elaeis guineensis* appears as the most likely candidate to be mixed with palm oil. Understanding of the factors that influence on the formation of precipitates in biodiesel are fundamental to control this phenomenon since it defines the chart to follow in not only the developing of strategies to limit the presence of the influential minor components but also the establishment of ideal storage and handling of biodiesel. Perhaps it's not possible to avoid the formation of precipitates, because of the low solubility of sterol glucosides in biodiesel and the high concentration of both free and acylated sterol glucosides in some crude oils, but perhaps it's possible to find a set of minor components concentration at which the fluid properties through the filter is maintained. Removing of free sterol glucosides from biodiesel has made great progress in the last years; however efforts on optimizing the removal of sterol glucosides during refining of feedstock should be performed in order to avoid the inclusion in the transesterification chain of an extra step that adds cost and complexity to the process.

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