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Evaluation and enhancement of cold flow properties of palm oil and its biodiesel

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ABSTRACT

Cold flow properties are the main issue to regular usage of Palm biodiesel as alternative fuel to diesel. The inferior cold flow property of biodiesel causes gum formation and crystallization of fuel particles which can be enhanced by winterization, blending and addition of cold flow improvers. The objective of this study is to improve cold flow properties of biodiesel obtained from palm oil. Blending and using of cold flow improver were adopted among various methods to enhance the cold flow properties. Results of the study show that with B20 blend of biodiesel using petroleum diesel and kerosene has significant improvement of the cold flow properties. Diesel improves CP and PP by 57.61% and 78.57% whereas kerosene improves CP and PP by 62.94% and 85.78% respectively for B20 blend. Ethanol had remarkable impact as 20% addition improves CP and PP by 60.48% and 63.96% respectively. The investigation concludes that PE80 is recommended as a fuel for engine operation under low temperature regions. For improving the cold flow properties, addition of cold flow improver is best method to attain the desired values of cold flow properties for biodiesel.

1. Introduction

With continuous rise in population, energy requirements have also increased which has resulted in the extensive use of the fossil fuel resources. Due to high rate of fossil fuels consumption, these are going to be exhausted. So need of hour is to look beyond conventional sources of fuel and develop alternate sources of fuel (Dwivedi and Sharma, 2013). One of the viable options to counter the excessive usage of petroleum diesel can be biodiesel, because it possesses comparable fuel properties as of diesel. Moreover, biodiesel is mainly derived from renewable feedstocks like edible, non-edible oils or animal fats (Verma and Sharma, 2015; Dwivedi and Sharma, 2014b). Biodiesel can be defined as the fatty acid alkyl esters of edible oils, non-edible oils, animal fats or waste oils. The most followed technique for producing biodiesel is the transesterification reaction, in which triglycerides are reacted with alcohol in presence of catalyst (acid or base) to obtain methyl esters and glycerol as a by-product (Giraldo et al., 2013; Verma et al., 2015b; Wang et al., 2014; Altaie et al., 2015). Cold flow properties of diesel fuel are generally determined by the following parameters viz. CP (cloud point), PP (pour point), CFPP (cold filter plugging point) and LTFT (low temperature filterability test). When biodiesel is subjected to lower temperatures, the solid wax crystal nuclei was easily formed. Further decrease in temperature causes the crystal nuclei to grow and become visible, and this temperature is termed as CP. When the temperature is further decreased, the crystal nuclei aggrandize and thus prevent free pouring of fluid, this temperature is termed as PP. Therefore CP and PP are the essential parameters, which defines the cold flow property. Continuous efforts are being done to enhance the cold flow properties of biodiesel. To overcome the disadvantages arising at the low temperature, certain techniques are used to lower the CP and PP (Verma et al., 2015a; Jurac and Zlatar, 2013; Cao et al., 2014b,a; Verma and Singh, 2014).

2. Literature review

The main problem associated with biodiesel is its poor cold flow property, which results in degradation in quality of fuel and it may not be suitable for engine application. Various authors have

Abbreviations: BXX, XX percentage of biodiesel in blend; CP, Cloud point; PP, Pour point; CFPP, Cold filter plugging point; LTFT, Low temperature filterability test; PMA, Polymethyl acrylate; MO, Methyl oleate; POME, Palm-oil methyl ester; EVAC, Ethylene vinyl acetate copolymer; JCB, Jatropha curcas biodiesel; WCB, Waste cooking biodiesel; RBE, Rapeseed butyl ester; RME, Rapeseed methyl ester; OECP, Olefin-ester copolymers; PO, Palm oil; PB, Palm Biodiesel; POXX, XX percentage of palm oil in blend; PKXX, XX percentage of palm oil in blend of palm oil and kerosene; PBDXX, XX percentage of biodiesel in blend of palm biodiesel and diesel; PBKXX, XX percentage of biodiesel in blend of palm biodiesel and kerosene; POEXX, XX shows the percentage of oil in palm oil–ethanol blend; PBEXX, XX shows the percentage of oil in palm biodiesel–ethanol blend.

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investigated the phenomena of cold flow properties of various biodiesels. Giraldo et al. (2013) studied the effect of various additives in range of 1%–10% on cold flow properties of palm biodiesel and observed that 5% addition of 2-butyl esters gave best results among other additives. Cold Filter Plugging Point decreased from 16 °C to 10 °C whereas PP reduced to 8 °C from 14 °C.

Upon addition of 0.04% of polymethyl acrylate (PMA), PP & CFPP of biodiesel were reduced by 8 and 6 °C respectively. CP, PP and CFPP on adding 0.04% PMA by weight to waste cooking biodiesel were observed to be −9, −19 and −15 °C respectively, which were lowest among other samples with different concentrations of additives in biodiesel. PMA changed the crystallization behaviour of the crystals by altering the shape of crystals and stopping the formation of larger crystals, which caused in the improvement of the biodiesel cold flow properties (Wang et al., 2014). Altaie et al. (2015) examined the cold flow properties of methyl oleate (MO) and palm-oil methyl ester blends (POME). It was observed that upon 50% addition of MO cloud point and cold filter plugging point, which were reduced to 70.38% and 91.69%, respectively. Cloud Point for POME was 18 °C which declined to 5.33 °C when MO was introduced by 50% proportion. Jurac and Zlatar (2013) developed linear correlations cold flow properties of product formed from mixtures of raw materials, and cold flow properties of the product formed from pure raw materials. CFPP for rapeseed and sunflower biodiesel was found to be −15 °C and −10 °C respectively. Cao et al. (2014b) varied the proportion of ethyl acetoacetate from 0% to 20% by volume in biodiesel produced from waste cooking oil. Both PP and CFPP decreased by 4 °C at 20 vol% ethyl acetoacetate. Reduction in CP was observed with rise in ethyl acetoacetate proportion in biodiesel. Freezing point of ethyl acetoacetate is substantially low (−45 °C) which can be primary reason in lowering down of CP of biodiesel. Ethyl acetoacetate tends to be in bulk liquid phase due to its low melting point. Cao et al. (2014a) identified that cloud point, cold filter plugging point and pour point of B20 decreased by 8 °C, 11 °C and 10 °C, respectively, after 0.04 wt% ethylene vinyl acetate copolymer (EVAC) treatment. Serrano et al. (2014) observed cold flow properties for biodiesel form various vegetable oils and found that CFPP was −4 °C, −14 °C, −6 °C and 13 °C, for soybean, rapeseed, high oleic soybean and palm biodiesel. Rasimoglu and Temur (2014) identified better cold flow properties when alcohol-to-oil ratio was kept between 3.15:1 and 4.15:1. Optimum CP, PP and CFPP of the biodiesel from corn oil were found to be −4, −10 and −12 °C. Nainwal et al. (2015) experimented with jatropha and waste cooking biodiesel for improvement in cold flow properties and observed that CP and PP (pour point) for Jatropha Curcas Biodiesel (JCB) for B20 blends with petro diesel were reported as 14.9 °C and 14 °C respectively, however, for Waste Cooking Biodiesel (WCB) it was 12 °C and 11.5 °C respectively. Kerosene K20 samples were showing best results as the reported CP and PP were −1 °C and −2.2 °C respectively for JCB. However in case of WCB blends with kerosene, the reported CP and PP for K20 blends are −10.5 °C and −12 °C respectively. Zuleta et al. (2012) found −7 °C CFPP for B100 castor biodiesel. Blend having 75% jatropha and 25% castor had CFPP of −12 °C. Lv et al. (2013) observed CP, CFPP and PP for Palm biodiesel to be 18, 16 and 13 °C. On using additive DEP:PGE:PA w in ratio of 3:1:1 or 2:2:1, the CFPP of palm biodiesel was decreased by 7 °C. Phung et al. (2014) experimented with autoxidation of triglycerides and concluded that CP for autoxidised biodiesel from soybean and canola was −13 °C for both cases. Makareviciene et al. (2015) examined the effect of butanol blending with methyl and butyl esters of rapeseed oil. The addition of butanol results in a gradual decrease in the cloud point. For blends containing 60%–100% rapeseed oil butyl esters, the CP ranges between −6 °C and −8 °C. Esters blends with butanol of concentration no less than 50% have a CFPP −17 °C that complies with the requirements established for E-Class diesel fuel. As the amount of butanol in a blend is increased further, the CFPP steadily decreases until it reaches 30–31 °C below zero. CFPP of RBE blends are lower than those of RME blends of the same concentration because the CFPP of pure RBE is lower than that of pure RME. Wang et al. (2015) produced biodiesel via enzymatic process with help of fusel alcohol. The cold filter plugging point (CFPP) of the fusel alcohol esters was −11 °C, 16 °C lower than the methyl esters of the Waste cooking oil. Ali et al. (2016) suggested that B30 blend of palm biodiesel with petroleum diesel is optimum as per fuel property requirements. Reduction of the pour point from 14 °C for unblended biodiesel to less than 0 °C at a 30% biodiesel blending ratio. Boshui et al. (2010) made use of different cold flow improvers to check effect on soybean biodiesel. On use of olefin-ester copolymers (OECP) pour point and cold filter plugging point of biodiesel reduced significantly. 0.03% addition of OECP, PP was found to be −9 °C whereas CFPP was −6 °C. Joshi et al. (2011) used Ethyl Levulinate to improve cold flow properties of cottonseed oil. CP was lowered down by 4–5 °C, whereas PP and CFPP had 3–4 °C and 3 °C reduction respectively at 20 vol% ethyl levulinate. Numerous reports have been available regarding the poor cold flow property of biodiesel is the main cause for the plugging of fuel lines and filters, it also creates the fuel starvation in engine, which ultimately leads to ignition problem. Methanol ethanol, kerosene, Mg additives, etc. are reported to be useful by different researchers to enhance the cold flow behaviour of biodiesels (Misra and Murthy, 2011; Dwivedi and Sharma, 2014a, 2015a). The poor cold flow property for Palm biodiesel can be improved by several methods like winterization, addition of cold flow improver and blending. This paper investigates the cold flow properties of palm oil and its biodiesel and effect of diesel, kerosene and ethanol as cold flow improver on cloud point and pour point.

3. Methodology for biodiesel production

Palm oil (PO) was purchased from local market. All chemicals like KOH, methanol, were of AR grade and 99% pure. Palm oil was filtered to remove all insoluble impurities from the oil followed by heating at 100 °C for 10 min to remove all the moisture. The fuel properties of Palm oil and its biodiesel after refining were determined as per standard methods and reported in Table 1.

Table 1 shows that a FFA content of the oils is as 0.7%. Owing to low FFA content (<1%), here we have adopted base catalyzed transesterification processes. *Palm* biodiesel (PB) yield of 97.9% was achieved with methanol/oil molar ratio (10.5:1) using KOH as catalyst (1.25% w/w) in duration of 90 min at the temperature of 60 °C.

3.1. Palm biodiesel

The biodiesel samples were tested for physicochemical properties as per ASTM D-6751 and Indian IS 15607 specification and the properties are given in Table 1 which shows that although the PB meets most of the specifications but according to Indian Climate it cannot be used in winter season. The PB samples were analysed for ME formation at a pre-determined interval of time by Gas Chromatograph (Netal make) equipped with a flame ionization detector and a capillary column for injecting the sample (Anon, 2003). The GC oven was kept at 230 °C (5 °C/min). Nitrogen was used as carrier gas. Quantitative analysis of % ME was done using European standard EN 14,103:2003 (DIN EN, 1410). The% ME yield was calculated using Eq. (1).

$$\%\text{ of ME} = \frac{\sum A - A_{EI}}{A_{EI}} X \frac{C_{EI} - V_{EI}}{m} \times 100 \quad (1)$$