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Cold flow and fuel properties of methyl oleate and palm-oil methyl ester blends

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HIGHLIGHTS

- Methyl oleate was effective cold-flow improver for palm-oil methyl ester.
- Cold-flow properties were decreased about 14 °C.
- Methyl oleate reduced the crystallization points of biodiesel.
- Strong correlations were found for cold-flow properties.
- Methyl oleate did not deteriorate fuel properties of biodiesel.

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ABSTRACT

Biodiesel is a renewable, alternative diesel fuel derived from various oils or fats through transesterification. Biodiesel usually consists of alkyl esters of the parent oil. Palm-oil methyl ester (PME) is a prominent biodiesel in Southeast Asian countries such as Malaysia and Indonesia, which have a surplus production of palm oil. However, given the substantial amount of saturated fatty acids in palm oil, its methyl ester has poor cold-flow characteristics. In the present study, the physicochemical properties of specified blends of technical-grade methyl oleate (MO) and PME, namely, PME80/MO20, PME70/MO30, PME60/MO40, and PME50/MO50 (vol/vol%) were studied. The aim was to determine the optimum blend and achieve better cold-flow properties than neat PME. Differential scanning calorimetry analysis showed that increasing the MO proportion until 50% (vol%, vol%) led to maximum improvements in cloud point and cold filter plugging point, which were reduced to 70.38% and 91.69%, respectively. Important fuel properties (i.e., cetane number (CN), kinematic viscosity, density, gross heating value, net heating value, flash point, oxidation stability, and acid value) were also examined. All fuel properties of PME–MO blends were observed within the specified permissible limits of biodiesel standard (ASTM D 6751).

1. Introduction

Environmental awareness and global energy crises are rising. Consequently, biodiesel as an alternative fuel is receiving increased attention because of its environmental benefits. Biodiesel is derived from edible or non-edible vegetable oils, animal fats, or waste cooking oils. Homogeneous-based catalyst is widely applied in oil and fat transesterification, whereas methanol is preferred among other short-chain alcohols [1]. Biodiesel is advantageous over petroleum diesel because it is safe to handle, non-toxic, biodegradable, contains no sulfur, and has higher combustion efficiency and cetane number (CN) [2,3]. Pure biodiesel can be directly used in modern unmodified engines. However, biodiesel is more commonly blended with diesel fuel such as B20. Blends with higher biodiesel content are allowed, ASTM D975, whereas ASTM D7467 is specific to diesel blends from B6 to B20. Biodiesel (B100) must meet ASTM D6751 specifications before it can be

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commercially used as a fuel or blend component. In the European Union, EN 14214 and EN 590 are the two relevant certification standards for neat biodiesel and petrodiesel up to B5, respectively [4].

Soybean, rapeseed, sunflower, palm oil, cottonseed, and peanut clearly dominate worldwide feedstock as sources of biodiesel production [5]. Although biodiesel has many advantages, it exhibits worse cold-flow behavior than petrodiesel. This behavior is known as the low temperature flow property, which is a major biodiesel property that prevents its utilization as a neat fuel in temperate regions [6]. When vehicles and fuel systems are exposed to low ambient temperatures, biodiesel is susceptible to some performance problems in engine. These problems particularly arise during engine start-up because of poor cold-flow properties resulting from the crystallization of high-melting saturated fatty acid methyl esters (FAMEs), which may lead to fuel line and injection pump blockage. The key flow properties of winter fuel can be specified by the following temperature measures: cloud point (CP), pour point (PP), and cold filter plugging point (CFPP). The lowest temperature at which crystals start to become visible (diameter exceeds 0.5 μm), forming a hazy or cloudy suspension, is defined as the CP. The lowest temperature at which fuel lose its fluidity and becomes semi-solid (crystal agglomeration is sufficiently extensive to prevent free pour) is defined as PP. CFPP can be described as the lowest temperature, where 20 mL of fuel still flows through a 45 μm wire mesh filter under 0.02 atm vacuum within 60 s [7].

Conversion to biodiesel does not significantly alter fatty acid (FA) profile based on the parent lipid. The cold-flow properties of a biodiesel fuel depend on the quantity of high melting point (MP) saturated long chain FAs present. MP increases with increased carbon chain length, and decreases with increased double bonds [8]. Saturated components are solid at room temperature with 10 or more carbons, whereas unsaturated components, which have double bonds, are liquid at room temperature. Moreover, *cis* configurations with or without –OH group presence in FA chain can significantly reduce MP. In general, biodiesel structure is a multicomponent. On one hand, biodiesel with large amounts of low MP components, such as sunflower (<73% linoleic acid, MP of −35 °C), has a low CP (1 °C). On the other hand, biodiesel made from feedstock with high MP component level, such as palm oil (<43% palmitic acid, MP of 30.5 °C), has a high CP (16 °C).

The major problem associated with palm oil biodiesel use is poor low temperature properties. Palm oil is the main biodiesel feedstock used in tropical regions and is considered the highest yielding oil crop that annually produces about 4–5 tons/ha. However, the poor cold-flow properties of palm oil are a critical issue that requires a solution because room temperatures lower than CP and PP can be easily reached in regions located at high altitudes [9].

Various methods have been investigated in order to predict the best quality of cold-flow properties of biodiesel. Among the most commonly used are the following: (i) blending with petroleum diesel [10–12], (ii) transesterification with branched chain alcohol [13,14], (iii) use of additives [15–18], (iv) winterization to reduce the amount of saturated fatty esters [19], and (v) blending of biodiesels from different sources [20–22], which has been widely utilized. Moreover, FAMEs from highly saturated raw material are usually blended with other FAMEs that have better cold-flow properties to obtain satisfactory performance at low temperature. Using more saturated FAMEs with cheaper FAMEs in the blend can reduce feedstock costs [23]. Moreover, some FAME properties can also be enhanced. Zuleta et al. [21] investigated CFPP and oxidation stability of palm oil biodiesel, castor, jatropha, and sacha-inchi blends. The properties of these blends depended on methyl ester constitutes. A blend with high oxidation stability exhibits poor CFPP. Sarin et al. [24] reported that the optimum mixture of jatropha methyl ester with palm oil methyl ester (PME) can enhance low temperature properties and oxidation stability. Jatropha methyl ester had a CFPP of 2 °C with oxidation stability of 3.23 h, whereas PME had a poor CFPP of about 12 °C but with good oxidation stability of about 14 h. The results showed that at least 60% of palm oil biodiesel needed to be blended with jatropha biodiesel to get a lower CFPP of about 0 °C, and to meet oxidation stability specification of 6 h per EN 14112 standard.

Wang et al. [25] mentioned that the ability to modify the fatty acids of feedstock, it is possible to have a "designer". A feedstock that is mostly monounsaturated (i.e., oleate) enhances balance the tradeoff between cold flow properties and oxidation stability. Polyunsaturated fatty acids improve cold flow behavior but decrease stability. Saturated feedstocks such as palm oil has better oxidation stability but tend to crystallize more rapidly in cold weather conditions.

This study aimed to evaluate the improvement of cold-flow properties of PME with the addition of MO. Effects of increasing the MO proportion on important fuel properties (i.e., CN, kinematic viscosity, density, gross heating value, net heating value, flash point, and oxidation stability) were studied. Differential scanning calorimetry (DSC) was used to investigate the low-temperature crystal morphology and crystallization behavior of PME and its blends.

2. Materials and methods

2.1. Materials

Refined palm oil was purchased from a local refinery (Golden Jomalina Food Industries Sdn. Bhd., Klang, Selangor, Malaysia). MO (70% technical grade) was purchased from Sigma–Aldrich (St. Louis, MO, USA). The chemicals and reagents with analytical purity grade were acquired from Merck Chemical (Darmstadt, Germany).

2.2. PME production

2.2.1. Alkali-catalyzed process

Refined palm oil was combined with methanol (25 v/v% of oil) and NaOH (1 *w*/*w*% of oil) in a jacket reactor at 60 °C using a circulating water bath. Stirring of the mixture was adjusted to 600 rpm using a motor stirrer for 2 h. The reacted material was shifted to a separation funnel and kept in equilibrium state for 12 h to complete the separation of two divergent phases. The upper layer of the two clearly separated phases consisted of methyl ester, whereas the lower layer consisted of glycerol and impurities (unused methanol, unreacted catalyst, soap derived during the reaction, some suspended ester, and partial glycerides).

2.2.2. Post-treatment process

The methyl ester was washed using distilled water to remove the residual impurities and glycerin. A total of 50% (v/v) distilled water at 55 °C was mixed with the ester and gently shook. This process was repeated several times until the pH became neutral. The biodiesel was then subjected to vacuum distillation using a rotary evaporator at a temperature of 65 °C for 1 h to remove residual methanol. The product moisture was absorbed using sodium sulfate, and the final purified product was collected after filtration via No. 42 Whatman filter paper. The methyl ester quantity produced was calculated according to the following equation:

$$\text{Yield of methyl esters } (\%) = \frac{\text{grams of methyl esters produced}}{\text{grams of oil used in reaction}} \times 100$$