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Effect of cold flow improvers on flow properties of soybean biodiesel

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ABSTRACT

The influence of three cold flow improvers, namely, olefin-ester copolymers (OECP), ethylene vinyl acetate copolymer (EACP) and polymethyl acrylate (PMA), on the low-temperature properties and viscosity–temperature characteristics of a soybean biodiesel was evaluated on a low-temperature flow tester and a rotatory rheometer. The crystal morphologies of the biodiesel at low temperatures were investigated through a polarizing microscope. The results indicated that the ability of the cold flow improvers differed in improving the cold flow properties of soybean biodiesel, of which OECP was the best candidate. OECP can significantly reduce pour point (PP) and cold filter plugging point (CFPP) of biodiesel and retard viscosity increase of biodiesel at low temperatures when incorporated into biodiesel at the additive contents of 0.03%. On the other hand, OECP functioned by inhibiting the wax crystals from growing to a larger size and provided a barrier to crystal agglomeration at low temperatures, thus improving the cold flow properties of soybean biodiesel.

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1. Introduction

In the last decades, the awareness of energetic and environmental problems encouraged many researchers to explore the possibility of using alternative fuels instead of petroleum and its derivatives. Biodiesel, derived from renewable vegetable oils or animal fats with a process of transesterification and commonly referred to as fatty acid methyl esters (FAME), has proven itself as an prominent candidate for petroleum diesel fuel. Since the beginning of the 1990s, a considerable interest has been taken in developing biodiesel [1–5]. Virtually, biodiesel is technically competitive with conventional petroleum diesel fuel and offers a number of advantages over petroleum fuels, such as enhanced biodegradability, reduced toxicity, lower emissions and increased lubricity [6]. Although the above attributes of biodiesel have drawn attention to this renewable resource as a substitute of petroleum fuel, there exist some significant drawbacks that have limited its application. One of the major problems associated with the use of biodiesel as the diet of diesel engines is poor low-temperature flow property. It has been found that crystallization or thickening of biodiesel at low temperatures causes fuel starvation and operability problems as solidified materials clog fuel lines and filters, mainly due to its high amount of saturated FAME components [7,8]. In recent years, several approaches to the low-temperature problems of biodiesel have been investigated including blending with conventional diesel fuels, winterization, additives, branched-chain esters, amongst which treatment with chemical additives seems to be the most convenient and economical, and thereby the most attractive [9–13]. Although some additives have so far been reported to be effective in improving the cold flow property of biodiesel [14–16], improvement of the low-temperature flow characteristics of biodiesel by the addition of additives still

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Table 1 – Typical specifications for the cold flow improvers.

Item	OECP	EACP	PMA
Appearances	Light yellow viscous	Brownish yellow oily	Light yellow viscous
Density (20 °C, $g\,cm^{-3}$)	0.886	0.853	0.878
Freezing point (°C)	−5	−7	−3
Kinematic viscosity (100 °C, $mm^2\,s^{-1}$)	18.64	15.58	17.45

remains a challenge and needs further investigation. The present work deals with the influence of some polymeric cold flow improvers on the cold flow properties of soybean-based biodiesel.

2. Materials and methods

2.1. *Soybean oil*

As a biodiesel origin, the soybean oil used for the production of the FAME in the present study was a bland, greenish-yellow, bright and clear oily liquid obtained from Chongqing Grain and Oil Corporation, China. It has been well processed (hydration- and phosphoric acid-degummed, caustic-neutralized, water-washed, bleached and deodorized) to remove undesirable substances such as free fatty acids, phosphatides, color bodies, sterols, ketones, and peroxides, with the appropriate color for cooking and baking applications. Chromatographic analysis has shown that the major unsaturated fatty acids in the soybean oil are 6.9% alpha-linolenic acid (C-18:3), 55.4% linoleic acid (C-18:2), and 23.4% oleic acid (C-18:1). The soybean oil also contains the saturated fatty acids of 3.7% stearic acid and 10.6% palmitic acid.

2.2. *Cold flow improvers*

Three commercial diesel fuel cold flow improvers, namely, HS-J015, KT1103 and XFT122, were selected for testing. Virtually, HS-J015 is chemically a mixture of olefin-ester copolymers (OECP) provided by Huashen Hi-Tech Co. Ltd., Xi'an, China. KT1103 is an ethylene vinyl acetate copolymer (EACP) provided by Kangtai Petrochemicals Co. Ltd., Shenyang, China, while XFT122 is polymethyl acrylate (PMA) obtained from Xiefeng Chemicals Co. Ltd., Nanjing, China. Shown in Table 1 are typical specifications for the three cold flow improvers. Prior to the testing, appropriate amount of the cold flow improvers was incorporated into soybean biodiesel in the mass percentages of 0.00%, 0.01%, 0.03% and 0.05%, respectively. The formulated biodiesels were thoroughly mixed under 60 °C and were thereafter ready for testing.

2.3. *Preparation of soybean biodiesel*

Soybean biodiesel (SME) was prepared by reacting 700 g of soybean oil, 151 g CH_3OH and 7 g NaOH. The reaction was carried out for 100 min under reflux at 60–65 °C with agitation. After reaction, the reaction mixture was allowed to stand overnight and the methyl ester layer was separated from the glycerol layer using a separatory funnel. Residual amount of glycerol in the crude methyl ester was removed by centrifugation. The methyl ester was purified by distilling-off the unreacted methanol under atmospheric pressure, washing several times with water, centrifugation and drying with anhydrous Na_2SO_4.

2.4. *Pour point and cold filter plugging point measurements*

Pour point (PP) and cold filter plugging point (CFPP) are important indices related to low-temperature operability of diesel fuels. The pour point is the temperature at which a fuel can no longer be poured due to gel formation, while the cold filter plugging point is the temperature at which a fuel jams the filter due to the formation of agglomerates of crystals. In the present test, PP and CFPP of the formulated soybean biodiesels were measured on a low-temperature flow tester following the SH/T0248 procedures. (SH/T0248 is a Chinese method for determining PP and CFPP. Determinations of PP and CFPP by this method well correspond to ASTM D-97 and EN 116, respectively).

2.5. *Viscosity measurements*

Diesel fuel viscosity not only affects atomization and density, but also influences the cold flow property. In the present investigation, dynamic viscosities of biodiesels at different temperatures but the same shear rate were measured on a VIARMES 95270 rotary rheometer (Sanchez Technologies, France). Duplicate measurements were made for each sample and the results were averaged.

2.6. *Crystal morphology observation*

Crystal morphologies of soybean biodiesel at low temperatures were observed using a polarizing microscope modeled DMLP (Leica, Germany). The microscope is equipped with a cooling system and, prior to observation, biodiesel samples were progressively cooled with liquid nitrogen from room temperature at the rate of 2 °C per minute. When biodiesel began to gel at certain temperatures, the cooling rate was slowed down and carefully controlled at 1 °C per minute so as to ensure plenary growth of wax crystals.

3. Results and discussion

3.1. *Effect of additives on cold flow properties*

The impacts of three cold flow improvers on the pour point and cold filter plugging point of soybean biodiesels are listed in Table 2.

From Table 2 it can be seen that the effects of OECP, EACP and PMA on the cold flow properties of soybean biodiesel were different, of which OECP was the most effective. With 8 °C decreases in the pour point and 6 °C decreases in the cold filter plugging point, OECP was very efficient in decreasing both PP and CFPP of soybean biodiesel at the additive content of 0.03%,

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