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Effect of poly-alpha-olefin pour point depressant on cold flow properties of waste cooking oil biodiesel blends

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HIGHLIGHTS

- PAO is an effective pour point depressant for waste cooking oil biodiesel blends.
- PAO could effective improve the low-temperature viscosity of biodiesel blends.
- PAO modified the crystallization behavior of biodiesel blends.
- B20 treated with 400 ppm PAO exhibited the best depression on cold flow properties.
- Other fuel properties of formulated B20 were determined and satisfied ASTM D7467.

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ABSTRACT

Improving the flow ability at a low temperature is vital for the utilization and popularization of biodiesel. The cold flow properties of waste cooking oil biodiesel–0# diesel blends with poly-alpha-olefin (PAO) pour point depressants were studied. Here results showed that B20 (20 vol.% biodiesel-80 vol.% diesel) treated with 400 ppm PAO exhibited the best depression in cloud point, cold filter plugging point and pour point by 8 °C, 9 °C and 7 °C, respectively. The other fuel properties of B20 were also determined and compared with the limits indicated in the ASTM D7467 standard. Viscosity–temperature curves, polarized optical microscopy, low-temperature X-ray diffraction, and differential scanning calorimetry were used to explore the performance mechanism of PAO in biodiesel blends; and results presented that PAO could effectively lower the low-temperature viscosity, delay the aggregation of wax crystals and modify their crystallization behavior by transforming the shape of crystals and depressing the formation of large wax crystals.

1. Introduction

Biodiesel, one of the promising biofuels, is a mixture of fatty acid esters derived from the transesterification of animal fats or vegetable oils with short alcohols [1,2]. It is considered as the best alternative for diesel fuels in diesel engines because it has similar physicochemical properties as petro-diesel [3]. The advantages and disadvantages of biodiesel are quite well documented [4]. First, biodiesel is renewable, possesses extensive raw material sources and has the potential to reduce the dependency on petro-diesel [5,6]. Second, biodiesel productions can ease the high consumption of diesel transportation and boost the local economies by providing employment. Furthermore, biodiesel is nontoxic, nonflammable, non-explosive, biodegradable and environmentally friendly compared with conventional diesel [7,8]. In fact, the oxygenated compositions in biodiesel not only ensure efficient combustion, but also produce less harmful pollutants and gases [3,9]. However, a critical inherent problem that currently limits the utilization and popularization of biodiesel is its relatively poor cold flow properties [4,10,11]. At a low temperature, the saturated fatty acid methyl esters with high melting point in biodiesel crystallize easily and cause filter plugging, which is one of the main reasons for the poor low-temperature performance of biodiesel [10,11].

To the best of our knowledge, winterization [12,13], modifying structures [14,15], blending with petro-diesel [16,17], and adding additives [4,18,19] are the major methods to mitigate the poor cold flow problem of biodiesel. Blending biodiesel with petro-diesel and

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adding pour point depressants have received much attention from many researchers and have been reported in some literatures [16–19]. Nevertheless, almost all improvements on the cold flow properties of biodiesel are conducted by using only one of these two methods; each of them alone cannot always yield satisfactory results [4,16–18]. In order to actualize an efficient improvement, research on low-temperature behaviors of biodiesel–diesel blends treated with cold flow improvers must be enriched, particularly in the performance mechanism of biodiesel blends.

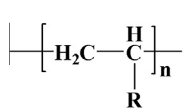
Poly-alpha-olefin (PAO) pour point depressant is a sticky liquid polymer primarily derived from the polymerization of alpha-olefin at certain temperatures, pressures and viscosity modifier in the presence of catalysts. It has been proven to be an effective cold flow improver, which is used primarily in lubricating oil [20–22]. In our previous investigation [20], PAO was studied as a pour point depressant in pure biodiesel fuel; the cold flow properties of treated biodiesel obviously decreased. However, a paucity of technical data exists in other published studies that clarify the effect of PAO on biodiesel-diesel blends consisting of waste cooking oil biodiesel and petro-diesel. In addition, the performance mechanism has not yet been sufficiently studied. In this regard, a systematic investigation of biodiesel–diesel blends treated and untreated with PAO pour point depressant is necessary. The results of the present investigation are expected to be beneficial for the utilization of traditional cold flow improvers and could facilitate the further development in biodiesel and its blends.

In China, approximately 4.5 million tons of waste cooking oil (WCO) is generated and used to produce biodiesel annually [8]. Therefore, WCO is considered as a promising feedstock for biodiesel in China because of its wide sources and inexpensive benefits [23,24]. In this study, biodiesel from waste cooking oil (BWCO) was prepared through an alkali-catalyzed transesterification reaction. The effects of PAO pour point depressant (T803D) on the cloud point (CP), cold filter plugging point (CFPP), and pour point (PP) waste cooking oil biodiesel–0# diesel blends were evaluated. Other properties, such as acid value (AV), kinematic viscosity (υ), oxidation stability (OS), and flash point (FP), were also examined and compared with those in the ASTM D7467 standard. Furthermore, viscosity–temperature curves, low-temperature X-ray diffraction (XRD), polarized optical microscopy (POM), and differential scanning calorimetry (DSC) were used to explore the performance mechanism of PAO in biodiesel blends.

2. Experimental

2.1. Materials

Songjiang 0# diesel was obtained from Shanghai Songjiang Gas Station, China. Refined WCO with an acid value of 0.98 mg KOH/g was supplied by Shanghai Zhongqi Environment Technology Co., Ltd., China. The PAO pour point depressant (T803D) was supplied by Jinzhou Xinxing Petroleum Additive Co., Ltd., Liaoning, China. The structure of PAO is shown below



where R is the mixture of C7–C20 long-chain alkyl.

The typical specifications of the pour point depressant are characterized and listed in Table 1.

Table 1
The typical specifications of the PAO pour point depressant in this study.

Pour point depressant	Appearance	Freezing point (°C)	Density (20 °C, g/cm^3)	Kinematic viscosity (100 °C, mm^2/s)	Flash point (°C)
PAO	Light yellow viscous	−31	0.932	25.37	⩾120

2.2. Biodiesel production

BWCO was produced with a relatively high yield (⩾97 wt.% with respect to oil) through the transesterification of WCO and methanol with 0.8% sodium hydroxide (w/w% oil) as the catalyst. The reaction was carried out at a 7:1 M ratio of methanol/oil at 65 °C for 120 min in a three necked flask equipped with a reflux condenser and a mechanical stirrer. After the fruition of the reaction, the reaction mixtures allowed to stand for 6 h in a separation funnel to separate glycerol from biodiesel. Residual glycerol and methanol in crude biodiesel were eliminated via centrifugation and rotary evaporation at 70 °C. Subsequently, the resulting biodiesel was washed with hot deionized water until the water became clear and finally dried with anhydrous calcium sulfate to obtain purified biodiesel.

2.3. Gas chromatography–mass spectrometry (GC–MS) analysis

Qualitative and quantitative analyses of the prepared biodiesel were conducted via GC–MS (Shimadzu QP 2010/Plus). An FID detector and an HP-Innowax quartz capillary column, RXi-5Sil MS (30 m × 0.25 mm × 0.25 μm), were used. The capillary column temperature was initially increased by 10 °C/min from 50 °C to 140 °C, followed by 5 °C/min from 140 °C to 170 °C and then 2 °C/min from 170 °C to 250 °C. Helium (99.9%) was utilized as the carrier gas at gas flow rates of 1.0 mL/min. The interface and ion source temperatures were 200 °C, and the injection temperature and volume were set to 270 °C and 1.0 μL, respectively.

2.4. Preparation of biodiesel/diesel blends

PAO was doped with the biodiesel blends (B0, B20, B40, B60, B80, and B100) at 0, 200, 400, 600, and 800 ppm by weight. The formulated biodiesel blends were stirred at a maintained speed of 200 rpm and temperature of 50 °C for 0.5 h to ensure the miscibility of the blend.

2.5. Determination of cold flow properties

Cold flow behavior is an essential property of biodiesel/diesel bends, particularly when used at a low temperature [25,26]; it is always analyzed based on CP, CFPP and PP [16,20]. The CP of a fuel is defined as a highest temperature at which a cloudy wax crystal appeared. The CFPP of a fuel is the lowest temperature where a fuel could filter through the standardized wire mesh filter within a specified time limit. PP refers to the highest temperature where the sample oils lose its fluidity [16]. The CP, CFPP, and PP of biodiesel/diesel blends were determined according to the specifications of ASTM D2500 [27], ASTM D6371 [28], and ASTM D97 [29], respectively.

2.6. Determination of other fuel properties

Other fuel properties, such as AV, FP, OS, υ and density, are also the critical indicators of biodiesel blends. Those properties of fuel