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Ethylene vinyl acetate copolymer: A bio-based cold flow improver for waste cooking oil derived biodiesel blends

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HIGHLIGHTS

- EVAC is an effective bio-based CFI for waste cooking oil derived biodiesel blends.
- The CP, CFPP and PP of biodiesel blends decreased with adding EVAC at 0.04 wt.%.
- The impacts of EVAC on other important fuel properties of B20 were also determined.
- Every formulated sample for B20 satisfied the ASTM D6751.

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ABSTRACT

This study was conducted to determine the cold flow properties of biodiesel–diesel blends (waste cooking oil derived biodiesel blended with 0# diesel) with ethylene vinyl acetate copolymer (EVAC) as the cold flow improver. The cloud point, cold filter plugging point and pour point of B20 (20 vol.% biodiesel + 80 vol.% 0# diesel) decreased by 8 °C, 11 °C and 10 °C, respectively, after 0.04 wt.% EVAC treatment. The impacts of EVAC on the kinematic viscosity, total glycerol, oxidation stability, acid value and flash point of B20 were also determined. The B20 samples treated with EVAC satisfied ASTM D6751. The crystallization behavior of the blend was investigated via differential scanning calorimetry. The crystallization rate and crystal content of B20 decreased. EVAC is therefore an effective bio-based cold flow improver for biodiesel blends.

1. Introduction

Biodiesel can be produced from animal fat or vegetable oils and is a good fuel alternative to diesel. Biodiesel development has attracted considerable interest because of its environmental benefits [1–3].

Biodiesel exhibits poor cold flow properties, which is a major disadvantage compared with petro-diesel [4–8]. Biodiesels generally crystallize at higher temperatures than petro-diesel. The crystals clog filters and fuel lines during cold weather, thereby impairing engine performance [5].

Several approaches, such as adding cold flow improvers (CFIs) [4,5,9–13], blending with petro-diesel [14–16], winterization [17–19], and branched-chain esters [20], have been developed to address the problem of crystallization. The addition of CFI is feasible, but the quantities of biodiesel CFIs are insufficient, and its effect does not meet the demand. The use of biodiesel–diesel blends added with CFIs can remarkably improve the low-temperature performance of such fuels. Although studies [9,21–23] have investigated the behavior of biodiesel–diesel blends at low temperatures, further studies on biodiesel–diesel blends with CFIs are still needed.

Ethylene vinyl acetate copolymer (EVAC) is a CFI typically used in petro-diesels. EVAC is primarily bio-based because it is derived from ethylene and vinyl acetate [24–26]. Ethylene can be produced via ethanol dehydration, and ethanol is obtained from sugar fermentation. Vinyl acetate is derived from ethylene and acetic acid, which can be obtained from biomass fermentation. Some scholars have reported on the effects of adding EVAC on the cold flow properties of various biodiesel/diesel fuel blends [11,12]. However, there is a paucity of technical data in the literature explicitly showing the effects of EVAC on the cold flow properties of waste cooking oil derived biodiesel blends.

Waste cooking oil has been used in the past several years as a substitute edible oil for biodiesel production because of its

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environmental benefits and low price [27–32]. Biodiesel was produced from waste cooking oil in the present study, and the effects of EVAC on the cold flow properties of the biodiesel blends were determined. Fuel properties, such as kinematic viscosity (v), total glycerol (TG), oxidation stability (OS), acid value (AV), and flash point (FP), were also determined. The crystallization behaviors of the formulated biodiesel blends were also investigated via differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

EVAC was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). Waste cooking oil was bought from Shanghai Zhongming Chemical Co. Ltd. (Shanghai). Hejiawan 0# diesel was bought from a Hejiawan gas station (Shanghai). Methanol (CH_3OH) and sodium hydroxide (NaOH) were purchased from Aladdin Reagent Co. Ltd. (Shanghai).

2.2. Biodiesel production

Waste cooking oil (500 g), CH_3OH (108 g), and NaOH (5 g) were used to prepare the biodiesel. The reaction was performed under reflux for 120 min at 60 °C. When the reaction was completed, the upper layer was evaporated to remove unreacted methanol. The crude biodiesel was then dried to obtain biodiesel from waste cooking oil (BWCO).

2.3. GC–MS analysis

GC–MS analysis was performed using Agilent 7890A-5975c GC–MS. An hp-Innowax quartz capillary column (60 m × 0.25 mm × 0.25 μm) was used. The capillary column temperature was increased from 70 °C to 160 °C (10 °C/min) then from 160 °C to 230 °C (5 °C/min). Both injector and interface temperatures were 260 °C, and a high-purity helium carrier (1 ml/min, 100:1) was used.

2.4. Measurement of cold flow properties

Cloud point (CP), cold filter plugging point (CFPP), and pour point (PP) are crucial indicators related to the low-temperature operability of biodiesel/diesel fuels. In this study, the CP, CFPP and PP of the treated biodiesel blends were evaluated in accordance with ASTM D 2500-11 [33], EN 116 [34] and ASTM D97 [35], respectively.

2.5. Other fuel properties

The other fuel properties of the sample for which EVAC showed the most significant cold flow improvement were determined based on the measurement of cold flow properties as follows: v (mm^2/s), ASTM D445 [36]; TG (mass%), ASTM D6584 [37]; OS (h, 110 °C), EN 14112 [38]; AV (mg KOH/g), AOCS Cd 3d-63 [39]; and FP (°C), ASTM D93 [40].

2.6. Crystallization behavior observation

The DSC (DSC27HP, Mettler Corporation, Swiss) curve was obtained using 8 mg to 10 mg of the samples from 30 °C to −60 °C (5 °C/min).

In the present investigation, average values for a minimum of triplicate measurements were reported in the figures and tables with a relative standard deviation of <3% in all cases.

3. Results and discussion

3.1. Properties of prepared biodiesel

The components of the prepared biodiesel (Table 1) are consistent with previously reported results [4,30]. The v, TG, OS, AV, and FP of the biodiesel were determined. The prepared biodiesel satisfied the specifications for biodiesels (Table 2).

3.2. Low-temperature properties

Table 3 shows that EVAC significantly affected the CP, CFPP, and PP of B0 (neat diesel), B20 (20 vol.% biodiesel + 80 vol.% 0# diesel), and B40 (40 vol.% biodiesel + 60 vol.% 0# diesel). The effects of EVAC on the CP, CFPP, and PP of B60 (60 vol.% biodiesel + 40 vol.% 0# diesel), B80 (80 vol.% biodiesel + 20 vol.% 0# diesel), and B100 (neat biodiesel) were minimal. EVAC showed little effect on the biodiesel blends with more than 40 vol.% biodiesel. Thus, EVAC exhibited weak sensitivity to the biodiesel blends with high biodiesel content. The addition of 0.04 wt.% additive resulted in the lowest CP, CFPP, and PP values. Table 3 shows that the CP, CFPP, and PP of B20 without additive were −4 °C, −5 °C, and −8 °C, respectively. The CP, CFPP, and PP of B20 decreased to −12 °C, −16 °C, and −18 °C, respectively, after 0.04 wt.% EVAC treatment. It indicates

Table 1
GC–MS analysis of biodiesel from waste cooking oil.

Peak No.	Retention time (min)	Name of fatty acid methyl esters	Corresponding acid	Mass percent (%)
1	42.21	Methyl tetradecanoate	C14:0	1.36
2	49.35	Methyl hexadecanoate	C16:0	20.42
3	49.70	Methyl 9-hexadecanoate	C16:1	1.63
4	55.37	Methyl octadecanoate	C18:0	20.10
5	55.83	Methyl oleate	C18:1	22.22
6	57.28	Methyl linoleate	C18:2	30.28
7	58.76	Methyl linolenate	C18:3	3.99

Table 2
Selected specifications of biodiesel standard and properties of prepared biodiesel.

Specification	v, 40 °C, mm^2/s	TG, mass%	OS, 110 °C, h	AV, mg KOH/g	FP, °C
ASTM D6751	1.9–6.0	0.24 max	3 min	0.50 max	130 min
BWCO	2.96	0.19	5.8	0.35	136

v = kinematic viscosity, TG = total glycerol, OS = oxidation stability, AV = acid value, FP = flash point, ASTM D6751 = American Society for Testing and Materials' details standards and specifications for biodiesels blended with middle distillate fuels, BWCO = biodiesel from waste cooking oil in this study.