

Ethyl acetoacetate: A potential bio-based diluent for improving the cold flow properties of biodiesel from waste cooking oil



Leichang Cao, Jieni Wang, Kuojin Liu, Sheng Han*

School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China

HIGHLIGHTS

- Ethyl acetoacetate (EAA) is a potential bio-based diluent for improving the cold flow properties of biodiesel.
- The cold filter plugging point (CFPP) and pour point (PP) of biodiesel decreased with adding EAA.
- The impact of EAA on kinematic viscosity, acid value, oxidative stability and flash point was determined.
- Every sample satisfied the ASTM D6751 except flash point (≥ 10 vol% ethyl acetoacetate).

ARTICLE INFO

Article history:

Received 5 May 2013

Received in revised form 4 September 2013

Accepted 17 September 2013

Available online 12 October 2013

Keywords:

Ethyl acetoacetate

Bio-based

Diluent

Biodiesel

Waste cooking oil

ABSTRACT

Ethyl acetoacetate was investigated as a potential bio-based diluent for improving the cold flow properties of biodiesel from waste cooking oil. Waste cooking oil generally has relatively high saturated fatty acid content, meaning that the cold flow properties of the converted biodiesel are more challenging than the properties of biodiesel from conventional vegetable oils. The cold filter plugging point (CFPP) and pour point (PP) of biodiesel decreased after adding ethyl acetoacetate at 0%, 2.5%, 5%, 10% and 20% (vol). Both PP and CFPP decreased by 4 °C at 20 vol% ethyl acetoacetate. The effect of ethyl acetoacetate on kinematic viscosity, acid value and flash point was determined. Every sample satisfied ASTM D6751 except for the flash point (≥ 10 vol% ethyl acetoacetate), but the 5 vol% blends were all acceptable. Oxidative stability was improved with the addition of ethyl acetoacetate. Overall, ethyl acetoacetate appears acceptable as a bio-based diluent for improving the cold flow properties of biodiesel.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Biodiesel has been studied as an excellent alternative for petroleum diesel. It is eco-friendly because it is biodegradable, non-toxic, and able to produce exhaust gas free of aromatic compound and sulfur [1–5]. Extensive researches have been conducted on biodiesel since the beginning of the 1990s [6–13]. Recent biodiesel studies have primarily focused on producing biodiesel from inexpensive raw materials, such as non-edible plants oils, waste cooking oil and by-products of the refining vegetable oils.

Waste cooking oil is considered a good alternative because it is inexpensive and prevents environmental pollution. By 2005, E.U. states occupy 89% of the total global biodiesel production, in which Germany alone produces 1.9 billion L (51%) [14]. Asia including China has lagged behind Europe and U.S. in biodiesel production [14]. However, a number of private companies, local governments, and other organizations in China have recently begun to increase the production of biodiesel from a variety of waste oils [15]. The

amount of waste cooking oil generated in homes and restaurants is increasing rapidly because of the tremendous growth in human population [16]. The United States alone generates approximately 10 million tons of waste cooking oil annually [17]. In China, approximately 4.5 million tons of waste cooking oil are generated every year [17], which requires economic and environment-friendly disposal methods, such as utilization of waste cooking oil in biodiesel production [18]. The price of waste cooking oil is two to three times cheaper than that of vegetable oils, which leads to a significant reduction in the total processing cost [19]. By transesterification process, numerous researchers have prepared biodiesel from waste cooking oil [20–25]. Therefore, in the present study, we prepared biodiesel from waste cooking oil. In addition, the properties of biodiesel with or without ethyl acetoacetate were investigated.

Compared with petroleum diesel fuel, poor cold flow property is a critical defect of biodiesel. In the past several years, some methods have been investigated to solve the low temperature flaw of biodiesel, such as additives, biodiesel–diesel blending, branched-chain esters and winterization. Among the methods mentioned, adding additives seems to be the most effective because it is more

* Corresponding author. Tel.: +86 18917950352.

E-mail address: hansheng654321@sina.com (S. Han).

Table 1

The selected specifications of biodiesel standard.

Specification	FG, mass%	TG, mass%	CP, °C	PP, °C	CFPP, °C	FP, °C	AV, mg KOH/g	IP, 110 °C, h	ν , 40 °C, mm ² /s
EN 14214	Max 0.02	Max 0.25	–	–	–	Min 101	Max 0.50	Min 6	3.5–5.0
ASTM D6751	Max 0.02	Max 0.24	–	–	–	Min 93	Max 0.50	Min 3	1.9–6.0

Table 2

GC–MS analysis of biodiesel.

Peak no.	Retention time (min)	Name of fatty acid methyl esters (FAME)	Corresponding acid	Mass percent (%)
1	42.13	Methyl tetradecanoate	C14:0	0.98
2	49.17	Methyl hexadecanoate	C16:0	20.09
3	49.67	Methyl 9-hexadecenoate	C16:1	1.75
4	55.57	Methyl octadecanoate	C18:0	14.87
5	55.86	Methyl oleate	C18:1	21.69
6	57.35	Methyl linoleate	C18:2	35.36
7	58.79	Methyl linolenate	C18:3	5.06

economical and convenient [26–29]. Despite some reported additives are available for biodiesel, the addition of additives for the improvement of biodiesel properties at low temperature is still a challenge and requires further research. Ethyl acetoacetate is derived from ethanol and is basically bio-based because ethanol is obtained from sugar fermentation. Furthermore, ethyl acetoacetate was never investigated to be an additive for biodiesel nor blended with biodiesel.

The purpose of this study was to determine the performance on fuel characteristics of blending ethyl acetoacetate with biodiesel. Cold filter plugging point (CFPP), pour point (PP), cloud point (CP), acid value (AV), induction period (IP), kinematic viscosity (ν), and flash point (FP) were determined using standard methods, which were provided by American Society for Testing Material (ASTM) and European Norm (EN). Finally, the properties of biodiesel blended with ethyl acetoacetate were compared with biodiesel fuel standards that are shown in Table 1.

2. Methods

2.1. Materials

Ethyl acetoacetate was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai). Waste cooking oil was bought from Shanghai Zhongming Chemical Co., Ltd. (Shanghai). All other chemicals were obtained from Aladdin Reagent Co., Ltd. (Shanghai).

2.2. Methanolysis of waste cooking oil

Biodiesel from waste cooking oil was prepared using ferric sulfate and potassium hydroxide as catalysts in a two-step reaction [30]. After reaction, the mixture was divided into upper and lower layers. The residual methanol was removed by evaporating the upper layer, and the crude biodiesel was then obtained. Residual soap and glycerol were removed by washing in hot water (85 °C) twice. Afterwards, biodiesel from waste cooking oil was obtained by drying the washed biodiesel.

2.3. GC–MS analysis

Agilent 7890A-5975c GC–MS was used to analyze the biodiesel composition. The GC operation conditions were as follows: hp-Innowax quartz capillary column (60 m × 0.25 mm × 0.25 μ m); capillary column temperature was initially raised by 10 °C/min from 70 °C to 160 °C, then raised by 5 °C/min from 160 °C to 230 °C, interface temperature was 260 °C; injector temperature

was 260 °C, the diffluent ratio was 100:1, high purity helium carrier, gas flow rate was 1 mL/min (high purity helium carrier); and the injection volume was 0.2 μ L.

2.4. Properties

Ethyl acetoacetate was added into biodiesel at the following levels, 0%, 2.5%, 5%, 10%, and 20% (vol). The measurement for fuel properties were implemented based on standard methods, such as total glycerol (TG, mass%) and (FG, mass%) free glycerol, ASTM D6584 [31]; PP: (°C), ASTM D5949 [32]; CP (°C), ASTM D5773 [33]; CFPP (°C), ASTM D6371 [34]; AV (mg KOH/g), AOCS Cd 3d-63 [35]; IP (h, 110 °C), EN 14112 [36]; ν (mm²/s), ASTM D445 [37]; FP (°C), ASTM D93 [38].

2.5. Data analysis

Employing the general linear model in the IBM SPSS Statistics (version 19.0), Variance Analysis (VA) was carried out. Using $\alpha = 0.05$, linear contrasts were used to test the performance of ethyl acetoacetate percentage on blend properties. The first linear contrast can determine whether biodiesel containing ethyl acetoacetate was different from the control. The other contrast checked whether varying ethyl acetoacetate content had impact on biodiesel properties.

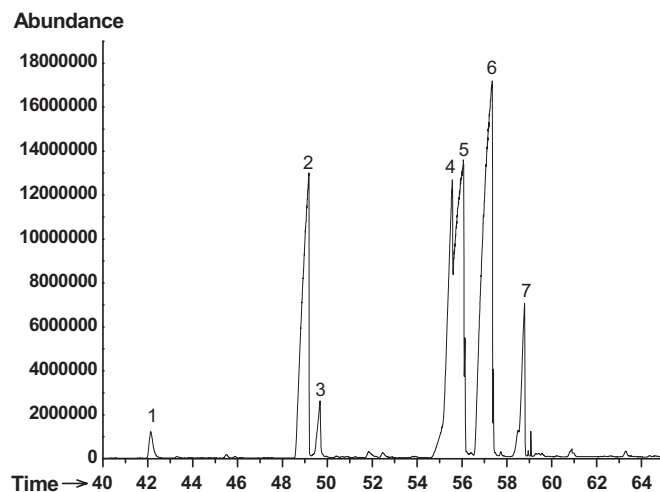


Fig. 1. Total ion chromatogram of biodiesel from waste cooking oil that shows FAME composition (1 = C14:0 2 = C16:0 3 = C16:1 4 = C18:0 5 = C18:1 6 = C18:2 7 = C18:3).

Download English Version:

<https://daneshyari.com/en/article/6691366>

Download Persian Version:

<https://daneshyari.com/article/6691366>

[Daneshyari.com](https://daneshyari.com)