Fuel 207 (2017) 503–509

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Crystallization behaviors and rheological properties of biodiesel derived from methanol and ethanol

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HIGHLIGHTS

- Compared to methyl biodiesel, T_{onset} and gelation point of ethyl ester decreased.
- Just below T_{onset} of methyl ester, amount of crystal from ethyl ester is much lower.
- Amount of crystal from methyl, ethyl ester is equal at a certain lower temperature.
- Just below T_{onset} of methyl ester, rheological property of ethyl ester is much better.
- Viscosity, storage modulus of ethyl ester is higher at relatively lower temperature.

ARTICLE INFO

Article history:
Received 5 April 2017
Received in revised form 24 May 2017
Accepted 27 June 2017

Keywords:
Biodiesel
Crystallization behavior
Rheological property
Methyl ester
Ethyl ester

ABSTRACT

Take palm oil and soybean oil biodiesels as example, crystallization behavior and rheological property of methyl and ethyl biodiesels were investigated. Differential scanning calorimeter (DSC) technique was used to analyze the crystallization behaviors of methyl and ethyl biodiesels, including the crystallization onset temperature and the variation of amount of crystal precipitation with temperature. Meanwhile, a thermodynamic model of regular solution was proposed and compared with the crystallization experiments. Comparisons suggested that the model can give a reasonable description of crystal precipitation of biodiesel. The rheological properties of methyl and ethyl biodiesels including the viscosity temperature curves as well as the variation of viscoelastic parameters with temperature during the cooling gelation process were measured by rheometer. Experimental results suggested that the crystallization onset temperature and the gelation temperature of ethyl biodiesels are decreased as compared with methyl biodiesels. When temperature is just below the crystallization onset temperature of methyl biodiesel, the crystal precipitation of ethyl biodiesel is much lower than methyl biodiesel, meanwhile, the same characteristic can be observed for the viscosity and storage modulus of methyl and ethyl biodiesels. As the temperature decreased, the crystal precipitation of ethyl biodiesel is gradually close to until equal to the methyl biodiesel. So as the temperature decreased, the differences between the viscosity, storage modulus of methyl and ethyl biodiesels are getting smaller, and then the viscosity and storage modulus of ethyl biodiesel are greater than those of methyl biodiesel.

1. Introduction

Take vegetable oils or animal fats and short chain alcohols as raw materials, biodiesel is usually produced by transesterification reaction in the presence of a catalyst [1]. Biodiesel has many advantages compared to petro diesel, including the lower exhaust emissions, renewable, biodegradability, higher flashing point, good performance in lubrication, etc. [2].

However, the main drawback of biodiesel is the poor low temperature flow properties which restrict the usage of biodiesel in areas of low temperature [3–5]. Saturated fatty acid alkyl ester (FAAE) and unsaturated FAAE are the main components of biodiesel. When the temperature is decreased, the saturated FAAE will precipitate from biodiesel because of its higher melting temperature, as the temperature decreased continuously, the crystal precipitation of biodiesel increases, and finally forms a network structure which causes the solidification of biodiesel [5]. At present, many techniques are used to improve this shortcomings of biodiesel, including addition of cold flow improvers [6,7], blending with petro diesel [8,9], fractionating by crystallization [10,11],

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http://dx.doi.org/10.1016/j.fuel.2017.06.121

blending of biodiesels with different compositions [12,13]. Another strategy to improve the low temperature fluidity of biodiesel is the use of alcohols with longer carbon chain instead of methanol [14–16]. The alcohol classically used for biodiesel production is methanol because of its high polarity, mild reaction conditions, low cost, easy phase separation [17]. However, there are also disadvantages in the application of methanol such as lower boiling point and higher toxicity, normally obtained from fossil sources [18]. Ethanol can be obtained from agricultural materials, so it has the following characteristics: renewable, non-toxic, and independent of petrochemical resources. Moreover, compared with fatty acid methyl ester(FAME), fatty acid ethyl ester (FAEE) shows better low temperature fluidity because of the lower melting temperature of ethyl esters [19]. So Ethyl esters have been produced from different materials for use as potential biodiesel fuels [20], especially in Brazil and Spain, the ethanol is the main alcohol used for biodiesel production.

Marcos Sánchez et al. produced biodiesels from Jatropha oil with methanol, ethanol, 2-propanol and 1-butanol, it was concluded that, the cold filter plugging point (CFPP) of Jatropha oil biodiesel derived from ethanol is lower than the CFPP of biodiesel derived from methanol [18].

Take crude Macauba almond oil and different alcohols including methanol, ethanol, isopropanol and isobutanol as raw materials, Larissa Noemi Silva et al. produced biodiesels with different ester groups by transesterification with homogeneous catalysts. Kinematic viscosity, density and CFPP of biodiesels derived from different alcohols were measured. It was suggested that the above properties of biodiesels with different ester groups were within the established limits of the European, ASTM and ANP standards for biodiesel. With the use of longer chain alcohols instead of methanol, the behavior of biodiesel at low temperature was obviously improved. Considering the ethanol has high sustainability, lower toxicity, can be obtained from a truly renewable resources, and the ethyl biodiesel can be mixed with the fossil jet fuel, the ethyl biodiesel was suggested to be the most promising one [21].

Claudia Cristina Cardoso et al. compared properties of biodiesel prepared from palm oil with different alcohols and observed that the crystallization temperature noticeably shifted to a lower temperature from the methyl to ethyl then to isopropyl moieties [22].

Kristaps Malins et al. studied the properties of rapeseed oil biodiesels with different ester groups. It was suggested the cold flow properties of FAAE has been obviously improved with an increase of the hydrocarbon chain length in alcohol moiety [23].

Rui Huang et al. produced biodiesel from wet microalgae cells with renewable ethanol and isopropanol through lipid transesterification. It has been found that the crystallization temperature of microalgae biodiesels derived from ethanol and isopropanol is 0.19 °C and −3.15 °C, respectively, which is lower than that with methanol (2.08 °C) [24].

However, these researches only studied the effect of alcohol on the characteristic temperatures (cloud point, CFPP, pour point) of biodiesel. The effect of alcohol on the crystallization behavior such as the variation of amount of crystal precipitation with temperature during cooling gelation process has not been studied at present. The crystallization behavior of biodiesel at low temperature is crucial for the low temperature fluidity of biodiesel. So in this work, the crystallization onset temperature and the variation of amount of crystal precipitation with temperature of methyl and ethyl biodiesels were measured by DSC method and predicted by regular solution model. Viscosity is one of the most important properties of biodiesel. Especially when the temperature is decreased, the crystal will precipitate from biodiesel and the precipitation will lead to the rapid increase in viscosity of biodiesel, which may cause the blockage of filters and lines. The effect of alcohol on the viscosity of biodiesel is mainly focused on the viscosity at 40 °C rather than the viscosity temperature curve. Therefore, the viscosity temperature curves of methyl and ethyl biodiesels were studied by rheometer. Meanwhile, the variation of viscoelastic parameters with temperature of methyl and ethyl biodiesels during cooling gelation process was also investigated by rheometer.

2. Materials and methods

2.1. Materials

Commercial soybean oil and palm oil were used as the source of biodiesel preparation and no treatment has been conducted on any of the oils. Analytical grade KOH, Na_2SO_4, hexane, reagent-grade methanol and ethanol were obtained from Aladdin Reagent Co. Ltd.(Shanghai).

2.2. Methyl and ethyl biodiesel production

Experiments were conducted in three necked flask connected to a reflux condenser and a magnetic stirrer. Methyl and ethyl biodiesels were prepared by transesterification of oils with alcohol (the molar ratio of alcohol/oil is 6:1) at 60 °C and KOH as the catalyst with the addition of 1% w/w. After 1 h of reaction time with methanol and 2 h with ethanol, the resulting upper alkyl ester layer was separated, washed with three or four times of distilled water, and the volume ratio of water to alkyl ester is 1:1. The emulsions formed during water washing process were separated by a centrifuge with a speed of 3000 round per minute. Then, the esters were dried with Na_2SO_4, and the remaining alcohol in biodiesel was evaporated under reduced pressure.

2.3. GC analysis

A 6890 series gas chromatograph equipped with a FID and a DB-WAX capillary column (30 m × 0.32 mm × 0.25 μm) was used to measure the composition of biodiesel samples. During the experiments, the detector temperature and inlet temperature were 250 °C and 260 °C, respectively. The initial column temperature was set at 100 °C and kept at this temperature for 1 min, subsequently heated to 150 °C with a heating rate of 10 °C/min and kept at 150 °C for 1 min, and then heated to 200 °C with a heating rate of 2 °C/min and kept at 200 °C for 20 min. The carrier gas was Helium and its flow rate was 2 mL/min. The flow rate of air was 400 mL/min and hydrogen was 30 mL/min. The injection volume of biodiesel sample was 1 μL. FAME composition was obtained by comparison of peak areas as well as retention times between methyl biodiesel and reference standards. A solution of methyl heptadecanoate in heptane was used as an internal standard. The FAEE peaks were determined by considering the sequence of retention times of FAEE is the same as that of FAME [23].

2.4. DSC analysis

The crystallization behaviors of methyl and ethyl biodiesels were analyzed by a DuPont Model 910 DSC equipment. The instrument was calibrated with n-pentacosane and indium. Liquid-nitrogen was used as refrigerant during the experiments. All biodiesel samples were heated to 30 °C and kept at 30 °C for 5 min to remove thermal history. And then the biodiesel samples were cooled down to −70 °C with a cooling rate of 5 °C/min.