Crystallization Behavior of Saturated Fatty Acid Methyl Esters in Biodiesel

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Abstract

The inferior cold flow property caused by crystallization of the saturated fatty acid methyl ester components in biodiesel is the main issue to regular usage of biodiesel as alternative fuel to diesel. In this study, the cold filter plugging point (CFPP) and the crystallization processes of palm biodiesel and it blending with -10PD are observed by CFPP tester and low temperature phase contrast microscope, respectively. The optical microscopic phase contrast images during temperature scan relate the effect of -10PD on crystallization onset temperature and crystal morphology which delayed the crystal formation with increase in crystal nucleation density and reduction in size of the crystals. -10PD shows altered crystallization morphology from regular polygon lamellar crystal structure to irregular dendritic crystal structure. The blending with -10PD reduces crystallization onset temperature (15.80 °C to 5.10 °C), forming the three dimensional network structures temperature (9.50 °C to -12.00 °C) and CFPP (10 °C to -11 °C) lower than that of -10PD having CFPP of -7 °C. So the poorer cold flow property of biodiesel can improved by blending with -10PD.

Keywords

Biodiesel, Crystallization, Crystallization morphology, Cold flow property.

1. Introduction

With diminishing resources of fossil fuels and environmental concerns, hence alternative renewable fuels have received increasing attention. One of the extensively researched alternative renewable fuels is biodiesel. Biodiesel is defined as the monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats [1].

The cold flow property is an important performance indicator for diesel fuels, and is highly relevant both to maintaining a normal supply of fuel for diesel engines, and to the storage and transportation of diesel, at low temperatures [2]. Study found that the cold filter plugging point (CFPP) of biodiesel is higher than that of conventional diesel fuels, such as CFPP of hogwash oil methyl ester (HME), Kentucky Fried Oil methyl ester (KFME), cottonseed oil methyl ester (CSME), palm oil methyl ester (PME) and peanut oil methyl ester (PNME) are 3, 5, 6, 10 and 13 ℃, respectively [3]. Biodiesel contributes to poorer cold flow property when compared to conventional diesel fuel. Hence, biodiesel has cold flow properties that limit widespread commercialization as fuels and fuel extenders during cooler weather in moderate temperature climates [4]. This is due to crystallization of the saturated fatty acid methyl ester components of biodiesel during cold seasons, which causes start-up and operability problems as solidified material clog fuel lines and filters [5].

In this paper, attempt has been made to investigate biodiesel crystallization process and saturated fatty acid methyl ester (SFAME) crystallization morphology in order to exploring the crystallization mechanism and the effects of crystallization on the cold flow property of biodiesel. Based on the fatty acid composition, color and CFPP of biodiesel (i.e. PME, composition: 31.04% palmitic acid methyl ester ($C_{16:0}$), color: light and CFPP: 10 ℃) PME [3], we choice PME as test oil. It can be expected to provide some help for the improvement of cold flow property of biodiesel.

2. Experimental

2.1 Materials

Homemade PME is prepared from commercial palm oil using an alkali-catalyzed transesterification procedure [6]. Based on the GC-MS analysis, it is determined that PME is composed of total 40.13% SFAME (mainly $C_{16:0}$ and stearic acid methyl ester ($C_{18:0}$), i.e. 31.04% $C_{16:0}$ and 6.64% $C_{18:0}$)) and 59.57% unsaturated fatty acid methyl ester (UFAME) (mainly oleic acid methyl ester ($C_{18:1}$) and linoleic acid methyl ester ($C_{18:2}$), i.e. 43.94% $C_{18:1}$ and 14.44% $C_{18:2}$)).

2.2 Cold Filter Plugging Point Measured

The CFPP of oil samples is measured in accordance to SH/T 0248-2006, using the SYP 2007-1 Cold Filter Plugging Point Tester (Shanghai BOLEA Instrument & Equipment Co., Ltd., China).

2.3 Crystallization Process Observation

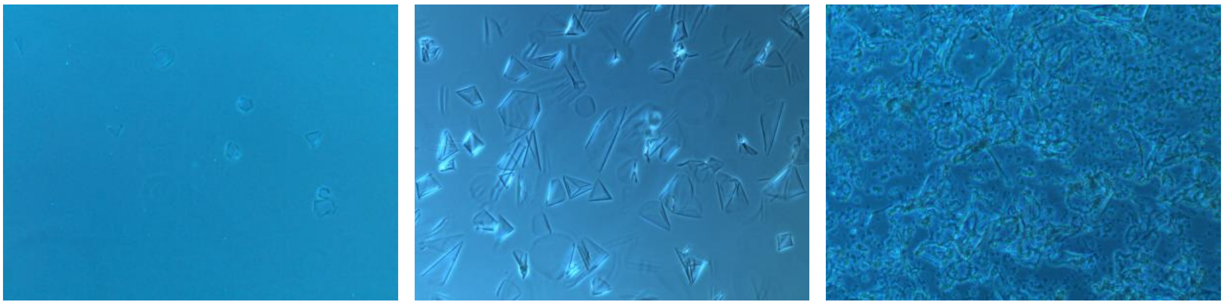
A Leica DM2500P (Leica Microsystems, Wetzlar, Germany) fitted with a Leica DFC295 digital camera was used for the microstructure studies. A Linkam LTS 120 temperature-controlled stage (Linkam Scientific Instruments, Tadworth, Surrey, UK) fitted to the polarized light microscope (PLM) is used to process thermally the samples. The sample (100~130 μL) in a quartz crucible is heated to 50.00 ℃ for 5 min to delete all crystal memory then cools down to 8.00 ℃ at 0.02 ℃/min. The temperature at which the first "spot" is observed in the PLM is recorded as the crystallization onset temperature. Temperature resolved images are measured at 100× magnification during cooling using the automatic multi-time image capture feature available in the PLM.

3. Results and discussion

3.1 Cold flow property

The CFPP of PME is 10 ℃, 13 ℃ higher than the that of petrodiesel (i.e. -3 ℃ 0 petrodiesel (0PD) and -3 ℃ -10 petrodiesel (-10PD)), and PME has relatively poor cold flow properties. Based to the main components of the PME, it may be considered a pseudobinary solution that is essentially a mixture of high melting points SFAMEs (30.5 ℃ $C_{16:0}$ and 39.1 ℃ $C_{18:0}$) dissolved in low melting points UFAMEs (-20.0 ℃ $C_{18:1}$ and 35.0 ℃ $C_{18:2}$) [6, 7]. SFAMEs content in PME reaches up to 40.13 wt.%. As temperatures fall, SFAMEs in PME begin to nucleate, form solid crystals and agglomerate. The CFPP of biodiesel increases with SFAMEs amount increasing. When the SFAMEs content is high, biodiesel is easier to crystallize, the CFPP of biodiesel is high, and the cold flow property would be poorer. In order to reduce the CFPP of biodiesel, it is very necessary to investigate biodiesel crystallization process.

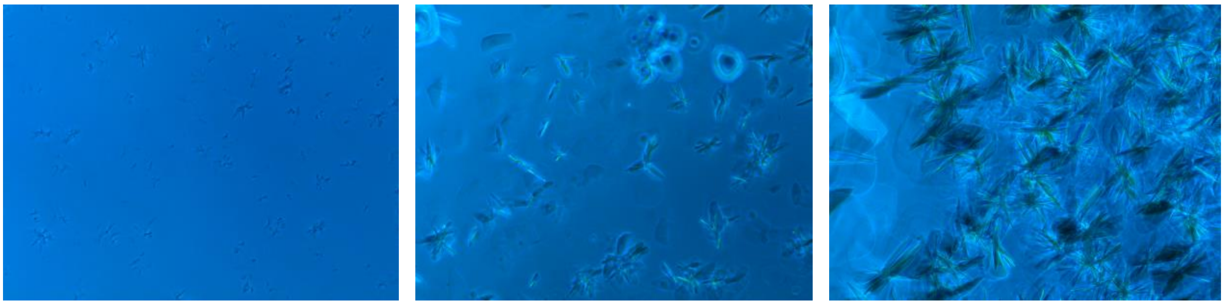
The crystal growth of neat PME at 15.20 ℃, 13.00 ℃ and 9.50 ℃ can be visualized through the PLM as shown in Fig.1. It can be observed that PME starts crystallization at 15.80 ℃. Fig.1(A)-(C) shows that the number of crystals and crystal size grow with decrease in temperature. Crystallization morphology is regular polygon lamellar crystal structure. With the further decrease in temperature, lamellar crystal increase continuously and aggregate together, forming the three dimensional network space structures. The cold flow property of PME is poor.



(A) 15.20 ℃ (B) 13.00 ℃ (C) 9.50 ℃

Fig.1 Microscope images of crystals of PME

The crystal growth of PME/-10PD at 2.00 ℃, -5.00 ℃ and -12.00 ℃ can be visualized through the PLM as shown in Fig.2. Blending with -10PD that is capable of altering crystallization nucleation, growth and morphology is preferred as it can delay crystallization and reduce the size of the crystals. It can be observed that B20 has lowered down the crystal growth initiation temperature to 5.10 ℃. Fig.2(A)-(C) clearly implicates that blending with petrodiesel has slowed down the crystal growth rate and reduced the crystal size. Crystallization morphology is irregular dendritic crystal structure. It shows that blending with -10PD can improve the cold flow properties of biodiesel.



(A) 2.00 ℃ (B) -5.00 ℃ (C) -12.00 ℃

Fig.2 Microscope images of crystals of B20

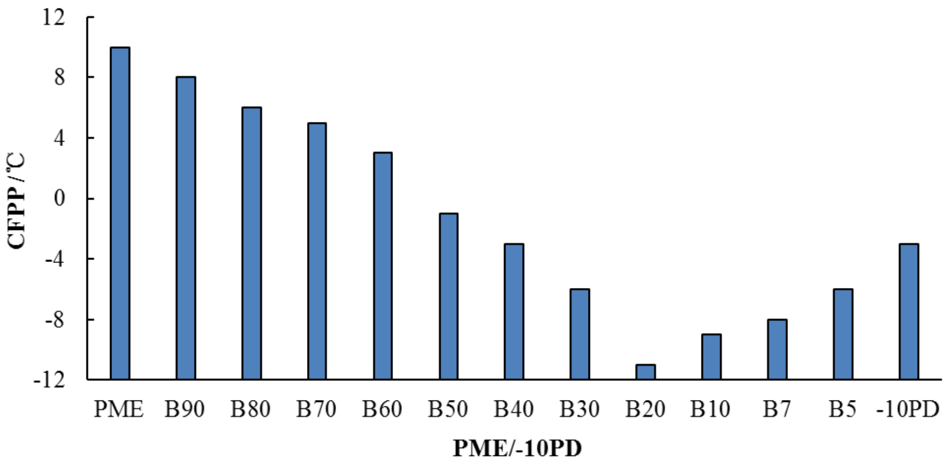


Fig. 3 The CFPP of PME/-10PD

The CFPP of PME/-10PD is showed in Fig.3. From Fig.3, the CFPP of PME/-10PD is the lowest to -11 ℃, which further supports the crystal results that blending with petrodiesel improved the cold flow properties of biodiesel.

4. Conclusion

The mass fraction of SFAME in PME is 40.13%. The crystallization onset temperature and forming the three dimensional network structures temperature are 15.80 ℃ and 9.50 ℃, respectively.

Crystallization morphology is regular polygon lamellar crystal structure. The CFPP of PME is as high as 10 ℃, and the cold flow property of PME is poor.

Blending with -10PD can delay crystallization, reduce the size of the crystals, and altering crystallization morphology. The crystallization onset temperature and forming the three dimensional network structures temperature of B20 decrease to 5.10 ℃ and -12.00 ℃, respectively. Crystallization morphology is irregular dendritic crystal structure. The poor cold flow property of PME is improved by blending with -10PD, and the CFPP of B20 decreases to -11 ℃.

Acknowledgements

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