Study on crystallization mechanism of saturated fatty acid methyl ester in biodiesel

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Abstract

The chemical composition, cold filter plugging point (CFPP) and the crystallization processes of palm oil methyl ester (PME) are observed by GC-MS, CFPP tester and low temperature phase contrast microscope, respectively. Bilayer crystallization mechanism is put forward. The study shows that PME is mainly composed of fatty acid methyl esters (FAME), and the contents of saturated fatty acid methyl ester (SFAME) is 40.13 w%. The CFPP of PME is as high as 10 °C, and the cold flow property of PME is poor. PME may be considered a pseudobinary mixture consisting of SFAME and UFAME. SFAME crystallization comprises three steps, viz., forming supersaturated solution, nucleation and crystal growth. The crystal morphology of SFAME is a bilayer regular polygon lamellar crystal structures.

Keywords

Biodiesel, Crystallization mechanism, Saturated fatty acid methyl ester.

1. Introduction

With diminishing resources of petroleum and environmental concerns, fatty acid methyl esters (FAMEs), known as biodiesel fuels, have received significant attention as alternative renewable fuels for compression ignition engines[1-2]. 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[3-5]. 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. It can be expected to provide some help for the improvement of cold flow property of biodiesel.

2. Experimental

2.1 Materials

Palm oil methyl ester (PME) is prepared by our laboratory, in line with GB/T 20828-2007 requirements.

2.2 Composition Analyzed

Oil samples are analyzed by gas chromatography-mass spectrometer (GC-MS) (Finnigan, Trace MS, FID, USA), equipped with a capillary column (DB-WAX, 30 m × 0.25 mm × 0.25 μm). The carrier gas is helium (0.8 mL/min). The sample injection volume is 1 μL. Temperature program is started at 160 °C, staying at this temperature for 0.5 min, heated to 215 °C at 6 °C /min, then heated to 230 °C at 3 °C /min, staying at this temperature for 13 min.

2.3 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).

2.4 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 °C for 5 min to delete all crystal memory then cools down to 8.00 °C at 0.02 °C/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 Composition

GC-MS is utilized to analyze the chemical composition of PME. The main fatty acid methyl ester (FAME) compositions are shown in Table 1.

Table 1 The main fatty acid methyl ester compositions of PME

PME	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{20:0}$	$C_{22:0}$	$C_{24:0}$	$C_{16:1}$	$C_{18:1}$	$C_{20:1}$	$C_{22:1}$	$C_{18:2}$	$C_{18:3}$
Content	1.44	26.95	6.40	0.72	0.21	0.14	0.42	42.13	0.34	0.15	18.20	1.59

Note: $C_{m:n}$ is the shorthand of fatty acid methyl ester; m means the carbon number of fatty acid; n means the number of C=C.

From Table 1, it can see that PME is is composed of total 40.13% saturated fatty acid methyl ester (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) $C_{16:1}$-$C_{22:1}$, $C_{18:2}$ and $C_{18:3}$.

3.2 Cold filter plugging point

The cold filter plugging point (CFPP) of PME is 10°C, the unfavorable cold flow properties of PME due to its higher amount of long-chain SFAME (40.13 wt.%). As temperatures fall, SFAMEs in PME begin to nucleate, form solid crystals and agglomerate, which become so thick that it can clog or restrict filter. The CFPP of biodiesel increases with SFAMEs amount increasing. In order to reduce the CFPP of biodiesel, it is very necessary to investigate crystallization mechanism of SFAME.

3.3 Crystallization mechanism

3.3.1 Molecular arrangement

SFAME with one straight and saturated hydrocarbon chain linked to a polar head-group is shown in Fig.1.

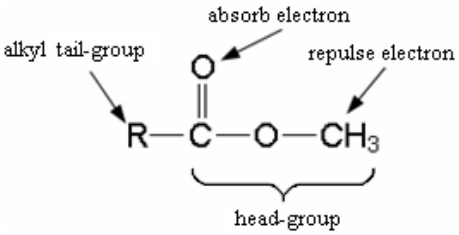


Fig.1 SFAME molecular structure schematic diagram

The SFAME molecules possess sufficient polarity in the carboxylic head-group, giving them an amphiphilic nature and allowing the formation of bilayer structures with head-groups aligned next to each other inside the crystal and away from nonpolar bulk liquid. Stacking structure schematic diagram of C16:0 molecular is shown in Fig.2.

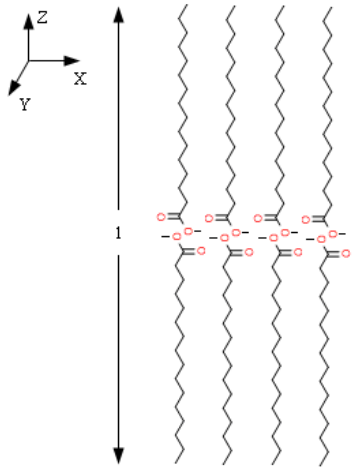


Fig.2 Stacking structure schematic diagram of C16:0 molecular

3.3.2 Pseudobinary solution

PME may be considered a pseudobinary solution that is essentially a mixture of high melting points SFAMEs ($C_{16:0}$, 30.5°C and $C_{18:0}$, 39.1°C) dissolved in low melting points UFAMEs ($C_{18:1}$, -20.0°C and $C_{18:2}$, 35.0°C).

3.3.3 Bilayer crystallization

The crystallization of SFAME in biodiesel comprises three steps, viz., forming supersaturated solution, nucleation and crystal growth. First of all, a sufficiently large thermodynamic driving force must be provided, viz., solution supersaturation by cooling. The temperature-concentration diagram is shown in Fig.3. Once this has been attained, nucleation can occur, whereby crystals are generated as a result of bringing growth units together so that a crystal lattice can be formed. From then on, proper crystal growth can proceed.

SFAME molecules possess sufficient polarity in the carboxylic headgroup, giving them an amphiphilic nature and allowing the formation of bilayer structures with headgroups aligned next to each other inside the crystal and away from nonpolar bulk liquid as shown in Fig.2. Crystal morphology is controlled by the relative rates of growth of the different crystal faces, which in turn depend on internal and external factors. In the crystal growth of SFAME in biodiesel, for instance C18:0, the slowest growth rate is {0 0 2} crystal face in Z-dimension. The crystal growth continues predominately in X-dimension and Y-dimension, and forming bilayer regular polygon lamellae crystal structures, see Fig. 4.

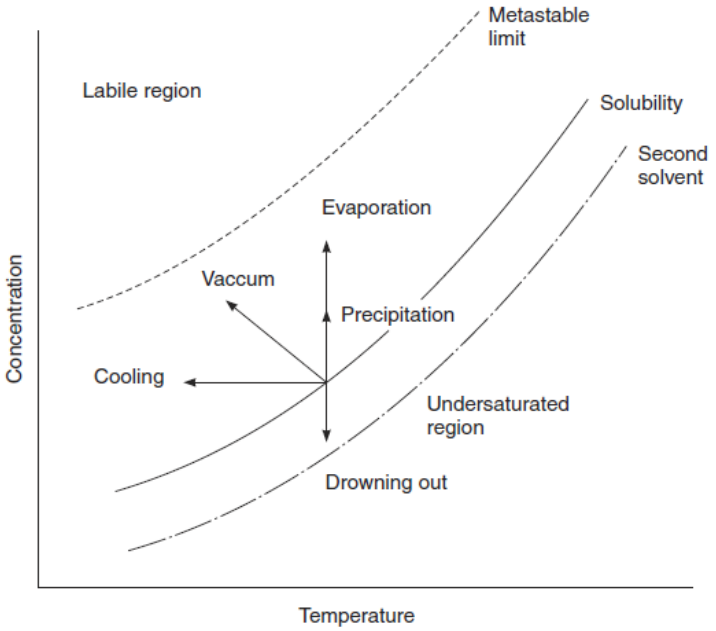


Fig. 3 Solubility-suspersolubility diagram

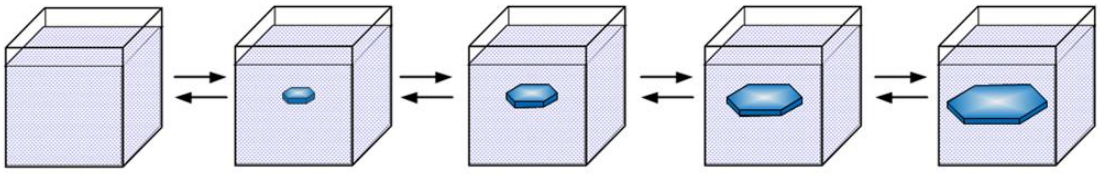
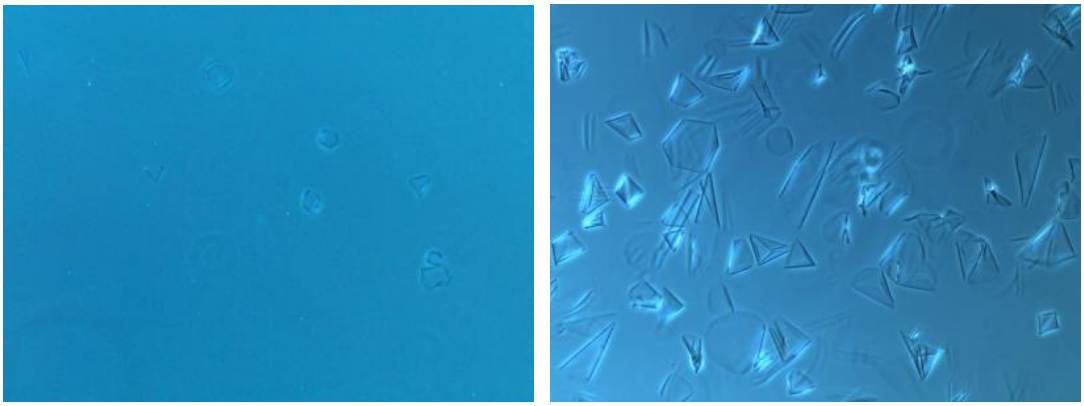


Fig.4 Crystallization process

The crystal growth of neat PME at 15.20 °C, 13.00 °C can be visualized through the PLM as shown in Fig.5. It can be observed that PME starts crystallization at 15.80 °C. Fig.5(A)-(B) shows that the number of crystals and crystal size grow with decrease in temperature. The regular polygon lamellar crystal structure is clearly visible in Fig.5.



(A) 15.20 °C (B) 13.00 °C

Fig.5 Microscope images of crystals of PME

The crystallization mechanism shows that improving cold flow property of biodiesel by delaying crystallization, reducing the size of the crystals, and altering crystallization morphology, such as blending with petrodiesel and treating with cold flow improver.

4. Conclusion

Based on the results of this study, we conclude that:

The mass fraction of SFAME in PME is 40.13%. The CFPP of PME is as high as 10 °C, and the cold flow property of PME is poor.

Bilayer crystallization mechanism: PME may be considered a pseudobinary mixture consisting of high-melting-point SFAME and low-melting-point UFAME. SFAME crystallization comprises three steps, viz., forming supersaturated solution, nucleation and crystal growth. The SFAME crystal grows predominately in X-dimension and Y-dimension, and forming bilayer regular polygon lamellar crystal structures.

Acknowledgements

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