Study on Crystallization Process of Biodiesel Derived from Palm Oil

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Abstract. The chemical composition of palm methyl ester (PME) was analyzed by Gas chromatography-Mass spectrometer (GC-MS). Cold flow properties of PME was studied by cold filter plugging point tester and kinematic viscosity tester, at the same time crystallization process was observed by low temperature phase contrast microscope. In this work, we show that PME is mainly composed of long chain fatty acid methyl esters (FAMEs): C14:0－C24:0, C16:1－C22:1, C18:2 and C18:3. The CFPP of PME is 10 ℃, and PME have relatively poor cold flow property. The crystallization of PME at a steady cooling rate is lamellar crystal for rules. With the reduction of temperature, lamellar crystal increases gradually, and aggregate together. The higher the cooling rate is, the smaller the lamellar crystal and the irregular shape is.

Keywords: Biodiesel, Palm Oil, Cold flow property, Crystallization.

1. Introduction

As a kind of green renewable biofuels, biodiesel has the advantages of non-toxic, biodegradable and environmentally friendly. It can not only relieve the strain on energy supply, reduce dependence on fossil fuels [1], but also the wide raw material sources. In recent years, it gradually get the attention of the governments [2].

The palm oil market supply and demand leveled off in recent years, palm trees planted area is very wide and it has many years history of the application study of palm oil. Therefore the study on PME not only has the good economic feasibility, also can extend the application field of palm oil, give full play to its scientific and practical value [3-4]. However, cold flow properties of PME is poor, it is easy to crystallization in low temperature environment, blocking pipeline and engine nozzle, leading to the abnormal use of the engine, hinder its practical application and popularization finally [5]. The main chemical composition of biodiesel are SFAME and UFAME, the more the content of SFAME and the longer the carbon chain is, the poor the cold flow property is [6-9].

In this work, firstly the chemical composition of PME was analyzed; then, represent cold flow property by measuring cold filter plugging point (CFPP) and kinematic viscosity of PME; finally, observing low temperature crystallization status of PME under the environment by the low temperature phase contrast microscope, exploring the cold flow properties of PME combined crystallization mechanism.

2. Experimental

2.1. Materials and Equipment.

PME: Lab homemade, in line with the national standard GB20828-2007.

SYP2007-1 type solidifying point, cold filter plugging point tester of petroleum products, Shanghai BOLEA Instrument & Equipment Co., Ltd. SYP1003-7 type kinematic viscosity tester of petroleum products, Shanghai BOLEA Instrument & Equipment Co., Ltd. Trace MS type Gas chromatography-Mass spectrometer, Finnigan, Trace MS, FID, USA).

Leica DM2500 P optical microscope, leica Microsystems Co., Ltd. Link am LTS120, Link am Scientific Instruments Ltd.

2.2. Analytical.

PME samples were analyzed by Gas chromatography-Mass spectrometer (GC-MS). Measuring cold filter plugging point (CFPP) and kinematic viscosity of PME according to SH/T 0248-2006, GB/T 265-1988.

Observing low temperature crystallization status of PME by the low temperature phase contrast microscope, cooling rate is respectively set to 0.01℃/min, 0.1℃/min, 1.0℃/min, 2.0 ℃/min.

3. Results and discussion

3.1. Chemical composition.

Main chemical compositions of PME are presented in Table 1.

Table 1 Main composition of PME

FAME	C14:0	C16:0	C18:0	C20:0	C22:0	C24:0	C16:1	C18:1	C20:1	C18:2	C18:3
PME	1.63	31.04	6.64	0.61	0.11	0.10	0.32	43.94	0.28	14.44	0.59

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

From Table 1 it can be seen that PME mainly consists of FAME, which composed of 14~24 even number of carbon atoms. Besides, the contents of SFAME and UFAME is 40.13% and 59.57%.

3.2. Cold flow properties.

CFPP. The CFPP of PME measuring by cold filter plugging point tester is 10℃. According to the main components of the PME, it might be considered as a pseudo binary component solution consisting of solute, those with high-melting-point SFAME, and solvent, those with low-melting-point UFAME [10]. Component of high melting point (SFAME) in PME is as high as 40.13%. Therefore, with the loss of the temperature, it is easy to crystallization precipitation of SFAME, lead to its higher CFPP.

Kinematic Viscosity. The kinematic viscosity of PME, 0PD and -10PD in different temperatures is shown in Fig.1.

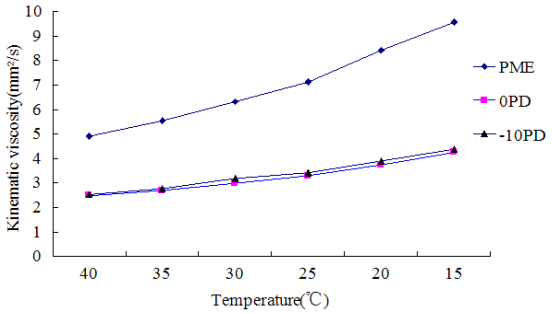


Fig. 1 The curve graph of kinematic viscosity of PME, 0PD and -10PD

The interaction between the molecules of a sample would change its flow performance. It is necessary to research its cold flow property combining of CFPP and kinematic viscosity of PME, since it cannot fully reflect cold flow property of PME which is based on the determination results of CFPP alone. According to GB/T 20828-2007, it can be used as diesel fuel when kinematic viscosity of the fuel oil was in 1.9~6.0 mm2/s under 40℃.

Table 2 the main chemical composition of petroleum diesel

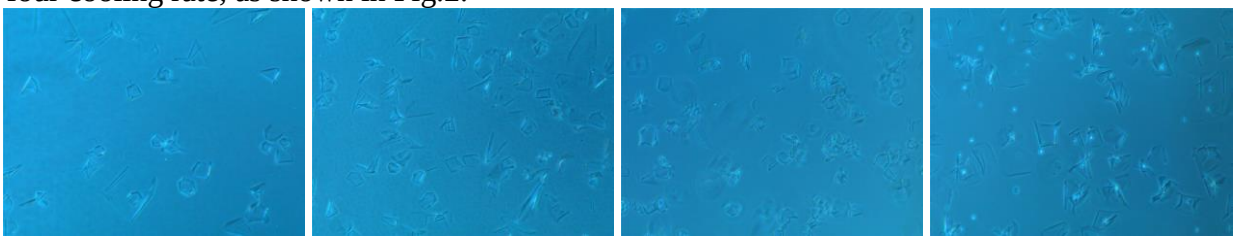
PD	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C24	C26
0PD	0	0	5.85	9.91	7.88	1.80	6.42	6.91	9.15	3.76	6.53	6.41	3.97	3.92	2.59	0	0
-10PD	0.36	1.75	5.51	4.09	6.70	2.24	4.37	12.69	3.83	6.65	1.38	0.81	1.35	8.52	0	0.74	0.27

In this experiment, kinematic viscosity of PME, 0PD, -10PD under different temperature were been measured, it can been seen from Fig.1, kinematic viscosity of PME, 0PD, -10PD under 40℃ can measure up GB/T 20828-2007, that would satisfied the daily use of the general area. However, the

quantity of long-chain SFAME ($C1_{4:0}$~$C_{24:0}$) in PME was larger than the quantity of long-chain alkane (C_{10}~C_{17}) (Table 2) in petroleum diesel. Therefore, the value of kinematic viscosity of PME (4.91mm2/s) is still bigger than 0PD (2.48mm2/s) and -10PD (2.53mm2/s).

3.3. Crystallization Process.

Cooling the sample by the low temperature cold machine, observing low temperature crystallization status of PME by the low temperature phase contrast microscope at different cooling rate, simultaneously under the action of a 100 times magnification. Filmed the crystallization images at four cooling rate, as shown in Fig.2.



(a)0.01℃/min (b)0.1℃/min (c)1.0℃/min (d)2.0℃/min

Fig.2 The crystallization of SFAME in PME at four cooling speeds

As can be seen from the Fig.2, the crystal morphology is mainly the lamellar crystal of regular polygon and a few irregular polygon. At the smaller cooling rate, the crystal grown slowly, it has a more gentle growth status. The amount of the crystal is smaller and its shape is more regular, the photo of the crystallization is shown in Fig.2(a) and Fig.2(b).

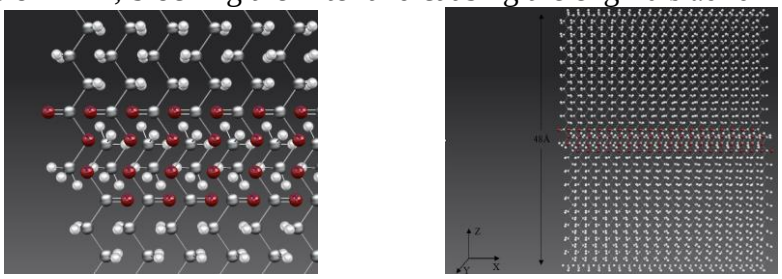
At the larger cooling rate, the crystal grown faster and the crystallization time is short, the growth condition of crystal is unstable. The shape of the crystal is irregular and the number is larger, the photo of the crystallization is shown in Fig.2(c) and Fig.2(d).

The crystallization of pseudo binary component solution is similar to other solution, the crystal growth of PME is also includes three processes: nucleation, growth and aggregation.

Nucleation. It can be known by the electronic effect theory[11], the headgroups of SFAME molecules are amphiphilic groups, the O is negatively charged and the -CH3 is positively charged in the headgroup, besides, the O and the -CH3 in one headgroup can attract each other with the -CH3 and the O in another headgroup. Two headgroups are mutually exclusive, as well as two tailgroups of SFAME molecules. Therefore, SFAME molecules can attract each other in the form of headgroup-to-headgroup and aggregate together, ultimately form a bilayer structure (Fig.3). With the reduction of temperature, when the force between the higher melting point SFAME molecules is greater than the forces between the SFAME molecules and other molecules in the solution, these SFAME molecules will gradually aggregate and form crystal nucleus.

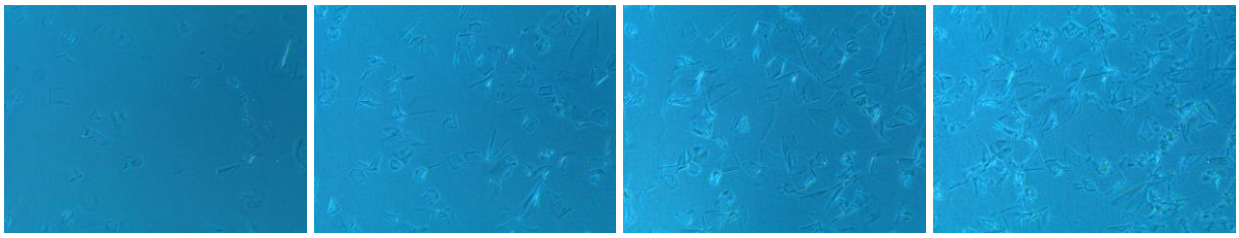
Growth. The bilayer structure constantly growing in both directions along X and Y axis (Fig.3) after crystal nucleus formed, other SFAME molecules constantly cover on lattice sites and gradually become lamelliform, this is the process of its growth. The crystal can grow into regular platelet (Fig.2) in relatively stable conditions, when there is enough growth space of crystal and a slower cooling rate.

Aggregation. As the crystal grow up gradually, lamellar crystal aggregate together, and become larger, forming a three-dimensional network structure (Fig.4). In the end, the FAME or other small parcel inside would been wrapped inside the three-dimensional network structure, resulting in poor cold flow properties of PME, blocking the filter and causing the engine's abnormal start, etc.



(a) (b)

Fig.3 Schematic of bilayer crystal structure of methyl stearate (C18:0)



(a) 15.0℃ (b) 14.0℃ (c) 13.0℃ (d) 14.0℃

Fig.4 Continuous growth of SFAME in PME at cooling speed of 0.1℃/min (×100)

4. Conclusion

PME mainly consists of FAME, which composed of 14-24 even number of carbon atoms, the contents of SFAME and UFAME is 40.13% and 59.57%. Therefore, the cold flow properties of PME is poor, its CFPP is as high as 10℃. The kinematic viscosity under different temperatures is larger than 0PD and -10PD.

The crystallization of PME in low temperature environment is regular polygon platelet. With the reduction of temperature, lamellar crystal increased gradually and aggregate together, wrapped PME or impurities in it, forming the three dimensional space structures, make the cold flow properties of PME poor. In addition, the slower the cooling rate and the more stabile the crystal growth environment is, the more slowly the crystal growth rate is, as well as the smaller number of crystal, the larger size and the more regular shape is. The faster the cooling rate is and the more quickly the crystal grows up, the larger number of the crystal, the smaller size and the irregular shape is.

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