Enhancing the cold flow properties of waste cooking methyl ester

Menghong Yuan, Li Dong, Shaowen Lan, Yifen Chen, Xiaoqi Guo, Xiu Chen[a]

School of Chemical Engineering, Anhui University of Science & Technology, Huainan 232001, China

[a]chenxiuhn@163.com

Abstract. The chemical compositions of waste cooking methyl ester (WCME) and -10# petroleum diesel (-10PD) were analyzed by Gas Chromatograph–Mass Spectrometer. The cold flow properties of WCME were studied by the cold filter plugging point tester and the kinematic viscosity tester. Through blending and adding cold flow improver, the cold flow properties of WCME were improved. The study shows that WCME is mainly composed of saturated fatty acid methyl esters (SFAME) and unsaturated fatty acid methyl esters (UFAME). The mass fraction of SFAME and UFAME are 27.63% and 71.81%, respectively. The cold filter plugging point (CFPP) of WCME is 0℃, and the viscosity of WCME is 4.41mm2/s at 40℃. Through blending, the CFPP of blending oils has decreased with the lowest being -13℃ at B20. With the decrease of the volume ratio of WCME, the kinematic viscosity of blending oils is lower than the WCME and near the -10PD. By adding of cold flow improver, the CFPP of WCME, B10 and B20 decreased from 0℃, -8℃, and -13℃ to -4℃, -26℃ and -25℃.

Keywords: Biodiesel, Waste Cooking Oil, Cold flow property.

1. Introduction

The raw material of biodiesel in our country at present are mainly animal and vegetable oils, which is probably contributed to adding the cost of biodiesel to some extent and again sting the use of biodiesel. In China, urban areas every year usually produce a lot of hutch garbage, which can be extracted waste cooking oil about more than 300 ten thousand tones. [1] It relieves the problem of biodiesel raw material shortage that using waste cooking oil to prepare biodiesel, which achieved the resource waste harmless treatment and avoided harm of waste cooking oil at the same time.

The waste cooking methyl ester contains more saturated fatty acid methyl esters (SFAME), and the cold flow properties of biodiesel are generally poor, which limits its using region. In recent years, researches about enhancing the cold flow properties of biodiesel included: blending, for instance, other biodiesel [2-3], petrochemical diesel [4-5], kerosene [6-7] or alcohol [8-9]; adding of the cold flow improver [10-11]; crystallization fractionation [4, 12]; double-bond epoxidation [13-14]. The most common and most effective method are blending with petrochemical diesel and adding of the cold flow improver.

In this paper, on the based chemical compositions analyzed by Gas Chromatograph–Mass Spectrometer, the objective of this study is using method of -10# petrochemical diesel and adding of the cold flow improver PDD.

2. Experimental

2.1. Materials and Equipment.

WCME was obtained from Nantong BIOLUX Bioenergy Protein Feed Co. Ltd., -10# petro diesel (-10PD) and PDD were obtained from China Petroleum & Chemical Corporation.

2.2. Chemical composition determination.

WCME was 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 × 0.25μm). The carrier gas was helium (0.8 mL/min). The sample injection volume was 1μL. Temperature program was started at 160 ℃, staying at this temperature for 0.5 min, heated to 215 ℃ at 6 ℃/min, then heated to 230 ℃ at 3 ℃/min, staying at this temperature for 13 min.

2.3. CFPP measurement.

The cold filter plugging point (CFPP) was measured in SYP2007-1 multifunctional low temperature tester (shanghai boli, China) following the GB/T 20828-2007 procedures.

2.4. Kinematic viscosity measurement.

The kinematic viscosity was measured in SYP2007-7 the kinematic viscosity tester (shanghai boli, China) following the GB/T 265-1988 procedures.

3. Results and discussion

3.1. Chemical composition.

The main chemical composition of WCME and -10PD by GC-MS is shown in Table 1 and Table 2, respectively.

Table 1 Main composition of WCME

WCME	C12:0	C14:0	C16:0	C18:0	C20:0	C22:0	C16:1	C18:1	C20:1	C22:1	C18:2	C20:2	C18:3
(w)%	0.09	0.83	20.66	5.78	0.19	0.08	1.64	36.77	0.55	0.43	29.41	0.1	2.91

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

Table 2 Main composition of -10PD

-10PD	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C24	C26
(w)%	0.36	1.75	5.51	4.09	6.7	2.24	4.37	12.69	3.83	6.65	1.38	0.81	1.35	8.52	0.74	0.27

Note: C_m is the shorthand of alkane; *m* means the carbon number of alkane.

From Table 1, it can be seen that the WCME was mainly composed of fatty acid methyl esters (FAME) of 14~24 even-numbered C atoms. They contained: saturated fatty acid methyl ester (SFAME) $C_{14:0}$~$C_{24:0}$, unsaturated fatty acid methyl esters (UFAME) $C_{16:1}$~$C_{22:1}$, $C_{18:2}$ and $C_{18:3}$. The mass fraction of SFAME and UFAME was 14.69% and 83.40%, respectively. -10PD was mainly composed of long chain alkane of 8~26 C atoms.

3.2. Cold flow properties.

CFPP. Using cold filtration point tester, determine the CFPP of WCME and -10PD is 0℃ and -7℃, respectively. In China, the CFPP is an important indicator of biodiesel cold flow property. The lower CFPP is, the better cold flow property of biodiesel is.

The mass fraction of SFAME of WCME was 27.63% (Table 1). From Table 3, as the growth of the carbon chain and the increase of unsaturation, the melting point of FAME is reduced. The melting point of fatty acid methyl esters increases as the growth of the carbon chain and the decrease of the unsaturation. The carbon in alkyl groups of SFAME formed the structure of zigzag pattern, which made SFAME closely packed and crystallize easily. As the temperature decrease, the structure of SFAME developed a 3D mesh "framework" structure. The mass fraction of UFAME of WCME was 71.81% (Table 1). UFAME are easy to be fixed in the "framework" structure, which made biodiesel loss of liquidity finally.

Table 3 Melting point (m.p.) of fatty acid methyl esters

WCME	C12:0	C14:0	C16:0	C18:0	C20:0	C22:0	C18:1	C18:2	C18:3
m.p /℃	5.2	18.5	30.5	39.1	54.5	55.0	-20	-35	-55

Kinematic Viscosity. Using the kinematic viscosity tester, the kinematic viscosity of WCME and -10PD is shown in Fig. 1.

The kinematic viscosity reflects the resistance of oil in the flow process. If the kinematic viscosity is too large, the friction may be increase, which is unfavorable for oil flow in the engine oil pipeline and filter. On the contrary, the kinematic viscosity is too small, the lubrication effect will reduce, which easy to cause mechanical wear and tear. Therefore, its range on the national standards (40 ℃) is from 1.9 mm^2/s to 6.0mm^2/s. The kinematic viscosity (40 ℃) of WCME and -10PD are 4.41mm^2/s and 2.53mm^2/s.

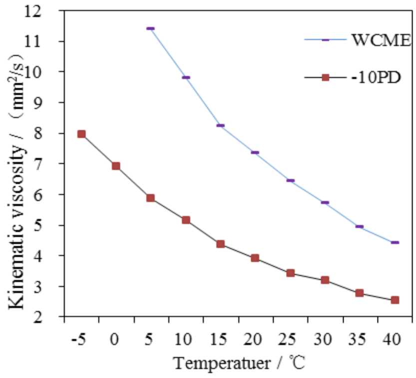

Fig. 1 The kinematic viscosity of WCME and -10PD

With the temperature decreases, WCME and -10PD gradually appeared crystallization. At the same time, the curves of viscosity-temperature became steep, which reflected that their flow properties had become worst. At the same temperature, the kinematic viscosities of WCME were greater than the -10PD. The mainly reason was different structure. WCME was mainly composed of 18 even-numbered C atoms FAME (74.87%).-10PD was mainly composed of long chain alkane of 10~17C atoms.

3.3. Improvement of Cold Flow Property.

Blending with -10PD. (1) CFPP. Using cold filtration point tester, determine the CFPP of bleeding oil. (Fig. 2)

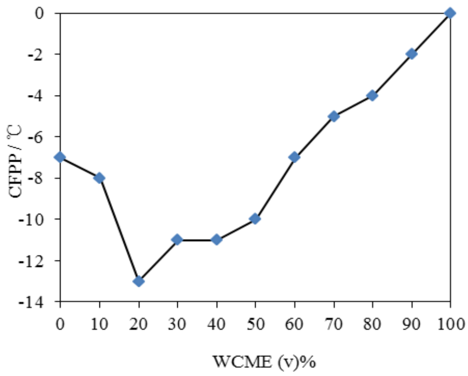

Fig.2 The CFPP of WCME / -10PD

With increasing WCME blending ratio, blending oil CFPP decreased from -7 ℃ to -13 ℃ with B0~B20 (Bn is biodiesel blended with petro diesel, the n indicates the volume fraction of biodiesel in the blend.), staying at -13 ℃ with B20, then increased to 0 ℃ (Fig.2). It was chiefly because WCME blending with -10PD decreased SFAME content, which could resistant to form the 3D mesh "framework" structure at low temperature. By blending, the long chain SFAME of WCME and long chain alkane of -10PD could form a eutectic mixture, with B10~B60. Therefore, the CFPP of blending oil was lower than that of WCME and -10PD.

(2) Kinematic viscosity. Using the kinematic viscosity tester, determine the kinematic viscosity of blending oil at different temperature, shown in Fig. 3.

With the temperature decreased, the kinematic viscosity of blending oil had reduced. Under the same temperature, with increasing WCME blending ratio, it decreased continuously, gradually reach to suitable the kinematic viscosity of -10PD. In blending oil, the less WCME, the less ester group, the less influence of ester base on kinematic viscosity.

Blending with -10PD. The economic and performance benefits of using cold flow improver to improve cold flow properties of biodiesel have been recognized. The effect of WCME/-10PD and WCME without / with PDD was research.

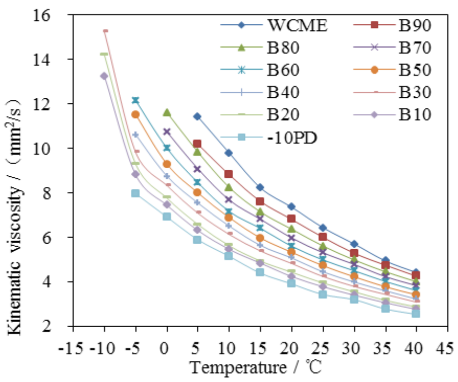

Fig. 3 The kinematic viscosity of WCME / -10PD

(1) CFPP. The actual used blending oil of WCME were B10 and B20. The optimum volume fraction of additives and the CFPP of B10, B20 and WCME without/with PDD is shown in Table 4.

Table 4 Influence of PDD on CFPP of WCME and WCME/-10PD

RME/-10PD	The optimum volume fraction(‰)	CFPP without PDD (℃)	CFPP with PDD(℃)
B10	6	-8	-26
B20	7	-13	-25
WCME	5	0	-4

From Table 4, it can be seen that PDD (5‰) reduced the CFPP of WCME reduced from 0℃ to -4℃. The cold flow improver was polymer polarity substances containing ester base. It may be the crystal nucleus in early crystallization, which made crystal become small. In the process of crystal growth, it played a role to absorption effect and co-crystallization, which had decreased the adhesion between crystals, and prevented the formation of crystal ball. So, small amount of PDD additives affected the CFPP of WCME. By adding the PDD, the cold flow properties of WCME was improved.

Adding the PDD, the CFPP of B10 and B20 significantly reduced to-23℃ and -26℃. After blended with -10PD, Concentration of the SFAME had reduced in blending oil. It inhibited the crystals from growing to a larger size and provided a barrier to crystal agglomeration at low temperatures, thus extending the range of fluidity of the biodiesel to lower temperatures.

(2) Kinematic viscosity. The kinematic viscosity's change of B10 and B20 without/with PDD was shown in Fig.4. The experimental results show that the kinematic viscosity's change of B10 and B20 without PDD was very small. small amount of PDD additives hardly affected the composition of blending oil. Therefore, adding the PDD can not fundamentally eliminate the influence of crystals on the kinematic viscosity.

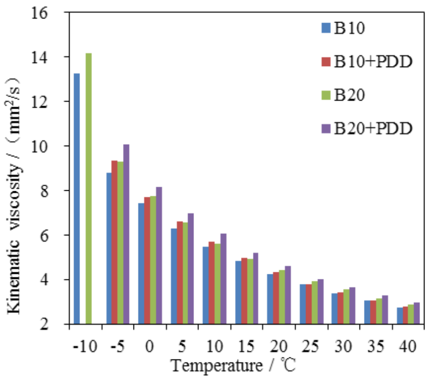

Fig.4 The kinematic viscosity of with/without PDD

4. Conclusion

(1) The WCME was mainly composed of fatty acid methyl esters (FAME) of 14-24 even-numbered C atoms. The mass fraction of SFAME and UFAME are 27.63% and 71.81%, respectively. The CFPP of WCME is 0℃, and the kinematic viscosity of WCME is 4.41mm^2/s at 40℃.

(2) The CFPP of blending oil decreased from -7 ℃ to -13 ℃ with B0~B20, staying at -13 ℃ with B20, then increased to 0 ℃. With increasing WCME blending ratio, the kinematic viscosity of blending oil decreased continuously.

(3) Adding with PDD decreased the CFPP of WCME, B10 and B20 from 0℃, -8℃, and -13℃ to -4℃, -26℃ and -25℃, which hardly affected to blending oil.

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