Cold flow properties and improvement of the cottonseed oil methyl ester and its blending oils

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Abstract. The chemical compositions of cottonseed oil methyl ester (CSME) were analyzed by the gas chromatograph- mass spectrometer (GC-MS). The cold flow properties of CSME and blending oils which made CSME to blend with 0PD were studied. Through adding Flow Fit the cold flow properties of CSME and blending oils were improved. The study shows that CSME is mainly composed of fatty acid methyl esters (FAMEs), and the contents of saturated fatty acid methyl esters (SFAMEs) and unsaturated fatty acid methyl esters (UFAMEs) are 27.69% and 71.65%, respectively. The cold filter plugging point (CFPP) of CSME is -1 ℃, and the viscosity at 40 ℃ of CSME is 4.63mm^2/s. The CFPP of blending oil decreases to -8 ℃ when the ratio of CSME is 50%, and at the same temperature the viscosity of blending oils are lower than CSME. Adding less than 3%(volume fraction) of Flow Fit, the CFPP of CSME, B50, B20, B10, B7 and B5 decreased from -1,-8, -5, -4, -3, -3 ℃ to -5, -16, -25, -24,- 25, -23 ℃.

Keywords: biodiesel, cottonseed oil, cold flow properties.

1. Introduction

With the deficiency of petrol resource and the deterioration of the environment, it becomes an urgent affair to develop diversification, renewable and clean energy sources. As an important supplement to petroleum diesel, biodiesel gets more and more attractions because of its renewable capability and environmental benefits [1]. However, biodiesel is easy to crystallize and block the fuel lines and filters at low temperature. Therefore, the cold flow properties of biodiesel have to be improved urgently.

In recent years, researches about cold flow properties of biodiesel concentrated in the influence factor of cold flow properties, development of cold flow improver, and the improving measures of cold flow properties. Knothe et al. [2-3] recommended that the cold flow properties of biodiesel were mainly determined by the amount and type of fatty acid methyl esters, cold filter plugging point (CFPP) of biodiesel increased with the increasing of content and the length of saturated fatty acid methyl esters (SFAMEs). Nestor et al. [4-6] used ozonized vegetable oils, methyl acrylic acid high carbon ester withα-hydroxyl, and the mixtures of cold flow improvers to improve biodiesel cold flow properties. Kerschbaum et al. [7-8] used winterization techniques on biodiesel which based waste cooking oil and peanut oil. Using this method, the CFPP of waste cooking oil and peanut oil biodiesel were decreased for 11 and 24 ℃. Wu Miaoxin et al. [9-11] tried to improve cold flow properties of palm oil, rapeseed oil, and pistacia chinensis oil biodiesel by blending with petroleum diesel and treating with cold flow improver respectively. The study showed that blending with petroleum diesel could decrease the CFPP of palm oil and rapeseed oil biodiesel from 8 and -1 ℃ to -12 and -15 ℃, adding cold flow improver could decrease the CFPP of three oils from 8, -1 and 3 ℃ to 2, -18 and -4 ℃. Meng Zhonglei et al. [12] used methanol and branched-chain alcohol to prepare the soybean oil biodiesel, which CFPP was 5-8 ℃ lower than biodiesel prepared from pure methanol. BaiYu et al.

[13] modified the main components of biodiesel to decrease the CFPP of biodiesel by 19 ℃. The objective of this study is to determine the chemical composition of cottonseed oil methyl ester (CSME) by gas chromatography - mass spectrometer (GC-MS), research the cold flow properties of CSME and its blending oil using CFPP tester and viscosity tester, construct a CSME viscosity-temperature prediction model with linear dependence, and improve cold flow properties of CSME and its blending oil by treating with Flow Fit.

2. Experimental

2.1. Materials and Equipment.

0 petroleum diesel (0PD) was provided by China Petroleum & Chemical Corporation; CSME which accorded with GB/T 20828 2007 was prepared in laboratory; Flow Fit was obtained from Liqui Moly, German.

Trace MS GC-MS; SYP2007-I CFPP tester; SYP1003-I viscosity tester.

2.2. Analytical methods.

2.2.1. Chemical Composition Determination. CSME was analyzed with a gas chromatograph-mass spectrometer (GC-MS) equipped with a capillary column (DB-WAX, 30 m × 0.25 mm × 0.25 μm). Sample injection volume was 0.1 μl. The carrier gas was He (0.8 ml/min). Temperature programming was from 160 ℃ (remaining for 0.5 min) to 215 ℃ by 6 ℃/min, then increased from 215 to 230 ℃ by 3 ℃/min, and maintained for 13 min.

2.2.2. Cold flow properties measurement. CFPP and viscosity of CSME are measured in accordance with SH/T 0248-2006 and GB/T 265-1988.

3. Results and discussion

3.1. Chemical composition.

The composition of 0PD and CSME were shown in Tables 1 and Table 2. The main chemical composition of 0PD is n-alkenes composed of 10 to 21 carbon atoms with mass fraction of 75.1%, while the composition of CSME is fatty acid methyl esters (FAMEs) of 14 to 22 carbon atoms, including SFAMEs and unsaturated fatty acid methyl esters (UFAMEs) with fractions of 21.69% and 71.65%.

Table 1 Main chemical composition of 0PD (*w*) / %

C_m	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}
Content	5.85	9.91	7.88	1.80	6.42	6.91	9.15	3.76	6.53	6.41	3.97	3.92

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

Table 2 Main chemical composition of CSME (*w*) / %

$C_{m:n}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{20:0}$	$C_{22:0}$	$C_{16:1}$	$C_{14:0}$	$C_{18:1}$	$C_{20:0}$	$C_{18:2}$	$C_{18:3}$	$C_{20:3}$
Content	0.98	23.36	2.90	0.30	0.15	0.72	19.54	0.10	50.96	0.26	0.07	0.98

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

3.2. Cold flow properties.

3.2.1. CFPP. The CFPP of CSME, its blending oil (CSME/0PD), and 0PD were shown in Fig.1. It is stipulated in GB/T 20828-2007 that the cold flow property of biodiesel is evaluated by CFPP. The lower the CFPP, the better the Cold flow property is. Biodiesel can be regarded as a pseudo-binary solution composed of high-melting-point SFAMEs and low-melting-point UFAMEs. The CFPP of biodiesel increased with SFAMEs amount increasing. Biodiesel was easier to crystallize, and the cold flow properties became poorer with SFAMEs content increasing. Therefore, the cold flow property of biodiesel was mainly determined by the content and distribution of SFAMEs. The content of SFAMEs in CSME reached up to 27.69%, and the CFPP was -1 ℃, which was higher than the that of 0PD (-3 ℃). So, the cold flow property of CSME was poorer than 0PD.

Fig.1 showed that with increasing CSME blending ratio, blending oil CFPP decreased at first and then increased. The CFPP decreased from -3 to -8 ℃, and then increased to -1 ℃. When the blending ratio reached 50%, the CFPP decreased to the minimum value of -8 ℃. This was because blending with 0PD decreased SFAME content, it became difficult to crystallize, and the CFPP of blending oil (CSME/0PD) was lower than CSME. In addition, the SFAME in CSME could form a eutectic mixture with the long-chain alkanes in 0PD, which made the CFPP of blending oil lower than CSME and 0PD. The CFPP of B50 was lowest with -12 ℃. When blending ratio was higher than 50%, SFAME content in the blending oil would increase, and it became easier to crystallize which could cause the increasing of blending oil CFPP. Blending with 0PD could change the composition of CSME. The size and shape of the crystals also have been changed under low temperature. It could prevent the formation of three-dimensional network structure effectively.

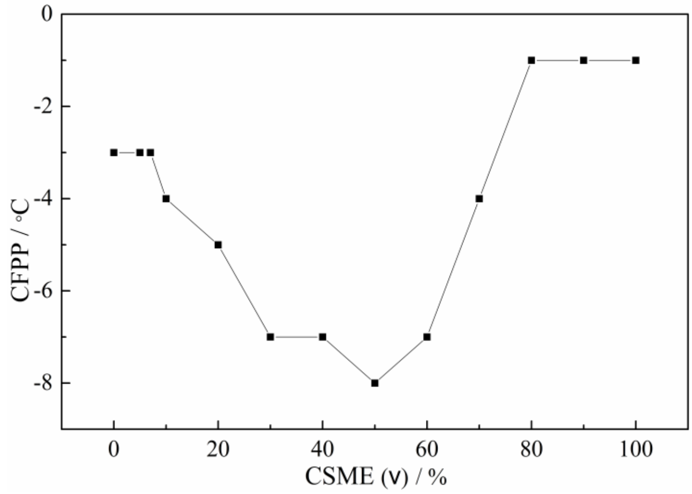

Fig. 1 CFPP of CSME/0PD

3.2.2. Viscosity-temperature characterization. Viscosity is the index to evaluate the flow ability of petroleum products. If viscosity is too high, the flow ability of oil would be poorer, but it would have a good lubrication performance. If viscosity is too low, the flow ability of oil would be good, but the lubrication performance would be poorer, which can cause mechanical wear. So it is stipulated in National Standard that the viscosity at 40 ℃ of diesel is 1.9 -6.0 mm^2/s.

3.2.2.1. CSME viscosity-temperature characterization and mathematical modeling. Viscosity - temperature characterization curve of CSME and 0PD were shown in Fig.2.

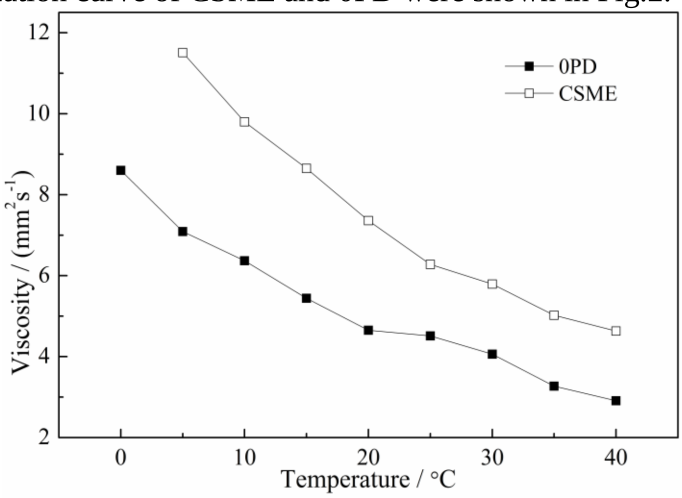

Fig. 2 Properties of viscosity versus temperature curves of CSME and 0PD

Viscosities of CSME and 0PD were 4.63 and 2.91 mm^2/s respectively, which were within National Standard. Under the same temperature condition, the viscosity of CSME was higher than that of 0PD. Differences between CSME and 0PD viscosity are mainly due to the different composition. CSME is mainly composed of FAME with 14-22 C atoms which contain long-chain SFAMEs. The SFAMEs in CSME is easy to crystallize by cooling, that will make CSME viscosity higher. Long-chain alkane content in 0PD was low, and average molecular weight of 0PD was smaller than CSME. So the viscosity of CSME was higher than 0PD at the same temperature. The viscosity of CSME and diesel both increased with temperature falling. They crystallize respectively when temperature was higher than CFPP. The SFAMEs is easier to crystallize in CSME. It also could form a three-dimensional expended framework filled with UFAMEs which could lead to poorer flow ability of CSME. It caused the difference between CSME and 0PD viscosity increasing, and the viscosity-temperature characterization curve of CSME was steeper than that of 0PD.

The mathematical model was thus established based on the linearity regression analysis having temperature as the independent variable, and CSME viscosity as the dependent variable.

The equation of the mathematical model is as follows.

$$y = 0.004x^2 - 0.37x + 13.21 \quad (1)$$

Where y is viscosity of CSME (mm^2/s) and x is temperature (℃).

3.2.2.2. Cold Flow Property of blending oil. The relation curves that blending oil (CSME/0PD) viscosity varies with temperature were shown in Fig.3. It could be seen that the viscosity of blending oil increased as the fraction of CSME increasing at same temperature, and the blending oil viscosity lied between 0PD and CSME. With temperature decreasing, CSME/0PD viscosity increased constantly. When the temperature was close to CFPP, the blending oil viscosity would leap, and the curves of viscosity-temperature became steep. It was mainly because the average molecular weight of CSME was greater than 0PD, and the viscosity of CSME was also greater than that of 0PD. The average molecular weight of blending oil increased with the increasing of CSME blending ratio, so did the viscosity at the same temperature. With temperature decreasing, the intermolecular forces increased, and solid-liquid phase transition occurs, the blending oil would crystallize gradually. The viscosity of blending oil would increase constantly, and the curves of viscosity-temperature also show a progressive rise. A little crystal can hardly affect the cold flow properties of blending oil, and the curves of viscosity-temperature decline slowly. When the temperature was near CFPP, large quantity of crystal would separate from blending oil, which could lead to the surge of blending oil viscosity. At last, crystallizing connection would take place, and the blending oil lost flow ability. CSME content were low in B5, B7 and B10, it had little influence on average molecular weight of blending oil. The viscosity of blending oil was close to 0PD as well as the curves of viscosity-temperature. This suggested that addition of CSME with a proportion of 5%, 7%, and 10% hardly affected viscosity of diesel, so CSME could substitute diesel partly. This could ease global petroleum crises to some extent.

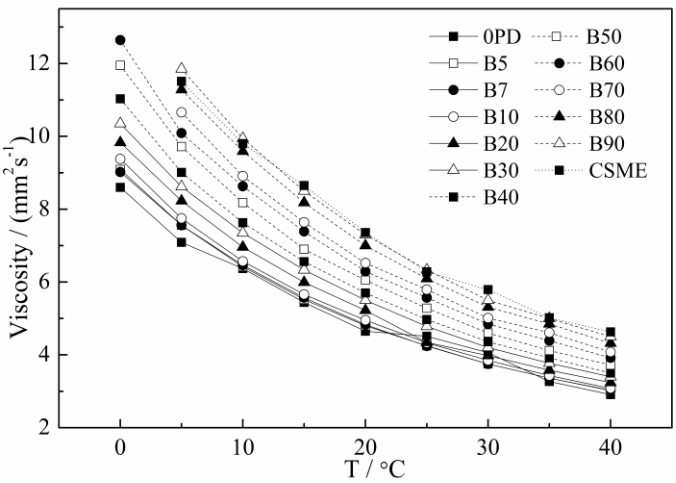

Fig. 3 Properties of viscosity versus temperature curves of CSME/0PD

3.3. Improvement of Cold Flow property.

Using Flow Fit is an economic and performance way for improving cold flow properties of biodiesel. Taking B5, B7, B10, B20, B50, and CSME as examples, the paper has analyzed the effect of Flow Fit on CFPP of CSME and CSME/0PD. The CSME and CSME/0PD without/with CFI is shown in Fig. 4.

From Fig.4, it could be seen that Flow Fit reduced the CFPP of CSME, B5, B7, B10, B20, and B50 from -1, -3, -3, -4, -5, and -8 ℃ to -5, -23, -25, -24, -25, and -16 ℃. With the improvement of the fraction of CSME, the addition quantity of Flow Fit increased. When blending ratio of CSME was low, adding low Flow Fit could also reduce the CFPP of CSME and improve its cold flow properties significantly. This was because the FAME in oil would be affected by Flow Fit during crystallization. Flow Fit could suppress the grain growth of crystal in CSME and CSME/0PD. Therefore, it was difficult to form a three-dimensional network structure, and the cold flow properties of CSME and CSME/0PD would not be affected.

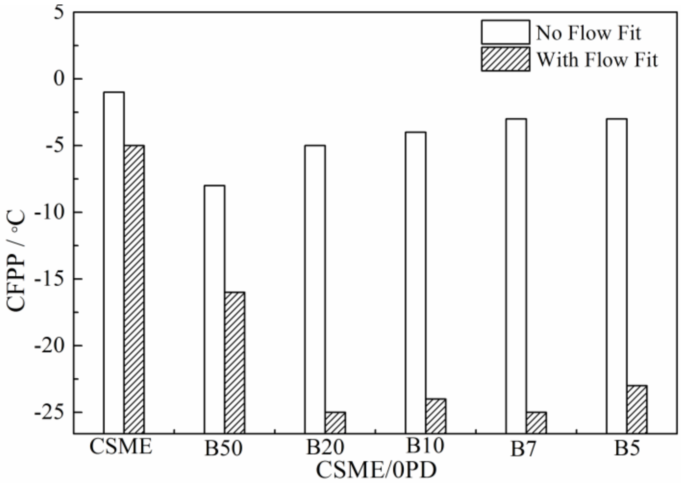

Fig. 4 CFPP of CSME and CSME/0PD without/with Flow Fit

4. Conclusion

(1) The main chemical composition of 0PD was n-alkenes composed of 8 to 21 carbon atoms. CSME was mainly composed of fatty acid methyl esters. The fractions of saturated fatty acid methyl esters and unsaturated fatty acid methyl esters were 27.69% and 71.65%, respectively. The CFPP of 0PD and CSME were -3 and -1 ℃. And the viscosity at 40 ℃ of 0PD and CSME were 2.91 and 4.63 mm^2/s respectively.

(2) The CFPP of blending oil depended on the composition of blending ratio. When the blending ratio of CSME was 50%, the CFPP was -8 ℃. The viscosity of blending oil was lower than that of CSME at the same temperature, and the viscosity increased with temperature decreasing.

(3) Treating with Flow Fit could improve cold flow properties of CSME and its blending oil. Flow Fit (volume fraction⩽3%) reduce the CFPP of CSME, B50, B20, B10, B7, and B5 from -1, -8, -5, -4, -3, and -3 ℃ to -5, -16, -25, -24, -25, and -23 ℃.

Acknowledgements

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