Fatty acid methyl esters composition and cold flow property of palm oil biodiesel

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Abstract

The chemical compositions and cold filter plugging point (CFPP) of palm methyl ester (PME) are investigated. Through blending with 0 petrodiesel (0PD) / -10 petrodiesel (-10PD) and treating with Flow Fit (FF) / Flow Fit K (FFK) / T818, the CFPP of PME is reduced significantly. The study shows that CSME is mainly composed of fatty acid methyl esters (FAME), and the contents of saturated fatty acid methyl ester (SFAME) and unsaturated fatty acid methyl ester (UFAME) are 35.86% and 62.83%, respectively. The CFPP of PME is 10 °C. Blending with 0PD and -10PD decreased the CFPPs of PME to -11°C and -13 °C, respectively. Treating with less than 8‰ (volume fraction) of FF, FFK and T818, the CFPPs of PME, PME/0PD and PME/-10PD decreased to 2 °C, -20 °C and -26 °C, respectively.

Keywords

Biodiesel, Palm oil, Cold flow properties, Cold Filter plugging point.

1. Introduction

One of the viable options to counter the excessive usage of petroleum diesel can be biodiesel, because it possesses comparable fuel properties as of diesel. There has been a considerable interest in developing woody biodiesel, viz., palm oil biodiesel as a substitute for an additive to petrodiesel in recent years due to its environmental benefits and because it is derived from renewable resources. But PME has poor cold flow property. When palm oil biodiesel is subjected to lower temperatures, biodiesel nucleate and form solid crystal. These crystals plug or restrict flow through fuel lines and filters during startup and can lead to fuel starvation and engine failure. In recent years, researches about cold flow property of biodiesel included: cold flow improver (CFI) [1, 2], and influences on cold flow property, viz., chemical composition of biodiesel [3, 4], blending reagent [5, 6] and CFI [1, 7]. In this study, we investigate chemical composition, cold filter plugging point and viscosity - temperature characteristics of palm oil biodiesel.

2. Experimental

2.1 Materials.

Palm methyl ester (PME) is prepared by our laboratory, in line with GB/T 20828-2007 requirements. 0 petrodiesel (0PD) and -10 petrodiesel (-10PD) is obtained from China Petroleum & Chemical Corporation. Flow Fit and Flow Fit K are provided by Liqui Moly, German. T818 was provided by SH Renyinglian Trade Development Co., Ltd., Shanghai, China.

2.2 Chemical composition analysis.

FAMEs of biodiesel are analyzed with a gas chromatograph-mass spectrometer (GC-MS) (Finnigan, Trace MS, FID, USA) equipped with a capillary column (DB-WAX, 30 m × 0.25 mm × 0.25 μm). Sample injection volume is 0.1 μl. The carrier gas is He (0.8 ml min-1). Temperature is programmed

as follows: 180 °C maintained for 0.5 min; 6 °C min-1 from 180 °C to 215 °C; and 3 °C min-1 from 215 °C to 230 °C maintained for 13 min.

2.3 Cold Filter plugging point measured.

CFPPs of biodiesel and blended biodiesel are measured with a SYP2007-1 Low Temperature Multi-function Tester (Shanghai BOLEA Instrument & Equipment Co. Ltd., China) in accordance with SH/T 0248-2006.

3. Results and discussion

3.1 Composition.

GC-MS is utilized to analyze the chemical composition of PME, 0PD and -10PD. The gas chromatogram is shown in Fig.1. The chemical composition is shown in Table 1 and Table 2.

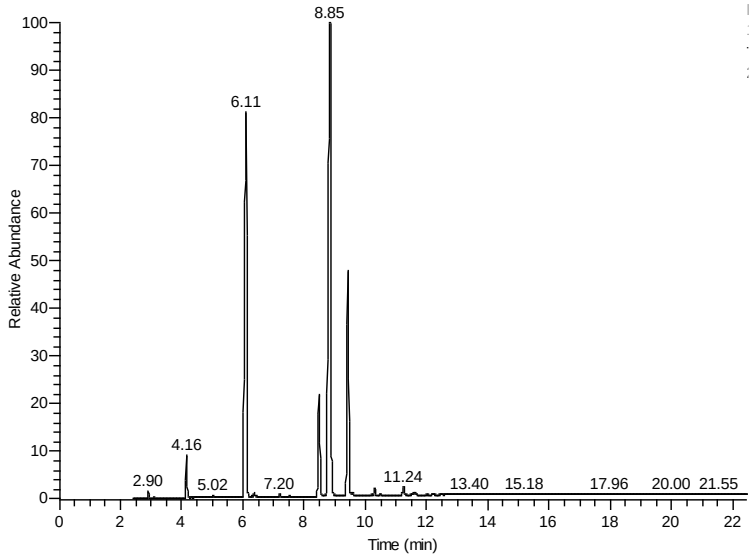

Fig. 1 The gas chromatogram of PME

Table 1 The main chemical composition of 0PD and -10PD (w)/%

Content	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{24}	C_{26}
0PD	0.00	0.00	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	0.00	0.00
-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	0.00	0.74	0.27

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

Table 2 The main chemical composition of PME (w)/%

RBME	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{20:0}$	$C_{22:0}$	$C_{24:0}$	$C_{26:0}$	$C_{16:1}$	$C_{18:1}$	$C_{20:1}$	$C_{18:2}$	$C_{18:3}$
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, the main chemical compositions of 0PD are the alkane composed by C_{10}-C_{22}, and -10PD by C_8-C_{26}. From Table 2, it can see that PME is mainly composed of long chain fatty acid methyl esters (FAME) of 14-24 even-numbered C atoms. They contain: saturated fatty acid methyl esters (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 fractions of SFAME and UFAME are 35.86% and 62.83%, respectively.

3.2 Cold flow property

PME has relatively poor cold flow properties due to its high amount of SFAME (35.86%). The CFPP of PME is 10 °C. It has limited the application in cooler weather.

3.3 Improvement of cold flow property

3.3.1 Crystallization fractionation

PME crystallization fractionation is carried out at cooling rate of 1°C/min and interval of temperature of 25-0°C, staying at this temperature for 24h. Then liquid-solid separation is carried out to obtain crystallization fractionation biodiesel (PME-CF), and yield is 68.2%. PME-CF chemical compositions are analyzed by GC-MS, and mass fraction of SFAME is 25.01%. Byproducts (solid) are used for summer biodiesel and oil chemical industry.

The CFPP of PME-CF is 2°C, it is 8 °C lower than that of PME. It is chiefly because amount of SFAME is decreased by crystallization fractionation. Biodiesel may be considered a pseudobinary solution consisting of high-melting-point SFAME (solute) and low-melting-point UFAME (solvent). According to solution crystallization theory, the more SFAME, the easier biodiesel crystallization, the higher CFPP, the poorer cold flow properties for biodiesel. The mass fraction of SFAME of PME and PME-CF was 35.86% (Table 1) and 25.01%, respectively. Crystallization fractionation was a useful way to reduce CFPP by reducing SFAME content.

3.3.2 Blending with petrodiesel

The CFPPs of PME/0PD and PME/-10PD are shown in Fig.2. It shows a relation between CFPP and the PME blending ratio. With the petrodiesel blending ratio increasing, the CFPP of PME/0PD and PME/-10PD decreased to -21 °C and -24 °C, respectively. That is chiefly because that blending with petrodiesel not only decreased SFAME content but also could form a eutectic mixture between PME long SFAME and petrodiesel long chain alkane. At the low temperature the component would change when the 0PD or -10PD are added into PME, it would effectively prevent crystals forming a three-dimensional network by changing the shape and size of crystals.

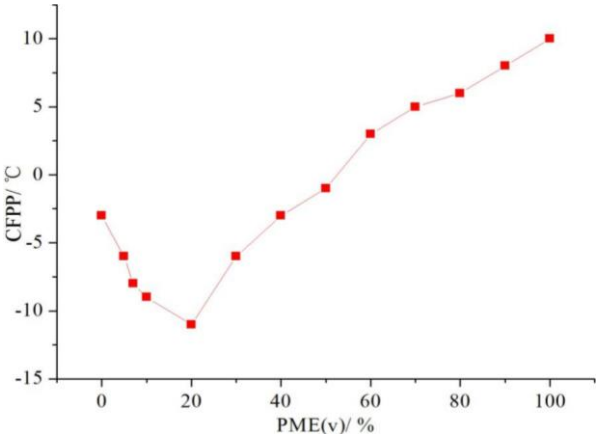

Fig. 2 The CFPP of PME/0PD

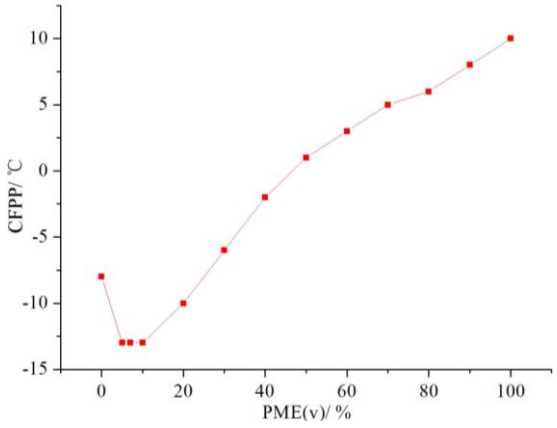

Fig. 3 The CFPP of PME/-10PD

3.3.3 Treating with CFI additives

The optimum volume fraction of additives is shown in Table 3. The CFPPs of PME/0PD and PME/-10PD treating with FF, FFK and T818 are given in Fig.4 and Fig.5, respectively. The CFPP of PME is reduced from 10 °C to 5 °C, 4 °C and 5 °C when add FF, FFK and T818, respectively. Meanwhile, the CFPPs of PME/0PD are decreased to -19°C, -19 °C and -20 °C, respectively; the CFPPs of PME/-10PD are decreased to -24°C, -24°C and -25 °C, respectively . It is mainly because that the crystallization behavior of FAME in oils is easily affected by CFI. FF, FFK or T818 which absorbs on the surface of crystals can hold up the process, that crystals grow up and stuck together with each other, and then that is difficult to form the three-dimensional network structure. It can be seen that treating with FF, FFK and T818 can reduce the CFPP of PME, PME/0PD and PME/-10PD efficiently.

Table 3 optimum volume fraction of CFI

Oil sample	PME	B90	B80	B70	B60	B50	B40	B30	B20	B10	B7	B5	PD
FF /v‰	6	6	6	6	6	6	6	6	6	3	3	3	1
FFK /v‰	8	8	8	8	8	8	6	3	3	1	1	1	1
T818 /v‰	8	8	8	8	8	8	6	6	3	1	1	1	1

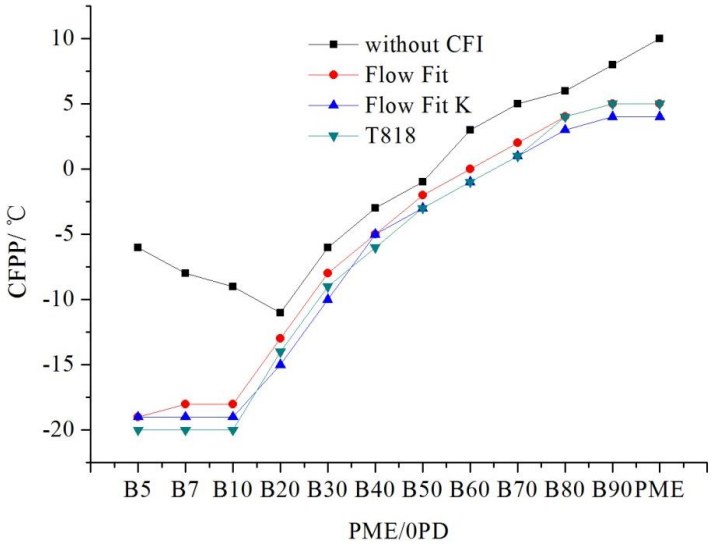

Fig. 4 CFPP of PME, PME/0PD without/with CFI

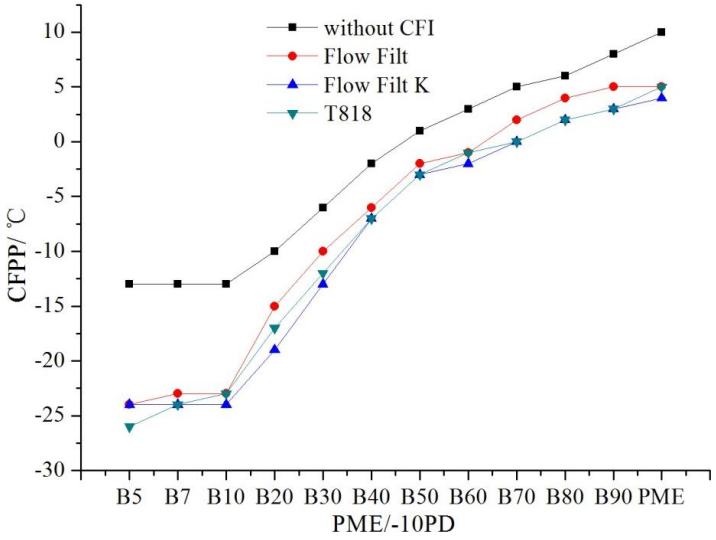

Fig.5 CFPP of PME, PME/-10PD without/with CFI

4. Conclusion

The PME is mainly composed of FAMEs: SFAMEs ($C_{14:0}$-$C_{24:0}$) and UFAMEs ($C_{16:1}$-$C_{22:1}$, $C_{18:2}$ and $C_{18:3}$), and their mass fractions are 35.86% and 62.83%, respectively. The CFPP of PME is 10 °C, it has relatively poor cold flow property. Three approaches for improving cold flow properties of PME are adopted. Crystallization fractionation decreases the CFPP to 2 °C. Blending with 0PD and -10PD decreases the CFPP to -11°C and -13 °C, respectively. Treating with FF, FFK and T818 (volume fraction ≤ 8 v‰) can decrease effectively the CFPP of PME and its blends. The lowest CFPPs of PME, PME/0PD and PME/-10PD are -13, -20 and -26°C, respectively.

Acknowledgements

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