Reducing Cold Filter Plugging Point of Biodiesel Produced from Cottonseed Oil

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Abstract

The chemical compositions, cold filter plugging point (CFPP) and kinematic viscosity of cottonseed methyl ester (CSME) are investigated. Through blending with -10 petrodiesel (-10PD) and treating with Flow Fit K (FFK) or Bang Jie depressant (BJD), the CFPP of CSME 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 32.41% and 66.24% respectively. The CFPP of CSME is 6 ℃. Blending with 0PD and -10PD decreased the CFPPs of CSME to -8 and -12 ℃. Treating with less than 5‰ (volume fraction) of FFK and BJD, the CFPPs of CSME, CSME/0PD and CSME/-10PD decreased to 2, -20 and -25 ℃, respectively.

Keywords

Biodiesel, Cottonseed oil, Cold filter plugging point, GC-MS.

1. Introduction

Biodiesel has received considerable attention as an alternative diesel fuel. However, the high costs of these feedstocks and their competition with food sources are the major bottlenecks for the commercialization of biodiesel especially in developing countries such as China with limited arable land per capita. China is one of the main cotton producing countries in the world. The total production of cotton is up to 5.61 million tons in 2015. It has certain risks of eating cotton oil since the presence of toxic gossypol in it. It is a new way to use cottonseed for the preparation of biodiesel just because of its low price and rich resources [1]. A further assertion is that the supplement problem of raw material for preparation biodiesel is also relieved. However cold filter plugging point (CFPP) of cottonseed methyl ester (CSME) is 6 ℃, the unfavorable cold flow properties of CSME since saturated methyl esters within CSME nucleate and form solid crystals at low temperature which can clog or restrict flow through fuel lines and filters or even become so thick that it even can't be pumped from the fuel tank to the engine, restrict its application and promotion in low temperature condition. Therefore, it is important to improve the cold flow properties of CSME, reduce CFPP. In the decade years, researches on CFPP of biodiesel are mainly concentrated in the three aspects including adjustment of winterization [2], blending with petrodiesel [3, 4], and treating with cold flow improver (CFI) [5-7]. The objectives of this study are to reduce CFPP of CSME by blending with petrodiesel and treating with CFI.

2. Experimental

2.1 Materials

Cottonseed oil is purchased from Dantu grain and oil chemical plant, China; 0 petrodiesel (0PD) and -10 petrodiesel (-10PD) are purchased from China Petroleum & Chemical Corporation. Flow Fit K (FFK) and Bang Jie depressant (BJD) are purchased from Germany Liqui Moly and China Petroleum & Chemical Corporation, respectively.

2.2 Biodiesel Preparation.

The cottonseed oil is transesterified with methyl alcohol to produce the biodiesel. The volume ratio of methyl alcohol to the rapeseed oil is set at 1:5. In this reaction 0.8 wt% of NaOH in relation to oil is dissolved in methanol, and then add to the oil being stirred at a constant temperature for 80 min. Then the mixture is decanted, and the lower layer, rich in glycerol and methanol, was removed. The top layer was washed with water three or four times to remove residual NaOH, methanol, and soap. The washed biodiesel was dried at 48 ℃ for about 5 min.

2.3 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, 30m × 0.25mm × 0.25μm). The carrier gas is helium (0.8mL/min). The sample injection volume is 1μL. Temperature program is started at 160 ℃, staying at this temperature for 0.5min, heated to 215 ℃ at 6 ℃/min, then heated to 230 ℃ at 3 ℃/min, staying at this temperature for 13 min.

2.4 Cold Filter Plugging Point Measured.

The CFPP of oil samples is measured in accordance to SH/T 0248-2006, using the SYP2007-1 Cold Filter Plugging Point Tester (Shanghai BOLEA Instrument & Equipment Co., Ltd., China).

3. Results and discussion

3.1 Composition.

The main chemical composition of CSME, 0PD and -10PD analyzed by GC-MS is shown in Table 1 and Table 2.

Table 1 The main chemical composition of CSME (w)/%

CSME	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{20:0}$	$C_{22:0}$	$C_{24:0}$
Content	0.05	0.24	1.28	24.04	5.71	0.69	0.23	0.17
CSME	$C_{16:1}$	$C_{18:1}$	$C_{20:1}$	$C_{22:1}$	$C_{16:2}$	$C_{18:2}$	$C_{20:2}$	$C_{18:3}$
Content	0.51	38.87	0.61	1.10	0.02	23.32	0.03	1.78

Note: Cm:n is the shorthand of fatty acid methyl ester; m means the carbon number of fatty acid; n means the number of C=C.

Table 2 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.

From Table 1, we can see that dominate the main chemical compositions of CSME are the fatty acid methyl ester (FAME) composed by 10-24 even number carbon atoms, and the mass fraction of saturated fatty acid methyl esters (SFAME) ($C_{10:0}$-$C_{24:0}$) and unsaturated fatty acid methyl esters (UFAME) ($C_{16:1}$-$C_{22:1}$, $C_{16:2}$-$C_{20:2}$ and $C_{18:3}$) is 32.41% and 66.24%, respectively. From Table 2, the main chemical compositions of 0PD and -10PD are the alkane composed by C_{10}-C_{22} and C_8-C_{26}, respectively.

3.2 Cold Filter Plugging Point.

The CFPP of CSME is 6 ℃. Compared to 0PD (-3 ℃) and -10PD (-7 ℃), CSME is higher. CSME can be regarded as pseudo two components in solution approximately which was composed of the high melting component SFAME (solute) and low melting component UFAME (solvent). As the temperature is decreased, SFAMEs within CSME nucleate and form solid crystals which can clog or restrict flow through fuel filters or even become so thick that it can’t flow. It results in CFPP higher, viz., unfavorable cold flow properties.

3.3 Blending with petrodiesel.

The CFPPs of CSME/0PD and CSME/-10PD are shown in Fig.1. It shows a relation between CFPP and the CSME blending ratio. With the petrodiesel blending ratio increasing, the CFPP of CSME/0PD and CSME/-10PD decreased to -8 ℃ and -12 ℃, respectively. That was chiefly because that blending with petrodiesel not only decreased SFAME content but also could form a eutectic mixture between CSME long SFAME and petrodiesel long chain alkane. At the low temperature the component would change when the 0PD or -10PD are added into CSME, it would effectively prevent crystals forming a three-dimensional network by changing the shape and size of crystals.

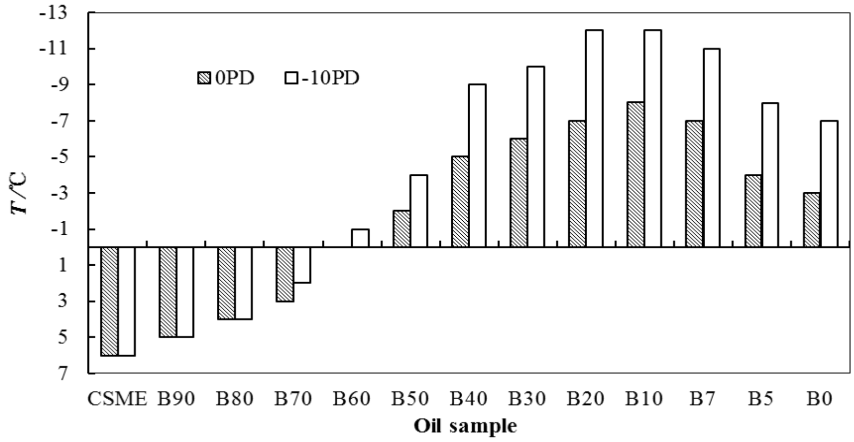

Fig. 1 The cold filter plugging point of CSME/0PD and RBME/-10PD

3.4 Treating with cold flow improver additives.

The optimum volume fraction of additives is shown in Table 3. The CFPPs of CSME/0PD and CSME/-10PD treating with FFK and BJD are given in Fig.2 and Fig.3, respectively. The CFPP of CSME is reduced from 6 ℃ to 2 ℃ when add FFK or BJD in it. Meanwhile, the CFPPs of CSME/0PD and CSME/-10PD are decreased to -20 and -25 ℃, respectively. It is mainly because that the crystallization behavior of FAME in oils is easily affected by CFI. FFK or BJD 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 FFK and BJD can reduce the CFPP of CSME, CSME/0PD and CSME/-10PD efficiently.

Table 3 The optimum volume fraction of CFI

Oil sample	SME	B90	B80	B70	B60	B50	B40	B30	B20	B10	B7	B5
Flow Fit /v‰	5	3	2	2	1	1	1	1	1	1	1	1
Flow Fit K /v‰	3	2	1	1	1	1	1	1	1	1	1	1

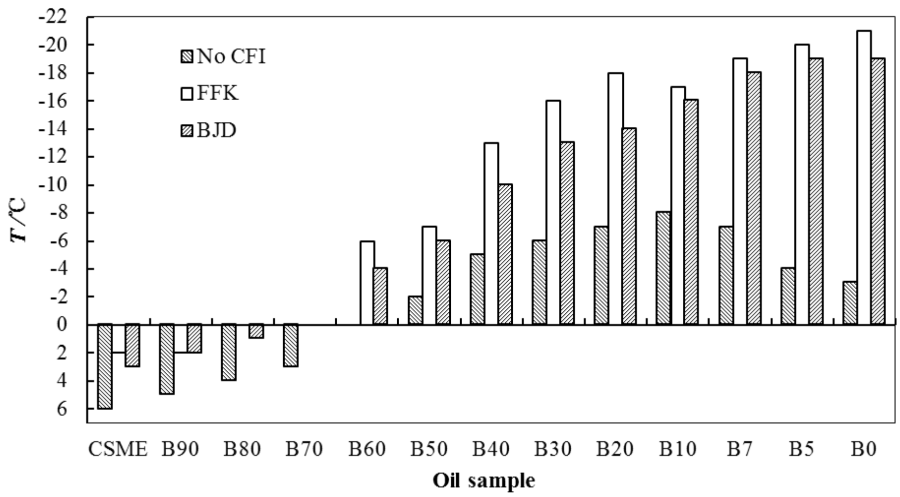

Fig. 2 The cold filter plugging point of CSME/0PD without/with CFI

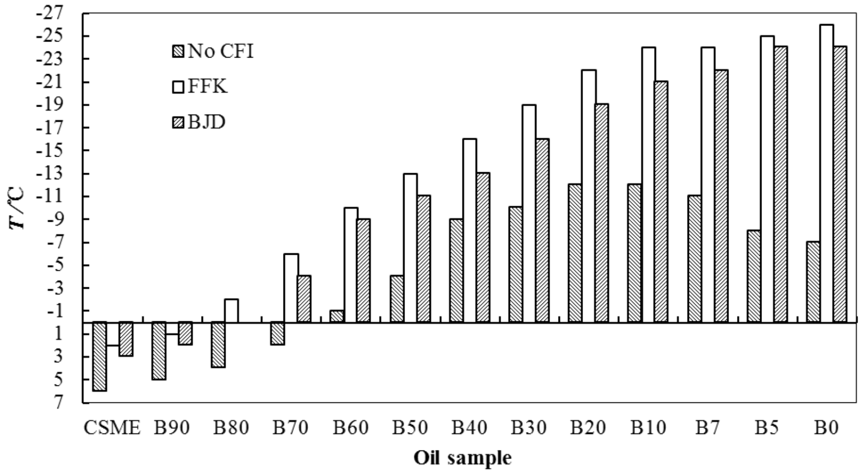

Fig. 3 The cold filter plugging point of CSME/-10PD without/with CFI

4. Conclusion

The CSME is mainly composed of FAMEs: SFAMEs ($C_{14:0}$-$C_{26:0}$) and UFAMEs ($C_{16:1}$-$C_{22:1}$, $C_{16:2}$-$C_{20:2}$ and $C_{18:3}$), and their mass fractions are 32.41% and 66.24%, respectively. The CFPP of CSME is 6 ℃, it has unfavorable cold flow property. Two approaches for improving cold flow properties of CSME are adopted. Blending with 0PD and -10PD decreased the CFPP to -8 and -12 ℃, respectively. Treating with FFK and BJD (volume fraction ≤ 5v‰) can decrease effectively the CFPP of CSME and its blends. FFK is the better CFI of CSME than BJD. The lowest CFPPs of CSME, CSME/0PD and CSME/-10PD are 2, -20 and -25 ℃, respectively.

Acknowledgements

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