Study on Cold Flow Properties of Rice Bran Oil Biodiesel and Improvement

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Abstract

The cold flow properties of rice bran oil biodiesel were studied by gas chromatography-mass spectrometry (GC-MS), multifunctional low temperature tester. Two approaches for reducing cold filter plugging point (CFPP) of rice bran oil methyl ester (RBME) were investigated: blending with petrodiesel and treating with cold flow improver (CFI) additives. The study shows that the RBME was mainly composed of fatty acid methyl esters (FAME): $C_{14:0}$-$C_{26:0}$, $C_{16:1}$-$C_{20:1}$, $C_{18:2}$ and $C_{18:3}$. The mass fractions of saturated fatty acid methyl esters (SFAME) and unsaturated fatty acid methyl esters (UFAME) were 20.73% and 79.26%, respectively. The CFPP of RBME was -2 ℃. Blending with 0 petrodiesel (0PD) and -10 petrodiesel (-10PD) decreased the CFPP to -11 and -15 ℃ respectively. Treating with CFI additives (volume fraction ≤ 0.5%) decreased the CFPP of RBME, RBME/0PD and RBME/-10PD to -6 -20 and -26 ℃, respectively. This study has effectively improved cold flow properties of RBME and provided guide for using RBME during cold weather.

Keywords

Biodiesel, Rice bran oil, Cold flow properties, GC-MS.

1. Introduction

There has been a considerable interest in developing rice bran oil biodiesel as a substitute for an additive to petrodiesel because it is a cheaper non-edible oil raw material. China is the largest rice producer of the world. 2015, rice yield is 208,245,000 ton/year. [1] Rice bran oil is a byproduct of rice. Depending on variety of rice and degree of milling, rice bran contains 15%–23% lipids. [2] But rice bran oil methyl ester (RBME) had unfavorable cold flow properties due to its higher amount of saturated fatty acid methyl esters (SFAME). As winter temperatures fall, SFAME nucleate and form solid crystal. These crystals can plug fuel lines and filters causing problems in fuel pumping and engine performance during winter operation. In recent years, researches about cold flow properties of biodiesel included: development of cold flow improver (CFI) [3, 4], and influences on cold flow properties, viz., chemical composition of biodiesel [5, 6], blending reagent [7] and CFI [3, 7]. The objective of this work was to study cold flow properties of RBME and improvement by blending with petrodiesel and treating with CFI additives.

2. Experimental

2.1 Materials.

-10 petrodiesel (-10PD) and 0 petrodiesel (0PD) were obtained from China Petroleum & Chemical Corporation. RBME is prepared by our laboratory, in line with GB/T 20828-2007 requirements. Flow Fit and Flow Fit K were provided by Liqui Moly, German. T818 was provided by SH Renyinglian Trade Development Co., Ltd., China. All other reagents were of analytical grade.

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 ℃ maintained for 0.5 min; 6 ℃ min-1 from 180 ℃ to 215 ℃; and 3 ℃ min-1 from 215 ℃ to 230 ℃ maintained for 13 min.

2.3 Cold Filter plugging point measured.

CFPPs of biodiesel and blended biodiesel are measured with an SYP2007-1 CFPP tester (Shanghai BOLEA Instrument & Equipment Co. Ltd., China) in accordance with SH/T 0248-2006.

3. Results and discussion

3.1 Chemical composition.

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

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 0PD and -10PD (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	0.36	16.37	2.20	0.73	0.29	0.49	0.29	0.30	42.74	0.64	34.19	1.39

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, we can see that dominate the main chemical compositions of RBME are the fatty acid methyl ester (FAME) composed by 14-26 even number carbon atoms, and the mass fraction of saturated fatty acid methyl esters (SFAME) ($C_{14:0}$-$C_{26:0}$) and unsaturated fatty acid methyl esters (UFAME) ($C_{16:1}$-$C_{20:1}$, $C_{18:2}$ and $C_{18:3}$) is 20.73% and 79.26% respectively.

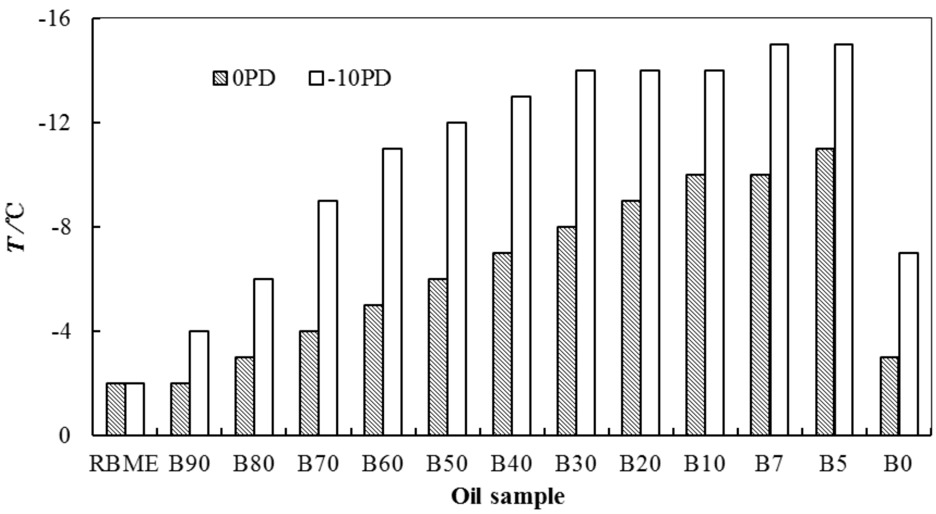


Fig. 1 The cold filter plugging point of RBME/0PD and RBME/-10PD

3.2 Improvement of cold flow property.

3.2.1 Blending with petrodiesel

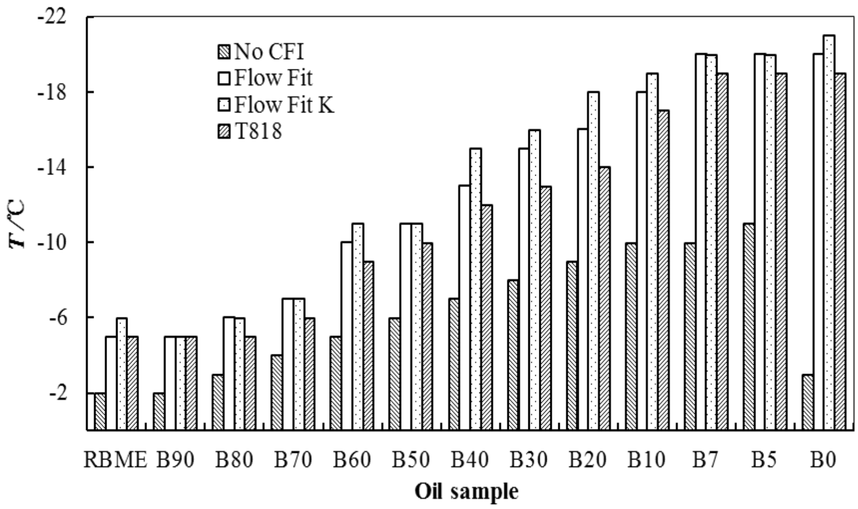
From Fig.1, with increasing petrodiesel blending ratio, CFPPs of RBME/0PD and RBME/-10PD decreased from -2 to -12 ℃ and from -2 to -15 ℃ with RBME-B5, respectively. (See Figure 1). It was chiefly because RBME blending with petrodiesel not only decreased SFAME content but also could form a eutectic mixture, viz., CFPP of blending oil was lower than that of RBME and petrodiesel. Hence blending with petrodiesel was an effective way to reduce CFPP of RBME.

3.2.2 Treating with cold flow improver additives

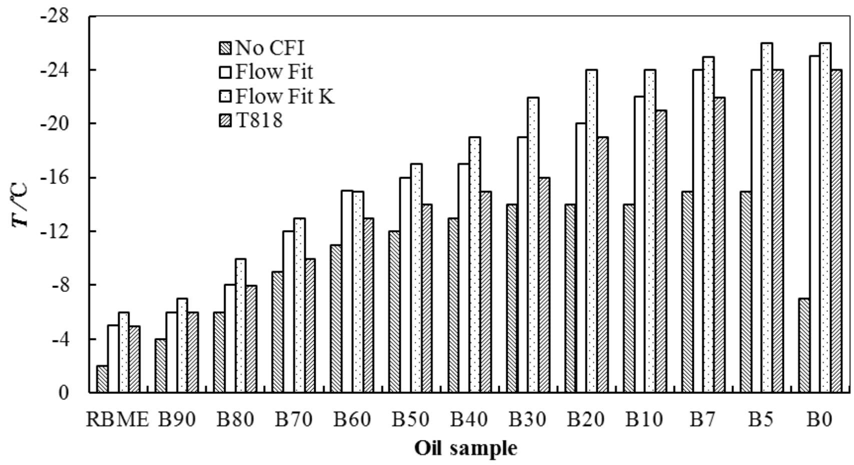
The economic and performance benefits of using CFI additives to improve cold flow properties of biodiesel have been recognized. The optimum volume fraction of additives is shown in Table 3. The CFPP of WME/-10PD without/with CFI is shown in Fig. 2.

Table 3 The main chemical composition of 0PD and -10PD (w)/%

Oil sample	RBME	B90	B80	B70	B60	B50	B40	B30	B20	B10	B7	B5
Flow Fit /v‰	5	3	3	3	3	3	3	3	3	3	3	3
Flow Fit K /v‰	5	3	2	2	1	1	1	1	1	1	1	1
T818 /v‰	1	1	1	1	1	1	1	1	1	1	1	1



(a) RBME/0PD



(b) RBME/-10PD

Fig. 2 The cold filter plugging point of RBME/0PD and RBME/-10PD without/with CFI

From Fig. 2, the optimum volume fraction of CFI additives is no less than 5‰. Among the Flow Fit, Flow Fit K and T818, Flow Fit K is the best CFI of RBME. It reduced the CFPP of RBME from -2 ℃ to -6 ℃. B5 of RBME/0PD and RBME/-10PD from -11 and -15 ℃ to -20 and -26 ℃, respectively. It can be seen that using CFI additives to improve cold flow properties of RBME was another kind of effective way.

4. Conclusion

Based on the results of this study, we conclude that:

The RBME was mainly composed of fatty acid methyl esters. This included: saturated fatty acid methyl esters ($C_{14:0}$-$C_{26:0}$) and unsaturated fatty acid methyl esters ($C_{16:1}$-$C2_{0:1}$, $C_{18:2}$ and $C_{18:3}$), and their mass fractions were 20.73% and 79.26%, respectively. The CFPP of RBME is -2 ℃, higher than 0PD. RBME had unfavorable cold flow property.

Two approaches for improving cold flow properties of RBME were adopted. Blending with 0PD and -10PD decreased the CFPP to -11 and -15 °C. Treating with CFI additives (volume fraction ≤ 5v‰) could decrease effectively the CFPP of RBME and its blends. Flow Fit K was the best CFI of RBME among the Flow Fit, Flow Fit K and T818. The lowest CFPP of RBME, RBME/0PD and RBME/-10PD were -6, -20 and -26 ℃, respectively.

Acknowledgements

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