Impact of Fatty Acid Methyl Esters Composition on Cold Flow Property of Biodiesel

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Abstract

This paper studies the chemical composition and molecular structure of biodiesel, cold flow properties, and the influence of chemical composition on cold filter plugging point (CFPP) by using the gas chromatograph-mass spectrometer (GC-MS) and CFPP tester according to the theories of hybridized orbital and crystallization. The study shows that biodiesel is mainly fatty acid methyl ester (FAME) that is composed of 14-24 even number carbon atoms. Saturated fatty acid methyl esters (SFAMEs) are mainly $C_{14:0}$～$C_{24:0}$. Unsaturated fatty acid methyl ester (UFAMEs) are mainly $C_{16:1}$～$C_{22:1}$, $C_{18:2}$～$C_{20:2}$ and $C_{18:3}$. The cold flow property of biodiesel is mainly decided by the content and distribution of FAME. The CFPP increases with the increase of the content of SFAME and the longer the carbon chains are, the greater the increase will be; the CFPP decreases with the increase of the content of UFAME and the higher the degree of unsaturation is, the greater the decrease will be.

Keywords

Biodiesel, Fatty acid methyl esters, Cold flow property, Cold filter plugging point.

1. Introduction

With the exhaustion of petroleum resources and deterioration of the environment, biodiesel has become a comparatively ideal partial alternative fuel for diesel engine because it is reproducible and environment-friendly. As ambient temperatures cool toward their saturation point, long-chain saturated fatty acid methyl esters (SFAMEs) present in biodiesel begin to nucleate and form crystals suspended in a liquid phase. These crystals plug or restrict flow through fuel lines and filters during start-up and can lead to fuel starvation and engine failure, thus restricting the use of the engine at the low temperatures. The cold flow properties of biodiesel mainly depend on its chemical composition, namely, the content and distribution of fatty acid methyl esters (FAMEs). [1-6] Given the vast territory, large-span temperature zone, and large difference between the north and south temperature (the minimum air temperature in the north is -44 ℃ and 0 ℃ in the south) in China, various kinds of raw oil (vegetable oil, animal fat, and waste oil) can be utilized to prepare biodiesel. Different raw oils have different chemical compositions and cold flow properties. For example, the Cold filter plugging point (CFPP) of peanut methyl ester and Chinese tallow methyl ester is 13 ℃ and -14 ℃, respectively. Given that the fatty acid moieties of biodiesel and raw oil are basically the same, basing on fatty acid moieties and determining the relation between the chemical composition of biodiesel and its cold flow properties are of practical

significance to the screening of feedstock for biodiesel production and feedstock or biodiesel blending (blending different kinds of feedstock or biodiesel with different fatty acids moieties).

2. Experimental

2.1 Materials

A total of 9 biodiesel samples are utilized in this study. The samples include four types of herbal biodiesel, namely, maize methyl ester (MME), peanut methyl ester (PNME), rapeseed methyl ester (RME) and soybean oil methyl ester (SME). Three types of woody plant biodiesel are also utilized, namely, Chinese tallow methyl ester (CME), jatropha curcas methyl ester (JME) and palm methyl ester (PME). The two types of waste oil biodiesel utilized are hogwash oil methyl ester (HME) and Kentucky fried oil methyl ester (KME). HME and KME are obtained from Changzhou Kate Petroleum Products Manufacturing Co., Ltd. and Hongkong Champway Technology Ltd., respectively. The other products are prepared in our laboratory.

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 of biodiesel

GC-MS is utilized to analyze the chemical composition of biodiesel. FAME composition is shown in Tables 1. The main chemical composition of biodiesel is FAME composed of 14 to 24 even-numbered carbon atoms, including SFAME ($C_{14:0}$ – $C_{24:0}$) and unsaturated fatty acid methyl esters (UFAME) ($C_{16:1}$ – $C_{20:1}$, $C_{18:2}$, and $C_{18:3}$).

3.2 Cold flow properties of biodiesel

The CFPPs of biodiesel are shown in Table 2. Chemical composition has an enormous effect on the cold flow properties of biodiesel. Among the 9 types of representative raw material biodiesel, $SFAME_{C\geq20}$ content in PNME and SFAME content in PME are high at 9.86 wt% and 40.13 wt%, respectively. The CFPPs of these two biodiesel samples reach up to 10 ℃ (13 ℃ and 10 ℃, respectively). The UFAMEs of CME and RME are high at 88.62 wt% and 87.46 wt%, respectively, causing their CFPPs to decrease to -10 ℃ (-14 ℃ and -9 ℃, respectively), thus affecting the serviceable range and climate adaptability of biodiesel.

3.3 Influence of chemical composition on cold flow properties

Table 3 shows that SFAME contents in JME and KME are 20.90 wt% and 35.67 wt%, respectively, and the CFPPs are -3 ℃ and 5 ℃, respectively. SFAMEC≥20 contents in SME and PNME are 1.51 wt% and 9.86 wt%, respectively, and the CFPPs are -5 ℃ and 13 ℃, respectively. High content and long chain length of SFAME allow for easy crystallization; therefore, CFPP is high. Table 4 shows that the MUFAME contents of HME and P70C30 are 40.95 wt% and 36.31 wt%, respectively, and their CFPPs are 3 ℃ and 5 ℃, respectively. Table 5 shows that the DUFAME contents of M60T40 and J40C60 are 40.95 wt% and 36.31 wt%, respectively, and their CFPPs are -9 ℃ and -5 ℃, respectively.

High content of UFAME entails difficulty in crystallization; therefore, CFPP is low. And DUFAME has a more significant influence on CFPP than on MUFAME. Therefore, the cold flow properties of biodiesel are determined mainly by SFAME content and chain length as well as the content and degree of unsaturation of UFAME.

Table 1. The chemical composition of biodiesel (wt%)

FAME	MME	PNME	RME	SME	CME	JME	PME	HME	KME
$C_{8:0}$	0	0	0	0	0	0	0	0	0.11
$C_{10:0}$	0	0.03	0	0	0	0	0	0.15	0
$C_{12:0}$	0	0	0	0	0	0	0	0.28	0.27
$C_{14:0}$	0.05	0.06	0	0.19	0.07	0.07	1.63	1.72	1.13
$C_{16:0}$	14.14	10.87	7.57	11.09	8.86	12.93	31.04	19.73	28.91
$C_{18:0}$	2.63	5.17	3.31	5.50	2.36	7.64	6.64	8.70	4.99
$C_{20:0}$	0.36	2.55	0.79	0.60	0.08	0.23	0.61	0.49	0.18
$C_{22:0}$	0.12	4.84	0.50	0.69	0	0.03	0.11	0.40	0.08
$C_{24:0}$	0.22	2.47	0.25	0.22	0	0	0.10	0	0
$C_{14:1}$	0	0	0	0	0	0	0	0	0.05
$C_{16:1}$	0.18	0.16	0.19	0.26	0.10	0.91	0.32	3.14	1.24
$C_{18:1}$	36.37	38.87	32.96	28.56	16.68	41.87	43.94	36.80	42.39
$C_{20:1}$	0.35	1.63	5.69	0.41	0.33	0.10	0.28	0.70	0.22
$C_{22:1}$	0	0.11	15.79	0.11	0	0	0	0.31	0
$C_{18:2}$	44.85	32.09	25.06	42.95	30.60	35.53	14.44	21.18	17.76
$C_{20:2}$	0	0.04	0.33	0.10	0	0	0	0.16	0.05
$C_{18:3}$	0.42	0.11	7.44	7.74	40.91	0.38	0.59	2.38	2.09

Table 2. The cold filter plugging point of biodiesel

Biodiesel	PNME	PME	KME	HME	JME	MME	SME	RME	CME
CFPP / ℃	13	10	5	3	-3	-5	-5	-9	-14

Table 3. The influence of SFAMEs on cold filter plugging point

Biodiesel	JME	KME	SME	PNME
SFAME /wt%	20.90	35.67	18.29	25.99
$SFAME_{C\leq18}$ /wt%	20.64	35.41	16.78	16.31
$SFAME_{C\geq20}$ /wt%	0.26	0.26	1.51	9.86
CFPP / ℃	-3	5	-5	13

Table 4. The influence of MUFAME on cold filter plugging point

Biodiesel	HME	$P_{70}C_{30}$
SFAME /wt%	31.47	31.50
$SFAME_{C\geq20}$ /wt%	0.89	0.60
MUFAME /wt%	40.95	36.31
CFPP / ℃	3	5

Table 5. The influence of DUFAME on cold filter plugging point

Biodiesel	$M_{60}T_{40}$	$J_{40}C_{60}$
SFAME /wt%	15.06	15.18
$SFAME_{C\geq20}$ /wt%	0.45	0.15
DUFAME /wt%	39.15	32.57
CFPP / ℃	-9	-5

4. Conclusion

Biodiesel is a mixture of long-chain FAMEs main composed of 14 to 24 even-numbered carbon atoms. The cold flow properties of biodiesel are determined mainly by FAME composition. CFPP increases with the increase in SFAME content. Long carbon chains promote the increase. CFPP decreases with the increase in UFAME content. A high degree of unsaturation enhances the decrease

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