Impact of saturated fatty acid methyl esters on cold filter plugging point of biodiesel

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Abstract

This paper studies the fatty acid methyl esters (FAMEs) composition and cold filter plugging point (CFPP) of biodiesel, and the influence of the saturated fatty acid methyl esters (SFAMEs) on CFPP by using the gas chromatograph-mass spectrometer (GC-MS) and cold filter plugging point tester according to the crystallization theory. The study shows that biodiesel is mainly FAMEs that are composed of 8-24 even number carbon atoms, i.e. $C_{8:0}$-$C_{24:0}$, $C_{16:1}$-$C_{20:1}$, $C_{18:2}$, and $C_{18:3}$. The SFAMEs of biodiesel have great influence on cold filter plugging point (CFPP). The CFPP of biodiesel increases with the increase in longer carbon chains $SFAME_{14\leq C\leq 24}$ content. Long carbon chains enhance the increase. The CFPP of biodiesel decreases with the increase in shorter carbon chains $SFAME8_{\leq C\leq 12}$ content.

Keywords

Biodiesel, Saturated fatty acid methyl esters, Cold filter plugging point.

1. Introduction

Biodiesel from renewable vegetable oils have many characteristics that make them attractive as a fuel for combustion in direct injection compression-ignition diesel engines [1]. As ambient temperatures cool toward their saturation point, long-chain saturated fatty acid methyl esters (SFAME) 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. So the SFAME composition of biodiesel plays a key role in determining cold flow property [2-5]. Different raw oils have different chemical compositions and cold flow properties. For example, the cold filter plugging point (CFPP) of peanut methyl ester (PNME) differs by 27 °C from Chinese tallow methyl ester (CTME), they are 13 °C and -14 °C, respectively [6].

In this study, the cold flow property of biodiesel is researched on the basis of the determination of its chemical composition with gas chromatography-mass spectrometer (GC-MS). In addition, the relationship between CFPP and SFAME of biodiesel is investigated.

2. Experimental

2.1 Materials

A total of 6 biodiesel samples are utilized in this study. The samples include four types of herbal biodiesel, namely, maize methyl ester (MME), PNME, rapeseed methyl ester (RME) and sesame oil methyl ester (SME). Two types of woody plant biodiesel are also utilized, namely, coconut oil methyl ester (CNME) and palm methyl ester (PME). CNME is obtained from Yunnan YingDing Bio-energy Co., Ltd., and 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 °C maintained for 0.5 min; 6 °C min-1 from 180 to 215 °C; and 3 °C min-1 from 215 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 Saturated fatty acid methyl esters composition

GC-MS is utilized to analyze the chemical composition of biodiesel. The gas chromatogram is shown in Fig.1. Fatty acid methyl ester (FAME) composition is shown in Table 1. The main SFAME composition of CNME is 8 to 20 even-numbered carbon atoms, i.e. $C_{8:0}$-$C_{20:0}$. And the other biodiesel are 14 to 24 even-numbered carbon atoms SFAME, i.e. $C_{14:0}$-$C_{24:0}$.

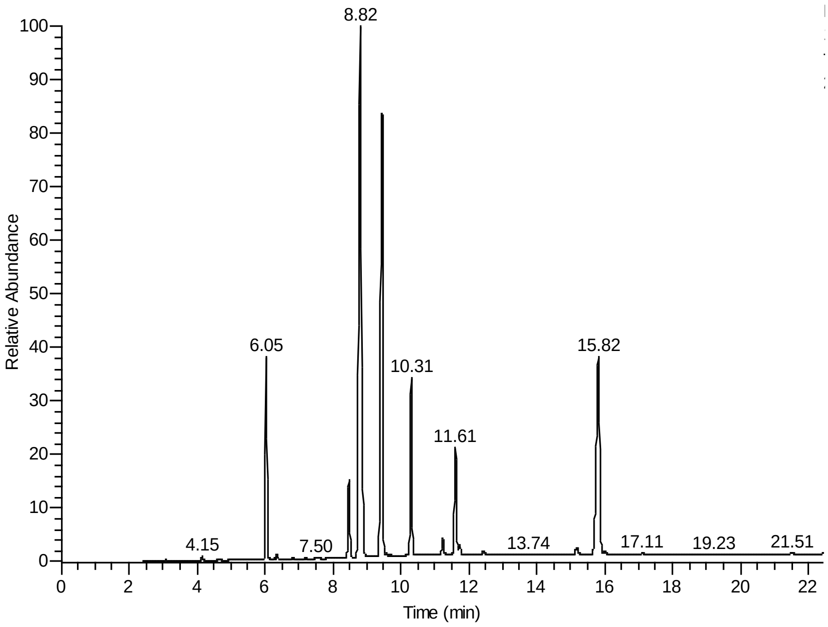

Fig.1 The gas chromatogram of RME

3.2 Cold filter plugging point

The CFPP of biodiesel tested with a SYP2007-1 Low Temperature Multi-function Tester is shown in Table 2. Among the 6 types of representative biodiesel, $SFAME20_{\leq C\leq 24}$ (SFAME in which fatty acid moieties include carbon atoms greater than or equal to 18, and less than or equal to 24) content in PNME and $SFAME14_{\leq C\leq 24}$ content in PME are high at 9.86 wt% and 40.13 wt%, respectively. The CFPPs of these two biodiesel samples reach up to above 10 °C. The $SFAME_{14\leq C\leq 24}$ content in RME, MME and SME are low at 12.42 wt%, 16.98 wt% and 18.70 wt%, respectively, and the $SFAME_{8\leq C\leq 12}$ content in CNME is high at 32.85 wt%, causing their CFPPs to decrease to below -3 °C. The SFAME has an enormous effect on the cold flow property of biodiesel. The SFAME contents and distributions vary with biodiesel such that large differences in CFPPs exist, thereby affecting the serviceable range and climate adaptability of biodiesel.

3.3 Impact of saturated fatty acid methyl esters on cold filter plugging point

The impact of SFAME on CFPP of biodiesel is shown in Table 3 – Table 5.

The $SFAME_{14\leq C\leq 18}$ and $SFAME_{20\leq C\leq 24}$ contents in CNME and PME are very close. The $SFAME_{8\leq C\leq 12}$ contents in CNME and PME are 32.85 wt% and 0 wt% respectively, 32.85% higher; the CFPPs of CNME and PME are -6 °C and 10 °C respectively, 16°C lower. The $SFAME_{8\leq C\leq 12}$ contents in RME and SME are zero. The $SFAME_{20\leq C\leq 24}$ contents in CNME and PME are very close. The $SFAME_{14\leq C\leq 18}$ contents in SME and RME are 17.20 wt% and 10.88 wt% respectively, 6.32% higher; the CFPPs of SME and RME are -3 °C and -9 °C respectively, 6 °C higher. The $SFAME_{8\leq C\leq 12}$ and $SFAME_{14\leq C\leq 18}$ contents in PNME and MME are very close. The $SFAME_{20\leq C\leq 24}$ contents in PNME and MME are 9.86 wt% and 1.51 wt% respectively, 8.35% higher; the CFPPs of PNME and MME are 13 °C and -7 °C respectively, 20 °C higher.

According to crystallization theory, molecular crystals are crystals combined by intermolecular forces (Van der Waals forces). The arrangement of the molecules is closed-packed owing to the lack of saturation and orientation of the Van der Waals force, as shown in Fig.2. As for the homologous compound, which refers to SFAME, the difficulty of molecular crystallization depends on molecular weight. Van der Waals force increases with molecular weight, that is, the length of the carbon chain; therefore, it is easy to crystallize.

Table 1 The gas chromatogram of RME

FAME	MME	PNME	RME	SME	CNME	PME
$C_{8:0}$	0	0	0	0	4.17	0
$C_{10:0}$	0	0.03	0	0	4.02	0
$C_{12:0}$	0	0	0	0	24.66	0
$C_{14:0}$	0.06	0.06	0	0.19	18.83	1.63
$C_{16:0}$	11.96	10.87	7.57	11.42	16.77	31.04
$C_{18:0}$	3.45	5.17	3.31	5.59	3.62	6.64
$C_{20:0}$	0.91	2.55	0.79	0.65	0.09	0.61
$C_{22:0}$	0.27	4.84	0.50	0.64	0.03	0.11
$C_{24:0}$	0.33	2.47	0.25	0.21	0	0.10
$C_{16:1}$	0.29	0.16	0.19	0.22	0.30	0.32
$C_{18:1}$	33.20	38.87	32.96	29.70	19.79	43.94
$C_{20:1}$	0.66	1.63	5.69	0.45	0.13	0.28
$C_{22:1}$	0.84	0.11	15.79	0	0	0
$C_{16:2}$	0.02	0	0	0	0	0
$C_{18:2}$	45.84	32.09	25.06	41.30	6.95	14.44
$C_{20:2}$	0.05	0.04	0.33	0.06	0	0
$C_{18:3}$	1.23	0.11	7.44	7.12	0.17	0.59
$C_{20:4}$	0	0	0	0.14	0	0

Table 2 The cold filter plugging point of biodiesel

Biodiesel	RME	MME	CNME	SME	PME	PNME
CFPP /°C	-9	-7	-6	-3	10	13

Table 3 Impact of SFAME8≤C≤12 on CFPP

Biodiesel	*SFAME* /%	$SFAME_{8\le C\le 12}$ /%	$SFAME_{14\le C\le 18}$ /%	$SFAME_{20\le C\le 24}$ /%	*CFPP* /℃
PME	40.13	0	39.31	0.82	10
CNME	72.19	32.85	39.22	0.12	-6

Table 4 Impact of SFAME14≤C≤18 on CFPP

Biodiesel	*SFAME* /%	$SFAME_{8\le C\le 12}$ /%	$SFAME_{14\le C\le 18}$ /%	$SFAME_{20\le C\le 24}$ /%	*CFPP* /℃
RME	12.42	0	10.88	1.54	-9
SME	18.70	0	17.20	1.50	-3

Table 5 Impact of SFAME20≤C≤24 on CFPP

Biodiesel	*SFAME* /%	$SFAME_{8\le C\le 12}$ /%	$SFAME_{14\le C\le 18}$ /%	$SFAME_{20\le C\le 24}$ /%	*CFPP* /℃
MME	16.98	0	15.47	1.51	-7
PNME	25.99	0.03	16.10	9.86	13

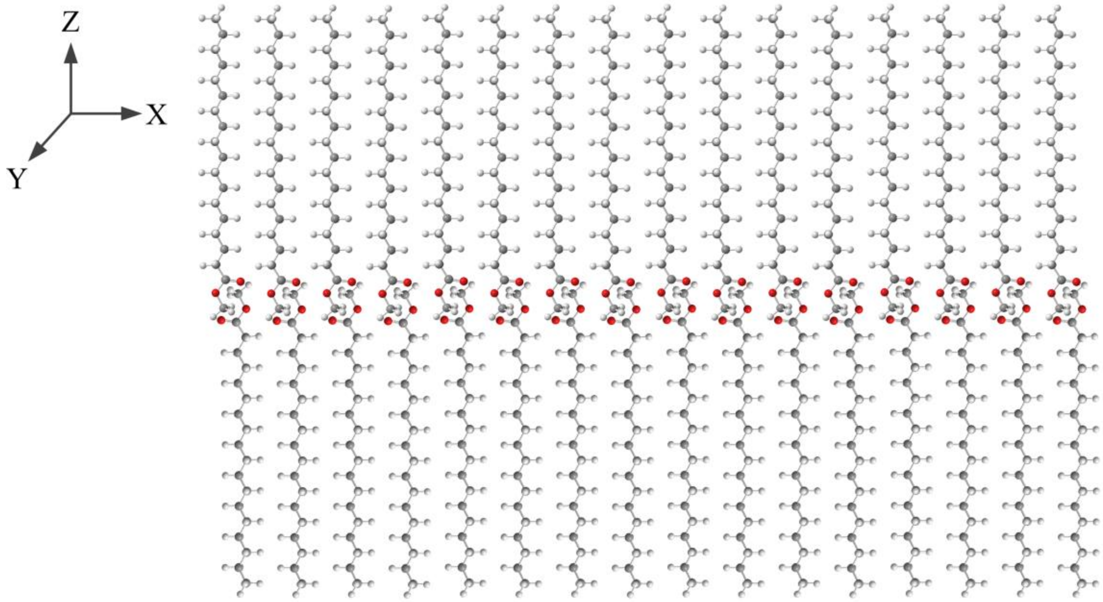

Fig.2 Molecular arrangement and distribution of methyl stearate

The results show that the effect of contents and carbon chains length of SFAME on CFPP is very significant. The CFPP of biodiesel increases with the increase in longer carbon chains SFAME14≤C≤24 content. The longer the carbon chain is, the more significant the effect is. The CFPP of biodiesel decreases with the increase in shorter carbon chains $SFAME_{8\le C\le 12}$ content.

4. Conclusion

Biodiesel mainly consists of long-chain FAMEs of 8 to 24 even-numbered carbon atoms, among which SFAMEs composed of C_8-C_{24}. The cold flow property of biodiesel is determined mainly by contents and carbon chains length of SFAME. The CFPP of biodiesel increases with the increase in longer carbon chains $SFAME_{14\le C\le 24}$ content. Long carbon chains enhance the increase. The CFPP of biodiesel decreases with the increase in shorter carbon chains $SFAME_{8\le C\le 12}$ content.

Acknowledgements

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