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Influence of Fatty Acid Esters on the Cold Flow Properties of Waste Cooking Oil Biodiesel

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Abstract

The cold flow properties are the main issue to the popularization and application of biodiesel as alternative fuel to diesel. In this study, the cold flow properties of waste cooking oil methyl ester (WCOME) and its blends with different fatty acid esters were investigated, including different chain lengths, different degree of unsaturation, and different ester group. Results showed that shorter chain length, more double bonds, and longer/branched chain ester group could effectively reduce WCOME cold filter plugging point (CFPP).

Keywords

Biodiesel, Oxidation stability, Waste cooking oil, Cold flow property, Fatty acid esters.

1. Introduction

Biodiesel is an alternative diesel fuel, mainly fatty acid methyl esters (FAME), provides an excellent solution to resolve problems related to environmental pollution and depletion of fossil based petroleum fuel. [1] It relieves the problem of biodiesel raw material shortage that using waste cooking oil (WCO) to prepare biodiesel, which achieved the resource waste harmless treatment and avoided harm of WCO at the same time. In China, urban areas every year usually produce a lot of hutch garbage, which can be extracted WCO about more than 500 ten thousand tones. [2].

Cold flow property is one of the important criteria concerning fuel properties. The main hinder with the use of biodiesel as fuel is its poor cold weather characteristics causing crystallization of biodiesel at low temperatures that led to the clogging of filters or cause fuel pumping difficult due to viscosity during engine operation, thereby, creating fuel starvation and operational problems. This is due to the presence of saturated fatty acid methyl etsters (SFAME) in biodiesel and reduces the crystallization temperature resulting in the deterioration of its cold flow property. [3-5]

This study discusses the effects of different ingredients and different structures of components in biodiesel on its cold flow properties. Then, fatty acid esters were divided into four types: different chain lengths; different double bond numbers, and different ester group to discuss the effects and their action mechanism on biodiesel cold flow properties.

2. Materials and Methods

2.1. Materials

WCOME was purchased from Nantong BIOLUX Bioenergy Protein Feed Co. Ltd.. All other chemicals were purchased from Aladdin Reagent Co., Ltd. (Shanghai).

2.2. Gas Chromatography–Mass Spectrometry (GC-MS) Analysis

A Finnigan, Trace MS GC-MS was used to analyze biodiesel composition under the following operating conditions: DB-WAX (30 m × 0.25 mm × 0.25 μm); capillary column temperature, started at 160 °C, staying at this temperature for 0.5 min, heated to 215 °C at 6 °C /min, then heated to 230 °C at 3 °C /min, staying at this temperature for 13 min.

2.3. Methods for Biodiesel Properties

Cold filter plugging point (CFPP, °C) was determined according to SH/T 0248-2006. Other properties were measured according to the following methods: GB/T 13377-2010 for density (ρ, 20°C, g·cm−3); GB/T 265-1988 for kinematic viscosity (KV, 40°C, mm2·s−1); GB/T 261-2008 for flash point (FP, °C); and GB/T 5096-2017 for copper strip corrosion (3h at 50°C, rating).

3. Results and Discussion

3.1. Waste Cooking Oil Methyl Ester Composition

According to GC-MS analysis, the result is shown in Table 1. WCOME mainly contained methyl palmitate (C16:0), methyl stearate (C18:0), methyl Palmitoleate (C16:1), methyl oleate (C18:1), methyl linoleate (C18:2), and methyl linolenate (C18:3). Among these FAMEs, the contents of C16:0, C18:1, and C18:2 in WCOME showed a wide variation; they were 19.73%, 36.80%, and 21.28%, respectively.

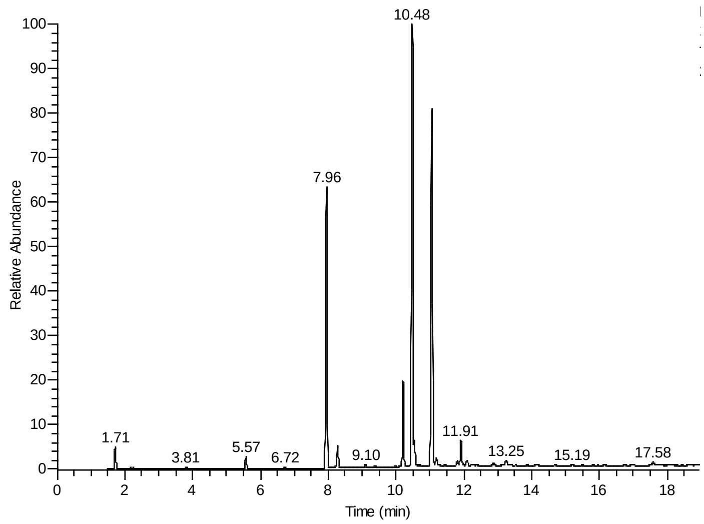

Fig 1. Chemical structures of antioxidants used in the present study.

Table 1. GC-MS analysis of waste cooking oil methyl ester

WCOME	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{20:0}$	$C_{22:0}$	$C_{16:1}$	$C_{18:1}$	$C_{20:1}$	$C_{22:1}$	$C_{18:2}$	$C_{20:2}$	$C_{18:3}$
(w)%	0.15	0.28	1.72	19.73	8.70	0.49	0.40	3.14	36.80	0.70	0.31	21.28	0.16	2.38

$C_{m:n}$: m means the number of fatty acid carbon atoms; n means the double-bond number in fatty acid group.

3.2. Properties of Waste Cooking Oil Methyl Ester

As shown in Table 2, all the fuel properties of WCOME satisfied the regulations in GB/T 20828-2015. However, WCOME presented poor cold flow property. It is precisely because of chemical composition that studying the effects of different ingredients and structures in WCOME on its cold flow property made sense.

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Table 2. Standards and physico-chemical properties of waste cooking oil methyl ester

Property	GB/T 20828	WCOME
ρ at 20°C, $g\cdot cm^{-3}$	820 - 900	879
KV at 40°C, $mm^2\cdot s^{-1}$	1.9 - 6.0	5.1
FP, °C	101min	>140
CFPP, °C	-	3
Copper strip corrosion, 3h at 50°C, rating	class 1	class 1

3.3. Effects of Different FAMEs on the CFPP of WCOME

3.3.1 Chain length (saturated)

As shown in Fig. 2, for WCOME, little amount of C14:0 (i.e. 2.5%, 5%) or C16:0 (i.e. 2.5%) affected almost nothing; however, as C14:0 and C16:0 increased, CFPP increased. With the increase of C18:0, C20:0, or C22:0, CFPP increased. Especially a longer carbon chain could raise the CFPP of biodiesel more rapidly than that of a shorter carbon chain. Thus, longer carbon chain SFAME (C14:0 - C22:0) was worse for biodiesel cold flow property.

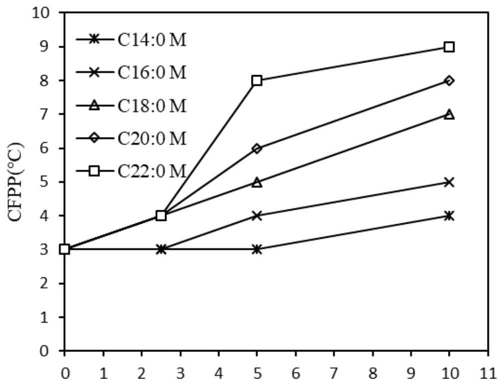

Fig 2. Effects of chain length (saturated) on CFPP.

3.3.2 Chain length (monounsaturated)

Fig. 3 depicts the variation tendency of CFPP with monounsaturated fatty acid methyl esters (MUFAME). Little amount of C16:1, C18:1, and C20:1 affected almost nothing (i.e. 2.5%); however, as they increased, CFPP decreased. Up to 10%, CFPP values were reduced by 4, 3 and 2°C, respectively. C22:1 was added up to 10%, CFPP remained basically unchanged. Considering the contents of C16:1 - C22:1 in WCOME, one can conclude that the more the C18:1 in biodiesel, the lower the biodiesel CFPP would be.

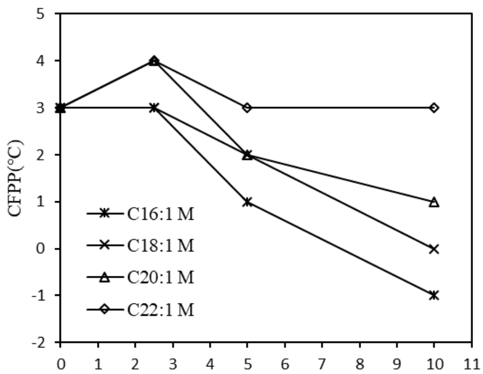

Fig 3. Effects of chain length (monounsaturated) on biodiesel CFPP.

3.3.3 Unsaturation degree

Since $C_{18:1}$ could improve the biodiesel cold flow properties, it was much better than that of C18:0. Then, $C_{18:2}$ was taken into consideration to investigate the effect of double-bond number on biodiesel cold flow properties. As shown in Fig. 4, $C_{18:2}$ could also improve biodiesel CFPP. When 10% $C^{18:2}$ was added, CFPP value was reduced by 5°C. In addition, double-bond number did play a great role in biodiesel cold flow properties: the more the double bond number was, the better the biodiesel cold flow properties would be.

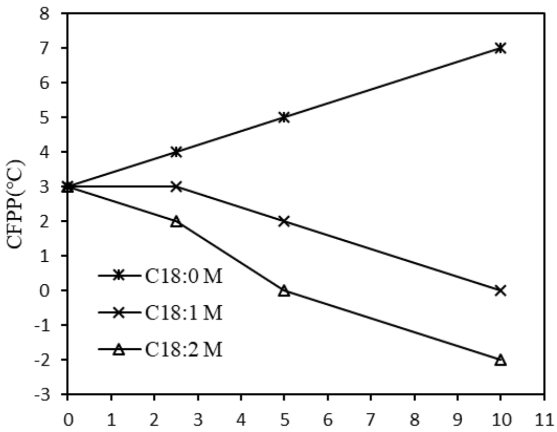

Fig 4. Effects of unsaturation degree on CFPP.

3.3.4 Ester group

Fig. 5 shows that a small quantity of $C_{18:0}$ E and $C_{18:0}$ M almost had the same effect, but 10% could obviously highlight the difference between them. As $C_{18:0}$ E had a longer ester group chain than $C_{18:0}$ M, a large amount of $C_{18:0}$ E would worsen the CFPP. Regarding $C_{18:0}$ I, $C_{18:0}$ I could decrease CFPP. Up to 10%, CFPP value was reduced by 4°C.

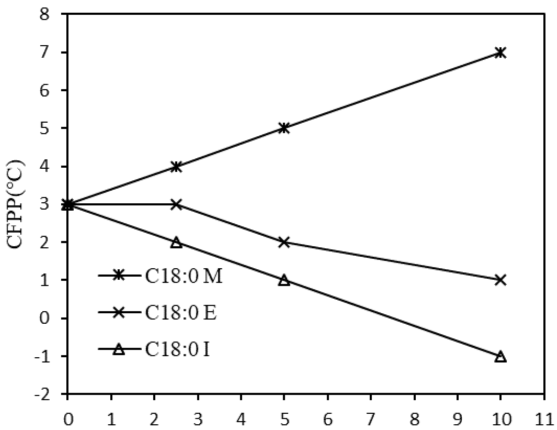

Fig 5. Effects of ester group on CFPP.

4. Conclusion

The contents and molecular structures of FAMEs did play significant roles in deciding biodiesel cold flow properties. (1) Biodiesel with more short carbon chain ($C_{m:0}$, m ≤ 16) FAMEs would possess better cold flow properties. (2) When biodiesel contained more unsaturated FAMEs ($C_{m:1}$, m ≤ 20), the biodiesel CFPP could be lower. (3) The more the double-bond number in

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FAMEs ($C_{m:n}$, m ≤ 22, n ≥ 1) was, the better the biodiesel cold flow properties would be. (4) Ester group with a branched one could effectively improve biodiesel cold flow properties.

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