

## Study on Cold Flow Properties of Waste Cooking Methyl Ester and Its Blending Oils

Xiu Chen<sup>1, a</sup>, Jiamin Hu<sup>1</sup>, Yongbin Lai<sup>2</sup>, Lei Zhong<sup>1</sup>, Menghong Yuan<sup>1</sup>

<sup>1</sup> School of Chemical Engineering, Anhui University of Science & Technology, Huainan, Anhui, 232001, China

<sup>2</sup> School of Mechanical Engineering, Anhui University of Science & Technology, Huainan, Anhui, 232001, China

<sup>a</sup>chenxiuhn@163.com

**Abstract:** The chemical composition of waste cooking methyl ester (WCME) was analyzed by gas chromatograph-mass spectrometer. The cold flow properties of WCME and its blending with OPD (WCME/OPD) were studied by the cold filter plugging point tester and the dynamic viscosity tester. Through adding cold flow improver, the cold flow property of WCME and WCME/OPD were improved. The study shows that WCME is mainly composed of saturated fatty acid methyl esters (SFAME) and unsaturated fatty acid methyl esters (UFAME). The mass fraction of SFAME and UFAME are 27.63% and 71.81%, respectively. The cold filter plugging point (CFPP) of WCME is 0 °C, and the viscosity of WCME is 4.41mm<sup>2</sup>/s at 40 °C. When the ratio of WCME is 40%, the CFPP of WCME/OPD decreases to -4 °C. With the decrease of the volume ratio of WCME, the viscosity of WCME/OPD is near the OPD. By adding less than 1(v) % of CFI, the CFPP of WCME decreased from 0 °C to -4 °C, and the CFPP of WCME/OPD respectively decreased from -3 °C to -24 °C, -24 °C, -23 °C, -24 °C and -8 °C.

**Keywords:** Biodiesel; Waste cooking Oil; Cold flow property; Cold filter plugging point

### INTRODUCTION

The production cost issue has been affect the popularity of biodiesel. Plants and animals oil prices were rising, which led to the high cost of biodiesel. Using waste cooking oil prepared biodiesel, which achieved the resource waste harmless treatment and avoided harm of waste cooking oil at the same time.

The waste cooking methyl ester (WCME) contains saturated fatty acid methyl esters (SFAME), and the cold flow properties of biodiesel are generally poor, which limits its using region. The actual used method is blending with petrochemical diesel. In recent years, researches about cold flow properties of biodiesel and blending oil concentrated in the influence factor of cold flow properties, development of cold flow improver. The cold flow property of biodiesel was mainly determined by the amount and type of fatty acid methyl esters and the types of alcohol for biodiesel production. CFPP of biodiesel increased with the increasing of content and the length of saturated fatty acid methyl esters (SFAME) [Jin *et al.*, 2011; Chen *et al.*, 2010; Bryan *et al.*, 2012]. The CFPP rapeseed methyl ester prepared from butanol smaller than methanol preparation 6 °C [Smith *et al.*, 2010]. The cold flow property of blending oil was mainly determined by blending ratio and composition of biodiesel. With increasing petrochemical diesel

blending ratio, blending oil CFPP decreased, then increased. By blending, blending oil could form a eutectic mixture. Therefore, the CFPP of blending oil was lower than that of biodiesel and petrochemical diesel [Lv *et al.*, 2011; Chen *et al.*, 2010; Joshi *et al.*, 2007]. By adding the cold flow improver, the cold flow properties of biodiesel and blending oil was effectively improved. The study showed that adding cold flow improver could decrease the CFPP of palm oil methyl ester, soybean oil methyl ester and rapeseed oil methyl ester from 8 °C, 0 °C, 3 °C to 2 °C, -6 °C, -4 °C [Chen *et al.*, 2010; Chen *et al.*, 2010; Wu *et al.*, 2008].

China, the CFPP is an important indicator of biodiesel cold flow property. The lower CFPP is the better cold flow property of biodiesel is. The CFPP reacted whether biodiesel can normal flow at different temperatures. It comprehensive evaluated flow properties of biodiesel under different temperature by the CFPP combined with kinematic viscosity. In this paper, the objective of this study is cold flow properties of WCME and its blending oils. By the way, the change of adding of the cold flow improver PDD was studied.

### EXPERIMENTAL

**Corresponding Author:** Xiu Chen, School of Chemical Engineering, Anhui University of Science & Technology, Huainan, Anhui, 232001, China.

**Materials and Equipment**

WCME was obtained from Nantong BIOLUX Bioenergy Protein Feed Co. Ltd. 0# petrochemical diesel (OPD) and PDD were obtained from China Petroleum & Chemical Corporation.

**Chemical Composition Determination**

WCME was analyzed by gas chromatography-mass spectrometer (GC-MS) (Finnigan, Trace MS, FID, USA), equipped with a capillary column (DB-WAX, 30 m × 0.25 mm × 0.25µm). The carrier gas was helium (0.8 mL/min). The sample injection volume was 1µL. Temperature program was 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.

**CFPP Measurement**

WCME was analyzed by gas chromatography-mass spectrometer (GC-MS) (Finnigan, Trace MS,

FID, USA), equipped with a capillary column (DB-WAX, 30 m × 0.25 mm × 0.25µm). The carrier gas was helium (0.8 mL/min). The sample injection volume was 1µL. Temperature program was 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.

**Kinematic Viscosity Measurement**

The kinematic viscosity was measured in SYP2007-7 the kinematic viscosity tester (shanghai boli, China) following the GB/T 265-1988 procedures.

**RESULTS AND DISCUSSION**

**Chemical Composition**

The main chemical composition of WCME and OPD by GC-MS is shown in Table 1 and Table 2, respectively.

Table 1 The main chemical compositions of WCME

WCME	C <sub>12:0</sub>	C <sub>14:0</sub>	C <sub>16:0</sub>	C <sub>18:0</sub>	C <sub>20:0</sub>	C <sub>22:0</sub>	C <sub>16:1</sub>	C <sub>18:1</sub>	C <sub>20:1</sub>	C <sub>22:1</sub>	C <sub>18:2</sub>	C <sub>20:2</sub>	C <sub>18:3</sub>
(w)%	0.09	0.83	20.66	5.78	0.19	0.08	1.64	36.77	0.55	0.43	29.41	0.1	2.91

Note: C<sub>m:n</sub> 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 compositions of OPD

OPD	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>15</sub>	C <sub>16</sub>	C <sub>17</sub>	C <sub>18</sub>	C <sub>19</sub>	C <sub>20</sub>	C <sub>21</sub>	C <sub>22</sub>
(w)%	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

Note: C<sub>m</sub> is shorthand of alkane. m is the number of carbon atom in alkane.

From Table 1, it can be seen that the WCME was mainly composed of fatty acid methyl esters (FAME) of 14-24 even-numbered C atoms. They contained: saturated fatty acid methyl ester (SFAME) C<sub>14:0</sub>~C<sub>24:0</sub>, unsaturated fatty acid methyl esters (UFAME) C<sub>16:1</sub>~C<sub>22:1</sub>, C<sub>18:2</sub> and C<sub>18:3</sub>. The mass fraction of SFAME and UFAME was 14.69% and 83.40%, respectively. OPD was mainly composed of long chain alkane of 10~22 C atoms.

**Cold Flow Properties**

The main chemical composition of WCME and OPD by GC-MS is shown in Table 1 and Table 2, respectively.

**(1) CFPP**

Using cold filtration point tester, determine the CFPP of WCME, OPD and WCME/OPD (Fig. 1).

The CFPP of WCME and OPD were 0 °C and -3 °C. The mass fraction of UFAME of WCME was 71.81% (Table 1). The C=C in carbon chains of WCME bended the chain. The symmetry of UFAME was below on SFAME. From Table 3, as the growth of the carbon chain and the increase of unsaturation, the melting point of FAME is reduced. The lower melting point, the easier crystal. Biodiesel could be regarded as pseudo two components in solution approximately which was composed of the high

component SFAME (solute) and low melting component UFAME (solvent). The carbon in alkyl groups of SFAME formed the structure of zigzag pattern, which made SFAME closely packed and crystallize easily. As the temperature decrease, the structure of SFAME developed a 3D mesh "framework" structure. UFAME are easy to be fixed in the "framework" structure, which made biodiesel loss of liquidity finally.

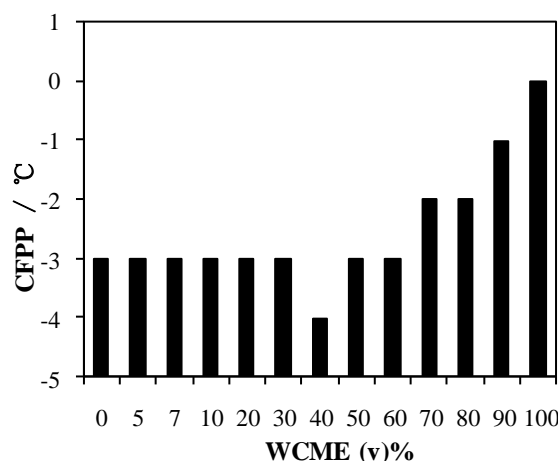


Fig.1 The CFPP of WCME, OPD and WCME/OPD

With increasing WCME blending ratio, blending oil CFPP decreased from -3 °C to -4 °C with B0~B40 (Bn is biodiesel blended with petro diesel, the n indicates the volume fraction of biodiesel in the blend.), staying at -4 °C with B40, then increased to 0 °C (Fig.1). It was chiefly because WCME blending with OPD decreased SFAME content, which could

resistant to form the 3D mesh "framework" structure at low temperature. By blending, the long chain SFAME of WCME and long chain alkane of OPD could form a eutectic mixture, with B40. Therefore, the CFPP of blending oil was lower than that of WCME and OPD.

Table 3 Melting point (m.p.) of fatty acid methyl esters

WCME	C <sub>12:0</sub>	C <sub>14:0</sub>	C <sub>16:0</sub>	C <sub>18:0</sub>	C <sub>20:0</sub>	C <sub>22:0</sub>	C <sub>18:1</sub>	C <sub>18:2</sub>	C <sub>18:3</sub>
m.p./°C	5.2	18.5	30.5	39.1	54.5	55.0	-20	-35	-55

**(2) Kinematic Viscosity**

Using the kinematic viscosity tester, determine the kinematic viscosity of WCME, OPD and blending oil (WCME/OPD) at different, shown in Fig. 2.

It can be seen from Fig.2 that kinematic viscosity of WCME and OPD were 4.41mm<sup>2</sup>/s and 2.53mm<sup>2</sup>/s respectively at 40 °C, which were within national standard (1.9-6.0 mm<sup>2</sup>/s). The viscosity of WCME was higher than that of OPD under the same temperature. It was mainly because of the difference between the composition of WCME and OPD which made the average molecular weight of WCME higher than OPD.

With temperature decreasing, WCME/OPD viscosity increased constantly. It could be seen that the kinematic viscosity of blending oil increased as the fraction of WCME increasing at same temperature, and the blending oil viscosity lied between OPD and WCME. Kinematic viscosity said resistance in the process of flow. The main source of resistance was intermolecular interactions. Reaction between the polar molecules and nonpolar molecules was greater than reaction between the nonpolar molecules and nonpolar molecules. It was less than reaction between the nonpolar molecules and

nonpolar molecules. So, the blending oil kinematic viscosity lied between OPD and WCME.

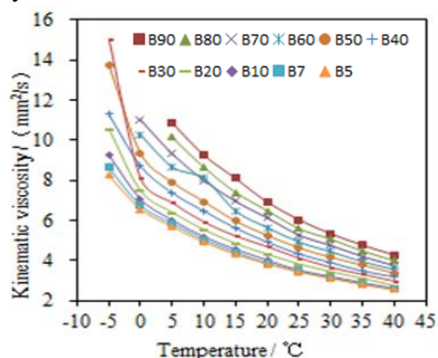


Fig. 2 The kinematic viscosity of WCME, OPD and WCME / OPD

**(3) Adding the PDD**

The economic and performance benefits of using cold flow improver to improve cold flow properties of biodiesel have been recognized. The optimum volume fraction of additives and the CFPP of WCME/OPD and WCME without/with PDD are shown in Table 4.

Table 4 Influence of PDD on CFPP of WCME and WCME/OPD

RME/OPD	The optimum volume fraction (%)	CFPP without PDD ( °C)	CFPP with PDD ( °C)
B5	0.3	-3	-24
B7	0.3	-3	-24
B10	0.2	-3	-23
B20	0.3	-3	-24
B50	1	-3	-8
WCME	0.5	0	-4

Using PDD is an economic and performance way for improving cold flow properties of biodiesel. The PDD functioned by reducing the size and amount and altering the shape of the wax crystals of biodiesel, which it was difficult to form a three-dimensional

network structure. That is, it inhibited the crystals from growing to a larger size and provided a barrier to crystal agglomeration at low temperatures, thus extending the range of fluidity of the biodiesel to lower temperatures.

From Fig.4, it could be seen that PDD reduced the CFPP of B5, B7, B10, and B20 from -1, -3, to -23 °C. With blending ratio of WCME increased, the CFPP of B50, and WCME Small changed, which reduced from -3 °C and 0 °C to -8 °C and -4 °C. By adding the PDD, the cold flow properties of WCME and WCME/OPD was effectively improved.

#### CONCLUSION

(1) The WCME was mainly composed of fatty acid methyl esters (FAME) of 14~24 even-numbered C atoms. The mass fraction of SFAME and UFAME are 27.63% and 71.81%, respectively. The cold filter plugging point (CFPP) of WCME is 0 °C, and the kinematic viscosity of WCME is 4.41mm<sup>2</sup>/s at 40 °C.

(2) The CFPP of blending oil depended on blending ratio. When the blending ratio of WCME was 40%, the CFPP was -4 °C. The viscosity of blending oil was between WCME and OPD. At the same temperature, and the viscosity increased with temperature decreasing.

(3) By adding the PDD, the cold flow properties of WCME and WCME/OPD was effectively improved. The CFPP of WCME decreased from 0 °C to -4 °C. The CFPP of B5, B7, B10, B20 and B50 decreased from -3 °C to -24 °C, -24 °C, -23 °C, -24 °C and -8 °C.

#### ACKNOWLEDGMENT

This research is supported by Anhui Provincial Natural Science Foundation (1408085ME109).

#### REFERENCES

- Bryan R. M., Steven F. V., 2012, "Efficacy of fatty acid profile as a tool for screening feeds tocks for biodiesel production", *Biomass and Bioenergy*, vol.307, pp 31-41.
- Chen B. S., Sun Y. Q., Fang J. H., et al, 2010, "Effect of cold flow improvers on flow properties of soybean biodiesel", *Biomass and bioenergy*, vol.34, pp 1309-1313.
- Chen X., Lai Y.B., Shao Q., 2010, "Study on Cold Flow Properties of Biodiesel from Typical Materials", *Chemical engineering of oil and gas*, vol.39, pp 391-393.
- Chen X., Yuan Y.N., Lai Y.B., 2010, "Flow properties of biodiesel at low temperature and its improvement", *Transactions of the CSAE*, vol.26, pp 277-280.
- Jin X., 2011, "Technology and policy research about using of waste oil in hutch garbage to product biodiesel", *Energy of China*, vol.33, pp 39-45.
- Joshi R. M., Pegg M. J., 2007, "Flow properties of biodiesel fuel blends at low temperatures", *Fuel*, vol.86, No.4, pp 143-151.
- Lv Y., Li J. Ouyang F. S., 2011, "Effect of biodiesels blending on their low temperature fluidity", *Journal of Fuel Chemistry and Technology*, vol.39, pp 189-193.
- Smith P. C., Ngothai Y., Nguyen Q. D., et al., 2010, "The addition of alkoxy side-chains to biodiesel and the impact on flow properties", *Fuel*, vol.89, pp 3517-3522.
- Wu M. X., Wu G. Y., Wang D., 2008, "Improving Low-Temperature Flowing Property of Biodiesel from Rapeseed Oil," *Journal of the Chinese Cereals and Oils Association*, vol.23, pp 90-94.