Study on the Rheological Properties of Biodiesel

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Abstract

The rheological properties and influencing factors of three kinds of bio diesels were studied systematically with AR-G2 rheometers. The results show that the rheological properties of bio diesel are affected by temperature and shear rate. The viscosity of bio diesels rise sharply when close to the cold filter plugging point (CFPP), leading to the viscosity-temperature curves having a turning point. And the turning point is close to but higher than the CFPP. The bio diesels show characteristics of non-Newton fluid at low shear rate along with the shear thinning phenomenon while showing characteristics of Newton fluid at high shear rate, and the shear thinning phenomenon at high temperature is more significant than low temperature. Above the temperature of the CFPP, three kinds of bio diesels all show the characteristics of plastic fluid, which can be better described by the Bingham model.

Keywords

Biodiesel, Rheological properties, Bingham model.

1. Introduction

The environmental pollution caused by a large amount of fossil fuels burning has become a major challenge for the whole world. In this environment, many countries have accelerated the pace of developing alternative energy. Due to the superior environmental performance of bio diesel, many countries and researchers have focus on it [1-3]. Compared to petroleum diesel fuel, bio diesel has many advantages including biodegradation, low emission, low toxicity, superior lubricity, high flash point, low sulfur [4-7]. But the rheological properties of bio diesel are poor. When the environmental temperature is low, bio diesel is prone to crystallization and gelation, resulting in the viscosity of bio diesel increases sharply. While the high viscosity of bio diesel will lead to poor engine start performance and filters and lines clogged. Therefore, how to improve the low temperature rheological properties of bio diesel is an urgent problem to be solved.

Some achievements have been made in the research on the low temperature rheological properties of bio diesel. The low temperature rheological properties of bio diesel mainly depend on the type and content of fatty acid methyl ester. While the CFPP is related to unsaturated fatty acid methyl esters and length of the molecular chain. The research from N. A. Santos [8] indicated that the low temperature crystallization increased the viscosity of palm oil bio diesel and resulted in Newtonian fluid changing into pseudo plastic fluid. Alexandra A. Alicke [9] pointed out that rheological properties were greatly affected by the shear history and thermal history. Chen [10] has studied the low temperature rheological properties of bio diesel and its blending oil by rotary rheometer and polarized light microscopy, which found that dynamic viscosity of biological diesel oil and its blending oil increased sharply with the temperature decrease below the CFPP ,while dynamic viscosity and shear rate showed a linear relationship above the CFPP.

The rheological properties and influencing factors of three kinds of bio diesels were discussed in this paper, providing the biological diesel oil with a reference of storage, transportation and application.

2. Experimental

2.1 Materials and Equipment.

Cottonseed oil: Dantu oil refinery; rice bran oil: Huainan Panyu Liangyou Xinyuan grease; rapeseed oil: Huainan oil refinery; 0 petrodiesel (0PD) and -10 petrodiesel (-10PD): Sinopec.

AR-G2 rheometer: TA Instruments; Trace MS gas chromatography mass spectrometer: the Finnegan; SYP2007-1 petroleum products cold filter plugging point tester: Shanghai Boil Equipment Limited Company.

2.2 Analytical.

The chemical composition of bio diesel and petrochemical diesel were analyzed by GC-MS. SYP2007-1 cold filter point tester was used to determine the cold filter plugging point according to China SH/T0248-2006 standard method. Temperature, viscosity, shear rate, shear stress of the samples was determined by AR-G2 rheometer.

3. Results and discussion

3.1 Index analysis.

The distribution of fatty acid methyl ester from cotton seed oil biodiesel (CSME), rice bran oil biodiesel (RBME) , and rapeseed oil bio diesel (RME) were determined . And the results were shown in Table 1. The CFPP of CSME, RBME, RME, 0PD and -10PD were determined, results shown in Table 2.

Table 1 Relative contents of fatty acid methyl esters in several kinds of biodiesels

Fatty acid	Content *w*/ %		
	CSME	RBME	RME
$C_{14:0}$	0.98	0.36	0.33
$C_{16:0}$	23.36	16.37	9.35
$C_{16:1}$	0.72	0.30	0.44
$C_{18:0}$	2.90	2.20	3.51
$C_{18:1}$	19.54	42.74	40.33
$C_{18:2}$	50.96	34.19	25.25
$C_{18:3}$	0.26	1.39	7.38
$C_{20:0}$	0.30	0.73	0.79
$C_{20:1}$	0.10	0.64	3.05
$C_{22:0}$	0.15	0.29	0.49
$C_{22:1}$		0.49	6.95
$C_{20:2}$			0.22
$C_{24:0}$			0.22
Unsaturated fatty acid	71.58	79.75	83.62

Table 2 Cold filter plugging point of oil biodiesel and diesel

Sample	CSME	RBME	RME	0PD	-10PD
CFPP / ℃	-1	-2	-9	-3	-8

Table 1 shows that the descending order of relative content of unsaturated fatty acids is RME, RBME and CSME. Table 2 shows that the descending order of CFPP is CSME, RBME, RME, and the CFPP of the three are all above zero. As Yuan Yinnan [11] said, the CFPP increased linearly with the decrease of the content of unsaturated fatty acid methyl ester.

3.2 Temperature effect.

The apparent viscosity of CSME, RBME, RME and -10PD under different temperature was determined by AR-G2 rheometer, and the viscosity-temperature curve was shown in Fig. 1.

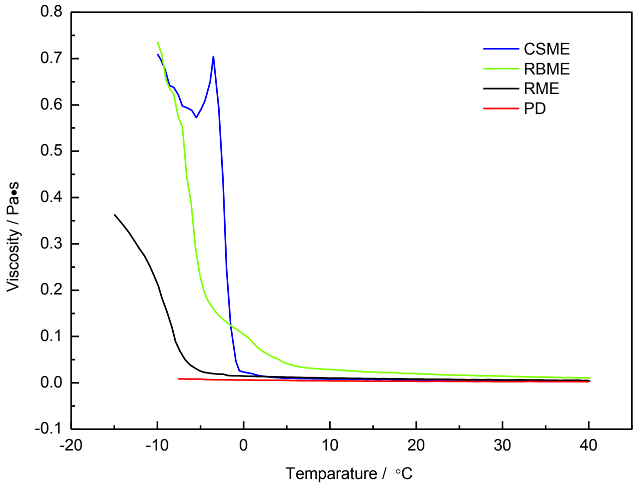


Fig. 1 Properties of viscosity- temperature curves of bio diesels and petrol diesel

It can be seen that the viscosity-temperature curves can be divided into two sections and a turning point. Before the turning point, the viscosity-temperature curves are flat. After turning point, the viscosity-temperature curves become very steep. The reason is that the temperature of bio diesel decreases to its CFPP, resulting in a sharp increase in viscosity. The viscosity of diesel oil changes a little with the temperature decreased. Viscosity of diesel oil can be kept at low temperature. So the low temperature rheological properties of diesel oil are better than other three kinds of bio diesels. The viscosity-temperature curve of diesel oil does not have obvious turning point, while the viscosity-temperature curves of bio diesels all have a obvious turning point. The temperatures of the turning points are, respectively, the RME (- 7℃) , the RBME(- 1℃)and the CSME (- 1℃);while the corresponding CFPP are 9 ℃, - 2℃ and -1℃. It indicates that the turning point is close to CFPP but higher than CFPP. Low temperature crystallization causes viscosity of the bio diesel oil suddenly rise and bio diesel oil flow from the Newton fluid into non -Newton fluid.

3.3 Effect of shear rate.

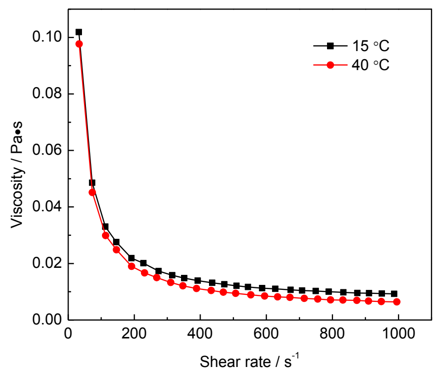
The viscosity-shear rate curves of CSME, RBME and RME under different temperature were shown in Fig. 2.

It can be seen from the Fig. 2 that at the shear rate of about 200 (1/s), the viscosity-shear rate curves have a sharp decrease. When the shear rate is less than 200 (1/s), the viscosity-shear rate curves are steep. While the shear rate is more than 200 (1/s), the viscosity-shear rate curves are more flat and the viscosity remains almost unchanged. The results show that at low shear rate the three kinds of biodiesel oil behave as the non-Newton fluid characteristics, while at high shear rate showing Newton fluid characteristics. Three kinds of biodiesels all have shear thinning phenomenon, and high temperature is more obvious than low temperature.

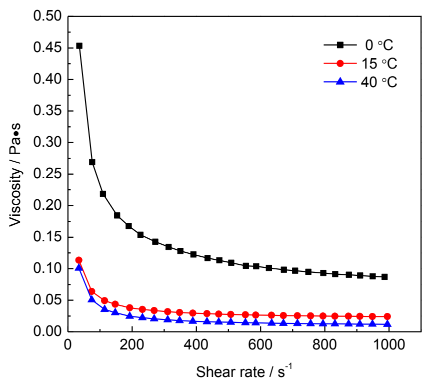
3.4 Flow curve and Bingham model.

The flow curves of CSME, RBME and RME under different temperature were shown in Figure 3.As is shown in Fig. 3, above the CFPP shear stress is proportional to shear rate; and the lower the temperature, the steeper the flow curve. These results suggest that above the CFPP, three kinds of bio diesels flow show plastic fluid or Bingham fluid characteristic.

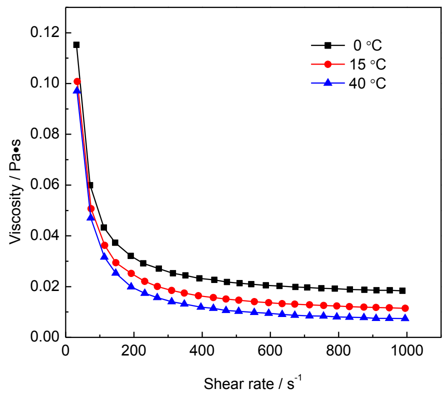
The flow curve fitting of CSME, RBME and RME based on the Bingham model under different temperature has been done in this paper. And the fitting equations and various parameters was shown in Table 3. Above the CFPP, the fitting correlation coefficient (r^2) of three bio diesels are are all larger than 0.99. The results illustrate that the Bingham model can better characterize the rheological properties of bio diesels above the CFPP. The plastic consistency coefficients (η_p) of three bio diesels all decrease with the temperature increasing, namely viscosity of bio diesel decreases with temperature increasing. The yield force (τ_0) of three kinds of bio diesels were all around 3P_a.



(a) CSME



(b) RBME

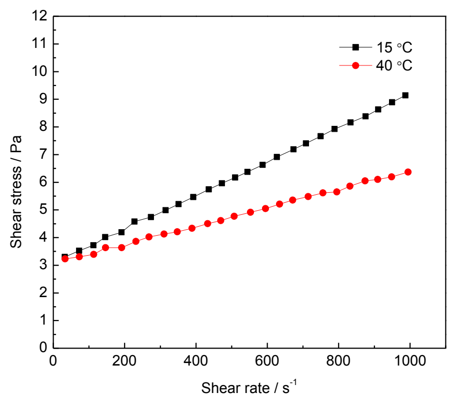


(c) RME

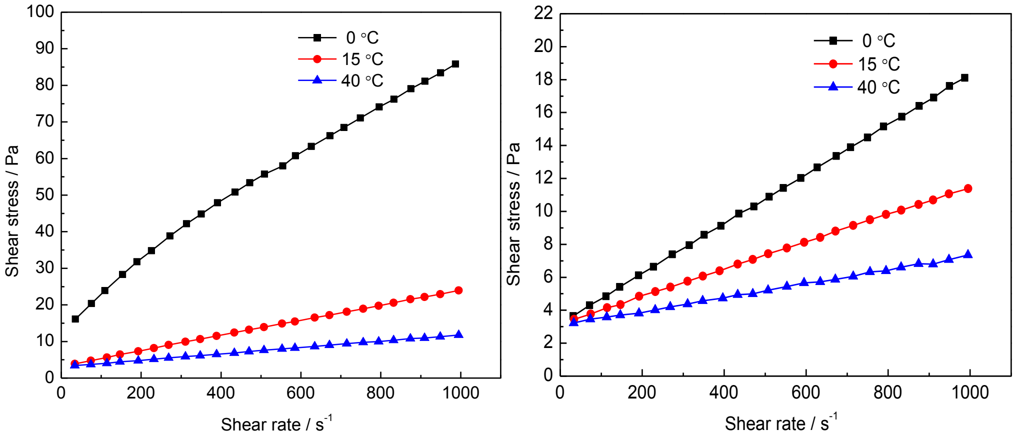
Fig.2 The crystallization of SFAME in PME at four cooling speeds

Table 3 Cold filter plugging point of oil biodiesel and diesel

Example	Temp. t/℃	Bingham equation	τ_0 /Pa	η_p /Pa·s	r^2
CSME	15	$\tau = 3.0801 + 0.0061\gamma$	3.0801	0.0061	0.9996
	40	$\tau = 3.0765 + 0.0033\gamma$	3.0765	0.0033	0.9983
RBME	0	$\tau = 18.083 + 0.0708\gamma$	18.083	0.0708	0.9930
	15	$\tau = 3.3644 + 0.0207\gamma$	3.3644	0.0207	0.9998
	40	$\tau = 3.147 + 0.0087\gamma$	3.147	0.0087	0.9996
RME	0	$\tau = 3.2097 + 0.0151\gamma$	3.2097	0.0151	0.9999
	15	$\tau = 3.1825 + 0.0083\gamma$	3.1825	0.0083	0.9998
	40	$\tau = 3.08 + 0.0042\gamma$	3.08	0.0042	0.9984



(a) CSME



(b) RBME (c) RME

Fig.3 Liquid Curves of CSME, RBME and RME

4. Conclusion

(1) The viscosity of bio diesels decreases with temperature increasing and rises sharply when close to CFPP, leading to the viscosity-temperature curves having a turning point. And the turning point is close to but higher than the CFPP.

(2) The bio diesels show characteristics of non-Newton fluid at low shear rate along with the shear thinning phenomenon while showing characteristics of Newton fluid at high shear rate, and the shear thinning phenomenon at high temperature is more significant than low temperature.

(3) Above the temperature of the CFPP, three kinds of bio diesels all show the characteristics of plastic fluid, which can be better described by the Bingham model.

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