Effects of fatty acids on oxidation stability and low temperature fluidity of biodiesel

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Abstract

In this study, the composition and content of the fatty acids methyl esters of biodiesel fuel samples, which were prepared from rapeseed oil, soybean oil, palm oil and waste frying oil, were analyzed. The oxidative stability of biodiesel was measured by Schaal Method and the low temperature fluidity of biodiesel was investigated. The technological parameters of biodiesel samples, such as peroxide value, acid value, TEP value, kinematic viscosity, cold filter plugging point and pour point, were also analyzed. The results showed that the higher content of the saturated fatty acidic methyl esters and the palm methyl ester in the fuel, the better the oxidative stability was; the higher the unsaturated methyl esters contents, the better the low temperature fluidity was; the high monounsaturated methyl esters contents improved both oxidative stability and low temperature fluidity of biodiesel.

Key words:biodiesel, fatty acids, oxidative stability, low temperature fluidity

Introduction

Biodiesel is defined to be the alkyl monoesters of vegetable oils, animal fats or recycled greases and used vegetable oils. Vegetable oils, such as soybean oil, rapeseed oil and tropical oils (palm oil and coconut oil) are the major sources of biodiesel. With these feedstock and alcohol (ethanol or methanol), transesterification reactions are carried out to produce monoesters known as biodiesel and glycerin in the presence of a catalyst. Because of its low cost, methanol is the most common alcohol used but ethanol is used in some cases. It is a renewable, biodegradable, cleaner burning alternative to petroleum fuels. Also biodiesel can be blended with diesel to form into a biodiesel blend which can be used in compression-ignition engines with little or no modifications (M.A. Kalam et al., 2002, Xu Ge et al., 2003).

Biodiesel as renewable biofuels has rapidly grown in the world market, but there are some problems which block its development. In storage time, the biodiesel fuel containing the polyunsaturated fatty acids such as linoleic acid and linolenic acid are inevitable to oxidation. The chemical changes in the fuel associated with auto-oxidation usually produce hydroperoxides, and then aldehydes and ketones, and the hydroperoxides can be also polymerized, which greatly reduce the performance of biodiesel (Sendzikiene E et al., 2005; Xu Ge et al., 2004, Robert O. Dunn, 2005). In addition to auto-oxidation of biodiesel, another drawback with the use of biodiesel is its poor cold flow properties compared with diesel fuel. In cold weather, some biodiesel will easily appear cloudy due to the wax crystals that can block the fuel lines and filters, because its cold filter plugging point, pour point and solid point are higher than diesel fuel (Sumit Tayal, 2006; Wu Miaoxin et al., 2005; Han Enshan et al., 2006). So vehicles running on biodiesel may experience more fuel system plugging problems than petroleum diesel fuel. It is necessary to enhance the storage stability and cold flow properties of biodiesel.

The oxidative stability and cold flow properties of biodiesel were studied in this paper. We used Schaal Method to investigate the oxidative stability of rapeseed methyl ester (RME), soybean methyl ester (SME), palm methyl ester (PME) and waste frying methyl ester (FWME), and determined their kinematic viscosity, cold filter plugging point and pour point; and we analyzed the effect of the profile of fatty acids methyl esters on The oxidative stability and cold flow properties of biodiesel.

Material and Methods

Materials

Crude rapeseed oil and soybean oil were purchased from Wuhan Zhongpai grain and oil Co., Ltd. Crude Palm oil was from the Wuhan food oil market, and waste frying oil was collected from some restaurants. Methanol analytical grade and sodium hydroxide analytical grade were supplied by Tianjin nankai Chemical Co., Ltd. . The Heptadecanoic acid methyl ester was obtained from Sigma－Aldrich Co..

Methods

Experimental methods

A sample of 1000 g crude oil was transferred to a two-neck flask equipped with a thermometer and a reflux condensator; and the oil was heated and stirred by a bar until the desired temperature was reached. A mixture of methanol and sodium hydroxide were added to the oil and the transesterification reaction began at 75°C. The reactor was kept at 75°C for 2 h. The procedure was carried out using a molar ratio of methanol/ crude oil which were 5 and a catalyst quantity equivalent to 1.0 %

mass of oil. At the end of the reaction period, the glycerol rich-phase was separated from the methyl ester layer in a decantation funnel. Then the latter phase was washed with a H_3PO_4 solution, and the biodiesel was separated from the H_3PO_4 solution. In the rotary evaporator, the remnant menthol in the biodiesel was distilled. The biodiesel was washed with hot water again, and the washed methyl esters were then dried with anhydrous sodium sulphate. The fatty acid composition of the samples was analyzed by GC.

The sample of 200 g of RME, SME, PME, FWME were transferred to the flasks which were put in the oven at 63°C±1°C., and the peroxide value, acid value, TEP value, kinematic viscosity, cold filter plugging point and pour point of biodiesel were determined in a time-interval

Analyses

The peroxide value(POV), acid value(AV), kinematic viscosity(KV) were examined at 40°C. Cold filter plugging point(CFPP) and pour point(PP) were carried out according to GB/T 5538, GB/T 5530, GB/265, SH/T0248, GB3535-83,respectively. The thiobarbituric acid(TBA) value was determined as follows: a sample of 10 g oil was transferred to evaporator flask with a reflux condensator, and a mixture of an HCl solution and wet olefin were added to the oil; the sample in the flask was heated through the vapor for 10 min, and collected the fraction at one time. The water was added to the fraction in 50ml container, and a mixture of 5ml of 50ml fraction and 5ml TEP was heated for 30 min at 100°C. The mixture was cooled in 10min, and its absorbency was determined in 532nm.

The methyl ester composition was obtained by gas chromatography using a HP6890N as Chromatograph, with DB-17HT capillary column. The temperature program was as follows: 160°C for 0.5 min, heating until 173°C at a rate of 40°C/min and holding at 175°C for 1 min; then heating until 245°C at a rate of 7°C/min and holding for 5min. The injector was set up for 260°C, as well as the FID detector. Helium was used as carrier gas, at a flux of 45 ml/min. Methyl heptadecanoate was used as an internal standard.

Results

Fatty acid distribution of biodiesel

The fatty acid composition of these biodiesel was analyzed by HP6890N Gas Chromatograph. Table 1 shows that FWME and PME contains saturated fatty acid methyl ester which mainly is palm methyl ester, higher than those of SME and RME. SME and RME containing the mass of unsaturated fatty acid methyl ester that reach 84.4% and 93.3%, respectively; the mass of linoleic methyl ester of SME is 50.1% and the mass of monoenoic acid methyl ester of RME is 71.7%. It was also observed that the order of the content of 18-carbon fatty acid methyl ester of biodiesel was as follows: SME>PME>RME>FWME, and fatty acid methyl ester(carbon number >18) of SME reaches 40.3%.

Table 1 Relative content of fatty acid methyl ester in biodiesel

	FWME	SME	RME	PME
C12:0 (%)	0.2	/	/	0.2
C14:0 (%)	1.0	0.1	0.1	0.9
C16:0 (%)	43.7	10.8	3.2	39.4
C16:1 (%)	0.5	0.2	0.3	0.4
C17:0 (%)	0.1	0.1	0.1	0.1
C17:1 (%)	/	0.1	/	/
C18:0 (%)	3.8	3.9	1.3	3.7
C18:1 (%)	39.9	24.7	33.4	43.1
C18:2 (%)	8.7	50.1	14.5	11.3
C18:3 (%)	0.4	7.4	7.0	0.3
C20:0 (%)	0.4	0.4	0.6	0.3
C20:1 (%)	0.2	0.7	8.7	0.4
C20:2 (%)	/	/	0.3	0.2
C22:0 (%)	0.1	0.3	/	/
C22:1 (%)	0.1	1.2	29.3	/
C22:2 (%)	/	/	0.4	/
C24:0 (%)	/	0.2	1.0	/

Comparison of the oxidation stability of biodiesel

The oxidative stability of RME, SME, PME and FWME was investigated by Schaal method. As shown in Fig. 1, the POV of FWME reaches 5.47meq/kg in 14d, which changes smaller than those of other biodiesel, and the POV of RME, SME and PME improve 102.09 meq/kg, 30.17meq/kg and 79.86meq/kg, respectively. From Fig. 1, it may be concluded that the oxidative stability of FWME is greater than that of RME according to the POV index, because their POV in 1d are pretty much the same thing. Fig. 2 indicates that the AV of RME, SME, PME and FWME increase 1.99mg KOH/kg, 1.88mg KOH/kg, 1.07mg KOH/kg and 0.25mg KOH/kg respectively, but the first value of FWME is lowest; so it can imply that the oxidative stability of FWME is the best among the four biodiesel and the oxidative stability of SME is poor. As can be seen from Fig. 3, the change of the TAB value of the samples shows the similar result compared with Fig. 2; the TAB value of

FWME is stable and the TAB value of SME enhances 14.54 mg/kg.

Comparison of the cold flow properties and kinematic viscosity of biodiesel

CFPP and PP have been used to characterize the cold flow operability of biodiesel fuels. The four samples were placed in the oven at 63°C±1°C, and the value of CFPP, PP and KV were termly evaluated. Table 2 and Table 3 indicate that RME has the lowest CFPP and PP in these biodiesel, but the values obviously altered when RME was gradually oxidated. The CFPP and PP of RME enhance 4°C and 10°C in 40d. Also the CFPP of SME increased from -2°C to 2°C and PP of SME increase from -3°C to -1°C, respectively. However, as shown in Table 2 and Table 3, the change of CFPP and PP of FWME and PME was inapparent as compared with RME and SME. The KV results at 40°C (Fig. 4) show that there is different variation among the four samples. The value of KV of SME increases from 4.629mm^2/s to 9.169mm^2/s, but that of PME, RME and FWME enhance 0.949mm^2/s,0.676mm^2/s and 0.527mm^2/s. It can be found that the results of the changes of KV, AV, TBA and CFPP are similar.

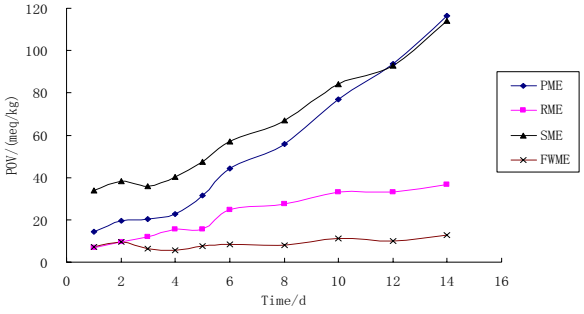

Fig. 1 Comparison for POV of four biodiesel

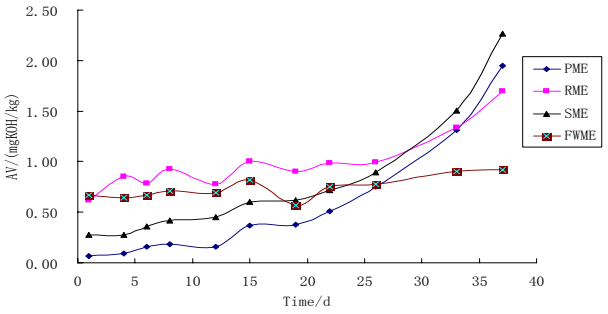

Fig. 2 Comparison for AV of four biodiesel

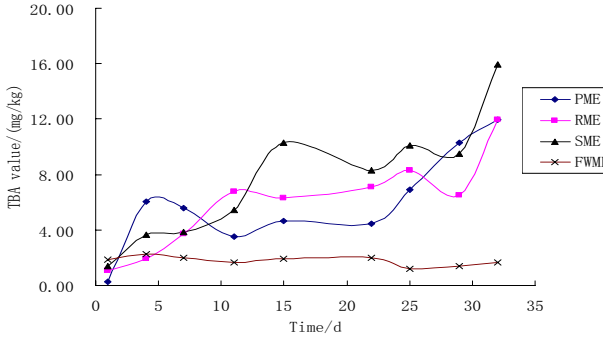

Fig. 3 Comparison for TBA value of four biodiesel

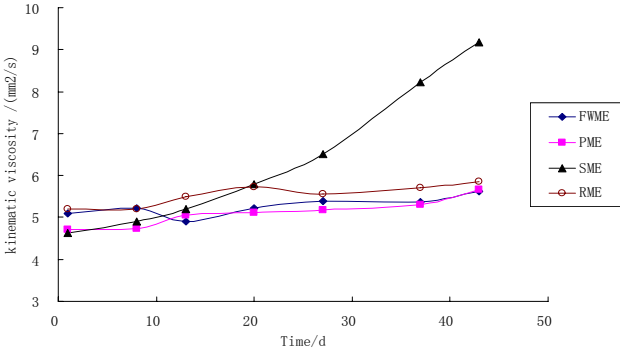

Fig. 4 Comparison for KV of four biodiesel

Table 2 Comparison for cold filter plugging point of four biodiesel (°C)

	FWME	PME	SME	RME
1d	11	11	-2	-11
20d	11	11	-1	-9
40d	12	11	2	-7

Table 3 Comparison for pour point of four biodiesel (°C)

	FWME	PME	SME	RME
1d	9	8	-3	-20
20d	9	9	-2	-17
40d	11	10	-1	-10

Discussion

One drawback of biodiesel is that biodiesel is prone to oxidation together with air exposure. Previous studies demonstrated that biodiesel stored at 4 and 20°C could degraded less than 10% within 52 weeks while nearly 40% degradation was found for those samples stored at a higher temperature, i.e. 40°C (D.Y.C. Leung et al.2006). Saturated compounds (C14:0, myristic acid; C16:0, palmitic acid; C18:0, stearic acid) have higher cetane numbers and are less prone to oxidation than unsaturated compounds but they tend to crystallize at unacceptably high temperatures (Mustafa Canakci, 2007).

As shown in the results, Biodiesel from soybean oil is highly unsaturated so its cold low properties are acceptable, for they have more linoleic methyl ester. However, it is more prone to oxidation than PME and WFME containing high saturated which has more palmtic methyl ester. RME has the best cold low properties among these biodiesel and good anti-oxidation performance relatively. It has been reported that the good order of biodiesel was RME>SM E>CME (cotton methyl esters) for the low temperature fluidity by compositions, solidifying point and CFPP (Xu Ge, 2004).The low-temperature fluidity of the biodiesel fuel depended on the content and distribution of the saturated fatty acid methyl esters in the fuel:the higher the esters content and the longer the carbon chains in the fuel, the worse the low-temperature fluidity was (Wu Miaoxin et, al.,2004).

Conclusions

The following conclusions may be drawn from the above study: the higher the saturated methyl esters and the palm methyl ester content in the fuel, the better the oxidative stability was; The higher the unsaturated methyl esters contents, the better the low temperature fluidity was; the high monounsaturated methyl esters contents improved the oxidative stability and low temperature fluidity of biodiesel.

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