Improving oxidation stability of biodiesel derived from cottonseed oil

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Abstract

Biodiesel, an ecofriendly and renewable fuel substitute for diesel has been receiving the attention of researchers around the world. Due to shortage of edible oil, the production of biodiesel from edible oil resources in China is not advisable. Therefore it is necessary to explore non-edible seed oils, like cottonseed oil for biodiesel production. The oxidation stability of biodiesel from cottonseed oil is unsatisfactory and therefore an idea is given to increase the oxidation stability of biodiesel by blending it with petrodiesel. Two pronged approaches have been adopted for improving the oxidation stability of COB: treating with antioxidant and blending with petrodiesel. The results have shown that COB, when treated with 1‰ antioxidant: butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and tert-butyl hydroquinone; blended with 0PD with less than 20% (v/v) would not need any antioxidants, maintains the international specification of oxidation stability.

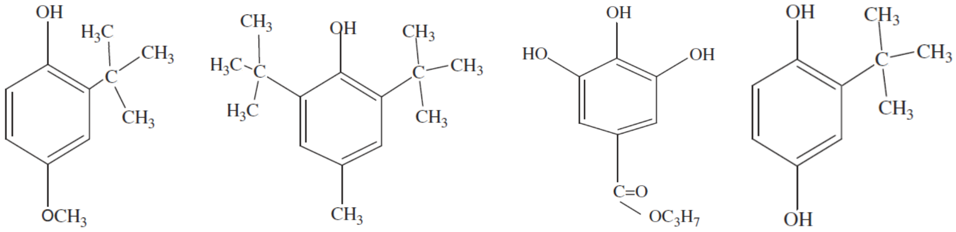
Keywords

Biodiesel, Oxidation stability, Cottonseed oil, Antioxidant additive.

1. Introduction

Biofuels especially biodiesels are receiving significant attention due to the environmental and energy concerns. Presently, commercial biodiesel is mainly produced from edible oil, such as palm oil, soybean oil and rapeseed oil, etc. [1]. Therefore, biodiesel is confronted with a severe challenge for petrol fuel because of expensive feedstock cost and increasingly aggravating tension between energy crisis and food security. In China, with abundance of cotton resources (an annual production of about 7 million tonnes), there are a high amount of inedible cottonseed oil, which have great potential for making biodiesel to supplement other conventional sources [2]. Cottonseed oil contains significant amounts of unsaturated fatty acids: oleic acid， linoleic acid and linolenic acid, etc. [3]. The fatty acid profile of cottonseed oil biodiesel (COB) i.e. the chain length and the level of unsaturation corresponds to that of cottonseed oil. It is the unsaturation fatty acid profile, which influences the oxidation stability of COB. When exposed to atmosphere, COB absorbs and reacts with oxygen to produce insoluble gums, aldehyde, alcohols, shorter chain carboxylic acids and sediments. These insoluble products result in plugging, fouling and corrosion of injection system and fuel storage tank [4].

In this article, the physicochemical properties and chemical composition of methyl biodiesel derived from refined cottonseed oil produced by our laboratory are reported. Method NB/SH/T 0825-2015 was employed to investigate the influence of four antioxidant additives: butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG) and Tert-butylhydroxyquinone (TBHQ) (structures in Fig.1[4]), and blending with 0PD on the oxidative stability of COB.



(a) BHA (b) BHT (c) PG (d) TBHQ

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

2. Experimental

2.1 Materials

Diesel: 0 petrodiesel (0PD) was purchased from China Petroleum & Chemical Corporation' Station in Huainan; COB is prepared using transesterification process in which triglyceride portion of the oil reacts with methanol and NaOH to form ester and glycerol. Antioxidant: BHA, BHT and PG were purchased from Henan Shengzhide Commerce and Trade Co., Ltd.; TBHQ was purchased from Guangzhou Yourui Biotechnology Co., Ltd..

2.2 Chemical composition analysis

The fatty acid methyl ester (FAME) composition of biodiesel 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.

2.3 Physico-chemical properties

The physico-chemical properties were measured following the GB/T 20828-2015 procedures.

2.4 Crystallization Process Observation

Rancimat instrument (NB/SH/T 0825-2015) was used to measure the oxidation stability of biodiesel with varying concentration. Fig. 2 shows the basic measurements principle of 873 rancimat tester. During testing, each biodiesel sample was heated to 110 °C and air was allowed to pass through each sample at constant rate of flow (10 L/h and then through the aqueous solution. Each measuring vessel was filled with 60 ml deionized water. After that, the conductivity of water is measured that was regularly monitoring using electrodes.

3. Results and discussion

3.1 Chemical composition

The main chemical components of COB were shown in Table 1.

Table 1 The main chemical compositions of COB (w)/%

COB	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{20:0}$	$C_{22:0}$	$C_{24:0}$	$C_{16:1}$	$C_{18:1}$	$C_{20:1}$	$C_{22:1}$	$C_{16:2}$	$C_{18:2}$	$C_{20:2}$	$C_{18:3}$
content	0.05	0.24	1.28	24.04	5.71	0.69	0.23	0.17	0.51	38.87	0.61	1.10	0.02	23.32	0.03	1.78

Note: $C_{m:n}$ is the shorthand of fatty acid methyl ester; *m* means the carbon number of fatty acid; *n* means the number of C=C.

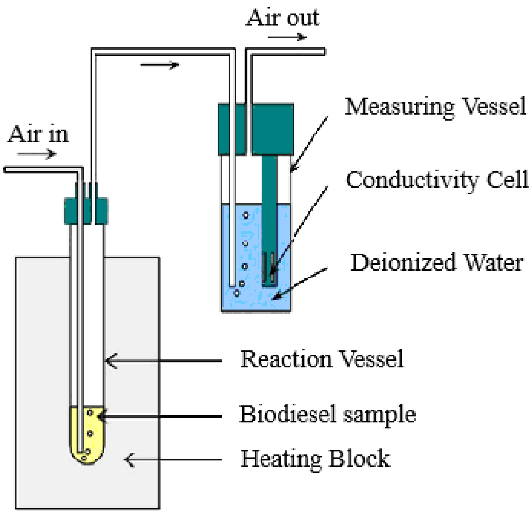


Fig. 2. Basic measurement principle of Rancimat instrument.

From Table 1, we can see that dominate the main chemical compositions of COB are the fatty acid methyl ester (FAME) composed by 10-24 even number carbon atoms, and the mass fraction of saturated fatty acid methyl esters (SFAME) ($C_{10:0}$-$C_{24:0}$) and unsaturated fatty acid methyl esters (UFAME) ($C_{16:1}$-$C_{22:1}$, $C_{16:2}$-$C_{20:2}$ and $C_{18:3}$) is 32.41% and 66.24%, respectively.

3.2 Physico-chemical properties

The synthesized COB samples were tested for physico-chemical properties as per GB/T 20828-2015 specification as given in Table 2. The table shows that although the COB met most of the specifications but failed in oxidation stability test according to NB/SH/T 0825-2015 limit of 6 h, due to presence of large amount of UFAME. It is clear from Table 1, the amount of polyunsaturated fatty acid methyl ester (PUFAME) with accounts for over 25% of COB, which highly influences the stability of the fuel sample.

Table 2 The properties of COB

Biodiesel	ρ at 20 °C (gcm^{-3})	v at 40 °C (mm^2s^{-1})	FP (closed cup) (°C)	CFPP (°C)	Copper strip corrosion 3h at 50°C	IP at 110 °C (h)
COB	881	4.63	>140	-1	1	3.22

3.3 Improvement of oxidation stability

Two pronged approaches have been adopted for improving the oxidation stability of COB. First approach deals with the doping of COB with antioxidants and four phenolic antioxidants, namely, BHA, BHT, PG, and TBHQ were used. Also the biodiesel is supposed to be blended with diesel while using in diesel engine and accordingly, another set of study was undertaken to blend COB with petrodiesel having good oxidation stability due to lack of UFAME.

(1) Treating with antioxidant

All the four antioxidants were doped in COB and Rancimat test was conducted to study the effectiveness of different antioxidants and the results are given in Table 3. Table 3 shows the effect of all phenolic antioxidants on the oxidation stability. The oxidation stability of COB has been found to be increase with all phenolic antioxidants, and at dosing of around 1‰ of antioxidants to meet NB/SH/T 0825-2015 specification for biodiesel oxidative stability.

Table 2 The properties of COB

Antioxidant	No antioxidant	1‰BHA	1‰BHT	1‰PG	1‰TBHQ	Antioxidant
IP (h)	3.22	6.47	6.51	8.59	13.33	IP (h)

(2) Blending with petrodiesel

Although, it is possible to meet the desired GB/T 20828-2015 specification by using antioxidant but there will be cost implications as antioxidants are costly chemicals. Also biodiesel is supposed to be blended with petrodiesel therefore COB blends with 0PD in different composition (B20, B40, B60 and B80) were prepared and then its effect on oxidation stability was studied and the results are shown in Table 4. It is clear from Table 4 that as the amount of 0PD is decreased in the blend, the IP also decreases, indicating the decrease in oxidation stability that can be attributed to the increase of UFAME in the blend. It has been found experimentally that minimum 80% 0PD is required to be blended with COB (B20) to meet the specification of IP of 6 h according to NB/SH/T 0825-2015. However, if we go beyond B20, the IP will decrease below 6 h and it will not be able to maintain the specification according to NB/SH/T 0825-2015. Therefore the antioxidants on oxidation stability is required beyond B20.

Table 2 The properties of COB

Oil sample	COB	B80	B60	B40	B20
IP (h)	3.22	3.51	3.71	4.38	6.09

4. Conclusion

COB, when treated with antioxidant and blended with petrodiesel leads to having efficient and improved oxidation stability. The results have shown that treating with 1‰BHA, BHT, PG, and TBHQ; blending with 0PD with less than 20% (v/v) would not need any antioxidants maintain the oxidation stability specification.

Acknowledgements

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References

[1] Z. Yaakob, B.N. Narayanan, S. Padikkaparambil, et al. A review on the oxidation stability of biodiesel, Renewable & Sustainable Energy Reviews, Vol. 35 (2014), p. 136-153.

[2] U. Rashid, F. Anwar, G. Knothe. Evaluation of biodiesel obtained from cottonseed oil, Fuel Processing Technology, Vol.90 (2009), No. 9, p. 1157-1163.

[3] R.D. Lanjekar, D. Deshmukh. A review of the effect of the composition of biodiesel on NOx emission, oxidative stability and cold flow properties, Renewable & Sustainable Energy Reviews, Vol. 54(2016), p.1404-1411.

[4] S. Kumar, R. Kumar, M. Kumar. Experimental investigations of oxidation stability of biodiesel produced from Prunus armeniaca oil (apricot oil) and effect of various antioxidants on stability, engine performance and emissions, Fuel, Vol. 216(2008), p. 861-869.