Improving Cold Flow Properties of Pistacia Chinensis Methyl Ester

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Abstract. The chemical compositions of PCME were analyzed by the gas chromatograph-mass spectrometer. The cold flow properties of PCME and blending oils which made PCME to blend with 0PD were studied in the article. The study shows that PCME is mainly composed of fatty acid methyl esters, and the contents of saturated fatty acid methyl ester and unsaturated fatty acid methyl ester are 18.6% and 81.09%, respectively. The CFPP of CSME is -6℃, and the viscosity of PCME is 6.06 mm2• s-1 when the temperature is 40℃. Blending with 0PD decreases the CFPP of PCME to -12℃. With temperature decreasing, the viscosity of PCME and blending oils increases. The lower the temperature is, the more differences the viscosity of PCME and blending oils are. Adding 0.4% (volume fraction) of PDD, the CFPP of PCME, B5 and B7 decreased from -3℃, -3℃to -23℃ and -21℃, respectively.

Keywords: Biodiesel, Cold flow property, GC-MS.

1. Introduction

The world faces the dual crisis of the fossil fuel depletion and environmental degradation, looking for a renewable alternative fuel is imminent, biodiesel because of its environmental friendliness is nations of the world's attention [1] Because of the cooking oil resources increasing nervous, the advantage of woody plants as a feedstock for biodiesel is more and more obvious. Pistacia are widely distributed in our country, Henan province is China's best suitable distribution area, pistacia existing natural distribution area of 200000 hectares, about 10 years of prostagland trees more than 900 strains. Using pistacia preparation of biodiesel can relieve the problem of shortage of raw material supply, But pistacia biodiesel (pistacia chinensis methyl ester, PCME) are easily crystallized at low temperature, blocking engine pipeline and filter, restricting its application and popularization in low temperature condition, so improving the PCME cold flow property in cold area to its use provides the technical support.

Studying the influence factors of biodiesel cold flow property and the inherent law, putting forward methods to improve the low temperature fluidity is the research focus of the biodiesel research. The study found that the biodiesel cryogenic liquid mainly depends on the fatty acid methyl ester in biodiesel (fatty acid methyl ester, FAME), the type and content of the biodiesel cold filtration point (cold filter plugging point, CFPP) with saturated fatty acid methyl ester (saturated fatty acid methyl ester, SFAME) increases with the increase of content and chain[2-3]; The method of improving biodiesel cold flow property basically have: with petroleum diesel blending[4-6] and added low temperature flow improver[7-9], longer chains or branched chain alcohol preparation of biodiesel[10], catalytic modification [11-12], crystal separation[13-15]. Our country adopts the CFPP as evaluation index of biodiesel cold flow property, but it cannot fully reflect the biological diesel oil under the condition of low temperature flow property, combine CFPP and motion viscosity can more fully reflect the cold flow property of biodiesel.

In this paper, we use GC instrument (GC - MS) to determine the chemical composition, two methods of PCME with 0# diesel fuel (0PD) blending and low temperature fluidity improver added to improve the PCME cold flow property.

2. Experimental

2.1. Materials and Instruments.

PCME: laboratory preparation; 0PD, Low temperature flow improver (PDD): sinopec.

Trace GCMS type instrument: Finnigan, companies in the United States; SYP2007-1 type cold filtration point tester, SYP1003-7 oil products kinematic viscosity at low temperature tester, kinematic viscosity tester SYP1003 -i petroleum products: Shanghai wee petroleum equipment manufacturing limited company.

2.2. Analysis Method.

Using GC-MS analysis PCME with 0 to the chemical composition of pd.Analysis conditions: chromatographic column: DB - idea (30 m×0.25mm×0.25 μm); Sample quantity: 0.1 mu L; The carrier gas: He; Temperature program: initial temperature is 160 ℃, keep 0.5 min. Heating rate 1 to 6 ℃•min^{-1}, up to 215 ℃; Heating rate of 2 to 3 ℃•min^{-1} up to 230 ℃, keeping 13 min.

According to SH/T 0248-2006 and GB/T 2006-265 respectively determine the CFPP of the oil viscosity and movement.

3. Results and discussion

3.1. Chemical composition.

Using GC-MS, 0PD measurement and the composition of PCME chromatograph chart as shown in Fig 1 and Fig 2, Main chemical compositions of 0PD and PCME are presented in Table 1and Table 2.

Table 1 Main composition of 0PD

Alkane	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22
0PD	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: Cm is the shorthand of alkane; m means the carbon number of alkane.

Table 2 Main composition of PCME

FAME	C14:0	C16:0	C18:0	C20:0	C22:0	C24:0	C16:1	C18:1	C20:1	C22:1	C18:2	C20:2	C18:3
PCME	0.06	15.56	2.33	0.30	0.28	0.15	1.66	46.16	0.93	3.52	27.21	0.04	1.57

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

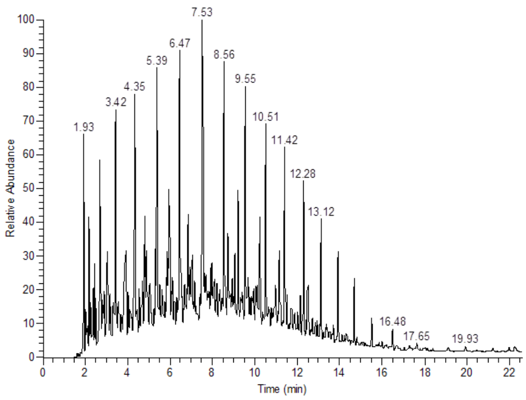

Fig.1 GC-MS spectra of 0PD

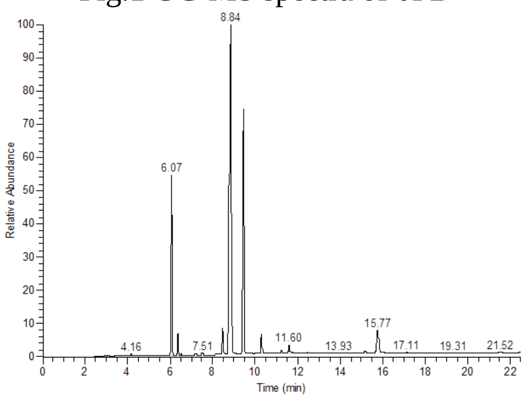

Fig.2 GC-MS spectra of PCME

From Table 1 an Table 2 it can be seen that 0PD is mainly composed of 10~22 carbon atoms of n-alkane, PCME mainly by $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, $C_{18:1}$, $C_{18:2}$ and $C_{18:3}$, $C_{22:1}$, accounting for 98.01% of the total mass, including SFAME and unsaturated fatty acid methyl ester (unsaturated fatty acid methyl ester, UFAME), SFAME and UFAME mass fraction of 18.6% and 81.09% respectively.

3.2. Kinematic Viscosity.

The relationship between viscosity and temperature of PCME, 0PD, and PCME/0PD are shown in Fig.3.

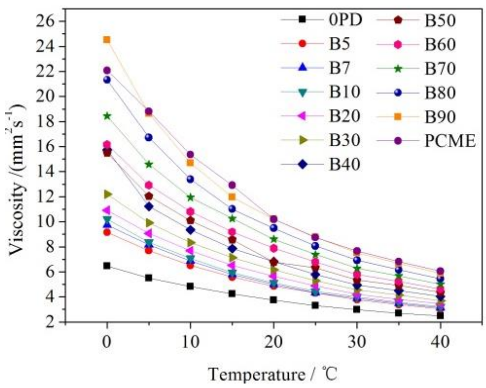

Fig.3 Properties of viscosity versus temperature curves of blending oils

The Fig.3 shows that when the temperature is 40℃, movement viscosity of PCME and 0PD respectively were 6.06 $mm^2 \cdot s^{-1}$and 2.48 $mm^2 \cdot s^{-1}$, under the different temperature, PCME movement viscosity of PCME was greater than movement viscosity of 0PD.With lower temperature, PCME and 0PD movement viscosity are increases gradually, gradually become illiquid. Because the PCME composition is given priority to with 18 carbon atoms of fatty acid methyl ester, accounting for 77.27% of the total mass, 0PD consisting mainly of 10~22 normal alkane carbon atoms, the average molecular weight is less than PCME, so as to make the PCME movement viscosity is higher than 0PD. However, with the increase of temperature, the movement of the blended oil viscosity is decreased. At the same temperature as the PCME volume increases, the movement of the blended oil viscosity value increases accordingly, gradually close to the PCME movement viscosity. Known from the analysis of PCME and 0PD: 0PD average molecular weight is less than PCME, under the same temperature, with the increase of PCME volume, average molecular mass of the blended oil increasing, motion viscosity value will increase accordingly. PCME in 40℃ kinematic viscosity of 6.06 $mm^2 \cdot s^{-1}$, slightly higher than the national standard regulations and through blending can make movement viscosity of PCME/0PD accord with diesel fuel in the standard, which provides the theoretical basis as alternative fuels.

3.2. The improvement of the cold flow property.

Blending with 0PD. CFPP of PCME/0PD, as shown in Fig 4.

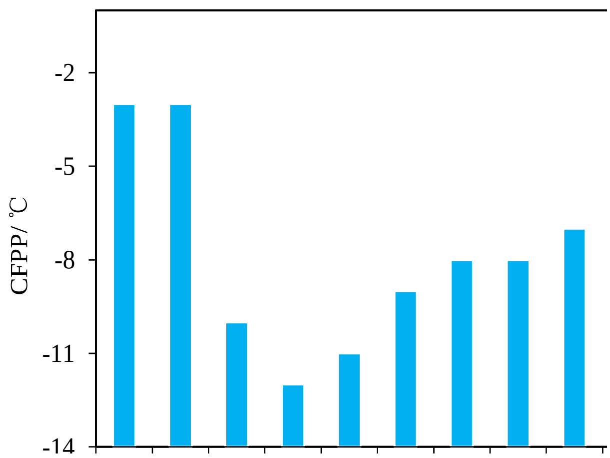

Fig.4 CFPP of blending oils

The Fig 4 shows, CFPP of PCME/0PD with PCME blending ratio has a close relationship. With the increase of PCME blend ratio, CFPP of PCME/0PD present the trend of increase with the decrease of the first CFPP of 0PD from -3 ℃ fell to the lowest - 12 ℃, then increase -3 ℃; When the blending ratio of 70%, PCME/ 0PD appeared the minimum CFPP for - 12 ℃. This is mainly because when PCME with 0PD after mixing, blending SFAME relative content is reduced, in the low temperature fluidity improves, this makes the PCME/0PD CFPP of are lower than that of the PCME;PCME long chain SFAME with long chain alkanes in -10PD can form eutectic material, makes the CFPP of PCME/0PD is lower than PCME,0PD,dropped to the lowest -12 ℃,which provides a favorable theoretical support for the PCME in northern cold region.

Add low temperature flow improver. Biodiesel and petroleum diesel blending to improve the low temperature fluidity effect is not very good, it can't meet their use in cold region, now combined blending and adding with PDD two methods to use, it can better to improve the cold flow property.

Selecting blending with 0PD proportion in B5 and B7 this two smaller sample added PDD. By adding 0.4% of the PDD, B5, B7 CFPP from 3℃ and 3℃ down to -23 ℃, 21℃ respectively; PDD adding the amount on a small scale can mitigate the CFPP of blending much, the effect is very obvious, improve the cold flow property effectively. This is mainly because the crystallization of the FAME of behavior is easily affected by PDD, PDD by adsorption on the surface crystallization make PCME/0PD grew up to the obstacles in the process of crystal grain size or adhesion between grains, which was difficult to form a three-dimensional network structure in the sample, so that the PCME/0PD under low temperature conditions produce crystal but does not affect the flow performance, so as to change its cold flow property.

4. Conclusion

(1) The main composition of 0PD is composed of 10~22 carbon atoms of n-alkane, CFPP was -3℃, and when the temperature is 40℃, movement viscosity of 0PD was 2.48 $mm^2•s^{-1}$; PCME's main composition contained SFAME and UFAME, the mass fraction of 18.6% and 81.09%, the CFPP was - 6℃, when the temperature is 40℃, movement viscosity of PCME was 6.06$mm^2•s^{-1}$.

(2) Blending with 0PD and adding the PDD to improve the cold flow property of PCME, the proportion of blending with 0PD between 20% ~ 80%, CFPP of PCME/0PD was lower than PCME, fell to the lowest -12℃, and the movement viscosity of PCME/0PD obviously lower than the PCME; When adding PDD volume fraction of 0.4%, B7 and B5 CFPP respectively from 3℃ and3℃ to-21 ℃, -23℃, improved the cold flow property of blended oil very well.

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References

[1] S. G. Chen, J. C. Jiang, X. A. Nie: The research progress of cold flow property of biodiesel, Journal of Biomass Chemical Engineering, Vol. 6 (2007), p.42-46. (In Chinese)

[2] X. Chen, Y. N.Yuan, Y.B. Lai, et al: The effect of biodiesel and component structure on its cold flow property, Journal of Oil (Oil Processing), Vol. 5(2009), p. 673-677. (In Chinese)

[3] E.F.S.M. Ramalho, J.R. Carvalho Filho, A.R. Albuquerque, et al: Low temperature behavior of poultry fat biodiesel: diesel blends, Fuel, Vol. 93 (2012), p. 601-605.

[4] B. S. Chen, Y. Q. Sun, J. H. Fang, et al: The research of biodiesel/mineral diesel blended fuel flow characteristics at low temperature and rheological properties, Journal of soybean science, Vol. 28(2009), p. 148-150. (In Chinese)

[5] Lee, Inmok, Johnson, et al: User of branched-chain esters to reduce the crystallization temperature of biodiesel. Source, Vol. 72(1995): 1155-1160.

[6] G. Xu, G. Y. Wu: Biological diesel oil and 0# diesel fuel blending performance research, Journal of Jiangsu polytechnic institute, Vol. 15 (2003), p. 16-18. (In Chinese)
[7] J. N. Wang, L. C. Cao, S. Han: Effect of polymeric cold flow improvers on flow properties of biodiesel from waste cooking oil, Fuel, Vol. 114 (2014), p. 876-881.
[8] H. W. Huang, F. Hong. Y. Mai: The research progress of biological diesel oil low temperature fluidity and improvement method, Chemical engineering progress, Vol. 26 (2007), p. 1395-1399. (In Chinese)
[9] H. Sheng, P. Wang. Y. Q. Song, et al: Impact of alkyl methacrylate–maleic anhydride–alkyl methacrylate terpolymers as cold flow improver on crystallization behavior of diesel fuel, Process Safety and Environmental Protection, Vol. 88 (2010), p. 41-46.
[10] O. Y. Sang, B. Subhash: Aluminum-containing SBA-15 as cracking catalyst for the production of biofuel from waste used palm oil, Microporous Mesoporous Mater, Vol. 102 (2007), p. 310-317.
[11] Z. L. Meng, X. Y. Li, J. C. Jiang: he study of branched chain alcohols impacting the low temperature properties of biodiesel, Forest chemical and industry, Vol. 28 (2008), p. 11-15. (In Chinese)
[12] A. Perez, A. Casas, C. Maria, et al: Winterization of peanut biodiesel to improve the cold flow properties, Bioresource Technology, Vol. 101 (2010), p. 7375-7381.
[13] Y. Lv, J. Li, F. S. Ouyang: Biodiesel blending to improve the performance of the cold flow property, Journal of fuel journal of chemistry, Vol. 33 (2011), p. 189-193. (In Chinese)
[14] X. Chen, Y. N.Yuan, Y.B. Lai, et al: Impact of compssiyion and molecular structure upon the cold flow properties for biodiesel, ACTA Petrolei Sinica (Petroleum Processing Section), Vol. 29 (2013), p.673-677. (In Chinese)
[15] S. X. Wu, G. Y. Wu, H. Xuan, ea al: Research on the effects of soybean biodiesel cold flow property, Journal of fuel chemistry journal, Vol. 6 (2005), p.698-701. (In Chinese)