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Study on Volatility of Palm Oil Biodiesel/-10 Petrodiesel by Thermogravimetric Analysis Technique

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Abstract

Palm methyl ester (PME) was prepared from palm oil through transesterification using NaOH as catalyst. Chemical composition of the PME and -10 petrodiesel (-10PD) was determined by gas chromatography-mass spectrometer (GC-MS). The PME and -10PD were characterized for their fuel properties including density, kinematic viscosity, and flash point, cold filter plugging point, sulfur content, copper strip corrosion and oxidative stability. Volatility was measured by thermogravimetric analysis (TGA). Volatile index was proposed to describe PME/-10PD volatility. A good correlation model was put forward for calculating the PME/-10PD volatility by PME blending ratio. The study showed that PME was mainly composed of long chain fatty acid methyl esters (FAMEs): C14:0 −C24:0, C16:1 −C22:1, C18:2 and C18:3. -10PD was mainly composed of long chain alkanes: C8 −C26. The fuel properties of PME were within the limits prescribed in the GB/T 20828-2007 standards for biodiesel. With respect to -10PD, volatilization of PME was stronger and quicker, but volatilization onset at higher temperature. The volatilization onset temperatures of PME and -10PD were 448.9 and 361.7 K respectively; and the volatile indexes were 1.76E-04 and 3.64E-05 respectively. The PME/-10PD volatility had relation to PME blending ratio. The volatility of B0 −B20 was very close to the -10PD. The volatility of B20 −B100 was better with increasing the PME blending ratio.

Keywords*: Biodiesel, Palm oil, Volatility, Thermogravimetry.*

1. Introduction

The limited resources of fossil fuels, increasing prices of crude oil, and environmental concerns have been the diverse reasons for exploring the use of vegetable oils for making biodiesel, viz., fatty acid methyl esters (FAMEs) as alternative fuels to petrodiesel. With respect to petrodiesel, FAMEs are generally safer to store and handle due to high flash point and an environmentally innocuous nature [1]. Combustion of FAMEs is known to reduce smoke, hydrocarbons, carbonyls (formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, butyraldehyde, and benzaldehyde), mono- and polycyclic aromatic hydrocarbons (MAHs and PAHs, respectively) emissions and slightly reduce carbon monoxide emissions while delivering comparable engine performance. The thermal efficiency is basically the same [2-4]. These are closely related to the fuel combustion process. It is the fuel and air mixing process of diesel engine that is key factors to influence combustion process. The fuel and air mixing process serves as a bridge

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connecting spray, igniting and combustion processes. It depends mainly on structure of diesel engine and volatility of fuel. Better volatility is beneficial for forming homogeneous mixed gas and igniting fuel. Hence, volatility has great influence on mixed gas forming, igniting quality, burning and emission of fuels in a compression ignition engine.

Study on combustion and emission characteristics of biodiesel is mainly conducted on engine bench test. The combustion characteristics include the fuel injection and atomization, premixed ignition, combustion and heat release processes [5-8]. The emission characteristics include the regulated and non-regulated pollutant emissions [4, 9]. Engine bench test requires not only engines and very large amount samples (typically dozens of kilograms). With respect to engine bench test, a thermogravimetric analysis (TGA) method for combustion characteristics requires very small samples (typically about 10mg) is rapid, and uses standard commercial advanced equipment, and has given a high accuracy. From TGA it is possible to follow the kinetics of thermally stimulated processes, like volatilization, decomposition, oxidation, reduction, crystallization, polymerization and combustion [10]. Little research has been conducted on biodiesel volatility. Lang et al [11] determines thermogravimetry (TG) curves of different esters from canola oil (CME: canola methyl ester; CEE: canola ethyl ester; CPE: canola 2-propyl ester; CBE: canola butyl ester), linseed oil (LME: linseed methyl ester; LEE: linseed ethyl ester; LPE: linseed 2-propyl ester; LBE: linseed butyl ester), rapeseed oil (RME: rapeseed methyl ester; REE: rapeseed ethyl ester), sunflower oil (SME: sunflower methyl ester; SEE: sunflower ethyl ester) and the diesel fuels (No. 1 winter DF and No. 2 summer DF). The TG curves at 5%, 10%, 50% and 90% weight loss indicates that biodiesel are the most volatile, and the volatility decreases as the alkyl group bulkier. The biodiesels are considerably less volatile than the conventional diesel fuels. Goodrum et al. [12] measures TG curves of RME, REE, CME, CEE, soybean methyl ester (SBME), soybean ethyl ester (SBEE), tallow methyl ester (TME) and tallow ethyl ester (TEE). Antonio et al. [10] measures TG curves of sunflower oil and SME at different heating rates (5, 10 and 20 °C/min). The TG curves indicate that the temperatures for volatilization of SME are lower than for sunflower oil. The value of the apparent activation energy for the volatilization process is higher for sunflower oil than for SME. The purpose of this work is to study the volatility of biodiesel (palm methyl ester, PME) and petrodiesel (-10# petrodiesel, -10PD) by TGA, and to put forward volatile index for describing biodiesel/petrodiesel volatility.

2. Materials and Methodology

2.1 Materials

Palm oil is purchased from Dantu grain and oil chemical plant, China. -10PD is obtained from China Petroleum & Chemical Corporation, China. All the chemicals used are analytical reagent grade. Used as a standard for chromatographic analysis, methyl heptadecanoate (P99.5% purity) is bought from Sigma-Aldrich, USA.

2.2 Apparatus

The main apparatus used include a TraceMS gas chromatography-mass spectrometer (GC-MS) (Finnigan Corp., USA); a SYP1026-1 Density tester, a SYP1003-6 kinematic viscosity tester, a SYP1002z-3 flash point tester, a SYP2007-I cold filter plugging point tester, and a SYP 1017-1 copper strip corrosion tester (Shanghai BOLEA Instrument & Equipment Co. Ltd., China); a 743 Rancimat (Metrohm Corp., Switzerland); a FLASH EA-1112A elemental analyser (Thermos Corp., Italy); a STA-449C simultaneous thermal analyzer (NETZSCH Group, Germany).

2.3 Palm Oil Biodiesel Preparation

Palm methyl ester (PME) is prepared from palm oil using an alkali-catalyzed transesterification method. The palm oil is transesterified with methyl alcohol to produce the biodiesel. The volume ratio of methyl alcohol to the palm oil is set at 1:5. In this reaction 0.8wt.% of NaOH in relation to oil is dissolved in methanol, and then added to the oil being stirred at 55 ℃ for 80 min. After standing and layering, the mixture is decanted, and the lower layer, rich in glycerol and methanol, is removed. The top layer is washed with water three or four times to remove residual NaOH, methanol, and soap. The washed biodiesel is dried at 48 ℃ for about 5 min.

2.4. Analytical Method

The chemical compositions of oil sample are determined by a Finnigan GC-MS system equipped with a DB-WAX capillary column (30 m × 0.25 mm × 0.25 μm) (Trace-Ultra/DSQ; Thermo Electron Co., Waltham, USA) and FDI. Helium is used as the carrier gas at a flow rate of 0.8 ml/min. Electron ionization mode (electron energy of 70 eV) is used for GC-MS detection. Sample injection volume is 0.1 μl. Temperature is programmed as follows: 160 ℃ maintained for 0.5 min; 6 ℃/min from 160 to 215 ℃; and 3 ℃/min from 215 to 230 ℃ maintained for 13 min.

Table 1. Standard Methods Applied for Biodiesel Characterization

Characterization tests	Standard methods
Density	GB/T 13377-2010
Kinematic viscosity	GB/T 265-1988
Flash point	GB/T 261-2008
Cold filter plugging point	SH/T 0248-2006
Sulfur content	SH/T 0689-2000
Copper strip corrosion	GB/T 5096-1985
Oxidative stability	GB/T 21121-2007

The properties of biodiesel such as density, kinematic viscosity, flash point, cold filter plugging point, sulfur content, copper strip corrosion and oxidative stability are measured according to the standard methods as given in Table 1.

Thermogravimetric analysis (TGA) is carried out using a STA-449C simultaneous thermal analyzer (NETZSCH Group, Germany). 10–20 mg of samples is added to 40 μl platinum pans under a N2 flow of 50 ml/min, at heating rates of 10 ℃/min and interval of temperature of 25–600 ℃.

3. Volatile Index

3.1. Eigenvalue

Eigenvalues derived from the thermogravimetry (TG) and differential thermogravimetry (DTG) curves include:

T_s is onset of volatilization, viz., temperature at 5% weight loss in N_2 atmosphere, K [11].

$(dM/d\tau)_{max}$ is the maximum rate of volatilization, viz., peak value of DTG curve in N_2 atmosphere, mg/min.

$W_{1/2}$ is the full width at half maximum (FWHM), viz. the FWHM of DTG peak in N_2 atmosphere, K.

3.2. Volatile Index

Volatile index:

$$V = \frac{(dM/d\tau)_{max}}{T_s \cdot W_{1/2}} \quad (1)$$

Where $(dM/d\tau)_{max}$ is the maximum rate of volatilization. Higher $(dM/d\tau)_{max}$ is, stronger volatile releases. T_s is onset of volatilization. The volatile is likely to release as T_s decreasing. $W_{1/2}$ is FWHM. Narrower $W_{1/2}$ is, quicker volatile releases.

Volatile index V indicates comprehensively volatility of biodiesel. The volatility is better with increasing volatile index V.

4. Results and Discussion

4.1. Characterization of Samples

The fuel properties of PME obtained following the above-mentioned procedure are summarized in Table 2 along with -10PD. It can be seen that PME had fuel properties comparable to those of -10PD are within the limits prescribed in the GB/T 20828-2007 standards for biodiesel.

4.2 Chemical Composition

The chromatograms of PME and -10PD analyzed by GC-MS are showed in Figure.1–Figure.2, and the main chemical compositions are showed in Table 3–Table 4.

PME is mainly composed of fatty acid methyl esters (FAMEs) of 14–24 even number carbon atoms, including saturated fatty acid methyl esters (SFAMEs) ($C_{10:0}$–$C_{24:0}$) and unsaturated fatty acid methyl esters (UFAMEs) ($C_{16:1}$–$C_{22:1}$, $C_{18:2}$ and $C_{18:3}$) with mass fractions of 35.86% and 62.83% respectively. -10PD is mainly composed of the n-alkenes of 8–26 carbon atoms. The n-alkanes and FAMEs molecular structure are shown in Figure.3.

Table 2. Fuel Properties of PME and -10PD

Property	Unit	PME	-10PD	GB/T 0828-2007
Density (20°C)	kg/m3	870	833	820–900
Kinematic viscosity (40°C)	mm2/s	4.91	2.53	1.9-6.0
Flash point	°C	>140	61	≥130
Cold filter plugging point	°C	10	-7	Report
Sulfur content	wt.%	0	0.16	≤0.005
Copper strip corrosion (50°C; 3 h)	Rating	1	1	≤1
Oxidation stability (110℃)	h	7.26	-	≥6.0

Table 3. Main Chemical Composition of PME

PME	C14:0	C16:0	C18:0	C20:0	C22:0	C24:0	C16:1	C18:1	C20:1	C22:1	C18:2	C18:3
Content /w%	1.44	26.95	6.40	0.72	0.21	0.14	0.42	42.13	0.34	0.15	18.20	1.59

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

Table 4. Main Chemical Composition of -10PD

-10PD	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C24	C26
Content /w%	0.36	1.75	5.51	4.09	6.70	2.24	4.37	12.69	3.83	6.65	1.38	0.81	1.35	8.52	0.74	0.27

NOTE: C_m is the shorthand of alkane; *m* means the carbon number of alkane.

4.3 Volatility of Petrodiesel and Biodiesel

Liquid volatilizing process comprises three steps: liquid absorbing heat, conquering molecules attractive forces, and liquid volatilizing. To organic compounds with similar composition and structure, substance volatility gets poor with increasing the molecule mass (the number of carbon) and molecule 3D-structure. This is mainly because the larger molecule mass is, the more energy of molecules kinematics needs; the larger molecule structure is, the larger molecules contact area is, the more energy of substance volatizing conquers molecules attractive forces.

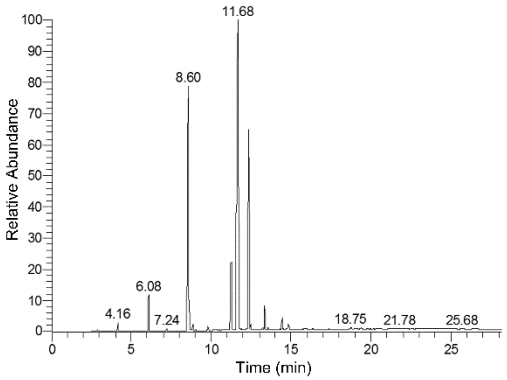

Figure 1. The Gas Chromatogram of PME

Volatility of -10PD and PME:TG-DTG curves of -10PD and PME are shown in Figure.4. -10PD is highly volatile. The volatilization onset temperature of -10PD is 361.7K (Table 5). The PME, being more viscous than the -10PD (Table 2), vaporized more slowly when heated up to 448.9k (volatilization onset temperature, viz., lost 5% of its initial weight) (Table 5). PME is volatile at a higher temperature than -10PD. Influences on fuel volatility are related to chemical composition. It is chiefly because -10PD is mainly composed of long chain n-alkane of 8–26 C atoms, and PME is mainly composed of long chain FAMEs of 14–24 even-numbered C atoms. Their composition and structure are similar (Figure.3). Small molecular mass of biodiesel (14 C atoms) is larger than petrodiesel (8 C atoms) (Table 3 and Table 4). Since PME carbon chain is curved by C=C and carboxylic end, the molecular 3D-structure of PME is also larger than -10PD (Figure.3). Hence, volatilization onset temperature of PME is higher than -10PD.

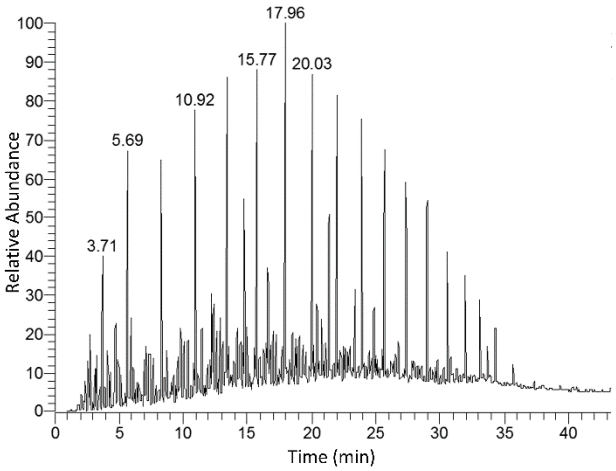

Figure 2. The Gas Chromatogram of -10PD

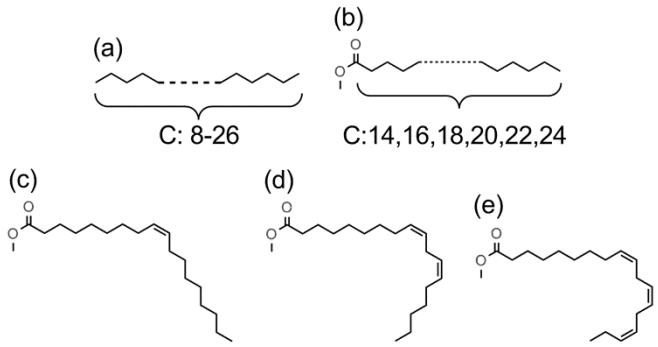

Figure 3. Molecular Structure
(a) n-alkane, (b) SFAME, (c) C18:1, (d) C18:2, (e) C18:3

The maximum rate of volatilization of -10PD is 1.65 mg/min lower than the PME, the FWHM of -10PD is 68.9 K wider than the PME (Table 5). Volatilization of PME is stronger and quicker than that of -10PD. It is chiefly because the range of PME carbon chain length (14–24 even-numbered C atoms) is relatively concentration in comparison to -10PD (8–26 C atoms) (Table 3 and Table 4).

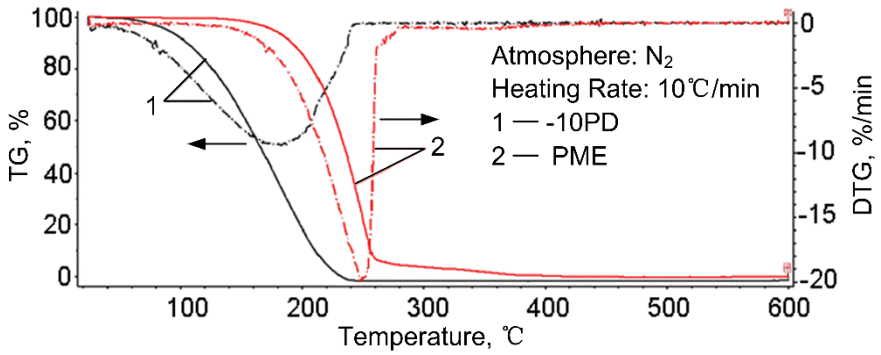

Figure 4. TG-DTG Curves of -10PD and PME

Table 5. Volatility Parameters of -10PD and PME

Diesel	T_s /K	$(dM/d\tau)_{max}$ /(mg/min)	$W_{1/2}$ /K	V
-10PD	361.7	1.42	107.8	3.64E-05
PME	448.9	3.07	38.9	1.76E-04

Based on the factors as above, volatile index of PME is higher than that of -10PD, and they are 1.76E-04 and 3.64E-05 respectively. Compared with the -10PD, PME is considerably better volatility and beneficial for igniting and burning. Wang et al. [13] arrives at the analogous conclusion. They examine combustion process of engine operating on petrodiesel and biodiesel by end scope high-speed photography: the ignition start of biodiesel is earlier and combustion speed of biodiesel is quicker.

Volatility of PME/-10PD: TG-DTG curves of PME/-10PD are shown in Figure.5. The volatile index for PME/-10PD remains more or less static within B0–B20, and then increases linearly with increasing PME addition (Figure.6). Namely, with increasing PME blending ratio, PME/-10PD volatility is very close to -10PD within B0–B20, and then gets better. This is mainly because adding a few amount of biodiesel (B0–B20) did not affect small molecular composition of petrodiesel. And with increasing biodiesel further, chemical composition of blending oil got closer and closer to the biodiesel.

From Figure.6, the following correlation is obtained:

$$V = \begin{cases} 3.64 \times 10^{-5} \ (0 \le PME < 20) \\ 1.84 \times 10^{-6} \times PME - 7.93 \times 10^{-6} \ (20 \le PME \le 100) \ (R^2 = 0.9934) \end{cases} \quad (2)$$

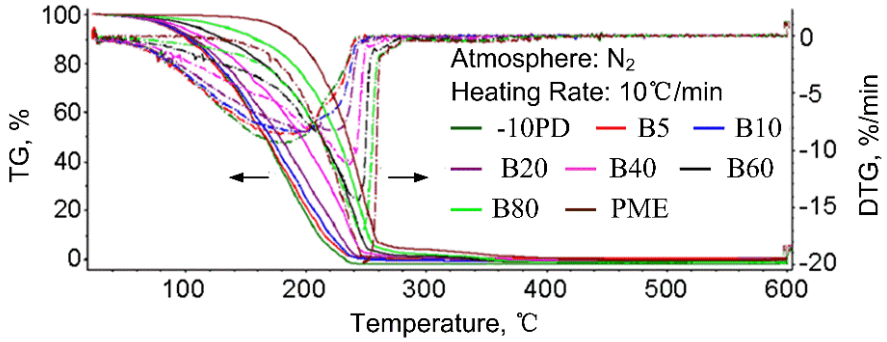

Figure 5. TG-DTG curves of PME/-10PD

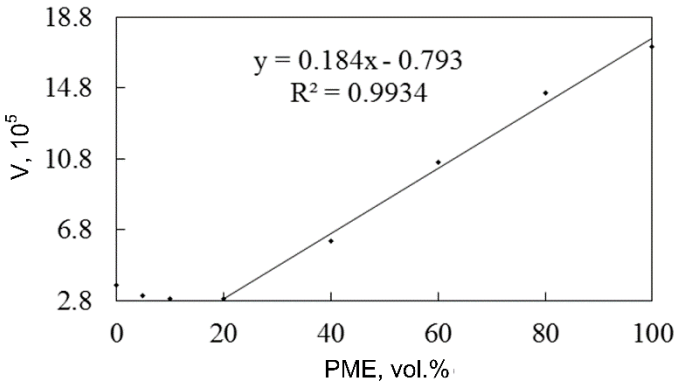

Figure 6. Impact of PME Ratio Upon Volatile Index for PME/-10PD

5. Summary

The above discussion shows that:

(1) PME is mainly composed of FAMEs of 14–24 even-numbered C atoms: $C_{14:0}$–$C_{24:0}$, $C_{16:1}$–$C_{22:1}$, $C_{18:2}$ and $C_{18:3}$, and the mass fraction of SFAMEs and UFAMEs is 35.86% and 62.83% respectively. -10PD is mainly composed of long chain alkanes: C_8－C_{26}. The volatility of fuel mainly depends on its chemical composition. The volatilization onset temperatures of PME and -10PD are 448.9 and 361.7 K respectively; and the volatile indexes are 1.76E-04 and 3.64E-05 respectively.

(2) The volatile index put forward can describe comprehensively fuel volatility. Based on volatile index, PME volatility is better than -10PD.

(3) Blending oil volatility is very close to -10PD within B0－B20, and then got better with increasing the PME blending ratio.

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