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Study of Ether Species Effects on Physicochemical Properties of Palm Oil Ether Monoesters as Novel Biodiesels

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***Abstract*—**Five palm oil ether monoesters utilized as novel biodiesels were synthesized and structurally identified in the paper. The investigation was made on the effect of ether species on physicochemical properties of the palm oil ether monoesters. The results showed that density, kinematic viscosity, smoke point, and solidifying point increase linearly with their $-CH_2$ group number in certain relationships. Cetane number is enhanced whereas heat value decreases linearly with $-CH_2$ group number. In addition, the influencing regularities of the volumetric content of the palm oil ether monoesters on the fuel properties were also studied when the ether monoesters are used as diesel fuel additives.

***Keywords*—**Biodiesel, palm oil ether monoester, ether species, physicochemical property.

I. Introduction

OVER the last decade, the petroleum oil shortness and serous atmospheric pollution caused by automobiles have promoted much research for clean alternative fuels. One of the most promising alternative energy sources is biomass. It contains much less sulfur and nitrogen which makes it more environmentally friendly than petroleum fuels. It is renewable and available at any part of the world presenting a bright future for practical application. Among the biomass resources developed, biodiesel has received much attention and seems to be the most promising renewable substitute for petroleum diesel fuels.

Conventional biodiesel is methyl ester of vegetable oil which is prepared through transesterification of vegetable oils with methanol, largely used species being methyl esters of rapeseed oil, soybean oil and waste cooking oil. Many studies manifested that biodiesel, containing certain amount of oxygen, can lead to remarkable reduction in diesel engine exhaust emissions [1]-[3] and has been called a kind of green fuel for diesel engine. However, since there is only one ester group, i.e. two oxygen atoms, existing in each monoester molecule, the oxygen content in conventional biodiesel is at comparatively lower level. Consequently, the reduction in smoke emissions is not just as significant as anticipated when diesel engine burns it or its mixture with diesel fuel. In addition, conventional biodiesel has low auto-ignition property with its cetane number generally between 55 and 45. In our previous studies about oxygenates used as clean diesel fuel additives, it was found that ether group can enhance auto-ignition property of oxygenates due to its easy decomposition into free radicals which can accelerate radical oxidation reactions of fuel in engine combustion flame [4], [5]. Recently, in order to enhance the engine-out emissions reduction performance and auto-ignition property of conventional biodiesel, a novel type of biodiesels of ethylene glycol alkyl ether palm oil monoesters were developed. These palm oil ether esters were synthesized utilizing palm oil and ethylene glycol alkyl ether as reactants and KOH as catalyst through transesterification reaction. Their chemical structures were also identified as palm oil ether monoester through FT-IR, ^{1}H NMR and GPC. As is well known, fuel physicochemical properties reflect its combustion performances and emissions characteristics when burning in engine. In this paper, investigation was made on the effect of ether species on physicochemical properties of palm oil ether monoesters as well as the influencing regularities of volumetric content of the palm oil ether monoesters on the fuel properties when the ether monoesters are used as diesel fuel additives.

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II. Preparation and Chemical Structure Characterization

The new palm oil monoesters were synthesized using a commercial refined palm oil and four ethylene glycol alkyl ethers and propylene glycol methyl ether. Initially, the selected palm oil was treated through extraction with ethanol as solvent at 50℃~60℃ to remove a tiny amount of organic fatty acid existing in it and then purified under vacuum condition. FT-IR analysis justified that there was no fatty acid left in the treated palm oil in that there was no –OH vibration absorption peak in the region of 3200cm^{-1}~3600cm^{-1}, indicating that there was little acid and ethanol in the purified palm oil.

The subsequent transesterification reactions to prepare the palm oil ether monoesters were carried out in a flask with the acid-free palm oil and ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol butyl ether and propylene glycol methyl ether under optimal conditions of molar ratio of alcohol to oil 8~10:1, usage of KOH catalyst 0.8%~1.2%(m) of palm oil used, reaction temperature 80~120℃ and reaction duration 90~120min. Upon completion of the reaction, the crude product was firstly neutralized with diluted HCl solution and separated from the water phase, and secondly purified with water vapor distillation treatment at 220℃~250℃ to remove ethylene glycol alkyl

ethers or propylene glycol methyl ether and palm oil left over in the crude product, and finally dried using 4A molecular sieve.

The chemical structure analysis of the five palm oil ether monoesters was conducted with FT-IR, ^{1}H NMR and GPC analytical techniques. IR analysis was performed on an EQUINOX55 FT-IR spectrometer. Its sample cell is KBr crystal. A superconducting NMR spectrometer of INOVA type made by VARIAN Company was employed to accomplish ^{1}H NMR analysis. The spectrometer operating frequency was 400 MHz. A GPC515-2410 apparatus by Waters Inc. was used to carry out their molecular weight determination. The chromatographic column was Styragel (HR2_HR3_ HR4E). THF was selected as moving phase with its flowing rate being 1ml/min. In the experiment polystyrene (PS) was chosen as standard sample. The GPC analytical system can measure molecular weight precisely within the range from 300 to 3,000,000.

TABLE I
ANALYTICAL DATA OF ^{1}H NMR OF ETHYLENE GLYCOL METHYL ETHER PALM OIL MONOESTER

Chemical shift/ppm	5.359	4.229	3.596	3.396
Proton peak spiliting	5	3	3	1
Peak area	1.00	1.37	1.45	1.88
Proton number	-	2	2	3

TABLE II
ANALYTICAL DATA OF ^{1}H NMR OF ETHYLENE GLYCOL ETHYL ETHER PALM OIL MONOESTER

Chemical shift /ppm	5.357	4.223	3.629	3.545
Proton peak spiliting	4	3	3	4
Peak area	1.00	1.23	1.28	1.24
Proton number	-	2	2	2

TABLE III
ANALYTICAL DATA OF ^{1}H NMR OF ETHYLENE GLYCOL PROPYL ETHER PALM OIL MONOESTER

Chemical shift /ppm	5.342	4.222	3.625	3.429
Proton peak splitting	3	3	3	3
Peak area	0.99	1.30	1.31	1.30
Proton number	-	2	2	2

TABLE IV
ANALYTICAL DATA OF ^{1}H NMR OF ETHYLENE GLYCOL BUTYL ETHER PALM OIL MONOESTER

Chemical shift /ppm	5.370	4.218	3.609	3.469
Proton peak splitting	3	3	3	3
Peak area	1.00	0.92	1.45	0.66
Proton number	-	2	2	2

TABLE V
ANALYTICAL DATA OF ^{1}H NMR OF PROPYLENE GLYCOL METHYL ETHER PALM OIL MONOESTER

Chemical shift /ppm	5.370	4.091	3.591	3.384
Proton peak splitting	4	8	7	1
Peak area	1.00	1.25	0.74	2.03
Proton number	-	2	1	3

These palm oil ether monoesters include ethylene glycol methyl ether palm oil monoester (EGMEPOM), ethylene glycol ethyl ether palm oil monoester (EGEEPOM), ethylene glycol propyl ether palm oil monoester (EGPEPOM), ethylene glycol butyl ether palm oil monoester (EGBEPOM), and propylene glycol methyl ether palm oil monoester (PGMEPOM).

FT-IR data showed that there are $-CH_3$, $-CH_2$, -C=C-, -C=O, -C-O-C- and $-(CH_2)_n$ ($n\geq4$) groups respectively in the molecules of the five novel biodiesels. Results of ^{1}H NMR spectra （chemical shift above 3.00ppm） analysis are respectively listed in Tables 1-5. In these tables, proton peaks of chemical shift 5.359 ppm, 5.357 ppm, 5.342 ppm and 5.370 ppm belong to protons of the groups H-C=C- and H-C=C-H in fatty acid (R). There also appeared more proton peaks of chemical shift below 3.00 ppm. However, they are not tabulated in the tables simply because they belong to protons of fatty acid(R).

TABLE VI
GPC DATA OF THE USED PALM OIL

Peak	Mn	Mw	Mp	Mz	Mv	d	Peak area/%
Peak 1	2605	2612	2585	2619	2611	1.0026	0.10
Peak 2	1360	1372	1349	1386	1371	1.0091	91.36
Peak 3	980	985	1006	990	984	1.0050	8.54

TABLE VII
GPC DATA OF ETHYLENE GLYCOL METHYL ETHER PALM OIL MONOESTER

Peak	Mn	Mw	Mp	Mz	Mv	d	Peak area/%
Peak 1	987	994	984	1003	993	1.0079	0.22
Peak 2	383	388	379	393	387	1.0112	99.78

TABLE VIII
GPC DATA OF ETHYLENE GLYCOL ETHYL ETHER PALM OIL MONOESTER

Peak	Mn	Mw	Mp	Mz	Mv	d	Peak area/%
Peak 1	1079	1138	954	1213	1128	1.0541	2.08
Peak 2	410	416	403	423	415	1.0149	97.92

TABLE IX
GPC DATA OF ETHYLENE GLYCOL PROPYL ETHER PALM OIL MONOESTER

Peak	Mn	Mw	Mp	Mz	Mv	d	Peak area/%
Peak 1	1095	1140	976	1192	1252	1.0408	2.28
Peak 2	430	436	426	443	435	1.0144	97.72

TABLE X
GPC DATA OF ETHYLENE GLYCOL BUTYL ETHER PALM OIL MONOESTER

Peak	Mn	Mw	Mp	Mz	Mv	d	Peak area/%
Peak 1	430	439	441	449	438	1.0212	77.31
Peak 2	190	194	172	199	194	1.0198	18.77

TABLE XI
GPC DATA OF PROPYLENE GLYCOL METHYL ETHER PALM OIL MONOESTER

Peak	Mn	Mw	Mp	Mz	Mv	d	Peak area/%
Peak 1	392	400	386	409	399	1.0204	78.14
Peak 2	191	194	172	198	194	1.0187	17.50
Peak 3							4.36

GPC analytical results of the used palm oil and the five novel biodiesels are respectively listed in Tables VI-XI. From the results shown in these tables, it is easily concluded that after the synthesis procedures mentioned above the novel biodiesels of quite low molecular weight were obtained.

These results demonstrated that there exist $-OCH_2CH_2-$,

$-OCH_3$, $-OCH_2CH_3$, $-OCH_2CH_2CH_3$, $-OCH_2CH_2CH_2CH_3$, and $-OCH(CH_3)CH_2-$ groups respectively in the five biodiesels. Their chemical structures are identified with EGMEPOM being $RCOOCH_2CH_2OCH_3$, EGEEPOM being $RCOOCH_2CH_2O-CH_2CH_3$, EGPEPOM being $RCOOCH_2CH_2OCH_2CH_2CH_3$, EGBEPOM being $RCOOCH_2CH_2OCH_2CH_2CH_2CH_3$ and PGMEPOM being $RCOOCH(CH_3)CH_2OCH_3$.

III. Influences of Ether Group Species on Properties of Palm Oil Ether Monoesters

Fuel blends of a commercial 0# diesel fuel with volumetric contents of the five biodiesels of 10%, 20%, 30%, 40%, and 50% were prepared for miscibility investigation. The fuel blends were stirred even firstly at 0℃ or 25℃, and then placed in static state for a certain time. It was observed that the fuel blends all stayed transparent and did not appear two layers. So the five biodiesels are respectively miscible with diesel fuel.

The measured physicochemical properties involve density, kinematic viscosity, smoke point, closed flash point, solidifying point, heat value and cetane number. These properties were measured in strict accordance with China national standard test methods. Cetane number was determined according to China national standard GB/T386. The used bench test apparatus was made by Waukesha Cooperation, USA. The selected standard fuels were mixtures of n-cetane(CN=100) and heptamethylnonane (CN=15). Density was measured according to GB/T1884, kinematic viscosity was according to GB/T265, smoke point was according to GB382, closed flash point was according to GB/T 261, solidifying point was according to GB/T510, heat value was according to GJB770A.

A. Density

The test results showed that all densities of the five palm oil ether monoesters are higher than that of diesel fuel. The reason is that molecular weights and chemical bond chain length of the five biodiesels is more than those of diesel fuels. Regarding density of palm oil ether monoesters themselves, it is not similar if the ether group species is different. Fig. 1 displays the density test results of four biodiesels of ethylene glycol alkyl ether palm oil monoesters. It is evident that with an increase in the number of $-CH_2$ group in the alkyl, density magnitude decreases linearly. The relationship between density (ρ) and $-CH_2$ group number(x) is obtained as $\rho = -0.057x + 0.8986$ (R^2=0.987).

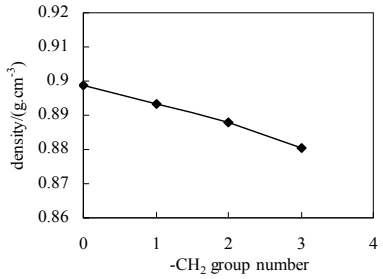

Fig. 1 Relation of density of ethylene glycol alkyl ether palm oil monoesters with $-CH_2$ group number

B. Kinematic Viscosity

Table XII lists kinematic viscosity of palm oil ether esters at 20℃ and 40℃. At these two temperatures, the viscosity of diesel fuel for comparison is 4.502mm^2/s and 2.840mm^2/s. All of the palm oil ether monoesters are higher than diesel fuel in density.

TABLE XII
Kinematic Viscosity of Palm Oil Ether Esters

Biodiesel	EGME POM	EGEE POM	EGPEP OM	EGBE POM	PGME POM
Viscosity/(mm^2/s) 20℃	9.826	13.10	15.07	16.39	12.99
Viscosity/(mm^2/s) 40℃	5.983	7.293	8.278	10.18	7.255

Fig. 2 displays the relationship of kinematic viscosity at 40℃ of ethylene glycol alkyl ether palm oil monoesters with $-CH_2$ group number. It is easily seen that their correlation is linear.

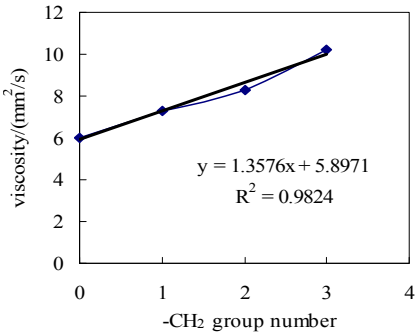

Fig. 2 Relation between viscosities at 40℃ of ethylene glycol alkyl ether palm oil monoesters with $-CH_2$ group number

Fig. 3 displays the effects of adding a content level of palm oil ether monoesters on fuel viscosity at 40℃ when the five biodiesels respectively were added to diesel fuel. Due to the higher viscosity of the palm oil ether monoesters compared with that of diesel fuel, their blends with diesel fuel has a higher viscosity than that of diesel fuel. It is clear that with increasing of the content level of palm oil ether monoesters in diesel fuel, the viscosity of the blends increases linearly.

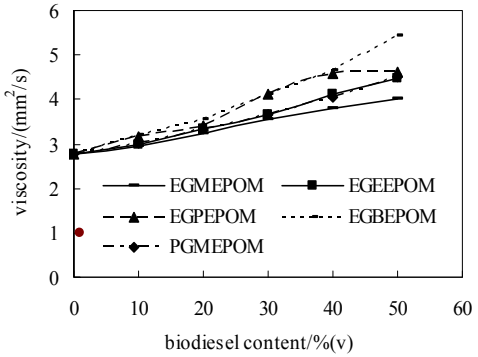

Fig. 3 Effect of addition of palm oil ether monoesters on viscosity at 40℃ of diesel fuel

C. Solidifying Point

Solidifying points of the palm oil ether monoesters were measured to be much higher than that of diesel fuel. Fig. 4 demonstrates the effect of $-CH_2$ group number on the solidifying point of ethylene glycol alkyl ether palm oil monoesters. It is observed that solidifying point (t) increases linearly with $-CH_2$ group number (x) and their relationship is $t = 1.3x + 7.3$ (R^2=0.9657).

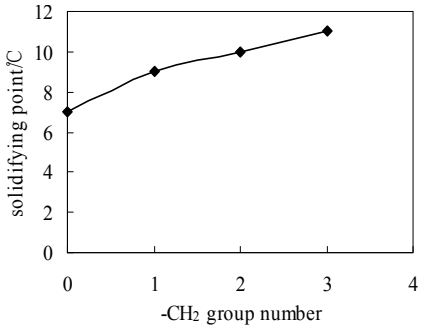

Fig. 4 Relation of solidifying point of ethylene glycol alkyl ether palm oil monoesters with their -CH_2 group number

In Fig. 5 are displayed the measured results of the effects of different biodiesels on fuel solidifying point when the palm oil ether monoesters were respectively added to diesel fuel. Due to the high solidifying point of the novel biodiesels compared with that of diesel fuel, fuel solidifying point increased with their content level in diesel fuel.

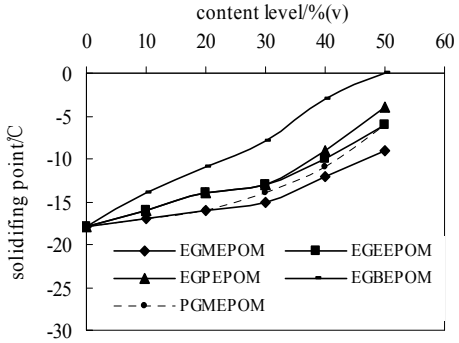

Fig. 5 Effects of palm oil ether monoesters on diesel fuel solidifying point

D. Smoke Point

Fig. 6 exhibits the effects of content level of the five palm oil ether monoesters on fuel smoke point when they were respectively added to two diesel fuels. Of the five palm oil ether monoesters, EGBEPOM and PGMEPOM were added to a diesel fuel respectively and EGMEPOM, EGEEPOM and EGPEPOM were added to another diesel fuel respectively. It is very evident that smoke point (h) increases linearly with the content level (x) of the palm oil ether monoesters. Correlation of h with x are obtained as $h = 0.1497x + 13.257$ ($R^2 = 0.9856$) for EGMEPOM, $h = 0.1383x + 13.143$ ($R^2 = 0.9751$) for EGEEPOM, $h = 0.1383x + 12.81$ ($R^2 = 0.9602$) for EGPEPOM, $h = 0.1466x + 9.0524$ ($R^2 = 0.9687$) for EGBEPOM and $h = 0.1586x + 8.5524$ ($R^2 = 0.9764$) for PGMEPOM.

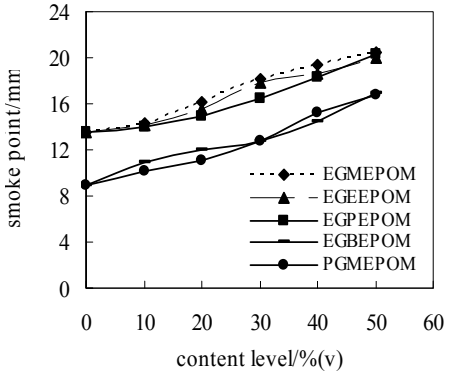

Fig. 6 Effects of content level of the five palm oil ether monoesters on fuel smoke point

E. Flash Point

In Table XIII tabulated test results of closed flash point of the 0# diesel fuel containing the novel biodiesels in different volumetric content levels are shown. From Table XIII, it can be easily seen that closed flash point of the fuel blend increases notably with the increase in the content of the novel biodiesels.

TABLE XIII
TEST RESULTS OF FLASH POINT/℃

Biodiesel content	EGME POM	EGEE POM	EGPEP OM	EGBE POM	PGME POM
0	57	57	57	57	57
10%	61	60	59	59	59
20%	62	62	62	64	61
30%	65	66	65	66	64
40%	70	69	68	68	67
50%	73	72	72	70	72
100%	190	185	185	198	185

F. Heat Value

High heat values of the five biodiesels were measured precisely, and the results are listed in Table XIV. Owing to containing a certain amount of oxygen in molecules heat values of the novel biodiesels are lower than that of diesel fuel. Due to the more $-CH_2$ group the lower oxygen content, heat value of the biodiesels becomes larger accompanying $-CH_2$ group number increasing. The relationship between heat value (H) and $-CH_2$ group number (x) is $H=0.3895x + 38.207$ (R^2=0.9945).

TABLE XIV
HIGH HEAT VALUES OF THE NOVEL BIODIESELS

biodiesel	EGME POM	EGEE POM	EGPEP OM	EGBE POM	PGME POM
heat value/ (MJ/kg)	38.174	38.650	38.978	39.363	38.242

G. Cetane Number

Cetane numbers of the five biodiesels were also measured precisely, and the results are tabulated in Table XV. It is easily seen that the novel biodiesels of palm oil ether monoesters have

higher cetane numbers than diesel fuels which have a cetane number of approximately 50. The reason why ether group can enhance cetane number of the biodiesels is in that ether group has C-O-C bond. As is well known the bond C-O-C is less thermally stable than C-C-C, and thus can decompose easily at a relatively lower temperature to produce more O, RO and R free radicals. These free radicals can promote the spontaneous ignition of biodiesel at a lower temperature which could decrease auto-ignition temperature of the fuel and hence increases the cetane number of the biodiesels.

TABLE XV
CETANE NUMBER OF THE NOVEL BIODIESELS

biodiesel	EGME POM	EGEEP OM	EGPEP OM	EGBEP OM	PGME POM
Cetane number	77.6	81.2	81.4	76.6	75.5

IV. CONCLUSIONS

1. Five palm oil ether monoesters were synthesized and structurally identified. The study was made about $–CH_2$ number in alkyl group influencing regularities on physicochemical properties of the ether monoesters. The investigation also included the effect of the content level of novel biodiesels on fuel properties when they are added to diesel fuel.
2. Because molecular weight becomes higher and intermolecular force tends stronger, such properties as density, kinematic viscosity, solidifying point and flash point of the novel biodiesel increase linearly with $–CH_2$ group number increasing, and such properties of their blends with diesel fuel also increase with their content level in diesel fuel.
3. Owing to oxygen content becoming lower, the heat value of the novel biodiesels decreases linearly with $–CH_2$ group number in alkyl increasing.
4. Due to easy decomposition of C-O-C in ether group, the novel biodiesels have higher cetane numbers than diesel fuel.

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