Characterization of Insoluble Impurities in Biodiesel from Palm Stearin

Parncheewa Udomsap*, Ukrit Sahapatsombut, Buppa Puttasawat, Pawnprapa Krasae, Vituruch Goodwin, Nuwong Chollacoop and Subongkoj Topaiboul

National Metal and Materials Technology Center
National Science and Technology Development Agency
114 Thailand Science Park, Phahonyothin Road, Klong 1, Klong Luang, Pathumthani 12120, Thailand
Tel: 0-2564-6500 x4630, Fax: 0-2564-6401, *E-mail: buachuu@mtec.or.th

Abstract

Biodiesel, defined as the alkyl ester of fatty acid, is a renewable fuel used in diesel engines. It is made from the transesterification reaction of vegetable oil with alcohol. It was reported in the industry that when biodiesel conforming to national standard were stored for a long period, insoluble impurities appeared as white sediment at the bottom. This white sediment was examined via Gas Chromatography to show the presence of mono- and di-glyceride resulting from incomplete reaction and saturated methyl ester, which are considered the harmful components affecting fuel filters or systems. Furthermore, these glyceride compounds could deteriorate cloud point property of biodiesel.

Keywords: insoluble impurities, biodiesel, sediment

1. Introduction

Biodiesel, the alkyl ester of fatty acid, is made from transesterification of vegetable oil or animal fat with alcohol by using alkali catalyst, the reaction as shown in Figure 1. Mechanism of transesterification of triglyceride (TG) is shown in Figure 2. There are three stepwise reactions with intermediate formation of diglyceride (DG) and monoglyceride (MG) resulting in the production of methyl ester and glycerol. Biodiesel has many advantages included its usage as fuel effectively in diesel engine and non-pollution [1]

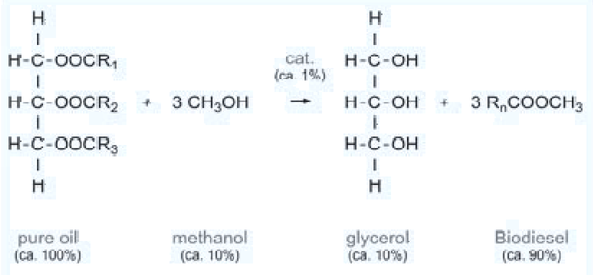

Figure 1. Transesterification reaction

$$TG + CH_3OH \rightarrow DG + R'CO_2CH_3$$
$$DG + CH_3OH \rightarrow MG + R'CO_2CH_3$$
$$MG + CH_3OH \rightarrow Glycerol + R'CO_2CH_3$$

Figure 2. Mechanism of Transesterification

The primary constituents in fats and oils are triglycerides but they also contain varying amounts of minor components such as monoglyceride and diglyceride etc., many of which significantly affect their chemical and physical properties. These substances dissolve in fatty acid and can be saponified by caustic treatment, often called the saponifiable matter. Besides, vegetable oil commonly contain 2% or more non-glyceride substances; whereas, animal fats contain much smaller quantities, also referred to as the unsaponifiable matter, consisting of phospholipids, tocopherols, sterols, resin, carbohydrates, pesticides, proteins, trace metals and pigments. These substances frequently dissolve in fatty acids, which cannot be saponified by caustic treatment. Some but not all of the non-glyceride materials are undesirable [2].

Characteristics of each biodiesel depend on fatty acid composition and organic compound that assemble in raw material. Palmitic acid and Stearic acid, which are saturate fatty acid, affect the cold flow properties [3] and sterol glucosides (SGs), which are organic compound or unsaponifiable matter as shown in Figure 3, have possibility to obstruct flow ability in biodiesel due to the high melting point of SGs (~240 degrees Celsius). The melting point is equivalent the pour point, which is the temperature for phase transition from solid to liquid or liquid to solid, vice versa. In addition, SGs can essentially be considered “dispersed fine solid particles” in biodiesel. These dispersed SG particles may also promote the crystallization of other compounds [4]. Therefore, the usage of biodiesel with these compounds poses high risk for clogging in engine system.

It was reported in the industry that when biodiesel that meet national standard is stored for a long period, insoluble impurities could appear as white sediment at the bottom. Therefore, the present study aims to characterize this white sediment via Gas Chromatography with the discussion on its effect on engine performance.

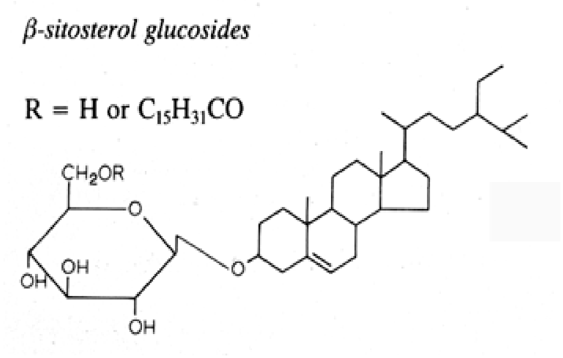

Figure 3. Sterol glucosides structure

.

2. Experimental

2.1 Materials

Biodiesel, Palm Stearin Methyl Ester (PSME), was received from commercial source as shown in Figure 4. Some physico-chemical properties of PSME were summarized in Table 1.

2.2 Methodology

When keeping the PSME under ambient condition, the white sediment becomes self-separated as a solid phase at the bottom and was collected them for GC analysis as shown in Figure 5. The sediment was examined by Determination of Ester and Linolenic Acid Methyl Ester Content and Determination of Free and Total glycerol and mono-, di-, triglyceride Content based on EN 14103 [5] and EN14105 [6] standards, respectively.

Figure 4. As-received palm stearin methyl ester

2.3 Instrumentation

The sediment, as shown in Figure 5, was analyzed by GC-2010 gas chromatograph with FID detector, equipped with DB-WAX column (30 m x 0.25 mm I.D) and injector at 180 ^{o}C with split ratio 180. An oven starting temperature of 180 ^{o}C was programmed at 5^{o}C/min up to 230 ^{o}C and hold for 15 min. Detector temperature was 250 ^{o}C, according to EN 14103. For EN14105, GC-2010 gas chromatograph provided with DB-1HT column (15 m x 0.32 mm I.D) and injector at 370 ^{o}C with split ratio 5.0. Gradient temperature of oven was set as follow: 60 ^{o}C hold for 1 min, programmed at 15 ^{o}C/min up to 180 ^{o}C, programmed at 7 ^{o}C/min up to 230 ^{o}C, programmed at 10 ^{o}C/min up to 370 ^{o}C, final temperature hold for 5 min.

Figure 5. The white sediment was collected

3. Results and discussion

PSME is produced from transesterification of palm stearin with methanol and using $NaOCH_3$ as catalyst. Properties of PSME were presented in Table 1.

The results in Table 1 show properties of PSME which meet Thai Biodiesel Standard [7]. PSME sample has little amount of Diglyceride and Triglyceride, which cannot be detected with the resolution of the equipment. However, white sediment was found in PSME, which was stored for a long period. The white sediment can melt upon heating to a temperature of 40-50 ^{o}C but re-appear upon cooling under ambient condition as a solid phase at the bottom again.

Table 1. Properties of Palm Stearin Methyl Ester (PSME)

Properties	*Method*	*Value*
Methyl Ester Content (%wt.)	EN 14103	96.9
Linolenic Methyl Ester Content (%wt.)	EN 14103	0.02
Monoglyceride (%wt.)	EN 14105	0.13
Diglyceride (%wt.)	EN 14105	N/D*
Triglyceride (%wt.)	EN 14105	N/D*
Free glycerine (%wt.)	EN 14105	0.01
Total glycerine (%wt.)	EN 14105	0.04
Density (g/cm^3)	ASTM D 4052	0.8739
Kinematic viscosity @ 40 ^{o}C (mm^2/s)	ASTM D 445	4.60

*Not detected

Comparisons between PSME and its white sediment are shown in Figures 6 and 7 as FAME compositon and glyceride compound compositions, respectively. Detailed chemical composition of white sediment is also presented in Table 2.

Methyl ester content of PSME presents high purity at 96.9 %wt, whereas sediment provides lower methyl ester content only at 47.68%wt which mainly contains palmitic acid methyl ester and oleic acid methyl ester. This result can be considered that PSME contains other chemical composition, which is not methyl ester, aggregating as sediment. When this composition is aggregated, it could induce methyl ester compositions to aggregate as well. This is consistent with the result in Figure 6 that relative composition of each methyl ester in both PSME and sediment are not significantly different. The sediment is hypothesized as glyceride compounds. Therefore, these samples were determined by GC to evaluate glyceride composition (Figure 7). As expected, there are much greater fractions of both mono- and di-glyceride in sediment than that in PSME. This is implied that even the biodiesel conforming to the specification limit for monoglyceride (with high melting point at 74-76 ^{o}C) could induce other methyl esters to co-precipitate as glyceride compounds.

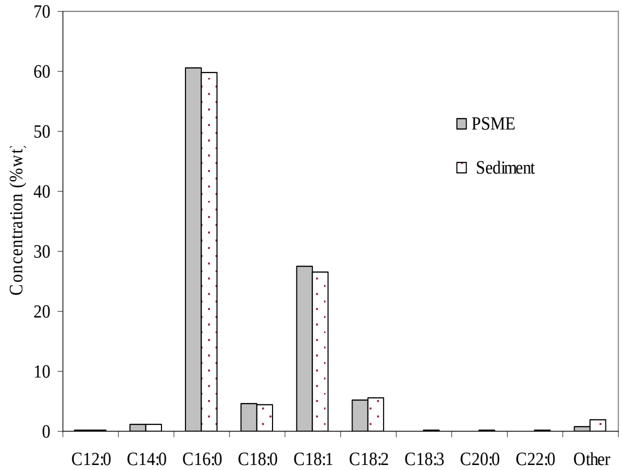

Figure 6. Fatty acid methyl ester composition of PSME and Sediment

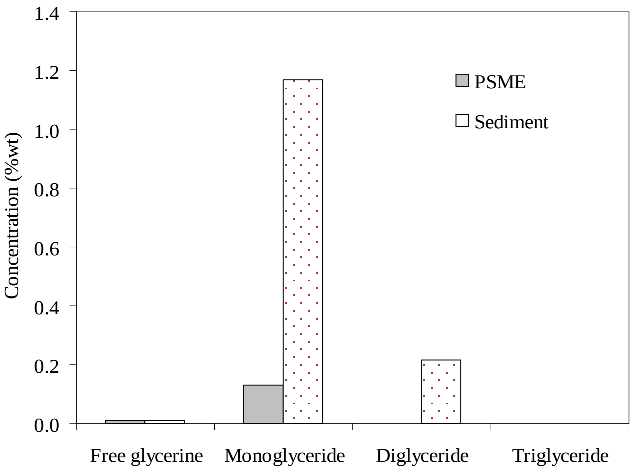

Figure 7. Free glycerine, Mono-, Di- and Tri-glycerine of PSME and Sediment

Table 2. Chemical composition of white sediment

Composition	*Found (%wt.)*	*Melting point (^{o}C)**
Lauric acid methyl ester	0.26	4 -5
Myristic acid methyl ester	1.07	18
Palmitic acid methyl ester	59.74	30-35
Stearic acid methyl ester	4.39	37-41
Oleic acid methyl ester	26.57	-19.8
Linoleic acid methyl ester	5.58	-35
Linolenic acid methyl ester	0.20	-
Arachidic acid methyl ester	0.10	45-48
Behenic acid methyl ester	0.22	
Monoglyceride	1.17	
Monopalmitin		74-76
Diglyceride	0.21	-
Triglyceride	N/D	-
Free glycerine	0.01	-

* Source: www.sigmaaldrich.com

All results show that the white sediment is composed of methyl ester, mono-, diglyceride and glycerin about 49 %wt. Others may be unsaponifiable substances such as aliphatic alcohols, sterols, pigments and hydrocarbons. These substances frequently dissolve in fatty acids, which cannot be saponified by caustic treatment, but they are soluble in the normal fat solvents. These unsaponifiable matters affect high cloud point and pour point of biodiesel and it can aggregate for clog in engine system (e.g. fuel injector nozzle and fuel filter), which decrease flow ability in engine at low temperature [8].

This problem can be solved by washing for removal the glycerol and glyceride from biodiesel, and unsaponifiable substances are eliminated via subjecting the biodiesel through a bed of diatomaceous earth [3]. However, if sediment has already appeared, it will be filtered before used. The fuel filter then needs to be replaced earlier. In addition, the white sediment can be melted at temperature of 40-50 ^{o}C, which is less than the operating temperature, posting less detrimental threat to the engine performance.

4. Conclusion

The biodiesel industries find white sediment and any other forms of sediment that contaminates in biodiesel. The preliminary effect is appearance. The white sediment was characterized to contain mono- and di-glyceride, which result from incomplete reaction. In addition, such sediment may contains unsaponifiable matters that affect and limit biodiesel usage in diesel engine at low temperature.

Acknowledgment

The authors greatly appreciate help and suggestion from Bangkok Renewable Energy Co, Ltd. All tests are conducted at Biofuel Testing Laboratory at MTEC.

References

1. Barnwal, B. K., and Sharma, M. P. 2005. Prospects of biodiesel production from vegetable oils in India. Renewable and Sustainable Energy Reviews, Vol. 9, pp.363-378.
2. O' Brien, R. D. 2003. Characterization of Fats and Oils. Fats and Oils: Formulating and Processing for Applications.
3. Pfalzgraf, L., Lee, I., Foster, J., and Poppe. G. 2007. The Effect of Minor Components on Cloud Point and Filterability. Biodiesel Magazine.
4. Lee, I., Pfalzgraf, L., Poppe. G., Powers. E., and Haines. T. 2007. The Pole of Sterol Glucosides on Filter Plugging. Biodiesel Magazine.
5. EN Standards: EN 14103 (2003). Fat and oil derivatives. Fatty acid methyl esters (FAME). Determination of ester and linolenic acid methyl ester contents.
6. EN Standards: EN 14105 (2003). Fat and oil derivatives. Fatty acid methyl esters (FAME). Determination of free and total glycerol and mono-, di-, triglyceride content.
7. Department of Energy Business (2007). Specification for industrial biodiesel (FAME grade)
8. Van Gerpen, J.H., E.G. Hammond, L. Yu, and A. Monyem. 1997. Determining the Influence of Contaminants on Biodiesel Properties, Society of Automotive Engineers, No. 971685, SAE. Warrendale, PA, 1997.