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Effect of Sterol Glucosides in Biodiesel Production

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***Abstract*—**The main objectives of this work is study cause of Sterol Glucosides (SG) formation in biodiesel production (methyl ester) based on industry process. In vegetable oils, SG is a common components that usually found in Acrylated Sterol Glucosides (ASG) form. During transesterification process, ASG can be converted to SG which their polarity was changed and restrictive solubility in biodiesel. When biodiesel has a high concentration of SG, that was formed to white precipitate in room temperature consistent with results from Fourier Transform Infrared Spectrometer (FT-IR) spectra show ASG and SG are major components of precipitate. Precipitate is causes of problems in engine using biodiesel as fuel will clog the plugging filter that fuel cannot get through and affect to the distribution of fuel in engine. A High-Performance Liquid Chromatography (HPLC) with an Evaporative Light Scattering Detector (ELSD) is method to analyze amount of ASG and SG in biodiesel and biodiesel precipitate found SG about 91 ppm and 462 ppm, respectively. Anywise this work is elementary data in order to reduce SG in biodiesel production.

***Keywords*—Acrylated Sterol Glucosides, Sterol Glucosides, Biodiesel, HPLC**

I. Introduction

NOWADAY biodiesel is the most interesting alternative fuel because friendly environmental, renewable and can be produced from common feedstock such as vegetable oils and animal fats. The advantages of biodiesel over petroleum diesel: improved lubricity, a higher flash point, lower toxicity, and biodegradability.

Sterols are the common minor components found in animal fats and vegetable oils and can found in many forms [1,2], such as free sterol, acylated (sterol esters), alkylated (sterol alkyl ethers), sulfated (sterol sulfate) and glucosides moiety (sterol glucosides) but in vegetable oil usually found in ASG form but during transesterification process with methanol and alkaline catalyst, ASG which structure of long chain hydrocarbon and ester group from Fig. 1(a), can be converted to SG by was decomposed chemically by removing the fatty acid side chain [3,8] which make restrictive solubility in biodiesel due to hydroxyl group was occurred show in Fig.1 (b). When biodiesel has a high concentration of SG, that was formed to white precipitate due to their polarity, poor solubility in biodiesel and high melting point of SG.

Precipitate make problems in engine that use biodiesel as fuel was precipitate in biodiesel will clog the plugging filter that fuel cannot get through and affect to the distribution of fuel in engine. In addition to, precipitate are formed both on the bottom of biodiesel storage tank and in pipeline of biodiesel production process. Amount of ASG and SG depend on temperature and time for storage and types of feedstock, Biodioli [6] reported 144 ppm of SG in palm oil and 35 ppm of SG in soybean oil.

The main objectives of this work is study cause of SG formation in biodiesel production (methyl ester) based on industry process. A HPLC-ELSD is method to analyze ASG and SG in biodiesel. As Daranee [1] and Moreau [5] reported that HPLC method has many advantages over GC method such as no derivatization of sample, shorter time of analysis and directly method to analysis biodiesel fuel that give result accurately.

(a)

(b)

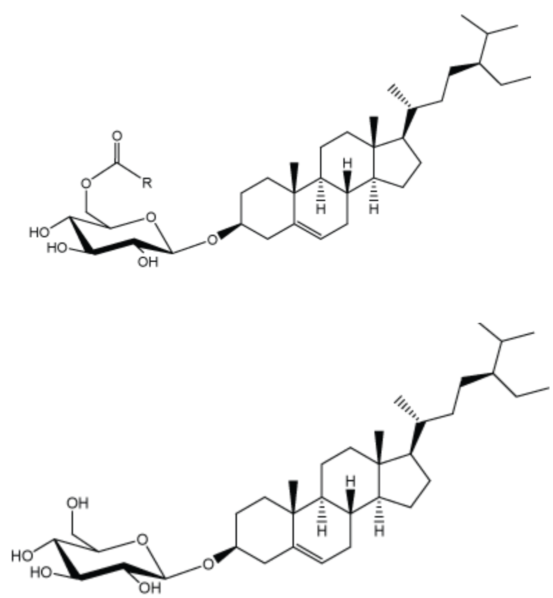

Fig. 1 Structure of (a) Acrylated Sterol Glucosides and (b) Sterol Glucosides[4]

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II. Material And Method

A. Material

Biodiesel and biodiesel precipitate were obtained from Biodiesel Industries (New Biodiesel Co.,Ltd., Suratthani, Thailand). Methanol, Sodiummethoxide and others chemical or reactants in transesterification process were obtained from Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops. Faculty of Engineering, Prince of Songkla University, Songkhla, Thailand.

ASG standard and SG standard were purchased from Matreya LLC (Pleasant Gap, PA) that ASG standard was dissolved in chloroform and SG standard was dissolved in chloroform/methanol/water (2:1:0.1 v/v). For measure concentration of ASG and SG in biodiesel precipitates using HPLC that dissolved in chloroform/methanol (85:5 v/v) 10 ml. Before analysis with HPLC method and purified with solid phase extraction (SPE) technique using LiChrolut Si (40-63 µm) was purchased from Merck KGaA.,Germany by conditioning SEP-PAK cartridge with chloroform, loading samples, washing with chloroform again and eluting with acetone/methanol (9:1 v/v). Chloroform, methanol, water and acetonitrile were purchased from RCI Labscan Ltd.

B. Fourier Transform Infrared Spectrometer (FT-IR) analysis

FT-IR is an analytical technique used to identify mainly organic material in precipitate from biodiesel. Before precipitate was analyzed with FT-IR that necessary to preparation sample step is "neat technique" by drop less amount spectrometer Bruker Equinox 55 with OPUS/IR software, operated at frequency range 4000-400 cm^{-1} and to achieved by using 8 scans 4 cm^{-1} resolution of the sample in KBr windows and splice its, due to it was inert liquids. Spectra were recorded using a FT-IR spectrometer Bruker Equinox 55 with OPUS/IR software, operated at frequency range 4000-400 cm^{-1} and to achieved by using 8 scans 4 cm^{-1} resolution of the sample in KBr windows.

TABLE I
GRADIENT CONDITION OF THE HPLC METHOD

Step	Time (min)	Chloroform (%)	Methanol/Water (%)
1	0	99	1
2	15	75	25
3	20	10	90
4	25	10	90
5	30	99	1

C. High-Performance Liquid Chromatography (HPLC) analysis

The HPLC analysis for quantify ASG and SG using an Agilent 1100 HPLC with autosampler and detect by Polymer Laboratories PL-ELS 1000 Evaporative Light Scattering Detector, operated at flow rate of nitrogen 1 ml/min, evaporative temperature 60ºC and nebulizer temperature 30 ºC. The stationary phase was LiChlospher Si 60 (125×4 mm i.d., Merck) and the mobile phase comprised of chloroform and methanol/water (95:5 v/v) and the flow rate was 1 ml/min (Table.1).

III. Result And Discussion

A. FT-IR spectra

FT-IR analysis results is an absorption spectra which provides information about the chemical bonding and molecular structure of a material. Fig. 2 shows FT-IR spectra

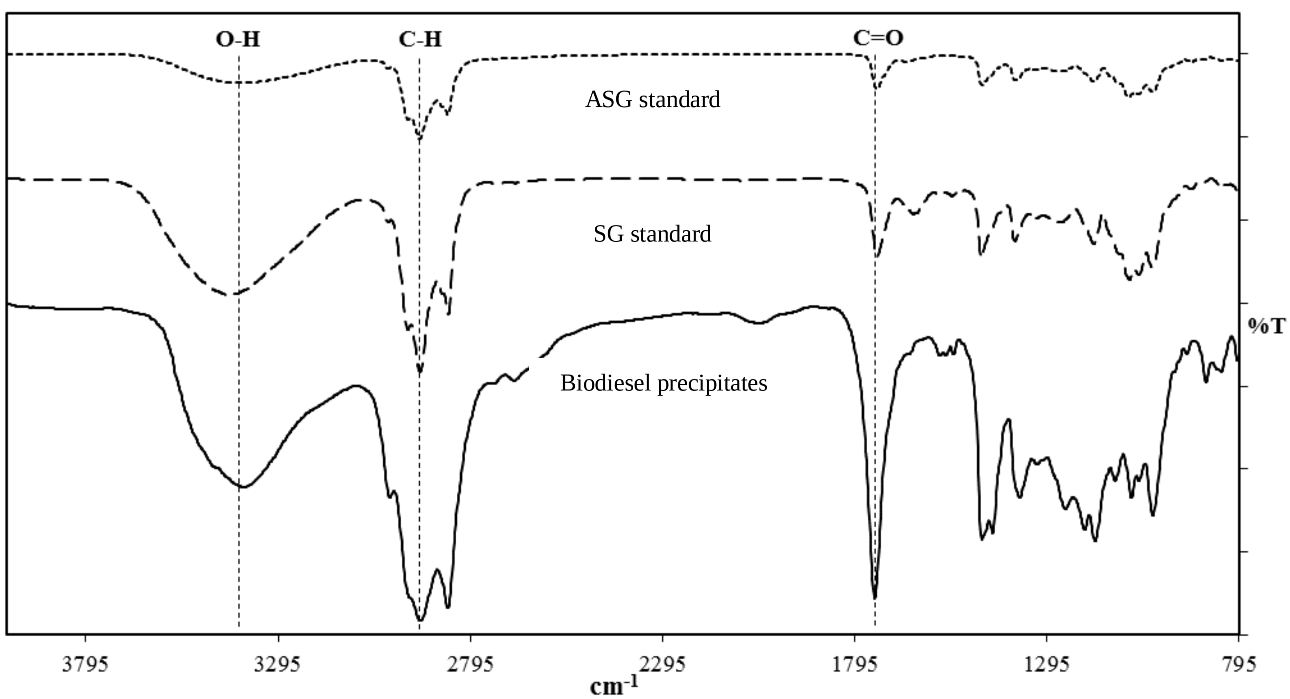

Fig.2 FT-IR spectra of Acrylated Sterol Glucosides standard, Sterol Glucosides standard and Biodiesel precipitates

obtained from the ASG standard, SG standard and biodiesel precipitates. ASG standard, SG standard and biodiesel precipitates show the strongest peak in the area of 1750-1735 cm^{-1} especially peak of biodiesel precipitates is due to the typical C=O stretching band of ester group. A C-H stretching band of alkanes normally visible at 3000-2850 cm^{-1} both standard and biodiesel precipitates show strong peak in this range. The typical O-H stretching band about 3300 cm^{-1} in the spectrum of biodiesel precipitates show the broad peak that imply the presence of hydroxyl group. The spectrum of SG standard shows the similar O-H stretching band as that of the biodiesel precipitates. In addition to in Fig. 1 show others strong adsorptions of the three spectra attributable CH_2 and CH_3 bend of alkanes at 1465 and 1367 cm^{-1}, respectively. Therefore, result of FT-IR spectra that can be explained which the major component of biodiesel precipitates is both of ASG and SG but mainly is SG.

B. HPLC calibration

Quantitative analysis of standard solutions with this gradient conditions for calibration curve in ranging of ASG standard from 200 to 1000 ppm and SG standard from 50 to 400 ppm that chromatogram found the retention time (RT) of ASG and SG were approximately 4.5 and 7.3 min, respectively. From fig. 3 shows the calibration curve of ASG and SG that fit the experiment data in nonlinear form due to capability in calculate response area of chromatogram to amount of ASG and SG at very low concentration and correctly. The polynomial equation from fitting the experiment data of calibration curve of ASG; $y=0.7809x^2-58.567x+29465$ and the polynomial equation of SG; y=0.4013x2+23.315x+622.69, where y is the peak area (mAu·s) and x represents the analyte concentration (ppm).

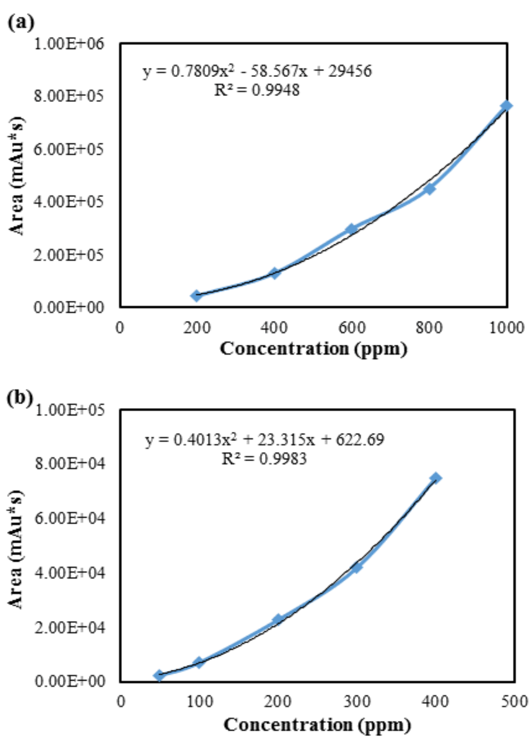

Fig. 3 The calibration curve of (a) Acrylated Sterol Glucosides and (b) Sterol Glucosides.

TABLE II
QUANTITY OF ACRYLATED STEROL GLUCOSIDES AND STEROL GLUCOSIDES IN BIODIESEL

Sample	ASG (ppm)	SG (ppm)
Crude Palm Oil	360	55
Refined Bleached Deodorized Palm Oil	-	-
Biodiesel [a]	-	39
Biodiesel [b]	202	33
Biodiesel Precipitates [c]	-	462

[a] Biodiesel produced from RBDPO on a lab scale by based on conditions of industrial
[b] Industrial biodiesel sample from a storage tank
[c] Precipitates in biodiesel that collect from bottom of storage tank

C. Quantification of Biodiesel and Biodiesel Precipitate

For amount of ASG and SG in crude palm oil (CPO), refined bleached deodorized palm oil (RBDPO), biodiesel and biodiesel precipitates from biodiesel production plant by HPLC-ELSD method found that ASG and SG of CPO as raw material in transesterification process equal 360 and 55 ppm, respectively. Afterward CPO was distillated under vacuum condition for remove free fatty acid and others contaminant into RBDPO which cannot detectable amount of ASG and SG and when RBDPO reacted with sodiummethoxide and methanol in transesterification reaction 3 times, and pass purification steps for purify biodiesel. Biodiesel from storage tank consist amount of ASG 202 ppm and SG 33 ppm. When we produced biodiesel from RBDPO on a lab scale by based on conditions of industrial found 39 ppm of SG as approximate to biodiesel from industrial but cannot found amount of ASG. Precipitates in biodiesel that collect from bottom of storage tank found only amount of SG is 462 ppm that consistent with result of FT-IR spectra.

IV. CONCLUSION

This paper study quantity of oil sample with HPLC-ELSD method since raw material found that include both ASG and SG, in vacuum distillation for remove FFA out of CPO that not found amount of ASG and SG in RBDPO, after transesterification process which make SG in biodiesel increase and found high amount of SG in biodiesel precipitates consistent with FT-IR spectra explain major component of biodiesel precipitates is both of ASG and SG but mainly is SG. Result from this paper is elementary data to study cause of SG formation in biodiesel production (methyl ester) based on industry process, further.

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REFERENCES

[1] D. Anupansakul, "The Metodology Study of Reducing Sterol Glucosides in Biodiesel Production," *M.S. thesis, Department of Chemical Engineering, Prince of Songkla University, Songkla, Thailand*, 2011.

[2] H. Wang, H. Tang, S. Salley, and K.Y. Simon Ng, "Analysis of Sterol Glycosides in Biodiesel and Biodiesel Precipitates," *J Am Oil Chem Soc*, vol. 87, pp. 215-221, 2010. http://dx.doi.org/10.1007/s11746-009-1489-x

[3] J. Haupt, G. Brankatschk and T. Wilham, "Sterol Glucosides Content in Vegetable Oils as a Risk for the Production of Biodiesel," *Proceedings of AGQM and OVID*, Berlin, Germany, Jul 30, 2009.

[4] Matreya LLC. Lipids and Biochemicals. Available: http://www.matreya.com

[5] R.A. Moreau, K.M. Scott and M.J. Haas, "The Identification and Quantification of Steryl Glucosides in Precipitates from Commercial Biodiesel," *J Am Chem Soc*, vol. 85, pp. 761-770, 2005.

[6] P. Bondioli, N. Cortesi and C. Mariana, "Identification and Quantification of Steryl Gucosides in Biodiesel," *Eur. J. Lipid Sci. Technol.*, vol 110, pp. 120-126, 2008. http://dx.doi.org/10.1002/ejlt.200700158

[7] T. Sugawara and T. Miyazawa, "Separation and Determination of Glycolipids from Edible Plant Sources by High-Performance Liquid Cromatography and Evaporative Light-Scattering Detection," *Lipids*, vol.34, no. 11, pp. 1231-1237, 1999. http://dx.doi.org/10.1007/s11745-999-0476-3

[8] V.V. Hoed, N. Zyaykina, W.D. Greyt, J. Maes, R. Verhe and K. Demeestere, "Identification and Occurrence of Steryl Glucosides in Palm and Soy Biodiesel," *J Am Chem Soc*, vol. 85, pp. 701-709, 2008.

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