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Study on the Quantitative Fatty Acids Correlation of Fried Vegetable Oil for Biodiesel with Heating Value

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Abstract

Quantitative analysis of palmitic acid (C16:0), oleic acid (C18:1) and linoleic acid (C18:2) in the fried vegetable oil cooked for 0, 15, 45 min and cooked oil sample was determined by Gas Chromatography–Flame Ionization Detector (GC-FID). As the results, the concentrations of C16:0, C18:1 and C18:2 showed in a range of 28–39, 40–54 and 4–13% v/v, respectively. After that, each of all samples was transesterified with methanol at the ratio of 3:1 and 0.40% KOH as a catalyst at 60°C for 8 hrs and cooled down to room temperature for 16 hrs to afford biodiesel. The percentage yields of the cooked oil for 0, 15, 45 min and the cooked oil samples were found to be 91.08, 89.28, 87.32 and 80.19% wt/wt, respectively. Heating value of the biodiesel, which was prepared from the cooked oil, was determined using bomb calorimeter to be in the range of 38,993–39,480 kJ.kg⁻¹, whereas from diesel displayed at value of 45,979 kJ.kg⁻¹.

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Keywords: biodiesel; transmethyl ester; transesterification; fried vegetable oil

1. Introduction

Since 2004, the crisis of petrol price to be high continually has effected to economy of Thailand. Due to the fact that the petrol importing from a board has worth 653,561 million baht/year especially diesel that was used 46.6% (43 million liter/day) of any fuels [1]. Recently, a scientist expected that a remaining amount of the petrol in a world can be used merely for 46 years in a future. In case of Thailand, the petrol can be used only 12 years because a production rate is not sufficiently by comparing with a current useful purpose [2]. Therefore, a scientist will research to focus on an alternative energy that will be used instead of the petrol from the foreign countries.

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Biodiesel as the non-toxic alternative fuel and biodegradable is the best choice. It also has the highest energy, which is used in any diesel engine without modification, of any fuels. The variable raw materials can be prepared for the biodiesel such as soybean oil [3-5], palm seed oil [5-6], coconut oil [6-7], flax seed oil [8] and castor oil [9]. However, the oil was cooked for many times to be a popular material [1, 10], because it is daily a plenty waste from cooking and easy to be available.

Generally, there are 2 systems of the transesterification, homogenous and heterogenous systems, using a vegetable oil or an animal fat as a starting material. Also, it was likely reacted with methanol [9, 11] because of a good efficiency and a catalyst such as H_2SO_4 and/or metal, $TiO_2.nH_2O/Zr(OH)_4$ [12] and $SO_4^{2-}SnO_2$, $SO_4^{2-}ZrO_2$ [7], HCl [13], KOH [11, 13], $NaOH$ [1, 14]. Beside of an alcohol type and a catalyst, the amount of free fatty acid of oil and fat were mostly an important factor to produce efficiently a high yield of biodiesel. Therefore, we hope that our study on the quantitative saturated and unsaturated fatty acids of the used vegetable oil and the correlation between them and their heating value will help to improve a quality of biodiesel in a future.

2. Materials and Methods

2.1. Preparation of oil sample

Three palm oil samples were fried for 0, 15, 45 min at 150-170°C as a controlled temperature. Also, a cooked oil sample was collected from the food shop at Nakhon Pathom Rajabhat University (NPRU).

2.2. Acid value analysis of oil sample

All samples were evaluated for their acid value which procedure was followed by AOCS Official of method Cd-3D-63. This result provided that the amount of potassium hydroxide (KOH) for biodiesel reaction.

Each sample (triplicate), 5.0000 g (m), was added into Erlenmeyer flask following by 50 mL of a mixture solvent between ethanol and diethyl ether (1:1) and 3 drops of phenolphthalein as an indicator. Then, it was shaken to mix and then titrated with a standard solution of 0.05 M KOH (C) until the end point of a mixture was changed from colorless into light pink color. Before using 0.05 M KOH, it was accurately analyzed of a concentration by titration with 0.05 M potassium hydrogen phthalate (KHP). The volumes of KOH were averaged to give V variable which was further in place of the acid value formula (1).

$$acid\ value = \frac{56.1CV}{m} \quad (1)$$

while V is the volume of KOH (mL)
 C is the concentration of KOH (M)
 m is the weight of oil sample (g)

2.3. Quantitative fatty acid of oil sample

The oil sample (0.5 μ L) was injected to Gas Chromatography instrument (GC14B, Shimadzu Co., Ltd) by a following condition;

column type: J&W DB-Wax (Polyethylene Glycol) capillary column 30) m \times 0.25 mm i.d; 0.25 μ m)
 column temp: 90°C hold 1 min; 90-190°C at 20°C/min hold 1 min; 190-210°C at 2°C/min hold

injector temp: 250°C
 detector temp: 250°C (FID)
 carrier gas: Helium 99.995% purity
 1 min; 210-230°C at 10°C/min hold 10 min

Total peak areas (A) from the GC chromatogram were quantitatively calculated by comparison with a calibration curve of three standard methyl esters of fatty acid, palmitic acid, oleic acid and linoleic acid. The standard graph was illustrated the correlation between A and a concentration (% v/v) of the methyl esters of the standard fatty acid.

The prepared concentration of methyl palmitate was 10, 20, 30 and 40% v/v. Also, methyl oleate was prepared at 10, 20, 30, 40, 50 and 60% v/v, whereas methyl linoleate was tested at 5, 10, 15 and 20% v/v.

2.4. Preparation of biodiesel

The oil sample, 100 g, was stirred with magnetic stirrer at 60°C. Then, a KOH solution (0.442 g KOH and 33.33 g MeOH) was slowly added over 5 min together with stirring for 8 hrs at 60°C and another 16 hrs at room temperature to afford a biodiesel mixture which was transferred into a separatory funnel. An upper organic layer was washed with warm water (3x100 mL) to yield a biodiesel as a yellow liquid. Next, the biodiesel was boiled at 110°C at least 20 min in order to be an anhydrous biodiesel.

2.5. Heating value evaluation for of biodiesel

The biodiesel was evaluated for heating value (5 times) using bomb calorimeter (IKA Co., Ltd. C5000) with ADIABATIC mode by comparison with diesel.

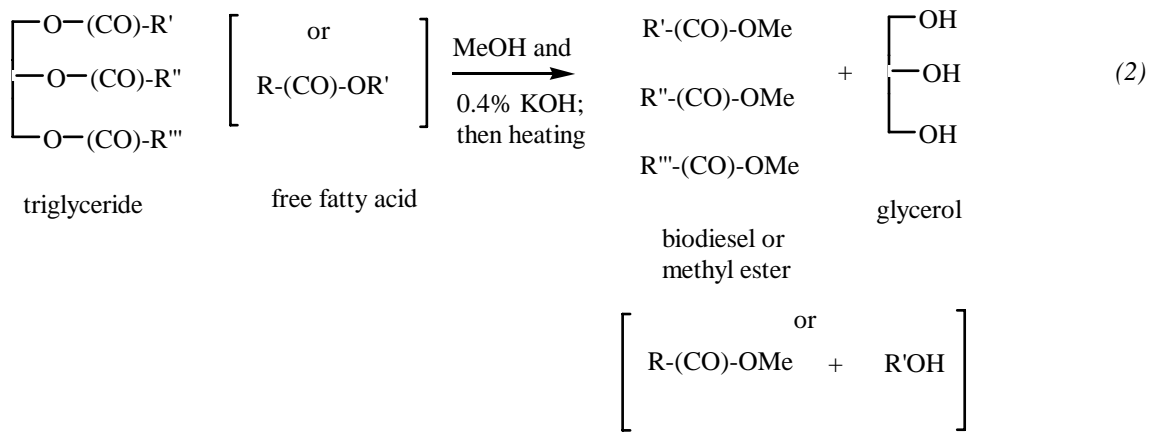
3. Results and Discussion

Three fried palm oil samples as a used vegetable oil, which were prepared at 150-170°C for 0, 15 and 45 min, including another collecting from the food shop at NPRU were analyzed of the acid value (Table 1). As the result, it showed that the fried palm oil for 45 min had consequently the acid value more than 15 and 0 min and vice versa. This means that a cooking time had directly influence to the acid value. In according to, the cooked oil sample which was collected from the food shop at NPRU with 3.22 mg-KOH/g of the acid value expected that it was fried at least 3 hrs. Meaningly, a triglyceride in oil could possibly hydrolyze and/or occur the thermal cracking after heating for a long time to afford a free fatty acids that caused increasingly the acid value [1].

Table 1. Acid values of four fried palm oil samples

samples	color	acid values (mg-KOH/g)
fried palm oil for 0 min	yellow	0.42
fried palm oil for 15 min	dark yellow	0.44
fried palm oil for 45 min	orange	0.54
cooked oil sample from the food shop	brown	3.22

All vegetable oil samples as a starting material, containing the triglyceride and/or the free fatty acids, were transesterified with MeOH in a 3:1 ratio using 0.4% wt/wt KOH as the catalyst during 24 hrs to yield the biodiesel or methyl ester (2).



The quantitative fatty acids, palmitic acid, oleic acid and linoleic acid, of each oil sample were evaluated using GC-FID to afford the GC chromatogram that contained five peaks (Fig. 1). Each peak of the GC chromatogram was confirmed using a standard addition method. Consequently, it was found that the third, fourth and fifth peaks were the identical peaks of methyl ester of palmitic acid (C16:0), oleic acid (C18:1) and linoleic acid (C18:2), particularly. This could be explained by London force as an intramolecular force in the derived fatty acid. Meaningly, the London force had directly correlation with molecular weight (MW) that conducted to boiling point (bp.) of the derived fatty acid. In according to the pb. of methyl palmitate (MW 270.46), oleate (MW 296.50) and linoleate (MW 294.48) gave 136, 169 and 206°C, respectively. Therefore, the methyl ester of palmitic acid was firstly separated following by oleic and linoleic acids.

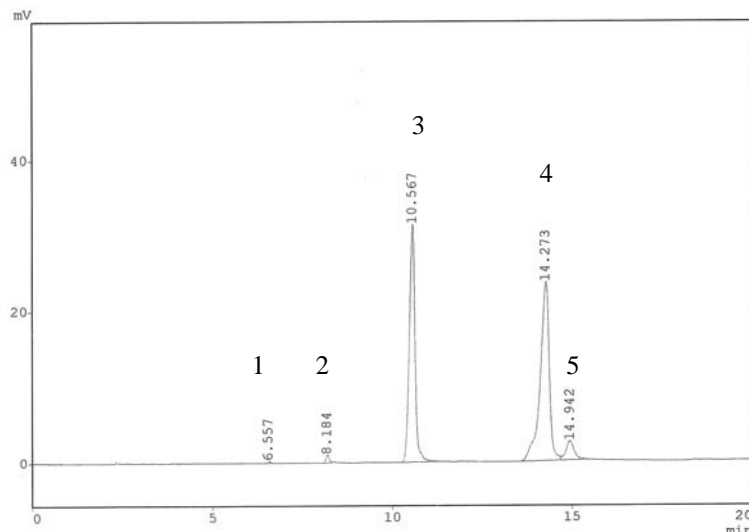


Fig. 1. An example of GC chromatogram of the oil sample

After analysis of all GC chromatograms, the results evaluated % saturated and unsaturated fatty acids of the oil samples which were further compared with their heating value (Table 2). Resulting, % yield of the biodiesel had inclined to decrease correlating to its period of an increasing fried time and a high acid value of the vegetable oil. Therefore, the preparation of the biodiesel to reach more than 90% yield should use the concentrations of palmitic, oleic and linoleic acids about 37, 50 and 12% v/v, respectively. Identically, the % unsaturated fatty acids should be at least 63% v/v composing a little amount of a double bond in a structure of the unsaturated fatty acid. Additionally, when an increasing percentage of the saturated fatty acid from the used vegetable oil and a decreasing acid value of the vegetable oil gave directly domination of the heating value, 38,993-39,480 kJ.kg⁻¹, from biodiesel and vice versa by comparison with diesel at value of 45,979 kJ.kg⁻¹.

Table 2. Correlation with % fatty acid of the oil sample, % yield and heating value of biodiesel

palm oil	% fatty acid of oil sample				% yield of biodiesel	heating value of biodiesel (kJ.kg ⁻¹)
	saturated		unsaturated			
	C 16:0	C18:1	C18:2	total		
fried for 0 min	36.8	51.3	11.9	63.2	91.08	39,450.00
fried for 15 min	35.6	51.5	12.9	64.4	89.28	39,438.60
fried for 45 min	37.0	49.6	13.4	63.0	87.32	39,479.60
from the food shop	38.7	55.7	5.5	61.2	80.19	38,993.00

4. Conclusion

The biodiesel was made through a chemical process called as a transesterification. In this process, the used vegetable oil reacted with methanol and potassium hydroxide as a catalyst in a 3:1 ratio. The percentage of the increasing saturated fatty acid and the decreasing acid value of the vegetable oil inclined to directly heating value of the biodiesel and vice versa.

By comparing to diesel fuel, biodiesel emission are substantially better for the environment and, in turn, better for the health of the environment's inhabitants. Specially, the emission of particular matter, carbon monoxide and total unburned hydrocarbons from biodiesel are much less than those from petroleum diesel. For this reason, the biodiesel has great potential in developing world. Using biodiesel will decrease our dependence on foreign oil and improve our domestic economy.

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