Biodiesel Synthesis from Used frying Oil through Phosphoric Acid Refined and CaO Catalyzed Transesterification

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Abstract. Used frying oil contains chemical components both from heating and fried food content. The frying oil is known as used cooking oil whose color is darker in color from yellow to brown and black. The purpose of this study is to understand the process of degumming in frying oil that is brown to black after chemical acid refining with Phosphoric acid (H3PO4). The analytical method used were GC-MS, supported by thermogravimetry and FTIR Analysis. Six (6) peaks with m / z 88 as ethyl ester fragment markers and allegedly there are two peaks of ethyl linoleate and ethyl oleate as unsaturated fatty acids in Gas Chromatography Mass Spectrometry. Volatile compounds detected by TGA. FTIR also shows an increase in absorbance so that the peak at wave number 2500-1500 cm$^{-1}$ is weak.

1. Introduction
The results of the food frying oil several times can make the fried taste less tasty known as used cooking oil to form new compounds so that it is not suitable for consumption. Non-consumable oil needs to be treated to function according to its designation, due to oil decomposition of fatty acids. The fat content in this oil will affect the results obtained. To understand this used cooking oil is chemically refined before the process of making biodiesel is developed at this time. The accumulation of inorganic material such as phosphoric acid in a long time will change the environment to be not according to its designation, the more toxic toxic substances and the composition of air, water, and soil change to become unhealthy.

Biodiesel is a renewable and an alternative fuel, containing volatile compounds. One of them is Fatty acid alkil ester (FAAE) is formed by fatty acid reacted with alcohol using acid and base catalysts [1]. FAAE such as methyl linolenate can be analyzed by GC-MS [2].

The acidic catalysts that can be used are hydrochloric acid, sulfuric acid, and phosphoric acid while the basic catalysts are sodium hydroxide and potassium hydroxide. Sulfuric acid has been used catalyst in making biodiesel with heating 60°C for 2 hours obtained the highest percentage of methyl 9-octadecanoate about 20% [3]. Hydrochloric acid activated in natural zeolite obtained optimum condition at 60°C with 2% w / w catalyst and physical properties in accordance with ASTM 2003 [4].

The reaction is an esterification reaction between an aliphatic alcohol and a fatty acid or a carboxylic acidic the reaction back and forth so that it needs to proceed with the transesterification reaction using a base catalyst. The methanol volume used in the transesterification process can decrease the physical properties of biodiesel such as viscosity [5]. The content of free fatty acids <3% can be done only by transesterification reactions as well as vegetable oils not required esterification reactions [6]. Vegetable oil from frying
known as jelantah that is frying oil many times need to do esterification reaction.

Biodiesel from used oil cooking oil (UCO) from restaurants using acidic catalysts, bases, and enzymes is said that the transesterification process can decrease viscosity but is highly dependent on molar ratio, reaction time and temperature and catalyst concentration [6]. Waste soybean oil and corn has been made bioemulsifier and biodiesel as an economical renewable source with the highest oleic acid content of more than 40% followed by palmitic acid about 30% [7].

The biodiesel yield of Cladophora vagabunda using chloroform-methanol solvent is greater than isopropanol, further GCMS analysis. The highest percentage is about 22% as methyl palmitate and myristate and linolenic acids respectively about 1% [8]. Biodiesel may be developed both in the manufacturing process, the selection of raw materials, reagents, and catalysts as well as the choice of analysis methods as characterization criteria.

2. Method and materials

2.1. Sample preparation
The procedure, as much as 100 mL of used cooking oil was heated to 35°C, added 20 mL of ethanol, stirred 5 minutes and added 0.5 mL of acid and then heated 2 hours at 60°C and then sterilized 24 hours. After cooling the solution was added 1.38 g CaO and 18.4 mL of ethanol after it was reheated at 55°C for 1 hour and then inserted into the separating funnel and allowed to stand for 1 hour. Further separated the top and bottom layer, then the top layer was washed with distilled water until the water wash. The solution was collected and CaCl$_2$ anhydrous was added, then filtered to obtain the biodiesel of FAEE then analyzed using GC-MS, TGA, and FTIR.

2.2. Method
The method of making biodiesel follows the refine process followed by a transesterification reaction with the following ingredients: cooking oil from food frying Household, 95-98% phosphoric acid (E. Merck), CaO, ethanol p.a. 99%, CaCl$_2$ anhydrous. Equipment such as a 2-neck flask, reflux, thermometer, funnel, measuring cup, measuring pipette, vial bottle, GC-MS QP 10 Shimadzu, Thermogravimetric Analysis, and FTIR.

3. Results and discussion

3.1. The result of Biodiesel from refining used oil
The pure coconut oil in Table 1 shows that lauric acid has the highest percentage followed by ethyl palmitate after frying of household food in coconut oil is obtained by cooking oil. Furthermore, cooking oil is reacted with ethanol with various catalysts in the esterification and transesterification process so that Biodiesel is obtained.

Biodiesel containing ester varied as in Figure 1 ester separation in household cooking oil biodiesel is reacted with ethanol using phosphoric acid catalyst, a very good analytical separation with peak via baseline with resolution meets the analytic criteria (Rs > 2). There are differences in the results obtained, the former oil refined using phosphoric acid first, then the next process is transeserification using heterogeneous catalyst (CaO) in Figure 2. The ester content in biodiesel using phosphoric acid catalysts is similar to the ester compound which is the highest percentage is ethyl laurate, followed by ethyl myristate, ethyl caprylate, ethyl decanoate, ethyl palmitate at m / z 88. Detected esters in the production of used cooking oil biodiesel with acid catalysts on esterification and basic catalysts in subsequent
tranesterification reactions are in accordance with those obtained [3, 8, 9, 10], and the percentage of ethyl palmitate the highest. Monthly of biodiesel production can be reported [11]. This depends on the source of used cooking oil and the result showed of qualitative and quantitative of biodiesel from coconut oil with ethanol using phosphoric acid as catalyst in Table 1.

Table 1 Qualitative and quantitative analysis of coconut oil biodiesel with ethanol and phosphoric acid catalyst by GCMS

| No | Compounds         | Retention time (minute) | Area     |
|----|-------------------|-------------------------|----------|
| 1  | Ethyl Octanoate   | 6.28                    | 177,344  |
| 2  | Ethyl Caprilate   | 9.27                    | 391994   |
| 3  | Ethyl Laurate     | 11.92                   | 2657968  |
| 4  | Ethyl Palmitate   | 14.29                   | 455258   |

Figure 1 Ester Compounds has detected in Biodiesel from waste oil with $\text{H}_3\text{PO}_4$ Esterification and CaO transesterification catalysts using Gas Chromatography-Mass Spectrometry

Figure 2 Ester Compounds has detected in Biodiesel from waste oil with $\text{H}_3\text{PO}_4$ refined and CaO transesterification catalysts using Gas Chromatography – Mass Spectrometry
The results of CaO analysis with and without phosphoric acid activation using Thermogravimetric were obtained as shown in Figure 3

![Figure 3 Moisture, Volatile, and ash compounds in CaO Catalyst measured using Thermogravimetric Analysis](image.png)

Phosphoric acid is able to refine used cooking oil in the transesterification process using CaO as a heterogeneous catalyst capable of increasing absorbance and reducing absorption peak at wave numbers 2500-1500 cm\(^{-1}\) such as Figure 4.

![Figure 3 Spectogram FTIR of Biodiesel with CaO and H\(_3\)PO\(_4\) catalysts compared with Biodiesel using H\(_3\)PO\(_4\) refined and CaO catalyzed transesterification](image.png)
4. Conclusion
The ester compounds detected in biodiesel are the various ester compounds with the highest ethyl laurate followed by ethyl myristate, caprylate, and palmitate with m/z specific being 88. Volatile compounds in CaO is detected by TGA and supported by FTIR showed an increase in absorbance so that the peak at wave number 2500-1500 cm\(^{-1}\) is weak.

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6. References
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