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Journal of Multidisciplinary Applied Natural Science Vol. 2 No. 1 (2022) https://doi.org/10.47352/jmans.2774-3047.90

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Research Article

Utilization of Breed Chicken Eggshells for Biodiesel Preparation from Waste Cooking Oil

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Received : April 30, 2021	Revised : October 28, 2021	Accepted : October 30, 2021	Online : November 01, 2021

Abstract

Chicken eggshell waste is a promising source of CaO which can be converted into heterogeneous catalyst materials. The purpose of this study was to utilize CaO heterogeneous catalyst derived from breed chicken eggshell toproduce biodiesel from waste cooking oil through the transesterification process. A total of 4 g ofcatalyst material was mixed with 200 g of waste cooking oil and 60 g of methanol, and then the mixture was stirred at a speed of 700rpm for 6 h at 60 ± 4^{0}C. The produced biodiesel was analyzed using GC-MS to elucidate the various methyl ester compounds. The produced biodiesel was found to have a density of 855kg/m^3, viscosity of 3.74 mm^2/s (cSt), and flash point of 135 ^{0}C. Based on these results, it can be concluded that breed chicken eggshells are potential sources for the preparation of CaO catalyst material to produce biodiesel from waste cooking oil. This finding is very useful for further optimization of masscatalysts heterogeneous CaO from breed chicken eggshells including the commercial production of biodiesel.

Keywords: biodiesel, CaO heterogeneous catalyst, transesterification, waste cooking oil, breed chicken eggshell

1. INTRODUCTION

Recently, it is well known that breed chicken eggshells are simply discarded polluting our environment. Whereas the breed chicken eggshells waste is a calcium resource that can be utilized as a raw material for the production of CaO heterogeneous catalyst [1]–[3]. Based on the composition of existing minerals, the eggshell is composed of $CaCO_3$ (98.43%), $MgCO_3$ (0.84%), and $Ca_3(PO_4)_2$ (0.75%) minerals. The $CaCO_3$ itself can be converted into CaO through the calcination process [4].

Catalyst materials are chemicals that can accelerate reactions. The production of a desired chemical compound can be performed using either homogeneous or heterogeneous catalyst. However, the main disadvantage of homogeneous catalysts is their difficulty to be recovered from the reaction system thus resulting in hazardous waste disposal, which is unfavourable [5]. In addition, homogeneous catalysts in free fatty acid (FFA) transesterification reactions can form soap making it difficult to separate glycerol thus reducing biodiesel yield. Homogeneous catalysts can be replaced with heterogeneous catalysts that are more environmentally friendly, highly stable at high temperatures, large pores, and low-cost material [6]–[9].

Among the other heterogeneous catalysts, CaO has high wetness thus CaO is widely used as a catalyst in the process of transesterificationof oil into biodiesel. Another advantage of CaO is its rigid structure so that it is easily recovered at the end of the biodiesel process [10]. The main drawback of CaO catalyst is that it reacts easily with water-containing air to form $Ca(OH)_2$ leading to a decrement in its catalytic activity [11].

Waste cooking oil (WCO) is a waste generated from vegetable cooking oil that has been used more than three times sothat it contains high levels of free fatty acids and peroxides. When WCO is still consumed by humans it can cause serious diseases including high blood pressure and cancer. Food processing using cooking oils leaves WCO and often it is discharged through public sewers, resulting in environmental pollution such as foam formation and sludge flotation. This problem is slowly but sure affects human life and requires expensive environmental remediation costs [12]–[15].

Researchers have reported the utilization of CaO catalysts to convert WCO into biodiesel products. Zhang et al. synthesize Au/CaO nanoribbons that can be used as recyclable catalysts with high activity for biodiesel production [16]. Yan et al.

Figure 1. The synthesis scheme of CaO heterogeneous catalysts from pure breed chicken eggshells.

used WCC with a dose of 6% to convert cooking oil waste in 82% biodiesel yield [17]. Alptekin et al. conducteda reduction of FFA content using acid catalysts and then produced biodiesel using alkaline catalysts [18]. Dang et al. convert WCO from canteen source to biodiesel [19]. Xiong et al. convert alcohol made from used cooking oil waste into biodiesel [20]. Marchetti conducted a study on the comparison of biodiesel products produced using raw materials for new cooking oil and used cooking oil, the results obtained were 40% of biodiesel products [21]. Agarwal et al. produced biodiesel by converting used cooking oil into biodiesel using a KOH catalyst in 98.2% yield [22]. Considering some of the aspects described above, the study aims to produce biodiesel from used cooking oil waste taking into account the advantages offered by the heterogeneous catalyst CaO made from pure breed chicken eggshells.

2. MATERIALS AND METHODS

2. 1. Materials

Used cooking oil and breed chicken eggshell samples were collected from the restaurant in Bandar Lampung City, Lampung, Indonesia. The other chemicals used include: methanol, *n*-hexane, cerium sulfate, and H_2SO_4 purchased from Merck SG.

2.2. Methods

2.2.1. Synthesize CaO heterogeneous catalysts

Pure breed chicken eggshells were washed several times and then boiled. The membrane layer was separated from the shell and then dried at room temperature. Furthermore, the eggshell was crushed into small particles and then filtered. After being crushed, then the material was calcined and sintered using a muffle furnace at 900 ^{0}C for 10 h to form a CaO structure [23]. The synthesis scheme of the CaO heterogeneous catalyst isshown in Figure 1.

2.2.2. Preparation of Biodiesel

As much as 200 g of used cooking oil was weighed, added with 60 g of methanol and 4 g of CaO catalyst, and then stirred at 60 ± 4^{0}C for 6 h. After that, the mixture was allowed to stand for 24 h until 3 phases are formed, namely biodiesel (top layer), glycerol (middle layer), and the catalyst material (bottom part). Crude Biodiesel and glycerol along with the catalyst are separated and placed in another container.

A certain amount of water was then added into the biodiesel mixture for a purification purpose. The crude biodiesel was washed repeatedly until the aqueous phase no longer contained soap and appeared as a clear solution. Finally, the biodiesel was heated at 60 ^{0}C for 10 min to evaporate the water which maystill be left.

Figure 2. Preparation scheme of biodiesel made from waste cooking oil using CaO heterogeneous catalyst.

Figure 3. Rf values of methyl ester produced.

3. RESULTS AND DISCUSSIONS

Based on the screening test using TLC, the obtained Rf values were 0.66 and 0.88 as shown in Figure 3. These results indicate that there were various types of methyl ester compounds with varying carbonchain lengths according to the degree of polarity where the value of 0.88 is relatively more non-polar and has a longer carbon chain than the compounds with an Rf value of 0.66.

Furthermore, the results of the characterization using GC-MS analysis obtained chromatogram data. A total of 18 peaks were observed in the chromatogram, and the first 2 peaks could not be identified because the intensity was too low to be considered satisfactory.

The chromatogram of identified compounds showed in Figure 4 and the composition was presented in Table 1. From Figure 4 and Table 1, the identification of methyl esters indicates that the transesterification of fatty acids in WCO took place already. The data also showed that methyl octadecanoate was found as the most prominent component of the sample, which was corresponded to the presence of palmitic acid as the most abundant component in WCO [24].

The information presented in Table 2 was an additional analysis to determine the three basic characteristics of biodiesel. Biodiesel standard values according to the Indonesian standard (SNI 7182-2015) are included in Table 2 for comparison. Compared to standard values, all three characteristics are acceptable. In the future, the determination of other parameters included in the standard is required for further commercialization of the produced biodiesel in this study [25]–[27].

4. CONCLUSIONS

The CaO-based heterogeneous catalyst derived from chicken eggshells can be used as a heterogeneous catalyst to produce biodiesel fuel from waste cooking oil as biodiesel raw material. The results of the TLC screening test and GC-MS analysis showed the formation of several methyl ester compounds.

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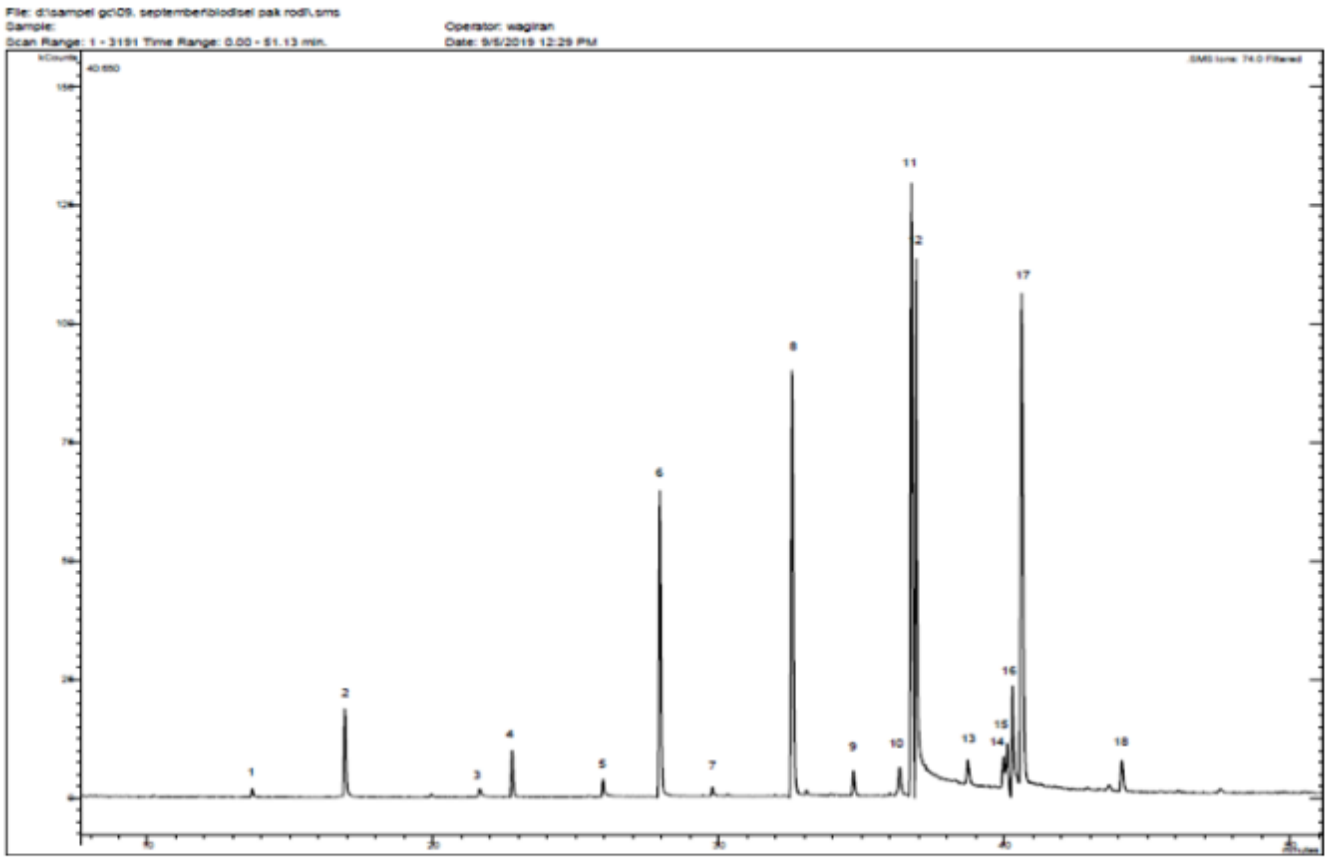

Figure 4. Chromatogram of typical biodiesel produced.

Table 1. The composition of biodiesel produced in this study based on GC-MS analysis.

Peak number	*Retention time (min)*	*MW*	*m/z*	*Compound Name*	*Relative percentage*
1	13.670			No hits	0.250
2	16.912			No hits	2.910
3	21.634	444	73	Dodecamethyl-ester	0.320
4	22.757	186	74	Decanoic acid, methyl ester	1.440
5	25.947	518	73	Tetradecamethyl-ester	0.570
6	27.934	214	74	Undecanoic acid, 10-methyl-, methyl ester	9.890
7	29.757	592	355	Hexadecamethyl-ester	0.310
8	32.564	242	74	Tridecanoic acid,12-methyl-,methyl ester	16.06
9	34.717	256	74	Pentadecanoic acid,methyl ester	0.870
10	36.323	268	74	9-Hexadecenoic acid, methyl ester, (Z)-	1.240
11	36.741	270	74	Pentadecanoic acid,14-methyl-,methyl ester	21.04
12	36.901	270	74	Pentadecanoic acid,14-methyl-,methyl ester	16.00
13	38.715	284	74	Hexadecanoic acid, 14-methyl-,methyl ester	0.890
14	39.967	294	67	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	1.110
15	40.099	294	67	8,11-Octadecadienoic acid,methyl ester	1.320
16	40.277	296	264	9-Octadecenoic acid,methyl ester, E-	4.200
17	40.589	298	74	Octadecanoic acid, methyl ester	20.10
18	44.108	326	74	Eicosanoic acid, methyl ester	1.470
				Total	**100.0**

Table 2. Comparison of produced biodiesel with Indonesian Standard for biodiesel.

Parameter Analysis	Result	Standard Value (SNI)
Density at 40^0C	855 kg/m^3	850-890 kg/m^3 (ASTM D-1298)
Kinematic viscosity at 40^0C	3.74 mm^2/s (cSt)	2.3-6.0 mm^2/s (cSt) (ASTM D 445)
Flash point (bowl closed)	135 ^{0}C	> 100 ^{0}C (ASTM D 93)

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ACKNOWLEDGEMENT

The author would like to thank the Ministry of Health of the Republic of Indonesia for the research funds provided through the Decree of the Director of the Tanjungkarang Health Polytechnics Number. HK.02.03/1.2/2712/2019

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