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To cite this article: L Qadaryah *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **543** 012072

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Biodiesel production from *Calophyllum inophyllum* L oil using Microwave with Calcium Carbonate catalyst

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Abstract. Biodiesel has become a promising renewable energy resource in recent years due mainly to the fluctuating global oil prices. *Calophyllum inophyllum* L seed has fairly high oil content of about 40-73 % by weight, thus, making it a great potential as raw material for producing biodiesel. This paper aims to study the effect of the microwave irradiation for biodiesel production from *Calophyllum inophyllum* L oil when solid CaCO_3 catalysts made from waste eggshells and synthetic were employed. Furthermore, the effects of operating conditions, including reaction time, microwave power, and amount of catalyst loading were also investigated. The initial step to produce *Calophyllum inophyllum* L biodiesel was degumming process, followed by the esterification and trans-esterification, respectively. The catalysts used are CaCO_3 synthetic and eggshell. The results of production biodiesel from *Calophyllum inophyllum* L oil give the highest yield of 65.36 % when performed with the microwave power of 300 Watt, 1 % eggshell catalyst and the reaction time of 10 minutes. Therefore, *Calophyllum inophyllum* L shown as potential biodiesel feedstock.

1. Introduction

Energy consumption in Indonesia mainly comes from fossil energy with crude oil (41.46 %), coal (35.81 %), and natural gas (19.36 %) [1]. However, due to the declining fossil fuel sources in the next few years and the increase of environmental issues caused by fossil energy, this has led to examine the prospect of using alternative energy resources such as biodiesel. Biodiesel is defined as the mono-alkyl esters of long chain fatty acids (FAME) derived from renewable lipids. Biodiesel is a biodegradable, nontoxic, low on emission, high cetane number, higher flash point, and give better lubricity on engine type of fuel [2]. thus, making it an ideal fuel for the future.

Biodiesel has a wide range of available feedstock with non-edible oils and therefore, regarded as second-generation biodiesel feedstocks. Biodiesel can be obtained from virgin vegetable oil like palm oil, waste frying oil, and palm oil mixtures [4]. One of the promising non-edible plants for biodiesel resource is *Calophyllum inophyllum* L, whose yield is known to be relatively higher than other plants (*Calophyllum inophyllum* L 40-73 %, Palm oil 45-70 %, *Jatropha curcas* 40-60 %) [5]. The composition of *Calophyllum inophyllum* L is shown on Table 1. With the Free Fatty Acid (FFA) content of 5.1%, crude *Calophyllum inophyllum* L oil needs to undergo pre-treatment process prior to transesterification, which consist of degumming and esterification. The purpose of degumming and esterification are to eliminate phosphatide gum from crude oil and to reduce the free fatty acid (FFA) content to less than 2%. [6]. High FFA in oil can result in saponification reaction instead of transesterification in the next process, therefore, the FFA content needs to be reduced by converting the FFA into methyl ester in an esterification process [7].

Microwave irradiation is the best method of accelerating and enhancing chemical reactions because it delivers the energy directly to the reactant. Therefore, heat transfer is more effective than in conventional heating and the reaction can be completed in a much shorter time and higher yields in the production of biodiesel can be obtained. It enhances the speed of the reaction and makes the separation process easier in comparison with conventional heating [8].



Table 1. *Calophyllum inophyllum* L oil fatty acid composition [3]

No.	Fatty Acid Composition	Percentage %	No.	Fatty Acid Composition	Percentage %
1.	Saturated fatty acid	35.83	2.	Unsaturated fatty acid	64.17
	-Myristic acid (C14:0)	0.09		-Oleic acid (C18:1)	37.57
	-Palmitic acid (C16:0)	14.6		-Linoleic acid (C18:2)	26.33
	-Stearic acid (C18:0)	19.96		-Linolenic acid (C18:3)	0.27
	Arachidic acid (C20:0)	0.94			
	Erucic acid (C22:1)	0.24			

Catalyst selection is important for transesterification process. Heterogeneous base catalysts are more effective than heterogeneous acid catalysts and enzymes. Heterogeneous catalyst could be operated in continuous processes, could give high quality products, reusable, and eco-friendly [9]. Calcium is common in the environment and is available at very low costs compared to other catalytic metals. The calcium carbonate catalyst is cheaper and is considerably more robust than calcium oxide particles. Traces of calcium carbonate released into the environment generally slightly affect the environment [10]. One of promising CaCO_3 source comes from waste chicken eggshell with 99% CaCO_3 [11]. Therefore an effort to achieve reduction in the biodiesel production cost there is needed to find an alternative low cost catalyst was derived from waste chicken eggshell and accelerating chemical reaction using microwave

The aim of this paper is to study the effect of the microwave irradiation for biodiesel production from *Calophyllum inophyllum* L oil when a solid CaCO_3 catalyst from waste eggshells and synthetic was employed. Furthermore, the effects of operating conditions, including reaction time, microwave power, and amount of catalyst loading are also investigated.

2. Methods

Calophyllum inophyllum L oil was commercially available from Cilacap area of Central Java and delivered in liquid form extracted by mechanical press. The oil that came out of the press machine was dark green with high viscosity. One neck flask was used as reactor with an inner volume of 1000 ml and reflux condenser as a cooling tower. Modified Microwave (Electrolux Co., model EMM 2308X) was used as energy source microwave equipped with magnetic stirrer. [12].

2.1. Catalyst Preparation

The waste eggshells were washed by tap water to remove dust and impurities, and then dried at 110 °C and crushed to 40 mesh size. The catalyst characterization was carried out in the form of X-Ray Diffraction (XRD).

2.2. Degumming

100 ml of *Calophyllum inophyllum* L oil were loaded and heated at a temperature of 80°C then followed by the addition of 85% phosphoric acid by 5 % (v/v). *Calophyllum inophyllum* L oil were mixed for 15 minutes using magnetic stirrer. The collected product was washed three times, each using warm aquadest (60°C), in a separation funnel. The upper oil phase was withdrawn and dried using an oven at 110°C to reduce the water content in the oil and result from degumming is analyzed accordingly.

2.3. Esterification

100 ml of post-degumming oil were loaded to reactor. Methanol was added to reactor alongside with the oil, the mole ratio of oil-methanol 1:40 and 98 % H_2SO_4 catalyst by 10% (w/w). The reactions were carried out with constant stirring (~300 rpm) at 450 W microwave oven for 20 minutes. After the radiation process, separation between methanol, oil and catalyst was using separating funnel, the top layer of methanol which can be recovered and the bottom layer was a mixture of oil and methyl ester (crude biodiesel). The solutions were cleansed, washed seven times, each using warm aquadest (60°C). The crude biodiesel product was dried in an oven at 110 °C and the result from esterification was analyzed

2.4. Transesterification

Mixed Crude biodiesel (30 mL) were loaded in a methanol (mole ratio of oil-methanol 1:9) and heterogeneous base catalyst was added in reactor. The reaction was carried out with constant stirring using magnetic stirrer under constant radiation in a microwave oven. The solution was washed ten times, each with warm aquadest (60°C) using a separator funnel. The oil was dried in an oven at 110°C to reduce the water content. The variables used were heterogeneous base catalyst type: CaCO_3 from eggshell and CaCO_3 synthetic; concentration (% v/v oil): 1 %; 2 %; 3 %, 4 %, and 5 %; microwave power (W): 150, 300, 450, and 600; as well as radiation time (minute): 2, 6, 10, 20, and 30. The biodiesel yield was then analyzed with gas chromatography at UBAYA University.

3. Results and discussion

3.1. Material Characteristic

A number of analysis were conducted to determine the characteristics of crude *Calophyllum inophyllum* L oil, including density, viscosity, % FFA, color and GC test (chemical component). The results are presented in Table 2.

Table 2. Characteristic of crude *Calophyllum inophyllum* L oil

Parameter	Results
Density (g/mL)	0,9387
Viscosity (cSt)	53,6259
FFA (%)	27,9011
color	blackish green

Tabel 3. GC Analysis of crude *Calophyllum inophyllum* L oil

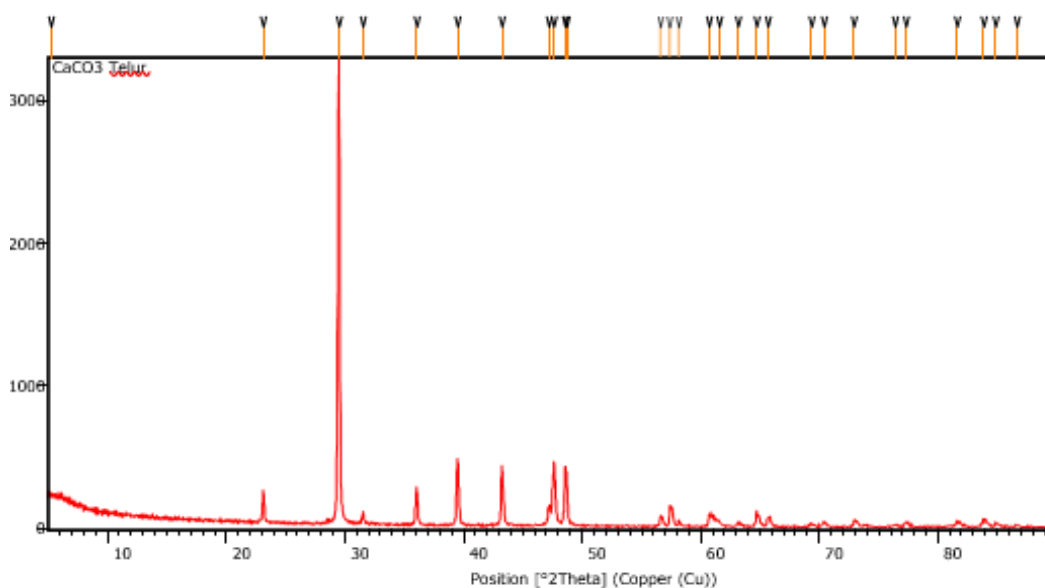
Components	(%)
Free Fatty Acid (FFA)	15,7568
Monoglycerol (MAG)	12,2459
Diglycerol (DAG)	4,6605
Triglycerol (TAG)	63,9121
Others	3,4247
Total	100

Table 3 represents the type of composition and purity of crude *Calophyllum inophyllum* L oil. Since the crude *Calophyllum inophyllum* L oil used in this study was extracted from the *Calophyllum inophyllum*

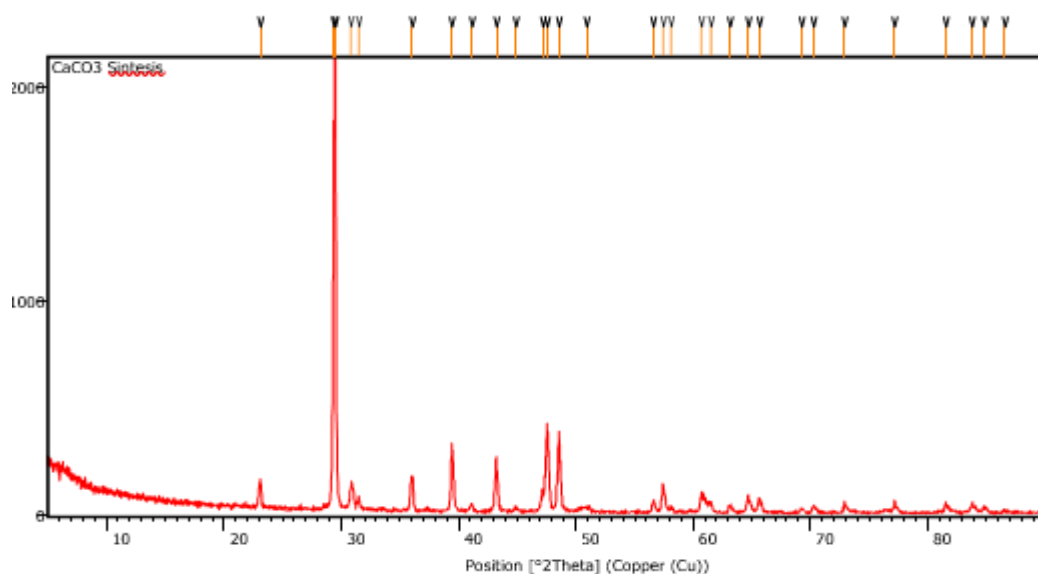
L seeds using mechanical extraction method, the oil contains relatively a lot of impurities, both from the skin and chemical compounds such as phosphatida, chlorophyll, karetenoid and others

3.2. Characteristic Catalyst

In order to characterize the crystallinity patterns of synthetic and egg shell calcium carbonate, XRD analysis was performed for both samples. The diffractograms in Figure 1 shows that diffraction patterns of synthetic and eggshell calcium carbonate have similar peaks. The patterns can be put upon being the differences only found in the intensity of the peaks. Both samples depicted same trends with one sharp peak at 2θ around 30° and weak peaks at 2θ around 40° - 50° . The sharp peaks of both samples are characteristic of the high crystallinity of the samples.



(a)



(b)

Figure 1. (a) XRD pattern of CaCO_3 eggshell ; (b)XRD pattern of CaCO_3 synthetic

3.3 Degumming

The degumming process is a process to remove impurities in the oil. The impurities that typically exist in the form of gum are phosphatida compounds which are carried from the previous process of oil pressing. The comparison between the parameters before and after degumming is presented in **Table 4**. As can be seen, there are some changes recorded on the density, viscosity, and color of the oil after the degumming. More importantly, there is also a quite significant decrease in the FFA content, i.e. from 27.9011% to 19.3069%.

Table 4. Characteristic of degummed *Calophyllum inophyllum* L oil

	Before Degumming	After Degumming
Density (gr/mL)	0.9387	0.9132
Viscosity (cSt)	53.6259	40.4428
Colour	Dark green	Reddish brown

3.4. Esterification

During the esterification stage, the triglycerides in the oil did not seem to react to produce methyl esters based on the fact that no formation of glycerol was identified. This shows that in oils with high FFA concentrations when present in acidic conditions, the reactions that occur tend to be between FFA and methanol (esterification) rather than between triglycerides and methanol (transesterification). The comparison of the oil parameters before and after the esterification process is shown in **Table 5**.

Table 5. Characteristic of esterified *Calophyllum inophyllum* L oil

	Before Esterification	After Esterification
Density (g/mL)	0.9132	0.9030
Viscosity (cSt)	40.4428	22.3905
FFA (%)	19.3074	0.4076

3.5 Transesterification

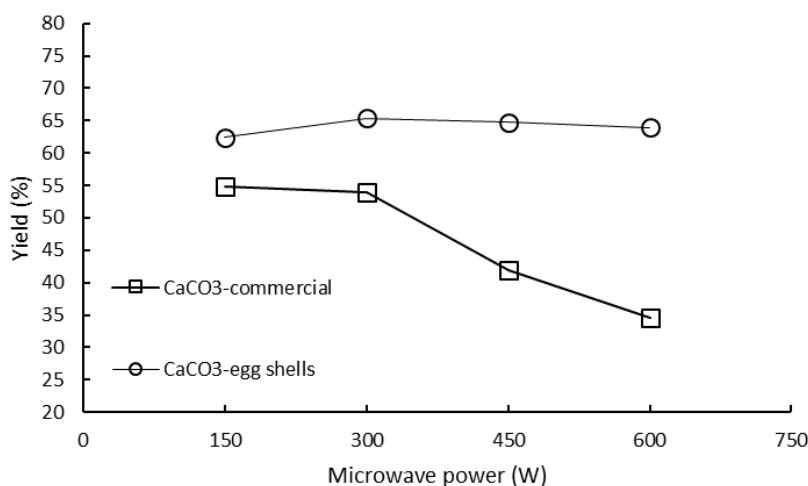


Figure 2. Effect of microwave power on biodiesel yield

Transesterification is the main process of biodiesel production, in which triglyceride contained in the oil is reacted with alcohol to form fatty acid methyl ester (FAME). **Figure 2.** shows the effect of microwave power on biodiesel yield on each CaCO₃ synthetic and eggshell catalyst. With increasing power from 150 to 300 W, the eggshell catalyst exhibits the increase of the biodiesel yield by 4.71 % (from 62.4 % to 65.36 %), however, for CaCO₃ synthetic catalyst indicates a decrease by 1.58% in the biodiesel yield

(from 54.76 % to 53.89 %). Furthermore, with the increasing microwave power, the biodiesel yields are decreasing for both catalysts. The final biodiesel yields at 600 Watt are 63.93 % for eggshell catalyst and 34.5 % for CaCO_3 synthetic catalyst. The highest biodiesel yield was obtained at 300 Watt for both catalysts. a research done by D. Y. C. Leung, X. Wu, and M. K. H. Leung carried out a biodiesel production from *Calophyllum inophyllum* L with dolomite rock and spiritus at 60 °C for operation condition and examined that base catalyst at high temperature was found to decrease the biodiesel yield due to the unwanted reaction in the form of saponification[13] .

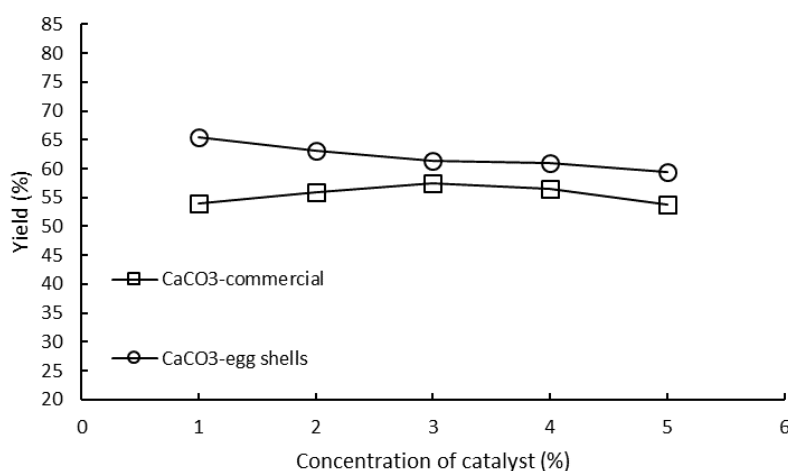


Figure 3. Effect of concentration catalyst on biodiesel yield

Catalysts have important roles in forming methyl ester to accelerate the transesterification reaction. To study the effect of catalyst concentration on biodiesel yield, a microwave power of 300 Watt was set for 10 minutes. As shown in **Figure 3**, when catalyst concentration is increased, the biodiesel yield increases and at one point the yield is decreasing for CaCO_3 synthetic catalyst. Yield increase from catalyst concentration 1% to 3% but decrease at concentration 3% to 5%. The optimum concentration catalyst (3%) give the highest yield 57.44% is for CaCO_3 synthetic. As for eggshell catalyst, the biodiesel yield is decreasing with increasing catalyst concentration. The highest yield (65.36%) is obtained at 1% concentration catalyst

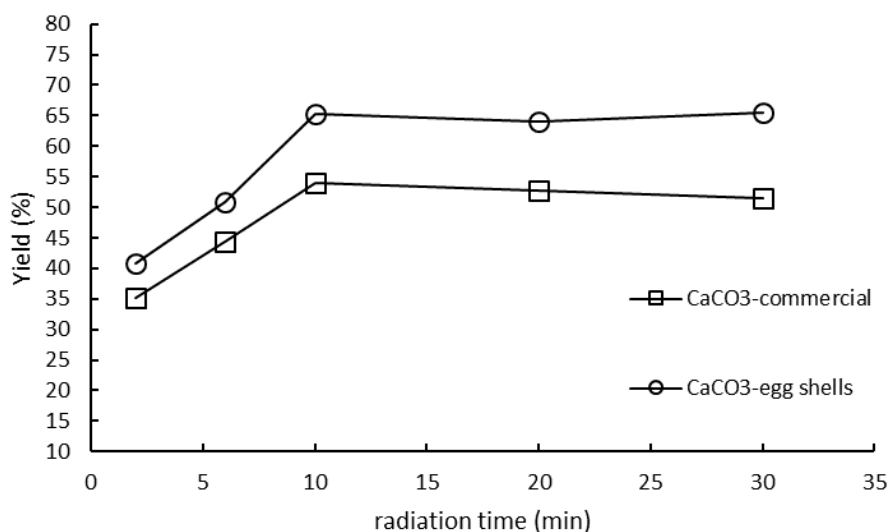
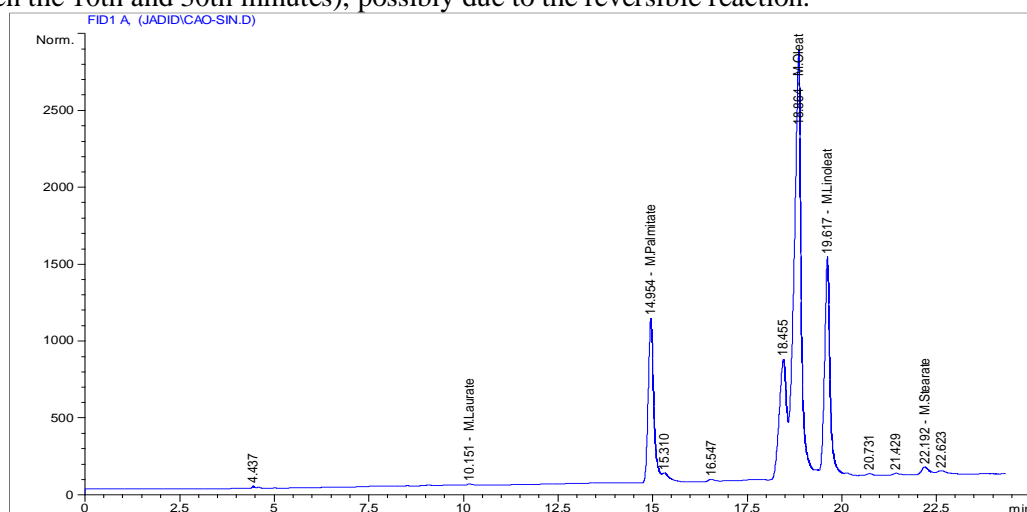


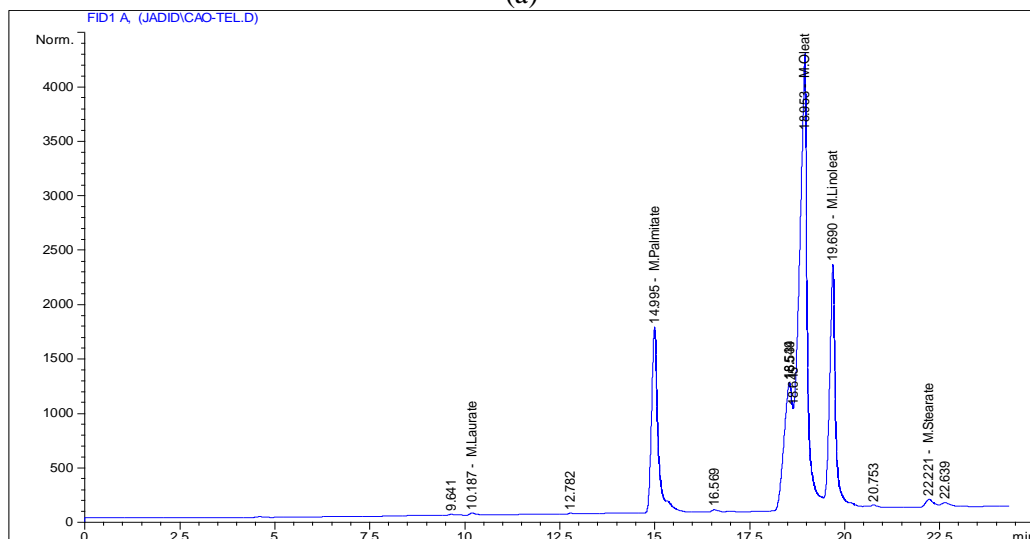
Figure 4. Effect of transesterification time on biodiesel yield

In this study, the effect of radiation time was investigated under the microwave power of 300 Watt with 1% (w/w) catalyst concentration. For both catalysts the biodiesel yields increase over time until 10

minutes before decreasing over the next minutes. For CaCO_3 synthetic from 2 to 6 minutes, biodiesel yield increases by 25.81 % (from 35.20 % to 44.29 %). From 6 to 10 minutes, biodiesel yield increases by 21.69 % (from 44.29 % to 53.89 %). However from 10 to 20 minutes, the biodiesel yield decreases by 2.00 % (from 53.89 % to 52.82 %). From 20 to 30 minute, biodiesel yield decreases by 2.66 % (from 52.82 % to 51.41%). For eggshell catalyst, from 2 to 6 minutes, biodiesel yield increases by 24.72 % (from 40.81 % to 50.90 %). From 6 to 10 minutes, biodiesel yield increases by 28.41 % (from 50.90 % to 65.36 %). However from 10 to 20 minutes, biodiesel yield decreases by 2.10 % (from 65.36 % to 63.99 %) and from 20 to 30 minute, biodiesel yield increases by 2.51 % (from 63.99 % to 65.60 %). The highest yield for CaCO_3 synthetic is 53.89 % at 10 minutes and for eggshell catalyst is 65.36 % at 10 minutes. When transesterification reaction is continued further over time, the biodiesel yield decreases (between the 10th and 30th minutes), possibly due to the reversible reaction.



(a)



(b)

Figure 5. (a) Chromatogram of biodiesel with 300 W, 1 % CaCO_3 synthetic catalyst, 10 minutes reaction; (b) Chromatogram of biodiesel with 300 W, 1 % eggshell catalyst, 10 minutes reaction

The gas chromatography (GC) test result indicates there is FAME formed. From **Figure 5(a)** the composition for FAME with CaCO_3 synthesis are laurate methyl 0.0483%, palmitic methyl 19.4538 %, oleic methyl 57.5571 %, linoleic methyl 22.1287 %, and stearic methyl 0.8121 %. As for the FAME composition from biodiesel with eggshell catalyst can be seen from **Figure 5(b)**, the results are hexanoat methyl 0.0167 %, laurate methyl 0.0463 %, palmitic methyl 18.3351 %, oleic methyl 58.1299 %, linoleic methyl 22.5343 %, and stearic methyl 0.9377 %.

Table 6. Density and viscosity of biodiesel yield

Catalyst	Density at 40°C (g/mL)	Viscosity at 40°C (cSt)
CaCO_3 synthetic	0,8980 – 0,9041	8,6867 – 12,1441
Eggshell	0,8955 – 0,9025	8,0788 – 9,7932

Unfortunately the density and viscosity of biodiesel yield are out of SNI standard range. The SNI standard for biodiesel density is 0.850 - 0.890 g/mL and for viscosity is 2.3 - 6 cSt. The closest density to SNI standard is 0.8980 g/mL for biodiesel with CaCO_3 synthetic catalyst with operation condition 450 W, reaction time 30 minutes, and catalyst concentration 3 %. While the closest density for eggshell is 0.8955 g/mL with operation condition 450 W, reaction time 20 minutes, and catalyst concentration 1%. A research done by J. Goli and O. Sahu [14] using chicken eggshell catalyst was measured and meet all the standards using 7% wt catalyst while in this research using maximum 5% wt catalyst. The closest viscosity to SNI standard is 8.6867 cSt for biodiesel with CaCO_3 synthetic catalyst with operation condition 300 W, reaction time 30 minutes, and catalyst concentration 1 %. While the closest viscosity for eggshell is 8.0788 cSt with operation condition 300 W, reaction time 30 minutes, and catalyst concentration 1%

4. Conclusion

It is concluded from this study that CaCO_3 synthetic and eggshell catalysts can be used for biodiesel production despite the fact that the yield is relatively low. The lowest yield is 35.20% using microwave power 300 W with 1 % CaCO_3 synthesis as catalyst and the reaction time of 2 minutes. The highest yield is 65.36 % using microwave power 300 W with 1 % eggshell as catalyst and the reaction time of 10 minutes. CaCO_3 can be calcined into CaO, which is another catalyst for biodiesel.

Acknowledgments

This work is financially supported by the Ministry of Research, Technology, and Higher Education of the Republic of Indonesia (KEMENRISTEKDIKTI) under the scheme of Penelitian Dasar Unggulan Perguruan Tinggi (PDUPT) 2018.

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