

# Al-alginate as acid catalyst for FAME synthesis using electrolysis process

Rudy Syah Putra<sup>1,2\*</sup>, and Tasyrifatur Rahma<sup>1</sup>

<sup>1</sup>Department of Chemistry and <sup>2</sup>New and Renewable Energy Research Group, Universitas Islam Indonesia, Jl. Kaliurang km. 14 Yogyakarta 55584, Indonesia

**Abstract.** A novel solid acid catalyst, which was prepared from sodium alginate and aluminum chlorides and characterized by SEM-EDS, XRD and FT-IR spectrometry. The catalyst was used for the synthesis of fatty acid methyl ester (FAME) via (trans)esterification reaction using electrolysis process. Purity and FAME components of biodiesel were measured by GC-MS. The results showed that the aluminum-alginate prepared in a cheap and easy way exhibited high catalytic activity. FAME conversion from used-cooking oil was obtained by 93.82% in the presence of 10 wt.% of catalyst dosage upon refluxing for 4 h of methanol and oil in a molar ratio of 6:1.

## 1 Introduction

Fossil fuel is now widely recognized as unsustainable resource. The limitations of fossil fuel had demanded to look for other energy sources that can be renewable. A candidate as renewable energy to substitute petroleum is biodiesel. Biodiesel is a mixture of fatty acid methyl esters (FAME) produced from free fatty acids via esterification and/or (trans)esterification with methanolysis process. Various biodiesel standard namely flash point, cold filter plugging point, sulphur content, and oxygen consumption of biodiesel are improved as compared with that of fossil-based diesel. Moreover, it was found out that biodiesel used as engine fuel can effectively reduce the emission of poisonous gases [1-2].

Typically, conventional biodiesel produces straight forwardly by means of homogeneous alkaline catalyst, such as NaOH and KOH. For high proportion of free fatty acid (FFA) and water containing in a low quality of used-cooking oil, homogeneous alkaline catalyst are markedly sensitive to FFA, leading to catalyst losses, saponification problem, lowering the efficiency and economics of the overall process [3]. The synthesis of biodiesel from used-cooking oil (UCO) by using electrolysis process had been reported by Guan and Kusakabe with the yield > 97% [4]. These methods have some advantages to produce biodiesel from used-cooking oil. For example, the high water content in the oil can be directly used in electrolysis process (i.e. the electron transfer emerged by the formation of H<sup>-</sup> and OH<sup>-</sup> ions) is derived indirectly as a catalyst in esterification and transesterification reaction at room temperature [5]. In this study, the enhancement of FAME synthesis from used-cooking oil using electrolysis process by Al-alginate as heterogeneous acid catalyst.

## 2 Methodology

### 2.1 Chemical and equipment

Used-cooking oil was provided from home industry activities. High grade of methanol, NaCl, AlCl<sub>3</sub>.6H<sub>2</sub>O and co-solvent THF were purchased from Merck, Germany and food grade of sodium alginate was purchased from local food industry in Yogyakarta province of Indonesia. Fig. 1 shows an electro-catalytic cell (250 ml) contains two graphite electrodes (Ø 0.8 mm x 130 mm) that were separated by a distance of 2.5 cm [5]. The qualities of used-cooking oil were determined by physicochemical analysis and the results were shown in the Tab. 1

**Table 1.** Physicochemical properties of used-cooking oil

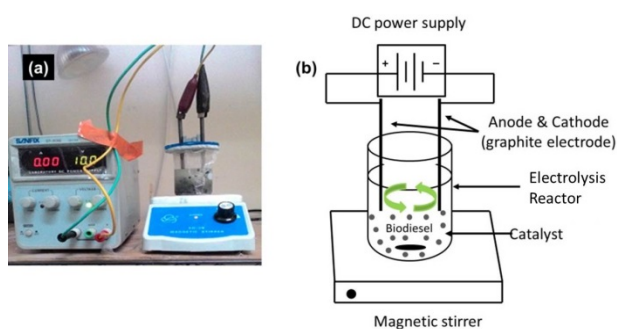
Oil	FFA (%)	Refractive index	$\rho$ , Kg/L	Moisture, %
UCO	1.89	1.462	0.956	0.099

### 2.2 Preparation and characterization of catalyst

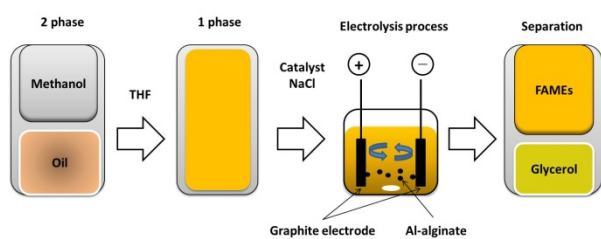
A novel solid acid catalyst of Al-alginate, which was prepared from sodium alginate and metal chlorides according to publish paper by Qiuyun et al. [6]. Briefly, 2 g of sodium alginate was added to 100 mL of 100 °C distilled water, followed by stirring at 700 rpm until a clear viscous solution was obtained. Then, the viscous solution was added drop wise into 100 mL of 0.1 M

\* Corresponding author: [rudy.syahputra@uii.ac.id](mailto:rudy.syahputra@uii.ac.id)

AlCl<sub>3</sub> solution. The resulting solution system was stirred vigorously for 13 h to form a white of Al-alginate complex. Finally, the Al-alginate granules were washed until a neutral pH and then dried at room temperature for 48 h. The X-ray diffraction (XRD) patterns of the catalyst were measured using a Bruker D2 Phaser diffractometer system (equipped with a monochromatic Ni filter using CuK $\alpha$  radiation). Fourier transform infrared (FTIR) spectra was recorded on a Perkin Elmer Spectrum Two equipped with the universal ATR. FTIR spectrophotometer without using the KBr disc technique (4000-400 cm<sup>-1</sup>) and Scanning electron microscope (SEM) was obtained from a Phenom ProX desktop equipped with an energy dispersive spectroscopy (EDS) detector to characterize the microstructures and chemical properties of as-prepared Al-alginate material. In addition, a PinAAcle 900 Perkin Elmer measured the sodium and aluminum concentration in the prepared alginate.



**Fig. 1.** Electrolysis reactor set up (a) and illustrated functional apparatus in the reactor (b).



**Fig. 2.** Steps on FAME synthesis using electrolysis process and Al-alginate as catalyst

### 2.3 Catalytic testing

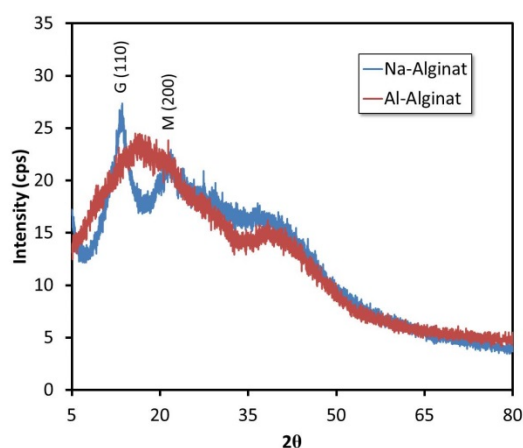
Effect of catalyst amount (5, 10 and 15 wt.%) was evaluated on the conversion of FAME from used-cooking oil. The reaction mixture was agitated using magnetic stirrer. The electrolytic cell was filled by 70 ml of reaction mixture containing used-cooking oil, methanol, THF as a co-solvent [5]. The methanol-to-oil molar ratio was 24:1, co-solvent-to-methanol molar ratio was 1:0.25 and NaCl concentration was added on the basis of oil weight (0.56 wt.%) of the entire reaction mixture, respectively. The electro-catalytic was carried

out at room temperature using a constant voltage of 18.6 V for 2, 4, 6 h. Fig. 2 shows a step of optimization process for biodiesel production in this study. The FAMES phase were separated from glycerol and the product was washed with deionized water to remove the residual inorganic components. FAME conversion and unreacted oils remaining in the product was measured by GC-MS.

## 3 Results and Discussion

### 3.1 Catalytic characterization

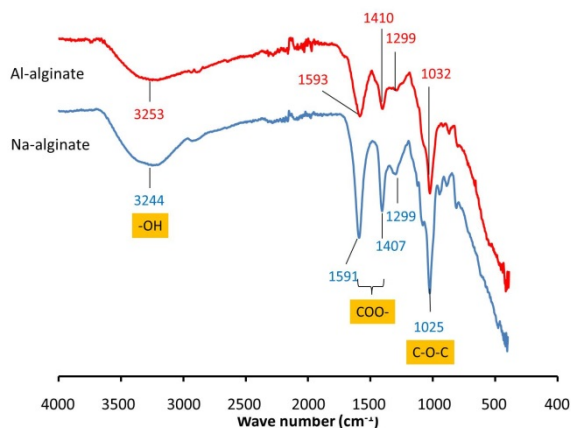
Fig. 3 shows the XRD patterns of Na-alginate and the Al-alginate catalyst. Crystalline of sodium alginate was formed by strong interaction between the alginate chains through intermolecular hydrogen bonding [7]. The degree of crystallinity of the alginate was estimated by using the software DIFFRAC.EVA version 4.0. The Na-alginate presents a 18.6% crystallinity degree; and the Al-alginate, a 11.0%. Three diffraction peaks at 2 $\theta$  values 13.5°, 22° and 39° were observed for sodium alginate due to the reflection of their (110) plane from polyguluronate unit, (200) plane from polymannuronate and the other from amorphous halo [8]. In case of Al-alginate sample, the intensity of diffraction peaks of alginate decreased notably which indicates that the formation of aluminum oxyhydroxide particles on the grid of alginate affected the crystalline nature of sodium alginate. In other words, this procedure is successful in the preparation of the aluminum-alginate catalyst. The broadening of the diffraction peaks in all prepared alginate indicates nature of the sample.



**Fig. 3.** XRD diffractogram of Na-alginate (a) and Al-alginate (b)

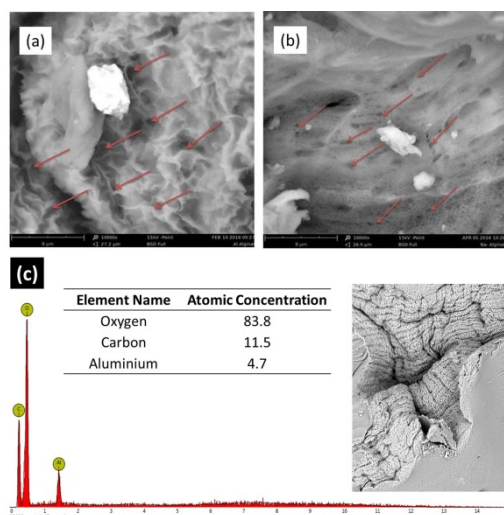
Fig. 4 shows the FTIR spectra of Na-Alginate and Al-Alginate. The FTIR spectrum of Na-alginate shows the characteristic peaks at 3242 cm<sup>-1</sup> (OH<sup>-</sup> stretching) [9], peaks at 1591 and 1407 cm<sup>-1</sup> (COO<sup>-</sup> asymmetric and symmetric stretching), 1081-1024 cm<sup>-1</sup> (C-O-C antisymmetric stretching), and carboxyl and carboxylate at peaks about 1000 to 1400 cm<sup>-1</sup> [10]. In FTIR spectra of

Al-alginate, the asymmetric band of carboxylate ion has shifted to lower frequencies from 1591  $\text{cm}^{-1}$  to 1593  $\text{cm}^{-1}$ , and the hydroxy band of sodium alginate has shifted from 3242  $\text{cm}^{-1}$  to 3253  $\text{cm}^{-1}$ , because of the interaction between sodium alginate and AlCl<sub>3</sub> [9]. The band at 1025  $\text{cm}^{-1}$  was given by the guluronic units [11] in all the spectra.



**Fig 4.** FTIR spectra of Na-alginate and Al-alginate

The results from SEM revealed that bigger micro architecture of Al-alginate formed than Na-alginate in terms of their pore sizes (Fig. 5). A wide and porous surfaces layer of the Al-alginate give a large catalytic activity so that increased the performance of esterification in electrolysis process. EDS spectra of the composite films clearly show the characteristic peaks of aluminum (AlCl<sub>3</sub>) used for the synthesis along with notable amounts of carbon and oxygen from alginate backbone.



**Fig. 5.** SEM images showing the topology of Al-alginate (a) and Na-alginate (b) in x10.000 magnificient. The red arrow indicated the porous surface in the material. Al-alginate images and its corresponding EDS analysis (c).

The quantify of ion exchange process between sodium alginate and the contacting AlCl<sub>3</sub> solution was measured by an atomic absorption spectrometer. Initial

sodium concentration in the Na-alginate was 0.00247 mg/Kg. While, aluminum concentration was 0.0648 mg/Kg in the Al-alginate. Therefore, the ratio of ion exchange between aluminum to sodium was 26.23 Al : Na.

### 3.2 FAME synthesis with electrolysis

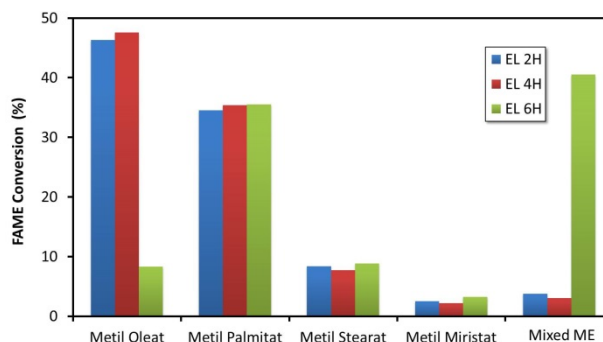
#### 3.2.1 Influence of electrolysis time

Tab. 2 shows the FAME yield increased by the increase of electrolysis time. It can be seen that the FAME yield rapidly reached up to 95.94% within 2 h. After 6 h of reaction, the conversion rate leveled off as the products attained a near-equilibrium composition as high as 96.51%. However, the optimum reaction time for electrolysis was 4 h since total FAME yield was the highest (see Fig. 6) and it was more efficient for electrolysis time. Fig. 6 shows typical of FAME conversion from used-cooking oil in the electrolysis process. When the FFA present in the used-cooking oil, the electrolysis process were successively subjected to esterification reaction with methanol, the high to low FFA conversion (%) from used-cooking oil was as follow oleic acid > palmitic acid > stearic acid > myristic acid, respectively.

**Table 2.** Effect of electrolysis time on the FAME yield without catalyst

Electrolysis time (hours)	FAME yield (%)
2	95,54
4	95,94
6	96,51

In this regards, the electrolysis was conducted at room temperature (25 °C) without catalyst.



**Fig. 6.** FAME conversion from used-cooking oil in the electrolysis process without catalyst.

### 3.2.2 Influence of catalytic loading

Tab. 3 shows the effects of wt.% catalyst to oil ratio on the FAME yield using electrolysis. The biodiesel yield increased by the increase of catalyst loading. It was discovered that excellent conversion rates (as high as 93.76% were obtained in 10 wt.% of catalyst loading since total FAME yield was the highest (see Fig. 7). This fact shows that aluminum-alginate was an appropriate solid catalyst that has a very high reactivity to catalyze esterification reaction. This study showed that the Al-alginate catalyst could be a good candidate to enhance the electrolysis conversion of cheap feed-stocks containing high amount of FFAs (such as inedible oils [12], waste vegetable oils [13], waste cooking oils [14], etc.) into biodiesel.

**Table 3.** Effect of catalyst loading on the FAME yield in electrolysis process

Catalyst loading (wt.%)	FAME yield (%)
5	87,55
10	93,76
15	93,82

In this regards, the electrolysis was conducted at room temperature (25 °C) in 4 hours process.

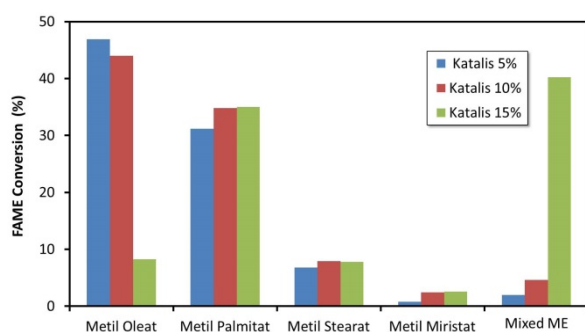


Fig. 7 FAME conversion from used-cooking oil in the electrolysis process enhanced by catalyst

## 4 Conclusions

The enhancement of FAME yield from the (trans)esterification of used-cooking oil using electrolysis process with Al-Alginate as acid catalyst had already evaluated. High catalyst concentration (10 wt.%) with 4 hours of electrolysis time at room temperature was required in order to get a high FAME yield as much as 93.82%. Future works will need to explore high specific catalytic surface of Al-Alginate aiming to enhance the catalyst in the electrolytic biodiesel production.

## Acknowledgement(s)

Authors would like thank to Ministry of RISTEK-DIKTI, the Republic of Indonesia for financial support through Penelitian Produk Terapan 2017. Furthermore, additional support from AIPT program 2016 of Universitas Islam Indonesia is gratefully acknowledged.

## References

1. Ng J H, Ng H K, Gan S. J. Applied Energy. 90(1): 58-67 (2012)
2. Ng H K, Gan S. J. Applied Thermal Engineering. 30(16): 2476-2484 (2010)
3. Kayser. H. Pienko, F. and Maria P.D. Fuel. 116:267-272 (2014)
4. G. Guan and K. Kusabe. Chem. Eng. 153:159–163 (2009)
5. R.S. Putra. P. Hartono and T. Julianto. Energy Procedia. 65:309–316 (2015)
6. Z. Qiuyun. L.H.Q. Wenting. L. Xiaofang. Z. Yuping. X.Wei. Y. Song. China Petrol. Process. Petrochem. Tech..14: 2033–2043 (2013)
7. D. Fang. Y. Liu. S. Jiang, J. Nie. and G. Ma. Carbohydrate Polymers, 85 (1): 276–279 (2011)
8. Fabia J. Ślusarczyk C. Gawłowski A. Fibres Text. East. Eur. 13(5): 114-117 (2005)
9. G. Lawrie, I. Keen, B. Drew, A. Chandler-Temple. L. Rintoul, P. Fredericks. and L. Grøndahl. Biomacromolecules. 8 (8), 2533–2541 (2007)
10. M.G. Sankalia, R.C Mashru. J.M. Sankalia. V.B. Sutariya. AAPS PharmSciTech (6) 2: E209-E222 (2005)
11. Pereira. L. Sousa. A. Coelho. H. Amado. A.M. and Ribeiro-Claro. P.J.A. Biomolecular Engineering. 20: 223-228 (2003)
12. R. Wang, M.A. Hanna, W.W. Zhou, P.S. Bhadury. Q.Chen, B.A Song. S. Yang. Bioresource Technology.102(2):1194-1199 (2011)
13. Ceclan R E, Pop A, Ceclan M. Chemical Engineering Transactions, 29: 1177-1182 (2012)
14. Gan S Y, Ng H K, Chan P H, et al. Fuel Processing Technology, 102, 67-72 (2012)