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Conversion of Methyl Ester from Used Cooking Oil: the Combined Use of Electrolysis Process and Chitosan

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Abstract

The conversion of fatty acid methyl ester from used cooking oil with a organocatalyst chitosan by using electrolysis process had been investigated. Fatty acid methyl ester yield was influenced by electrolysis time (2 h, 4 h, and 6 h), chitosan mass ratio (5 wt. %, 10 wt. % and 15 wt. %), co-solvent type (i.e. Tween 80 and Tetrahydrofuran) and methanol-to-oil molar ratio. The evaluation of the process was followed by GC-MS, determining the fatty acid methyl ester ratio at different operation variables. The results showed that the conversion of fatty acid methyl ester from used-cooking oil was obtained for 35.4 % in 4 h electrolysis process. When the combined use of electrolysis process and 10 % chitosan was applied in 4 h, the conversion of fatty acid methyl ester increased up to 59.1 %. However, the optimum conversion process was achieved without use of co-solvent.

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Keywords: Chitosan; electrolysis; fatty acid methyl ester; used cooking oil

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Nomenclature	
FAME	a type of fatty acid ester that is derived by transesterification of fats with methanol. The molecules in biodiesel are primarily FAMES, usually obtained from vegetable oils by transesterification
FFA	a fatty acid is a carboxylic acid with a long aliphatic tail (chain), which is either saturated or unsaturated. Most naturally occurring fatty acids have a chain of an even number of carbon atoms, from 4 to 28. Fatty acids are usually derived from triglycerides or phospholipids. When they are not attached to other molecules, they are known as "free" fatty acids
THF	an organic compound with the formula $(CH_2)_4O$. The compound is classified as heterocyclic compound, specifically a cyclic ether. It is a colorless, water-miscible organic liquid with low viscosity. THF has an odor similar to acetone. It is mainly used as a precursor to polymers. Being polar and having a wide liquid range, THF is a versatile solvent
Tween 80	an organic compound with the formula $C_{64}H_{124}O_{26}$. A nonionic surfactant and emulsifier often used in foods and cosmetics. This synthetic compound is a viscous, water-soluble yellow liquid
h	a symbol of hours
wt. %	a symbol of percentage of weight

1. Introduction

Biodiesel is a renewable energy source that can be made from vegetable oils, animal fats and waste cooking oils, and therefore is non-toxic, biodegradable and essentially free of sulphur and other harmful emissions [1]. Various production methods of biodiesel have been developed. Typically, conventional biodiesel is straightforwardly produced by means of homogeneous alkaline catalyst, such as NaOH and KOH [2-4]. For low quality used-cooking oil containing a high proportion of free fatty acid (FFA) and water, homogeneous alkaline catalyst are markedly sensitive to FFA, leading to saponification problem, catalyst losses, lowering the efficiency and economics of the overall process. To circumvent these issues, some industrial chemical plants incorporate an acid-catalyzed pre-step to firstly form of fatty acid methyl ester (FAME) from these FFA. Later on, the base-catalyzed step carries out the actual transesterification-based biodiesel synthesis [5-7].

Another approach to solve the problems derived from the presence of FFA is the incorporation of heterogeneous catalyst that could catalyze both trans- and esterification reactions at the same time. In these cases, saponifications observed in homogeneous alkaline catalysts would be overcome, thus leading to a simplified and cleaner process set-up (e.g. no need of a pre-step of acid-catalyzed esterification) [5,6]. Furthermore, there would not be need of setting an acid-catalyzed pre-step for esterifications, simplifying the process set-up as well. This aspect is of utmost importance for second generation biodiesel, whereby impure oils (e.g. used-cooking oil) containing significant amounts of free fatty acid (up to 5 wt.%) may be present [5,6].

The assessment of chitosan as a basic heterogeneous catalyst has been tested for (trans)esterification-based reaction for biodiesel synthesis. Some articles reported the adsorption on chitosan of different catalysts, namely inorganic oxide (e.g. CaO) [8] and heavy metals (e.g. Cu^{2+} and Co^{2+}) [9]. Direct use of chitosan as heterogeneous organocatalyst for biodiesel synthesis has been reported by other researchers [2,10]. For these reports, chitosan-cryogels are typically formed, aiming to enhance the specific surface of the catalyst and the amount of accessible amino groups for an adequate catalysis [2]. Advantageous, a modified chitosan-cryogels can be used directly as catalyst for transesterification of different oil (e.g. triolein and soybean oils) with methanol, with an operational frame (100 to 150) °C and with yields of up to 90 % FAME, bigger percentage that corresponding to the unmodified chitosan used in conversion of FAME from used-cooking oil (e.g. 88.4 % at 60 °C) [10].

The synthesis of biodiesel from used-cooking oil by using electrolysis process has been first reported by elsewhere researcher [1]. Simplify process of these methods have some advantages to produce biodiesel from used-cooking oil. For example, the high water content in the feedstock can be directly used in electrolysis process i.e.

hydrolysis of water at anode and cathode {see Eqs. (2) and (3)} and the process run at room temperature. Also, the electron transfer emerged by the formation of H^+ and OH^- ions in the mixture was derived indirectly as a catalyst of transesterification process of oil. Moreover, direct use of chitosan as heterogeneous organocatalyst combined with electrolysis process might contribute to enhance the biodiesel synthesis. For example, the esterification and transesterification reaction takes place in one stage due to the formation of H^+ and OH^- ions either in the electrolysis process or involved the catalysis reaction in the chitosan {see Eqs. (2), (3), and (6)}. Therefore, high FFA content in the oil does not cause undesirable side reactions such as saponification problems and catalysis losses. Furthermore, the combined electrolysis process and heterogeneous chitosan catalysts might simplify downstream processing operations such as separations, neutralizations, etc., as well as enabling the reuse of the catalyst with a diminished waste formation. Fig. 1 shows a step of biodiesel production from used-cooking oil using electrolysis method through the enhancement of catalytic reaction of chitosan.

In this study, an electrolysis method for the production of FAME from used-cooking oil at room temperature by the enhancement of basic heterogeneous catalyst, chitosan was carried out. Also, the effect of electrolysis time and chitosan weight, and additional of various co-solvent on the FAME yield were investigated.

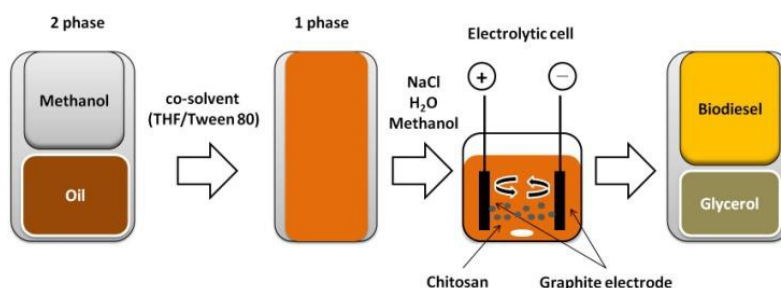


Fig.1 Schematic steps of biodiesel production from used-cooking oil by using electrolysis method through the enhancement of catalytic reaction of chitosan.

2. Material and method

2.1. Chemicals

Used-cooking oil was provided from home industry activities around of Universitas Islam Indonesia (UII) area. Methanol, NaCl, Tween 80 and THF were purchased from Merck, Germany and Chitosan (farmaceutic grade) was purchased from UPT BPPTK LIPI Gunung Kidul, Yogyakarta. The analytical methods used to determine the characteristics of the oil are referred to SNI (National Standard of Indonesia) recommendation. The following physical properties of the used-cooking oil were determined: density (pycnometry), refractive index (open prism refractometry), free fatty acid (alkaline titration), and water content (different weight), respectively. The physical properties of used cooking oil were shown in Table 1.

Tabel 1. Physical properties of used cooking oil

Parameters	Value
Density ($g \cdot mL^{-1}$)	0.828
Refractive index	1.462

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Table 1. Continued

Parameters	Value
Water content (%)	2.0
FFA (%)	0.488

2.2. Electrolysis methods

Fig. 2 shows an electrolysis cell consist of two graphite electrodes (\varnothing 0.8 mm x 130 mm) separated by 15 mm distance. The electro-assisted cell in 250 mL capacity was filled with 65 mL of reaction mixture containing used cooking oil, methanol, Tween 80, chitosan, deionized water and NaCl as a supporting electrolyte. The methanol-to-oil molar ratio and co-solvent-to-methanol molar ratio were adjusted to 24 : 1 and 100 : 1, respectively. NaCl concentration based on the oil weight was 0.56 wt.%. Based on the weight of the entire reaction mixture, 2 wt.% of deionized water was added. Electrolysis was carried out at room temperature using a constant voltage of 18 V (DC power supply, Marysol mp-7812). The effect of electrolysis time (2 h, 4 h and 6 h) and chitosan weight (based on oil weight, 5 wt.%, 10 wt.% and 15 wt.%) were evaluated for the conversion of FAME from used cooking oil. The reaction mixture was agitated using magnetic stirrer.

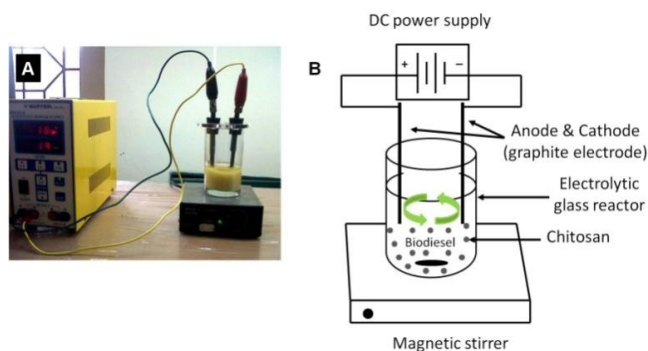


Fig.2. Photograph images of electrolytic cell (A) and designed apparatus for biodiesel production (B), respectively.

2.3. Methyl ester analysis

The product of ME phase was washed with deionized water to remove the residual inorganic components. Concentration of produced ME and unreacted oils remaining in the product were analyzed using a gas chromatography mass spectrophotometer (GC Agilent 6890N, MS Agilent 5975B MSD, USA). The sum of MEs and unreacted glycerides were represented by peaks separated in the chromatograph. The ME yield in the product was calculated by total sum of percentage area of ME in each product.

3. Results and discussion

3.1. Enhancement of electrolysis with base catalyst

The first use of a simple electrolysis method to produce biodiesel from corn oil and used-cooking oil at room temperature has reported by Japan researcher [1]. This novel process exhibited a high fatty acid FAME yield

(> 97 %) even in the presence of a relatively high water content (as high as 2 wt.% of the total reaction mixture) when using a low concentration of sodium chloride (< 1.2 wt.% based on oil weight). As shown in Eqs. (1) and (2), when the reaction mixture containing NaCl and H₂O was introduced into the electrolysis cell, the evolution of chlorine or oxygen might occur on the anode. On the other hand, hydroxyl ions and hydrogen were formed on the cathode (Eq. 3). The transesterification of triglycerides (TG) with methanol (Eq. 5) requires an active species, methoxide ion (CH₃O⁻), in order to obtain reasonable FAME yield.

Anodic reaction:



Cathodic reaction:



Methoxide ion can form when methanol reacts with hydroxyl ion (OH⁻) in the Eq. (4), and once formed; the methoxide ion is strongly nucleophilic and attacks the carbonyl moiety in glyceride molecules to produce ME and glycerol (Eq. 5). As a result, biodiesel fuel could be produced using this electrolysis method.

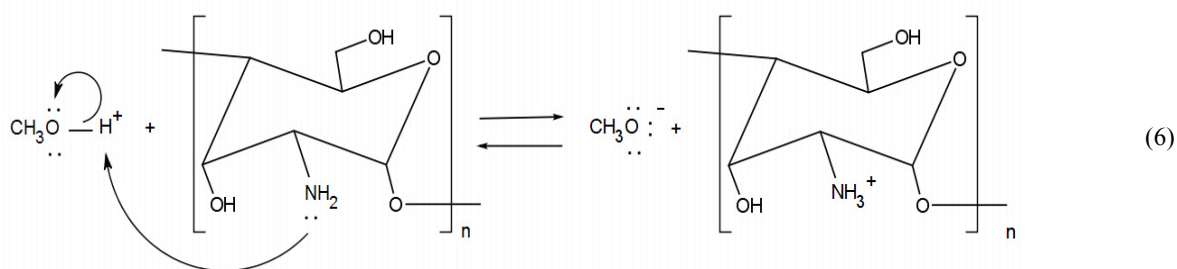
Proton transfer reaction:



Transesterification reaction:



Chitosan was employed in electrolysis process considering the potential enhancement of basicity of the system upon methoxide ion formation to produce biodiesel catalytically, through transesterification of used-cooking oil with methanol [2,10]. The presence of free amino groups-NH₂ on the chitosan backbone with unpaired electron in the nitrogen has expected as a base catalyst which is react with methanol to produce methoxide ion (Eq. 6). Therefore, the concentration of methoxide ions in the mixture has increased with the increase of chitosan concentration.



3.2. Effect of electrolysis time and chitosan weight

Fig. 3 shows the FAME yield has increased with the increase of electrolysis time. High FAME yield was reached 34.2 % for 4 h electrolysis process in the presence of 10 wt.% chitosan. Further increased the electrolysis time in 6 h, the conversion of FAME decreases to 5.1 %. Fig. 3 shows that further increased the chitosan weight do not affect to increase the FAME yield. On other hand, the FAME yield was as low as 10.9 % when the electrolysis was proceed in non-polar co-solvent (i.e. Tween 80) without use of chitosan (Fig. 4). However, when THF (i.e. polar aprotic solvent) was added in the transesterification of used-cooking oil, a high FAME yield (94 %) obtained in 2 h with

electrolysis process [1]. In addition, when electrolysis was not involved, the FAME yield as high as 88.4 % obtained from transesterification of used-cooking oil using 1 g chitosan [10]. The increasing of chitosan weight 2 g to 3 g a line with a reduction of FAME yield (76.1 % to 72.5 %). Having these consideration in mind, these results were the proof-of-concept a synergetic of using chitosan as an enhancement catalyst in the electrolysis process for (trans)esterification-based biodiesel synthesis.

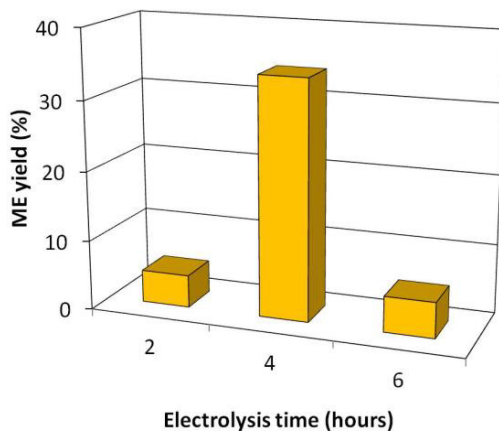


Fig. 3 Effect of electrolysis time on the FAME yield in the presence of 2 wt.% -water and 10 wt.% chitosan in Tween 80 (100 : 1, co-solvent-to-methanol molar ratio)

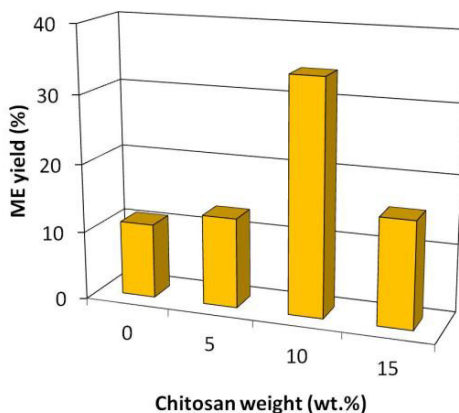


Fig. 4 Effect of chitosan weight on the FAME yield in the presence of 2 wt.% water and Tween 80 (100 : 1, co-solvent-to-methanol molar ratio) by the electrolysis process in 4 h.

3.3. Effect of co-solvent

Fig. 5 shows the effect of co-solvent on the FAME yield in the presence of 2 wt.% water and 10 wt.% chitosan by the electrolysis process in 4 h. The time when no co-solvent was added, a two-phase solution dispersed with methanol droplets was formed. However, the production of FAME by combined use of electrolysis and chitosan catalysis occurred, and the FAME yield was as high as 59.1 %, bigger percentage that corresponding the electrolysis

process in chitosan free system (Fig. 4). This fact can be attributed to the high electrical conductivity in the solution of co-solvent free system [1]. Similar results using THF as co-solvent for the heterogeneous transesterification of triglyceride has presented a reduction of 36 % and 18 % in the reaction yield compared to the system without co-solvent [11,12.] When ethanol and acetone were used as co-solvent, the authors observed an enhancement of about 15 % and 10 % on the yield of the reaction. These differences might be associated to the interaction between the chitosan and the solvent. In this case, as THF (polar aprotic solvents) are more adsorbed on the polar surface of heterogeneous catalyst, a competing for active sites on chitosan, tended to reduce the activity for both hydrolysis and transesterification [12] and being involved in side reactions with methanol [11]. In contrast, the presence of Tween 80 as a co-solvent, the conversion of triglyceride decreased, probably due to a non-polar and low kinematic viscosity has inducing in low catalytic activities of chitosan for transesterification and hydrolysis. Therefore, this result has concluded that the electrolysis reaction might be a dominance process compared with catalytic reaction

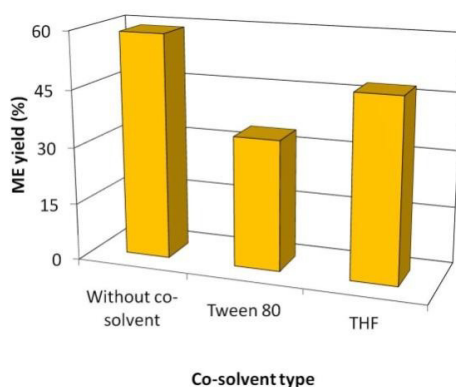


Fig. 5 Effect of co-solvent on the FAME yield in the presence of 2 wt.% water, 10 wt.% chitosan and co-solvent-to-methanol molar ratio (100 : 1) by the electrolysis process in 4 h.

4. Conclusion

The combined use of electrolysis process with chitosan as basic heterogeneous catalyst can be used to produce biodiesel-type transesterification from used-cooking oil containing relatively high content of FFA and water. The ME yield using this method is dependent on the polarity of co-solvent, electrolysis time and chitosan weight. Overall results deliver a promising concept for using electrolysis process through the enhancement of catalytic reaction of chitosan.

Acknowledgements

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