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Enhanced Electrocatalytic Biodiesel Production with Chitosan Gel (Hydrogel and Xerogel)

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Abstract

The production of biodiesel from used-cooking oil using the enhancement of electrolysis process with chitosan-gel (i.e. hydrogel and xerogel) as a base catalyst had been investigated. Previously, the optimized variables were evaluated by using soybean oil as a feedstock before using used-cooking oil on the biodiesel production. Biodiesel yield was influenced by chitosan-gel to oil mass ratio (0, 5, 10 and 15 wt. %), and electrolysis time (30, 60, 90 and 120 mnts). The methyl ester yields were determined by GC-MS on these operation variables. The results showed that the conversion of biodiesel increased with the increase of chitosan-gel to oil ratio thereby giving 98.0% yields respectively for 15 wt. % hydrogel, meanwhile in the similar mass ratio of chitosan-xerogel giving 94.5 wt. % yields, respectively. Contrary results showed that when electrolysis time increased, the conversions of biodiesel decrease thereby giving 99.4%, 98.5%, 97.1%, 98.2% yields respectively for 30, 60, 90 and 120 mnts. These optimized processes, e.g. 30 mnts and 15 wt. % catalyst, were then applied to convert biodiesel from used-cooking oil giving 90.3% for chitosan-hydrogel and 93.1% for chitosan-xerogel as a base catalyst, respectively.

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Keywords: Biodiesel; Chitosan-gel; Catalyst; Electrolysis; Used-cooking oil

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1. Introduction

Today petroleum is the largest source of energy consumption when compared with other energy sources so that today the world faces an energy crisis. The limitations of petroleum had demanded Indonesia to look for other energy sources that is renewable. Biodiesel is one of candidate as a substitute energy source for petroleum [1-2]. Used-cooking oil is abundant in Indonesia since regular consumption of Indonesian people for palm oil. Used-cooking oil can be converted into biodiesel through (trans)esterification reaction. The conversion of used-cooking oil into biodiesel has given three advantages in one namely economic value, waste management solutions, and produce a biodiesel.

The synthesis of biodiesel from used-cooking oil using simple electrolysis process has been first reported elsewhere [1]. Simplify these electrolysis processes have some advantages. For example, high water content (> 2%) in the feedstock supports the electrolysis, i.e. hydrolysis of water at anode and cathode emerged the electron transfer (formation of H+ and OH- ions) in the mixture was derived indirectly as an acid and base catalyst of (trans)esterification in one-pot process. Thus high FFA content in the oil does not cause undesirable side reactions such as saponification problems and catalysis losses. In addition, all the processes have been run in room temperature [3-4].

The assessment of direct use of chitosan as a heterogeneous catalyst has hardly been tested for (trans)esterification-based reaction for biodiesel synthesis [5-8]. Also, chitosan was used as an enzyme-immobilizing carrier to enhance of bio-catalytic esterification of lauric acid with lipase from Candida rugosa [9]. In this regard, chitosan was incorporated with graphene oxide in order to increase the superior mechanical integrity and low thermal conductivity. Putra et al. [3-4] reported the enhancement of electrolysis using chitosan as an organo-catalyst in the synthesis of biodiesel had yielded a low biodiesel as much as 59.1%. Thus, it is needed further study to increase the enhancement of catalyzed electrolysis process using chitosan as a base catalyst in the biodiesel production.

In this study, the chitosan-gels (i.e hydrogel and xerogel phase) were formed, aiming to enhance the specific basicity of catalyst with the amount of accessible amino groups for an adequate catalysis process. Thus, chitosan-gel were conducted as catalyst for (trans)esterification of oil with electrolysis process as well, using soybean oil and methanol as substrates (Scheme 1). The expected results would be a part of the development technology for the industrial-scale production of small and medium enterprises for biofuel. Fig. 1 shows a step of optimization process for biodiesel production.

Scheme 1 Chitosan-gel-catalyzed (trans)esterification of soybean oil and methanol to afford methyl ester
2. Material and Method

2.1. Chemical and equipment

Used-cooking oil was provided from home industry activities and soybean oil was obtained from supermarket. High grade of methanol, NaCl, and co-solvent THF were purchased from Merck, Germany and chitosan (pharmaceutical grade) was purchased from UPT BPPTK LIPI Gunung Kidul, Yogyakarta. As illustrated in Fig. 2, an electrolysis cell (70 ml) contains two graphite electrodes (Ø 0.8 mm x 130 mm) that separated by a distance of 15 mm. The electrolysis was carried out at room temperature (25 °C) using a constant voltage of 10 V.

2.2. Preparation of chitosan-gel

The preparation of chitosan-hydrogels and xerogels imply several steps. The first step is the formation of a hydrogel by reaction of a polymer solution with a gelling agent. Previously, the chitosan-hydrogel was prepared using a modified protocol reported in the literature [10]: 1 g chitosan (from shrimp shells, >75% deacetylated) was dissolved in 50 ml acetic acid solution (5.5 mM). The solution was then slowly precipitated into an aqueous NaOH solution (1 M) until appropriate of chitosan-hydrogel was formed. After 2 h, the chitosan-hydrogel was sintered and
washed with deionized water until constant pH was reached. The resulting chitosan-hydrogel was stored in water overnight and washed with deionized water before sintering. Chitosan-xerogel was prepared by atmospheric drying of hydrogel at room temperature. Volume shrinkage of the gel was obtained after drying.

2.3. Biodiesel synthesis

Previously, soybean oil was used as a feedstock to obtain optimal condition before implemented to used-cooking oil for biodiesel production. Fig. 3 shows a typical process of biodiesel production in this study. Effect of electrolysis time and catalyst amount (wt. %) were evaluated for the conversion of biodiesel from soybean oil. The reaction mixture was agitated using magnetic stirrer. The electrolytic cell was filled with 70 ml of reaction mixture containing soybean oil, methanol, THF as a co-solvent, and NaCl as a supporting electrolyte. The methanol-to-oil molar ratio and co-solvent-to-methanol molar ratio were adjusted to optimize the process, and NaCl concentration was added on the basis of oil weight of the entire reaction mixture, respectively.

![Typical biodiesel production in this study](image)

2.4. Product analysis

The product of biodiesel phase was separated from glycerol and washed with deionized water to remove the residual inorganic components. Concentration of produced ME and unreacted oils remaining in the product were analyzed using GC-MS. The sum of ME and unreacted glycerides were represented by peaks separated in the chromatograph. The biodiesel yield in the product was calculated by total sum of percentage area of ME in each product.

3. Results and Discussion

3.1 Effect of catalyst loading

In this study, effects of catalyst loading on the biodiesel yield were first investigated for the (trans)esterification of soybean oil. The use of soybean oil which is more unsaturation per triglyceride expected led to such high ME yields [10]. In this regards, the electrolysis process was conducted at room temperature (25 °C) in 120 mins. Tab. 1
shows the effects of wt. % catalyst to oil ratio on the biodiesel yield. The biodiesel yield increased with the increase of catalyst loading either in chitosan-hydrogel or chitosan-xerogel as a catalyst.

High concentration of methoxide ions present in the solution with the increase of catalyst amount. In this regard, chitosan was employed in electrolysis process considering the potential enhancement of basicity of the system upon methoxide ion formation to produce biodiesel catalytically [3-4,10]. However, experiments conducted at higher chitosan-gel loading led to severe swelling and mass-transfer limitation problems. Importantly, chitosan is known to be a widely malleable material, from which layers, beads or other different form and textures can be created in a straightforward way [11]. In this study, 15 wt. % of catalyst to oil ratio had produced a high yield of biodiesel as much as 98.02% and 94.51% respectively for chitosan-hydrogel and chitosan-xerogel. Detail catalytically mechanism of chitosan to enhance the electrolysis process was described elsewhere [3-4].

<table>
<thead>
<tr>
<th>Chitosan-gel</th>
<th>Catalyst / oil ratio, wt. %</th>
<th>Total ME, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogel</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>96.88</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>97.64</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>98.02</td>
</tr>
<tr>
<td>Xerogel</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>22.00</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>16.97</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>94.51</td>
</tr>
</tbody>
</table>

3.2 Effect of electrolysis time

Tab. 2 shows the biodiesel yield a quiet decreased with the increase of electrolysis time. In this regards, the electrolysis process was carried out at room temperature (25 °C) in 15 wt. % chitosan-hydrogel as catalyst to oil ratio. The increasing of electrolysis time leads to increase the solubility of glycerol in the product which had reduced the conversion of ME in the mixture [12]. In addition, swelling effects of chitosan-gel had considered in the increase of electrolysis time, leading some rheological problem in the reaction set-up [10]. Therefore, 30 mins electrolysis time had considered enough to produce a high yield of biodiesel. It may be expected that a better catalyst design of chitosan might certainly improve electrolysis process, providing more competitive synthetic performance of biodiesel.

Based on those optimized processes condition, the conversion of biodiesel from used-cooking oil has obtained as much as 99.3 % with chitosan-hydrogel and 93.1 % with chitosan-xerogel as a base catalyst. Importantly, this result had fulfilled the minimum criteria for industrial production [10]. One of the potential advantages of using heterogeneous catalysts with electrolysis process in the production of biodiesel from used-cooking oil is that esterification (trans)esterification may be conducted at the same time, provided that such heterogeneous catalysts and electrolysis may catalyst both reactions.
Table 2. Effect of electrolysis time on the biodiesel production

<table>
<thead>
<tr>
<th>Electrolysis time, mins</th>
<th>Total ME, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>99.39</td>
</tr>
<tr>
<td>60</td>
<td>98.52</td>
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<tr>
<td>90</td>
<td>97.08</td>
</tr>
<tr>
<td>120</td>
<td>98.17</td>
</tr>
</tbody>
</table>

4. Conclusion

The biodiesel yield from the (trans)esterification of soybean oil was used to optimize the enhancement electrolysis process using chitosan-gel as a base catalyst in the conversion of biodiesel from used-cooking oil. For the soybean oil, high catalyst concentration (15 wt. %) with short electrolysis time (30 mins.) was required in order to get a high ME yield. Similar results were obtained when using used-cooking oil as a feedstock of biodiesel production. Future works will need to explore high specific catalytic surface of chitosan-gel aiming to enhance the catalyst in the electrolytic biodiesel production.

Acknowledgements

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