

Carbon material@Chitosan composite as catalyst on the synthesis of FAME from used-cooking oil with electro-catalytic process

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Abstract. The conversion of fatty acid methyl ester (FAME) from soybean oil with a carbon@chitosan composite as alkaline catalyst using electrolysis process had been investigated. The carbon was added onto chitosan through sol-gel method. Carbon material@chitosan, featured with high electrical conductivity and large surface area and Scanning electron microscopy equipped with an energy dispersive spectroscopy (EDS) detector was performed to characterize the microstructures as-prepared alcogels composite. The evaluation of the synthesis process was followed by GC-MS, determining the fatty acid methyl ester (FAME) ratio at different operation variables (e.g oil:MeOH molar ratio at 1:6, THF:MeOH ratio at 1:1 v/v, 10 V and 60 mins). The results showed that the incorporation of carbon resulted in an observable change in the porous structure and an obvious increase in the conductivity strength. When compared with graphite@chitosan composite as catalyst, the carbon@chitosan composite exhibits remarkably FAME yields of 100% in 20 wt.% catalyst loading. The application of those processes was also evaluated when using used-cooking oil as a feedstock of biodiesel production.

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. With a global production of almost 60 million tonnes and a global vegetable oil market share of more than 35% by weight in 2012, palm oil is the most produced vegetable oil in the world [1]. Therefore, the amount of cooking oil consumption impacted directly the increase of use-cooking oil as raw material for biodiesel production. In addition, utilization of used-cooking oil as biodiesel diminishes the problem of contamination, because reusing of these greases can reduce the burden of the government in disposing of the waste, maintaining public sewers, and treating the oil wastewater [2].

The chitosan-catalyzed transesterification of soybean oil had used chitosan gel (i.e cryogel) as alkaline catalyst at high temperature (100-150 °C) was investigated by Kayser *et al.* (2014) [3] led to high FAME yields (up to 90%). Another researcher, Guan and Kusakabe (2009) [4] had used electrolysis process to afford FAME in high yields (> 97%) at room temperature reaction. In addition, the combined use of electrolysis and chitosan had been investigated by Putra *et al.* (2015) [5] with low FAME yields (up to 59.05%). Low yield on these synthesis processes due to lack of chitosan basicity which was influenced by low catalyst surface area and due to lack of electrical conductivity in the



reaction. However, direct use of chitosan as heterogeneous alkaline catalyst combined with electrolysis process had enhanced the biodiesel synthesis. For example, the esterification and transesterification reaction occurring in one step reaction through the formation of H^+ and OH^- ions either in the electrolysis process or involved the catalytic reaction in the chitosan [5]. Therefore, in this study the increasing of FAME conversion from used-cooking oil is proposed using a carbon material@chitosan composite as hydrogel catalyst. The purposes of these studies are to provide high added-value lightweight material with outstanding textural properties, i.e. high surface area, open porosity and electrical conductivity, respectively.

2. Materials 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. Fig. 1 shows an electro-catalytic cell (70 ml) contains two graphite electrodes (\varnothing 0.8 mm x 130 mm) that were separated by a distance of 15 mm. The qualities of pre-treatment of used-cooking oil were determined by physicochemical analysis and the results were shown in the Tab. 1.

The process involves direct filtration of oil using filter paper following absorption process [2]. A 50 g of used-cooking oil was heated until $100^\circ C$ after filtration to remove solid particle from oil. After that, a 5 g of activated carbon was poured into the oil and then stirred for 80 minutes. The mixture was then filtered and the filtrate was measured for physicochemical properties including density, refractive index, water content, and acid number (AN), respectively.

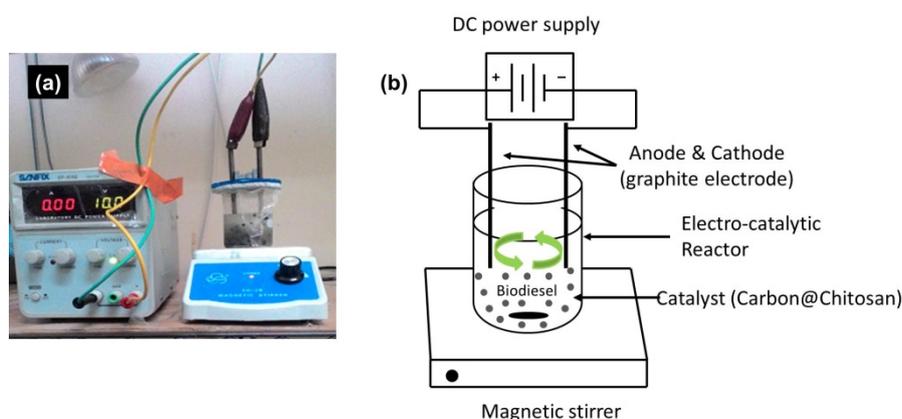


Figure 1. Electro-catalytic reactor set up (a) and illustrated functional apparatus in the reactor (b).

Table 1. Physicochemical properties of oil that was used as a feedstock in the experiment

Oil	Acid number	FFA, %	Refractive index	ρ , Kg/L	Moisture, %
Used-cooking	1.308	0.860	1.461	0.914	0.185
Soybean	0.378	0.263	1.469	0.920	0.217

2.2. Preparation of spherical carbon material@chitosan composite with sol-gel method

In order to evaluate the scope of carbon material@chitosan composite as catalyst, uniform-size spherical hydrogel beads were prepared by adaptation and modified of reported procedures based on the alkaline coagulation of an acidic viscous chitosan solution added using a peristaltic pump equipped with a dropping silicon pipe [6] as illustrated in Fig. 2. Graphite was used as a carbon material that was composited with chitosan as a preliminary study before testing with carbon. The first step was the formation of chitosan hydrogel by reaction of a polymer solution with a gelling agent, 1 g chitosan (from shrimp shells, > 61.4% deacetylated) was dissolved in 50 mL acetic acid glacial solution (1% v/v) and stirred for 15 mins. After that 0.5 g graphite was added into the mixture and continued to be stirred for 24 h. The solution mixture was then slowly precipitated into an aqueous NaOH solution (1 M) until appropriate of graphite@chitosan-hydrogel composite was formed. The carbon@chitosan-hydrogel composite was washed with deionized water until constant pH was reached (pH 6 ~ 7). The resulting graphite@chitosan-hydrogel composite was stored in deionized water before used it as alkaline catalyst in biodiesel synthesis. Similar procedure was also applied when carbon@chitosan composite prepared.

The micro-structures of the produced graphite@chitosan composite samples were characterized using a desktop scanning electron microscope (SEM, Phenom ProX, Phenom-World B.V., The Netherlands) equipped with an energy dispersive spectroscope (EDS) detector. In this regards, the corresponding dried gel beads were prepared by alcogel, a water-to-ethanol solvent exchange (5 steps EtOH/water 100:0) was carried out prior to analysis [7].

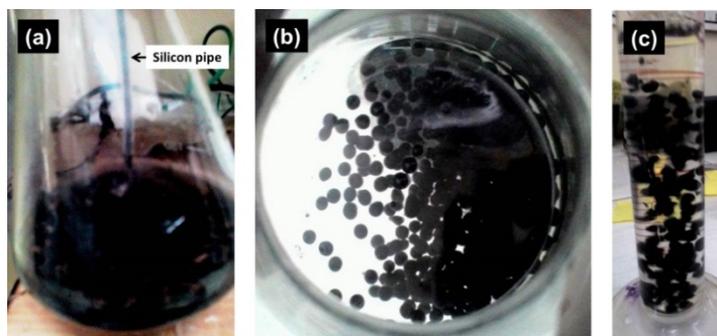


Figure 2. Experimental set-up used for the preparation of spherical graphite@chitosan with an average diameter of 3.0 ± 0.1 mm (a), and macroscopic view of milk-black colour graphite@chitosan beads after maturing (b, c).

2.3. FAME synthesis

Preliminary, soybean oil was used as a feedstock to obtain optimal condition before implemented to used-cooking oil for FAME synthesis. Effect of catalyst amount (10 wt.% and 20 wt.%) were evaluated for the conversion of FAME 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 was 6:1 and co-solvent-to-methanol molar ratio was 1:1, and NaCl concentration was added on the basis of oil weight of the entire reaction mixture, respectively. The electro-catalytic was carried out at room temperature (25 °C) using a constant voltage of 10 V for 60 mins. Fig. 3 shows a step of optimization process for biodiesel production in this study.

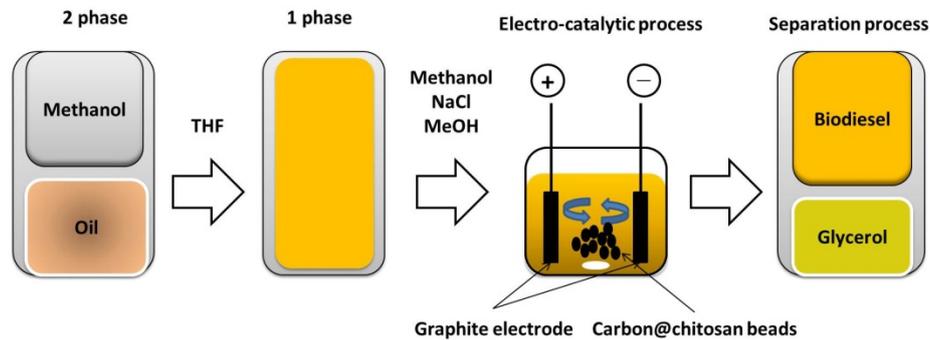


Figure 3. Steps on biodiesel production using electrolysis process and carbon@chitosan beads as catalyst.

2.4. FAME analysis

The biodiesel phase was separated from glycerol and washed with deionized water to remove the residual inorganic components. Concentration of produced FAME and unreacted oils remaining in the product were analyzed using GC-MS (GC-MS QP2010 Plus, Shimadzu Corporation, Japan) equipped with an electron ionization detector (EID) and a capillary column $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ (Restex 5MS). The sum of FAME 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 chromatographic peak of FAME in each product.

3. Results and Discussion

3.1. Composite characterization

The morphology of graphite@chitosan composite was investigated by SEM as shown in Fig. 4. According to the SEM images, Fig. 4a represents the SEM morphology of the prepared graphite@chitosan composite. The SEM image of the composite showed that graphite particles were covered by chitosan gel. Figure 4b shows that the surface of the carbon@chitosan composite was relatively homogeneous and smooth being similar to those from previous reports [8]. In addition, the energy dispersive spectroscopy (EDS) spectra of the graphite@chitosan composite (Figs. 5a and 5b) confirmed the presence of carbon material in the matrix composite.

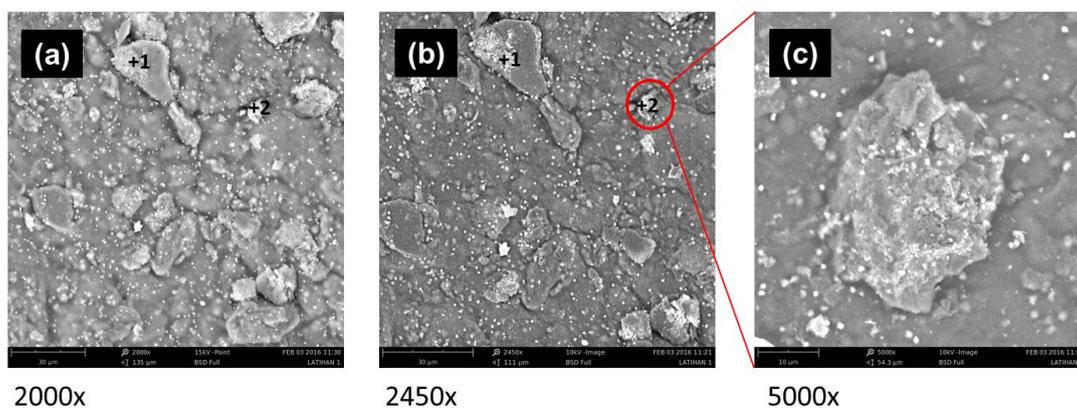


Figure 4. SEM images of graphite@chitosan composite with different magnification.

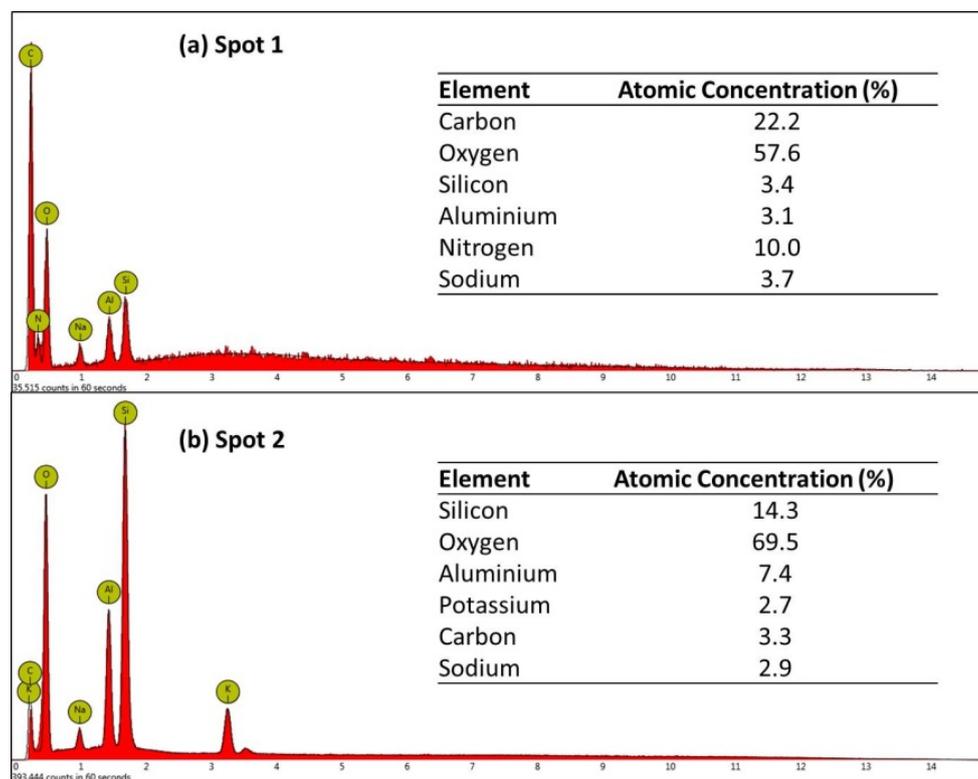


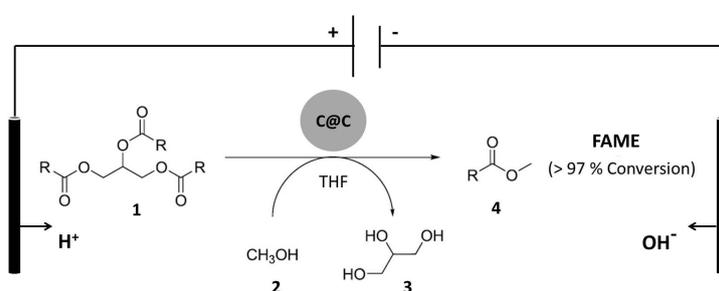
Figure 5. EDS spectra obtained from spot 1 and 2 in the SEM images of graphite@chitosan composite.

3.2 Washing effect of graphite@chitosan composite catalyst

One of the most critical aspects during the evaluation of the carbon material@chitosan composite catalyst is the meticulous washing protocol of the matured beads, thereby ensuring the removal of trapped hydroxyl ions (OH^-) from alkaline solution in the sol-gel process, which otherwise might influence the expected base catalysis by the free amino groups $-\text{NH}_2$ on the chitosan backbone, upon slow diffusion-controlled leaching of OH^- during the reaction [6]. In order to demonstrate this hypothesis, different batches of beads at different pH were prepared by tuning the wash procedure. The exact pH of the filtrate in each case was measured using a pre-calibrated pH meter. The general correlation of the pH of the filtrate with the internal pH of the beads was checked by extensive trituration-dissolution of the beads and measuring the pH of the resulting solution. Tab. 1 shows the correlation between pH of graphite@chitosan composite before and after washed to the FAME product by electro-catalytic process.

Neutral composite afforded 73.0% (Table 1, entry 4) of FAME conversion as well as alkaline composite before washed (Table 1, entry 1), which showed low conversion in the absence of the catalyst in the electro-catalytic process (Table 1, entry 5). In general, no significant improvement was observed by increasing two-fold washing cycle (Table 1, entry 3). However, it was high when neutral pH achieved. Those results indicating that simply the accessible free primary amino groups presented in these hydrogel beads of the native chitosan are active enough to promote satisfactorily the formation of the required methoxide ion (CH_3O^-) intermediate [5,6] under the present hydrogel conditions.

Table 2. Correlation between pH of graphite@chitosan composite before and after washed to the FAME product by electro-catalytic process



Entry	pH	Time (minute)	FAME, %
1	11.98	60	76.1 ^a
2	10.13	60	13.3
3	8.15	60	47.8
4	6.91	60	73.0 ^b
5	-	60	42.2 ^c

Reaction condition: soybean oil used as a feedstock; molar ratio methanol to oil, 6:1; volume ratio THF to methanol, 1:1; mass ratio of catalyst to oil, 10 wt.%; DC voltage in electro-catalytic, 10 V. Result of the composite ^abefore washed and ^bafter 3rd washing cycle. ^cControl experiment in which no catalyst was employed in electro-catalytic process at 18.2 V.

3.3 Electrical conductivity of carbon material@chitosan composite catalyst

Another critical aspect of the carbon material@chitosan composite is the electrical conductivity properties of the matured beads, thereby ensuring enhanced the electrical conductivity of the solution during the FAME conversion. Figure 6 shows the effect of carbon material@chitosan composite on the electrical conductivity of catalyst property. In the electro-catalytic process, a direct proportional to the hydrogen and hydroxyl ions formed at the anode and cathode as well as NaCl concentration enhanced electric current and conductivity of the reaction mixture during electro-catalytic process. Roughly, the electric current increased with the increase in the electrolysis voltage, which resulted in more hydrogen and hydroxyl ions formed on the anode and cathode [4,5]. The hydroxide ions are continuously produced at the cathode and might react immediately with nearby methanol and the oil transesterification reaction happened in methanol phase [4]. As a result, transesterification progressed mainly with the concentrated hydroxide ion that existed near the cathode. While, the electron transfer emerged by the formation of hydrogen ion that existed near the anode was derived indirectly as a catalyst of esterification process of oil (reaction scheme was showed in Tab.1).

The electrical conductivity during electro-catalytic process was also enhanced by the presenting of carbon material in the chitosan gel beads as a composite material. The electrical conductivity was measured in the aqueous media using conductivity meter at room temperature. It was showed that the electrical conductivity of carbon@chitosan higher than graphite@chitosan beads (Fig. 6).

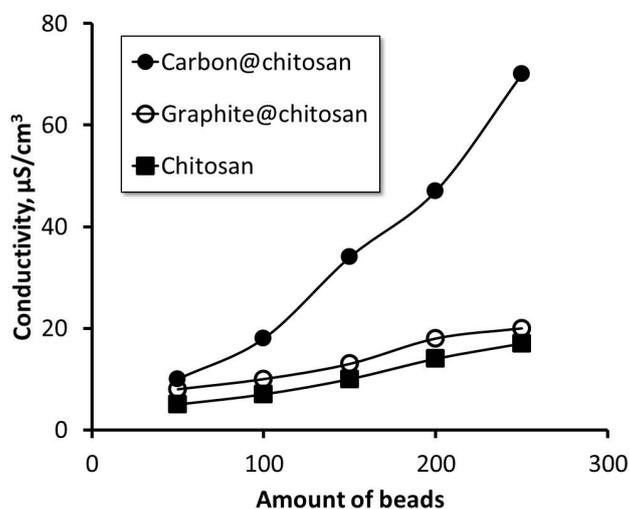


Figure 6. Effect of carbon material on the electrical conductivity of composite catalyst.

3.4 FAME conversion from soybean oil and used-cooking oil

For low quality used-cooking oil containing 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 [8-10]. Therefore, a pre-treatment process to reduce water content (<0.1 wt.%) and FFAs (<2.0 wt.%) are necessary in order to avoid an undesirable side reactions, such as saponification, which could lead to serious problem of product separation and low fatty acid methyl ester (FAME) yield. Tab. 1 shows that the pre-treatment process of used-cooking oil which used activated carbon as an adsorbent was able to reduce of water content (< 0.1%) and FFA (< 0.2%) in the oil significantly, which the results were similar to those from previous report [2]. In this study, effects of catalyst loading on the biodiesel yield was preliminary investigated for the transesterification of soybean oil before apply in used-cooking oil. The use of soybean oil which was more unsaturation per triglyceride expected led to such a high FAME yields [3].

Tab. 1 shows FAME conversion from oil (i.e soybean oil and used-cooking oil) did not reflect with the increasing of catalyst loading, but it was more affected by the carbon material@chitosan type as a composite catalyst. When compared with graphite@chitosan composite, the carbon@chitosan composite exhibits remarkably FAME yields of 100% in 20 wt.% catalyst loading when using soybean oil as feedstock. However, there were no good results when the process was used in the conversion of biodiesel from used-cooking oil.

Table 3. FAME conversion from oil using carbon material@chitosan type

Catalyst type	wt.% loading	FAME yield, %	
		Soybean oil	Used-cooking oil
Carbon@chitosan	10	0.00 ^a	- ^b
	20	100	33.6
Graphite@chitosan	10	73.0	37.6
	20	0.00 ^a	0.00 ^a

Reaction condition: molar ratio methanol to oil, 6:1; volume ratio THF to methanol, 1:1; DC voltage in electro-catalytic, 10 V; pH composite washed 6.91.
^aExperiment was repeated ($n = 2$) in which no FAME yield in the product confirmed. ^bThere is no experiment employed in this regards.

4. Conclusion

The incorporation of carbon material resulted in an observable change in the porous structure and an obvious increase in the electrical conductivity strength of composite as catalyst. Carbon@chitosan catalyst composite exhibits remarkably FAME yields of 100% in 20 wt.% of catalyst loading when using soybean oil as feedstock compared with graphite@chitosan composite as catalyst. In contrast, those results were not applied well on the FAME conversion from used-cooking oil.

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