Activation of Coconut Shell - Randu Wood Biochar and Its Use as Heterogeneous Catalyst Support for Biodiesel Production

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Abstract. In the last decade, biodiesel has been considered as one of attractive biofuels in function of replacing fossil-based diesel fuel and concerning on reduction of greenhouse gas release. For biodiesel production, the use of heterogeneous catalyst is a challenge to minimize problems related to the use of homogeneous catalyst. One of potential heterogeneous catalyst is activated carbon-based catalyst. This study investigated the effect of activating agents (hydrochloric acid and sulfuric acid), its concentration (0.5, 1.0, 1.5 and 2.0 N) and activation time (1.5, 3.0, 4.5 and 6.0 h) on iodine number of activated biochar (from coconut shell and Randu wood). The results showed that the highest iodine number (749.14 mg/g) was obtained from coconut shell biochar activated by sulfuric acid at concentration of 2 N and activation time of 6 h. Moreover, BET analysis of the best activated biochar resulted 30.88 m^2/gcat of surface area, 3.26 x 10^{-2} cm^3/g of total pore volume and 2.11 nm of average pore radius. The performance test of this potassium-impregnated activated biochar in batch transesterification reaction (palm oil-methanol) presented 29.44 % of biodiesel conversion.

1. Introduction

In the last decade, biodiesel is one of attractive biofuels in function of replacing fossil fuels which has been growing down in production [1]. In addition, the environmental concerns caused by the increasing level of CO_2 in the atmosphere has led to speed up the development of biodiesel production [2]. Biodiesel is known as a mixture of fatty acid methyl esters (FAMEs) generated from the reaction of fatty acid in renewable natural feedstocks and short-chain alcohol in the presence of catalyst [3]. It has several advantages, i.e. renewable, biodegradable, less toxic and environmentally friendly [4]. Currently, biodiesel is derived from some oil crops, such as palm oil [5], sunflower oil [6], jatropha oil [7] and soybean oil [8], because of their availability. For improving the economic value, biodiesel is also produced from low-cost feedstocks [9], such as used cooking oil [10] and palm fatty acid distillate [11]. Moreover, several studies have started to exploit microorganism as biodiesel feedstock, such as

microalgae [12]. By the fact, a lot of lipid-rich feedstocks in the world makes biodiesel potential to be developed [13].

Biodiesel synthesis requires catalyst to accelerate the reaction. The common catalyst used is homogeneous alkaline catalyst such as NaOH and KOH, which have high catalytic activity and affordable in price. Nevertheless, this condition results many problems: (i) corrosive to the equipment; (ii) difficulty in separation step; (iii) more wastewater production [14]. In order to minimize these problems, the use of heterogeneous alkaline catalyst is proposed. Besides, heterogeneous catalyst can be regenerated to be used again as catalyst after impregnation. However, the active site of catalyst has possibility to be leached seriously and perform as homogeneous catalyst [15]. It results problems in reducing the heterogeneous catalytic activity and removing leached catalyst from biodiesel [16].

Among the heterogeneous alkaline catalyst, activated carbon has been shown as one of potential catalyst support for accelerating the transesterification reaction. Activated carbon has been widely used as catalyst supporter in various industrial and environmental applications. Activated carbon has characteristics: (i) high surface area; (ii) durable in high pressure and temperature; (iii) chemically stable [17]. Many researchers have been conducted for studying several carbon-based heterogeneous alkaline catalysts. Fadhil et al. [18] reported methanolysis of bitter almond oil using potassium acetate loaded on activated carbon. Baroutian et al. [19] studied potassium hydroxide catalyst loaded on palm shell activated carbon for producing biodiesel from palm oil. Wan and Hameed [20] used activated carbon supported calcium oxide catalyst to transform palm oil into biodiesel.

There are two steps for producing activated carbon: carbonization and activation. Carbonization is a process for synthesizing carbon in the form of solid, such as pyrolysis by using thermal in air limitation or no air condition [21]. Solid carbon will be formed by heating hydrocarbon materials at temperature of 400 – 600 ^{o}C. After formation of solid carbon, activation treatment, physical and/or chemical, is needed to enlarge pores by breaking hydrocarbon bond or oxidizing surface molecules so the characteristics will change. Physical activation can be applied by using heat in the presence of vapor and CO_2 gas flow. Whereas chemical activation is carried out by using chemicals, which is called activator, such as HCl and H_2SO_4.

This work presents the activation comparison of biochar synthesized from coconut shell and Randu wood as heterogeneous catalyst support in biodiesel production by using iodine number analysis. The effect of activating agents (hydrochloric acid and sulfuric acid), its concentration (0.5, 1.0, 1.5 and 2.0 N) and activation time (1.5, 3.0, 4.5 and 6.0 h) on iodine number of activated biochar (from coconut shell and Randu wood) were investigated. Moreover, the BET surface area analysis was conducted on the best activated biochar (represented by the highest iodine number).

2. Experimental

2.1. Materials preparation

Materials used in this research were coconut shell and Randu wood biochar obtained from Yogyakarta, Indonesia. These biochar were reduced in size and then sieved at 20-30 mesh. Hydrochloric acid (37 %), sulfuric acid (≥98 %), potassium iodide (≥ 99.5 %) and sodium thiosulfate pentahydrate (≥ 99.5 %) were produced by Merck. Meanwhile, distilled water was manufactured by UD. Jaya Santosa, Yogyakarta, Indonesia.

2.2. Biochar activation

The sieved biochar was then activated by using acid solution (HCl and H_2SO_4) in batch reactor with stirring rate of 300 rpm. The biochar was put into 100 ml of acid solution at desired concentration (0.5, 1, 1.5 and 2 N) for various residence times (90, 180, 270 and 360 minutes).

2.3. Analysis of iodine number

Iodine number is defined as milligram amount of iodine which is adsorbed by one gram activated carbon. Highly ability of activated carbon to adsorb iodine means it has larger surface area. After activation was

finished, activated biochar was separated from the acid solution using filter paper and was then dried at 110 ^{o}C overnight. 0.5 g of dried activated biochar was put into 30 ml of 0.1 N potassium iodide solution and then stirred at stirring rate of 300 rpm for 15 min. The solution was separated between activated biochar and filtrate using centrifuge. 10 mL of filtrate was diluted with 30 mL of distilled water and then titrated with standardized sodium thiosulfate solution. Hereafter, the iodine number was calculated using Equation 1.

$$Iodine\ number = \frac{126.9\times(V_1-V_2)\times N}{W} \quad (1)$$

where, V_1 : volume of standardized sodium thiosulfate needed for titrating distilled water
V_2 : volume of standardized sodium thiosulfate needed for titrating diluted filtrate
N : normality of $Na_2S_2O_3$ solution
W : mass of activated carbon

2.4. Analysis of surface area by Brunauer–Emmett–Teller (BET)

Based on the analysis of iodine number, the best activated biochar was then analyzed the specific surface area of by Brunauer–Emmett–Teller (BET) method. This method determined the surface area of solid materials by nitrogen adsorption-desorption. Moreover, BET analysis also provided representation of pore size and pore volume of activated biochar.

2.5. Performance test

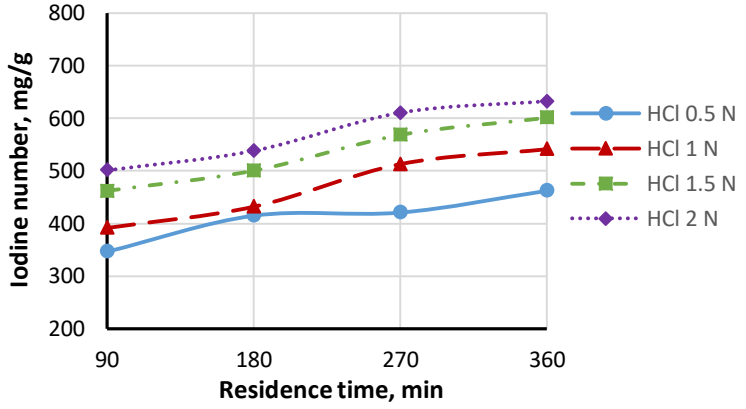
Furthermore, the best activated biochar was performed to produce biodiesel in batch stirred reactor. Selected activated biochar was firstly prepared to be basic catalyst by impregnating potassium. The impregnation procedures of potassium on activated biochar was presented in previous paper by Pradana et al. [22]. Before tested in transesterification process, the solid or heterogeneous catalyst was characterized using BET and Atomic Absorption Spectroscopy (AAS) method. The prepared catalyst was then used to drive transesterification of palm oil and methanol. The steps of transesterification and separation process, as conducted by Pradana et al. [22], were carried out at 60 ^{o}C of temperature, 6:1 of methanol-oil molar ratio, and 700 rpm of stirring rate for 4 h. At the end, the conversion was determined using Equation 2 by evaluating the bounded glycerol in biodiesel sample. G_T was presented as total glycerol content and G_F was presented as free glycerol content.

$$X = \frac{\left|\left(G_T - G_F\right)_{feed} - \left(G_T - G_F\right)_{sample}\right|}{\left(G_T - G_F\right)_{feed}} \quad (2)$$

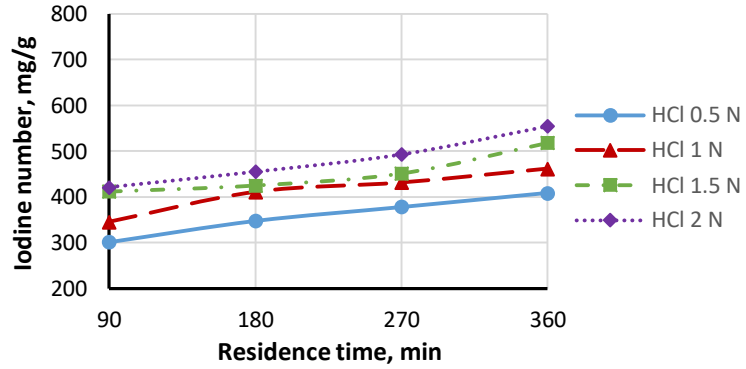
3. Results and Discussion

3.1. Effect of hydrochloric acid as activating agent

Figure 1(a) and (b) show the relation between iodine number of activated carbon from coconut shell and Randu wood, respectively, at various concentrations of hydrochloric acid (HCl) and residence times of activation step. Generally, the increase of HCl concentration and activation time were followed by iodine number increase. The highest iodine number of coconut shell activated carbon was 632.15 mg/g, obtained at 2 N of HCl concentration and 360 minutes of residence time. At the same condition, the highest iodine number of Randu wood activated carbon was reached (544.99 mg/g). This phenomena occurred because the higher concentration of HCl and the longer residence time of activation removed more impurities and opened the pores, resulting higher surface area (represented by higher iodine number).



(a)

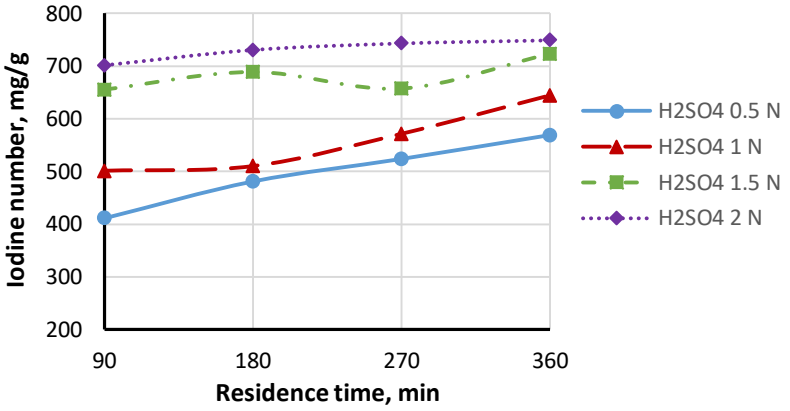


(b)

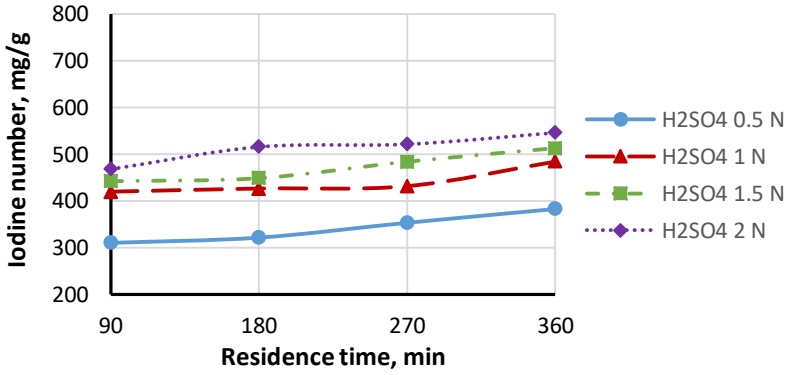
Figure 1. Effect of HCl concentration and residence time on iodine number of activated carbon from: **(a)** coconut shell [23]; and **(b)** Randu wood [24]

3.2. Effect of sulfuric acid as activating agent

Figure 2(a) and (b) show the relation between iodine number of activated carbon from coconut shell and Randu wood, respectively, at various concentrations of sulfuric acid (H_2SO_4) and residence times of activation time. These trends of H_2SO_4 performance as activating agent were similar with HCl, in which the increase of iodine number was proportionally affected by the more concentration of H_2SO_4 and activation time. Based on the results, the highest iodine number (749.14 mg/g) was obtained at 2 N of H_2SO_4 concentration and 6 hours of residence time. Meanwhile, the highest iodine number of Randu wood biochar was 556.64 mg/g. The higher concentration of sulfuric acid, refers to higher acid concentration, would remove tar and other impurities remained in the biochar and closing the pores [25]. As results, the more opened pores of biochar were generated and the adsorption of iodine was increase. Moreover, the longer residence time of activation positively affected on the iodine number. It indicated the higher activated surface area of biochar and the more pores formed.



(a)



(b)

Figure 2. Effect of H_2SO_4 concentration and residence time on iodine number of activated carbon from: **(a)** coconut shell [23]; and **(b)** Randu wood [24]

3.3. Brunauer–Emmett–Teller (BET) Surface Area

The highest iodine number analysis was 749.14 mg/g, resulted from coconut shell biochar activated by sulfuric acid at concentration of 2 N and residence time of 6 h. This activated biochar sample was then analyzed the specific surface area using Brunauer–Emmett–Teller (BET) method. The analysis result showed that the surface area, total pore volume and average pore radius were 30.88 m^2/gcat, 3.26 x 10^{-2} cm^3/g and 2.11 nm, respectively. Based on this result, the activated carbon was classified as very low surface area. However, these results were very possible and prospective to be developed further because of the heterogenic functions of activated carbon in all fields [21].

3.4. Performance Test

After potassium impregnation process, the prepared heterogeneous catalyst was characterized to compare with activated carbon, as reported in Table 1. It showed slight effect of potassium impregnation on the pore size enlargement, surface area and total pore volume addition compared to activated carbon. The impregnation was proven to give additional potassium (5.17 mg/gcat) on activated carbon. Furthermore, the performance test of potassium-impregnated activated biochar resulted 29.44% of biodiesel conversion. Its transesterification showed in low conversion and catalyst activity. This results were still far from the expectation, thus the development of higher activity and durable heterogeneous catalyst was always in the research program.

Table 1. Properties of K/AC catalyst.

Characteristics	K/AC Catalyst	Unit
BET surface area[*)]	34.4660	m^2/gcat
Total pore volume[*)]	4.09 x 10^{-2}	cm^3/gcat
Average pore size[*)]	2.3740	nm
Potassium addition	5.1700	mg/gcat

4. Conclusions

The higher concentration of acid (HCl & H_2SO_4) and the longer residence time of activation removed more impurities and opened the pores, resulting higher surface area (represented by higher iodine number). The results showed that the highest iodine number (749.14 mg/g) was obtained from coconut shell biochar activated by sulfuric acid at concentration of 2 N and activation time of 6 h. Moreover, BET analysis of the best activated biochar reported 30.88 m^2/gcat of surface area, 3.26 x 10^{-2} cm^3/g of total pore volume and 2.11 nm of average pore radius. In performance test, this potassium-impregnated activated biochar drove transesterification of palm oil-methanol to be 29.44% of biodiesel conversion.

Acknowledgements

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