RESEARCH ARTICLE

Comparison of Carbon-Based Heterogeneous Acid Catalyst from Water Hyacinth and Coconut Shell for Biofuel Production

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Abstract

Biofuels are one of the renewable fuels needed to replace fossil fuels. Making biofuels requires an acid/base catalyst to speed up the reaction, one of which is esterification. This study aimed to produce sulfonated carbon from coconut shells and water hyacinth, which was carbonized at 300 °C for 6 h. It was reacted with 96 % sulfuric acid at 150 °C with variations in sulfonation times and variations in sulfonation cycles. The highest acid concentration catalyst results were obtained on water hyacinth raw materials at 1.2 mmol/g and coconut shells at 1.215 mmol/g. The more sulfonation cycles will increase the acid concentration value. The value of the catalyst activity test in the esterification reaction of the water hyacinth catalyst can convert Free Fatty Acid (FFA) better than the coconut shell catalyst. Conversion of esters in the esterification process is 75.28 % in the water hyacinth catalyst and 57.62 % in the coconut shell catalyst. The coconut shell and water hyacinth catalysts were sulfonated in the presence of Fourier Transform Infra-Red (FTIR) absorption spectra at wave numbers 1,035.77 cm^{-1} for the coconut catalyst and 1,033.85 cm^{-1} for the water hyacinth catalyst, which is a strong S=O group. The Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) analysis results indicate that the carbon sulfonate acid catalyst is amorphous. The constant kinetics of the water hyacinth catalyst reaction is 0.0139 L/mol.h, while for the coconut shell catalyst, it is 0.0045 L/mol.h. Coconut shell and water hyacinth raw materials can be used as heterogeneous acid catalysts after sulfonation.

Keywords: Coconut shells, Water hyacinth, Esterification, Sulfonation, Heterogeneous acid catalyst, Sulfonated carbon

Introduction

The growth of industries and population will increase the global energy demand. The primary energy source worldwide is fossil fuels, which raise significant environmental, economic, and social issues. Fossil energy is non-renewable energy. Emissions originating from greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), and nitrogen dioxide (NO_2) result from the combustion of fossil energy. Global warming can be addressed by transitioning from fossil energy to new, renewable energy sources [1-3]. Dependence on the need for fossil fuels can be diverted by utilizing renewable energy, one of which is biodiesel. This renewable fuel has great potential to reduce the use of petroleum fuels. One alternative energy development is biofuel (biodiesel) [4]. Biodiesel is a vegetable-derived fuel from plant/animal oils and other biomass waste [5]. Biodiesel is a new renewable energy source in liquid form that can be decomposed in the environment, sustainable, environmentally friendly, and has low emissions [6-10]. The physical and chemical properties of biodiesel can reduce emissions of carbon monoxide (CO), carbon dioxide (CO_2), and hydrocarbons (HC) [3].

The process of making biodiesel requires the help of a catalyst to speed up the reaction. The process is very slow in biodiesel production without a catalyst and yields lower [4]. Catalysts can accelerate the rate of chemical reactions and lower the activation energy [11]. There are various types of homogeneous and heterogeneous catalysts [4]. The catalyst used can be homogeneous or heterogeneous, either acid or base. The use of homogeneous catalysts has the disadvantage of being difficult to separate, so it is necessary to re-process the separation and cause corrosion [12-14].

Heterogeneous catalysts can be an alternative in the manufacture of biodiesel. Heterogeneous acid catalysts can be used for raw materials with high FFA percentages, in the esterification of FFA and the transesterification of triglycerides in non-food oil feedstocks and used cooking oil waste. They can be easily separated from the resulting products, exhibit selectivity and are recyclable [15]. Several types of heterogeneous acid catalysts have been developed in recent years, including modified zeolite catalysts, silica-based catalysts, and metal oxide mixtures [16-19]. One type of heterogeneous catalyst used is a sulfonated carbon catalyst. The advantage of the sulfonated carbon catalyst is that it is relatively cheaper and is taken from biomass [3]. Liu's *et al.* [20] research successfully produced a sulfonated carbon-based catalyst derived from bagasse. Sulfonated carbon catalysts derived from bioglycerol have produced promising catalyst products [21]. Sulfonated carbon catalysts are synthesized from bamboo in research Tang and Niu [22].

The results showed that sulfonated carbon had the best performance in producing high conversions [23,24]. Carbon catalyst is an alternative catalyst that has thermal stability, good thermal properties, increased activity, and selectivity [25,26].

This coconut shell waste has a high enough cellulose content, so it has the potential to produce heterogeneous acid catalysts in the manufacture of biofuels. Coconut shell has a reasonably high cellulose content, namely 33.61 % cellulose, 19.27 % hemicellulose, 36.51 % lignin and the rest are other substances [27]. Water hyacinth contains 25 % cellulose, 33 % hemicellulose and 10 % lignin [28].

The main focus of this research is the manufacture of sulfonated carbon catalysts from water hyacinth and coconut shells and knowing the activation of the catalyst by esterification and conducting analytical tests through acid concentration tests, SEM, XRD and FTIR analysis to see the spectroscopic results on the sulfonated carbon catalysts and calculate the kinetics of the chemical reaction in the esterification process of oleic acid using carbon sulfonic acid catalyst.

Materials and methods

This research focuses on manufacturing sulfonated carbon-based heterogeneous acid catalysts from coconut shells and water hyacinth as raw materials and 96 % H_2SO_4 as the active catalyst material. The resulting catalyst was then tested for acid concentration, SEM (SEM, Tabletop Microscope-1000, Hitachi, Tokyo, Japan), XRD (XRD, Rigaku/Miniflex 600, Tokyo, Japan), FTIR (Perkin Elmer Spectrum-100), and test the catalyst activity in the esterification process.

Carbonization

The pre-treatment of raw materials from coconut shells and water hyacinth involves cleaning impurities and drying to eliminate moisture content at 105 °C. Carbon production in the carbonization process was carried out at 300 °C. The crushing of charcoal obtained from carbonization is done until it reaches a particle size of 60 mesh. Carbon material from carbonization results is the main raw material in manufacturing sulfonated carbon catalysts. The process occurs in the same way as the raw coconut shells and water hyacinth materials.

Carbon sulfonation

The carbon produced then goes through a sulfonation process using 96 % concentrated sulfuric acid with a process temperature of 150 °C and varying the time of sulfonation and the method of sulfonation used. The sulfonation times were varied to 4, 6 and 8 h. In addition, a variation of the sulfonation cycle was carried out to determine the effect of the sulfonation cycle on the acid density in the catalyst. After the sulfonation process, the sulfonated mixture is cooled using ice cubes to form a precipitate. Then, the mixture is filtered using Whatman filter paper. Filtering aims to separate the catalyst that has been produced. The catalyst is washed using a vacuum pump and neutralized using distilled water until it has a neutral pH.

Acid concentration test

The acid concentration is known by 1st soaking 1 g of sulfonated catalyst with 100 mL of 0.1 M NaCl solution. Then, the phenolphthalein indicator is added and titrated in duplicate with 0.02 M NaOH solution and calculated using the following formula:

$$\text{Concentration acid}_{\text{catalyst}} = \frac{\text{Volume}_{\text{NaOH}} \times \text{Concentration}_{\text{NaOH}}}{\text{Volume}_{\text{HCL}}} \times 1{,}000 \frac{\text{mmol}}{\text{mol}} \times 0.1 \frac{\text{L}}{\text{g}} \qquad (1)$$

Esterification test

Analysis of catalyst activity using the esterification reaction of oleic acid with methanol. The molar ratio of oleic acid: Methanol (1:4) with a catalyst of 5 % by weight of the oleic acid used and also for oleic

acid without a catalyst. The catalyst was activated in the oven for 2 h at 100 °C. The reflux method was used in this esterification, where methanol and catalyst were put into a 2-neck flask and then heated and stirred at 600 rpm to 60 °C. Then add oleic acid and heat at 65 °C for 2 h. Then titrated by NaOH with the addition of phenolphthalein indicator from oleic acid with a catalyst and oleic acid without a catalyst as a comparison. As for how to find out the content of FFA with the equation below [29]:

$$\%FFA = \frac{(\text{Normalitas NaOH} \times \text{Volume NaOH} \times \text{Relative Atomic Mass Oleic Acid})}{(\text{Sample Mass} \times 1000)} \times 100 \% \tag{2}$$

$$\%FFA\ Conversion = \frac{\text{Initial FFA} - \text{Final FFA}}{\text{Initial FFA}} \times 100 \% \tag{3}$$

Results and discussion

Carbonization
The carbonization process is carried out to obtain carbon, which will then be used in the sulfonation process.

Table 1 Carbonization result data.

Raw material	Total weight before carbonization	Total weight after carbonization	% Yield carbon
Coconut shell	138.333	61.0687	44 %
Water hyacinth	97.33	52.682	54 %

Table 1 shows that the carbonization process produces a yield carbon of 44 % in coconut shell and 54 % in water hyacinth. Water hyacinth yield carbon formation is greater than coconut shells because the cellulose content in water hyacinth is higher than in coconut shells [27,28]. The formation of carbon is influenced by the size of the material put into the porcelain crusher. The smaller and denser the size of the material, the faster the overall heat distribution of the material so that the process can run perfectly. The composition of cellulose and lignin in the material can affect the results of the formed carbon content.

Sulfonation
The sulfonation process in forming heterogeneous acid catalysts attaches sulfonate acid groups to carbon groups. Below is a schematic diagram of the sulfonation processes in the formation of heterogeneous acid catalysts:
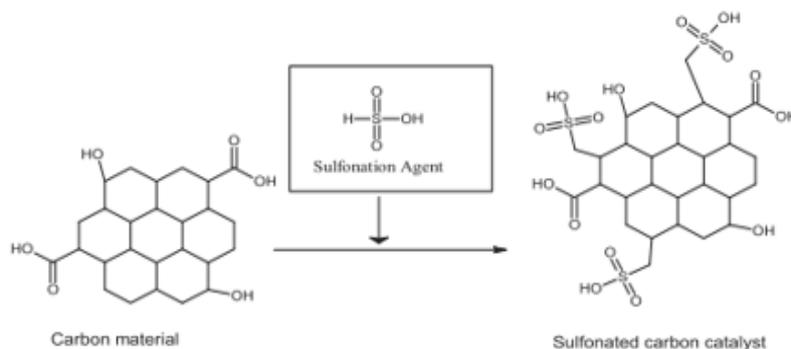

Figure 1 Schematic of the sulfonation process in the formation of heterogeneous acid catalysts [30].

The sulfonation process was carried out at 4, 6 and 8 h. Then, see the difference in value in acid concentration obtained from the sulfonated catalyst.

Table 2 Acid concentration.

Coconut shell		Water hyacinth	
Sulfonation (h)	**Acid concentration (mmol/g)**	**Sulfonation (h)**	**Acid concentration (mmol/g)**
4	0.58	4	0.56
6	0.608	6	0.61
8	0.736	8	0.872

Based on the data obtained, the sulfonation time affects the resulting acid concentration value. The sulfonation process will produce sulfonated carbon with a high brønsted acid [31]. Sulfonate groups and aromatic hydrocarbon groups will bind the charcoal obtained from carbonization and will be replaced by sulfonate acid groups. The longer the sulfonation time, the higher the acid concentration value. Therefore, the optimum sulfonation time is 8 h sulfonation. At optimum operating conditions, it is necessary to compare the acid concentration values of sulfonated catalysts made from water hyacinth and coconut shells.
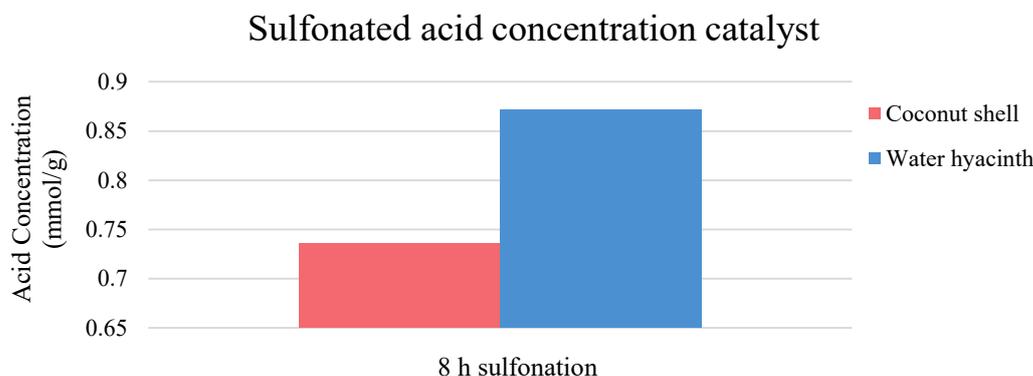

Figure 2 Comparison of acid concentration at the optimum sulfonation time.

Based on **Figure 2**, it can be seen that the acid concentration value of the water hyacinth catalyst is higher than that of the coconut shell catalyst. The acid concentration value for the water hyacinth catalyst was 0.872 mol/g while the acid concentration value for the coconut shell catalyst was 0.736 mmol/g The differences in acid concentration values are due to variations in preparation methods and the properties of the carbon precursor (or support) used in the sulfonation step. The sulfonation of carbon has an acid concentration range of 0.57 to 1.58 mmol/g [31].

Effect of sulfonation cycle

The effect of the sulfonation cycle was taken from the optimum sulfonation time of 8 h, both on carbon catalysts from water hyacinth and coconut shells. **Figure 3** shows the sulfonation cycle's effect on coconut shells and water hyacinths.
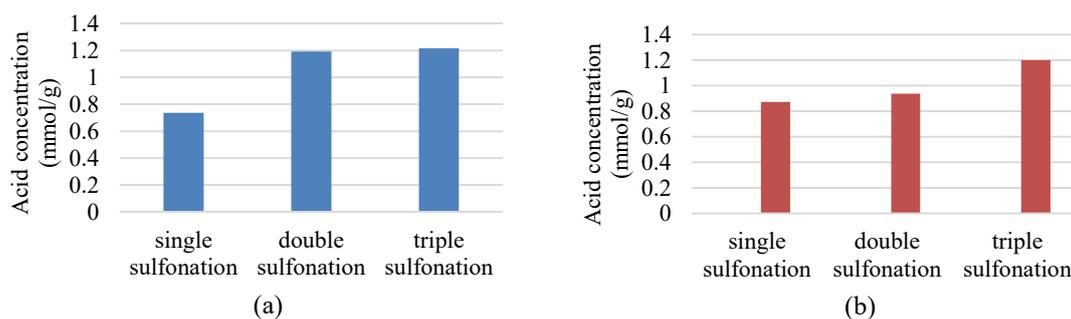
Figure 3 Effect of sulfonation cycle on acid concentration in 8 h sulfonation; (a) Coconut shell catalyst and (b) Water hyacinth catalyst.

Figure 3 shows that the treatment with the sulfonation method at the optimum operating time affected the resulting acid concentration value. The acid concentration value of coconut shell catalyst in single sulfonation, double sulfonation, and triple sulfonation treatment was 0.736, 1.192 and 1.215 mmol/g, while for water hyacinth catalyst, it was 0.872, 0.938 and 1.2 mmol/g. Triple sulfonation treatment on a coconut shell and water hyacinth catalysts achieved the highest acid concentration value. This research demonstrates that sulfonation time and cycles influence the synthesis of heterogeneous acid catalysts. The acid density or concentration on sulfonated carbon catalysts varies in the range of 0.05 - 7.3 mmol/g, depending on the sulfonation method used and the structure of the carbon support framework [31].

FTIR analysis

Sulfonation causes the –SO_3H groups to attach to the carbon atom, which causes the carbon atom to become acidic. With operating conditions at 150 °C, variations in time at 4, 6 and 8 h, and variations in single sulfonation, double sulfonation, and triple sulfonation methods, there was an increase in acid concentration values. The attachment of the –SO_3H group successfully to carbon was carried out by FTIR testing on coconut shell and water hyacinth catalysts, as shown in **Figure 3**. Sulfonated carbon can be identified by carbon materials that have formed covalent bonds with SO_3H groups [31].
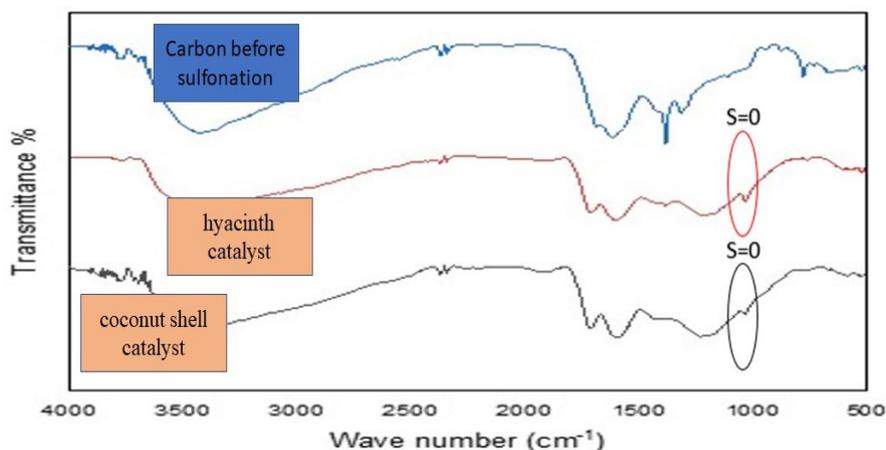

Figure 4 FTIR analysis results.

FTIR analysis results in **Figure 4** showed that the coconut shell and water hyacinth catalysts were sulfonated in the presence of an absorption spectrum at wave numbers 1,035.77 cm^{-1}, for the coconut catalyst and 1,033.85 cm^{-1}, for the water hyacinth catalyst, which was the S=O group showing the sulfonate. The absorption of the S=O group at –SO_3H is at wavelengths 1,020 - 840 and 1,130 - 1,020 cm^{-1} [32].

SEM analysis

Sulfonated carbon catalysts were analyzed using SEM. The results of the morphological analysis of the sulfonated carbon catalyst from coconut shell and water hyacinth are shown in **Figure 5**.
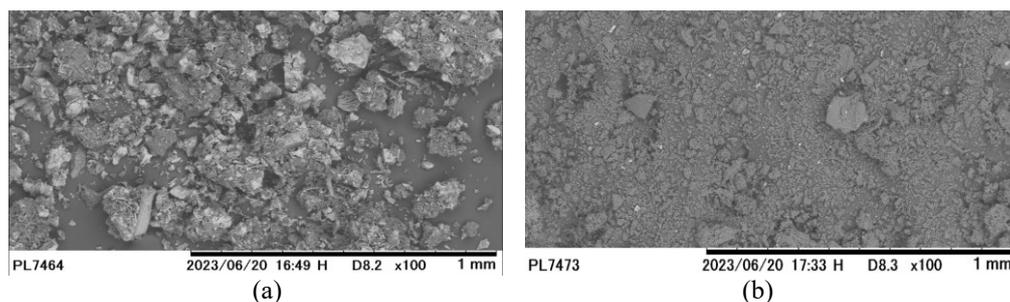
Figure 5 SEM analysis; (a) Coconut shell catalyst (b) Water hyacinth catalyst.

Based on **Figure 5**, the catalyst from coconut shell is larger than the catalyst from water hyacinth because the lignin content in coconut shell is greater than in water hyacinth [27,28]. Surface morphology in catalyst from coconut shell and water hyacinth is irregular, similar to the carbon catalyst produced by Kurji's research. Catalysts derived from water hyacinth are more uniform and fine compared to catalysts derived from coconut shells. Both of these catalysts have irregular and amorphous shapes. The particles in both catalysts tend to agglomerate, forming larger particles, similar to Kurji's research [33].

XRD analysis

The XRD pattern exhibits the amorphous nature of carbon-SO_3H, which is attached in **Figure 6**, showing a single broad peak. The peak for the carbon-SO_3H hyacinth catalyst is observed between 15 and 33 °, while for the carbon-SO_3H coconut shell catalyst, it falls between 15 and 32 °. These peak patterns align with the findings in research by Varkolu, which also indicated peaks in the range of 15 - 30 ° and 35 - 50 °, confirming that the carbon catalyst is amorphous [21].
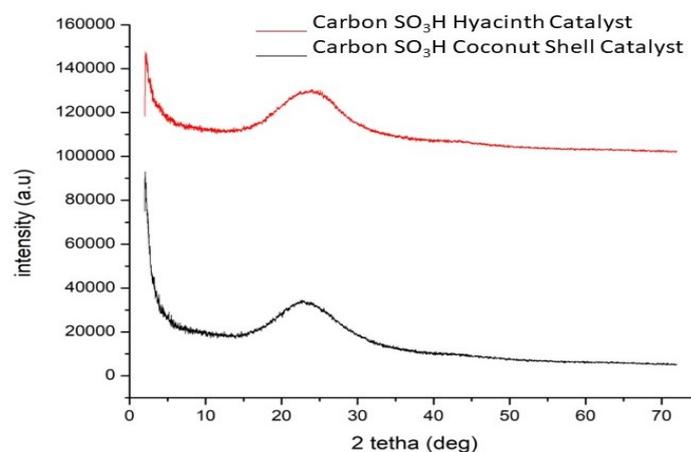

Figure 6 XRD analysis of carbon SO_3H hyacinth catalyst and Carbon SO_3H coconut shell catalyst.

Esterification test

The esterification test serves to determine the activity of the resulting catalyst. The addition of a heterogeneous acid catalyst in the esterification process can help the process of converting oleate with methanol into esters. The following is the esterification result of the resulting heterogeneous acid catalyst, which is attached in **Figure 7**.
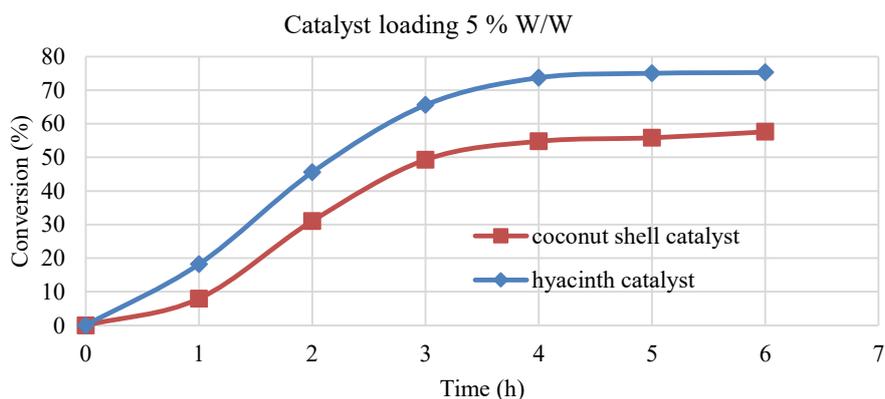
Figure 7 Sulfonated catalyst activity test.

Figure 7 shows that the heterogeneous acid catalyst used to convert oleic acid and methanol to esters is marked by a decrease in the FFA value from the beginning to the end of the process. A catalyst made from coconut shell can convert FFA to 57.62 %, while a catalyst made from water hyacinth can convert FFA to 75.28 %. The conversion results in the esterification reaction showed that the catalyst made from water hyacinth was better used for esterification than that made from coconut shells.

The increase in ester conversion occurred significantly at 0 - 4 h while slowly constant at 4 - 6 h. Constant slow ester conversion indicates that the esterification reaction with the help of heterogeneous acid catalysts is already at the endpoint of the process.

The esterification in this research was conducted using raw oleic acid and methanol materials under the operating conditions of 65 °C, 60 rpm and a reaction time of 2 - 6 h. After 4 h of the reaction, there was no increase in conversion value, indicating that the reaction had reached equilibrium. In a previous study by Hussain and Kumar [34], the esterification of oleic acid yielded a conversion rate of 90 % under the reaction temperature of 65 °C for 2 h using a solid acid catalyst derived from corn cob-H_2SO_4 [34].

Reaction kinetics

Calculating the kinetics of the reaction between the coconut shell catalyst and the water hyacinth catalyst aims to determine the speed of the reaction in the release of –SO_3OH. The reactions that occur are in the 2nd order so that the kinetic constants of the reactions can be seen based on the graphs in **Figure 8**.
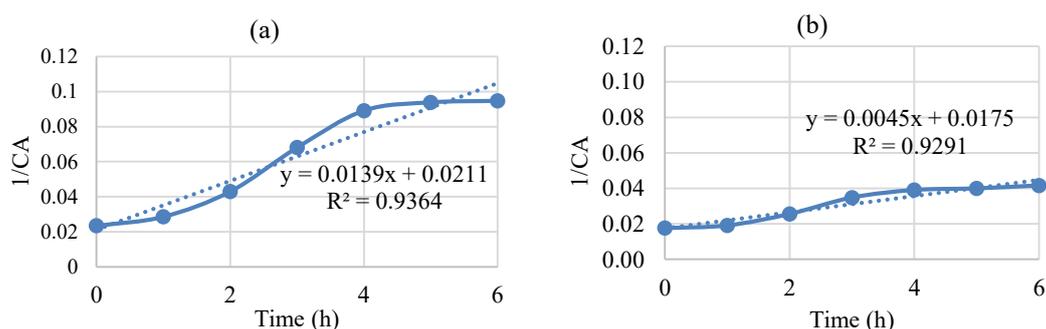

Figure 8 Kinetics constants of the 2nd order; (a) Water hyacinth catalyst reactions and (b) Coconut shell catalyst reactions.

Figure 8 shows the kinetics value of the reaction for the water hyacinth catalyst was 0.0139 L/mol.h, while for the coconut shell catalyst, it was 0.0045 L/mol.h. The kinetic constant value of the water hyacinth reaction rate is greater than that of the coconut shell catalyst, so it is better at converting esters in the esterification process.

Conclusions

Based on the results of this study, it can be concluded that coconut shell and water hyacinth raw materials can be used as heterogeneous acid catalysts. The water hyacinth catalyst was better than the coconut shell catalyst because the lignin composition in water hyacinth is less than in coconut shells. Conversion of esters in the esterification process is 75.28 % in the water hyacinth catalyst and 57.62 % in the coconut shell catalyst.

Sulfonation cycles affect the results of the acid concentration, and the more sulfonation cycles will increase the acid concentration value. FTIR analysis results show the presence of cluster attachment SO_3H on carbon catalysts made from water hyacinth and coconut shells. The coconut shell and water hyacinth catalysts were sulfonated in the presence of absorption spectra at wave numbers 1,035.77 cm^{-1} for the coconut catalyst and 1,033.85 cm^{-1} for the water hyacinth catalyst, which is a strong –S=O group. The SEM and XRD analysis results indicate that the carbon sulfonate acid catalyst is amorphous. The constant kinetics of the water hyacinth catalyst reaction is 0.0139 L/mol.h, while for the coconut shell catalyst, it is 0.0045 L/mol.h.

Acknowledgments

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