Synthesis and Application of a Sulfonated Carbon Catalyst for a Hydrolysis Reaction

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ABSTRACT

Biomass, such as wood waste, is one of the resources that can be potentially converted into a carbon product for catalyst applications. In this study, the sulfonated carbon was obtained through the pyrolysis method for wood waste at the temperature of 350°C, which was later sulfonated through the use of H2SO4 (8N) on the reflux for 4 h. The sulfonated carbon was then analyzed and characterized including its water content, ash content, volatile matter, fixed carbon, iodine adsorption as well as the H+ (acidity) capacity using ammonia adsorptions and functional groups and the Fourier Transform Infra-Red (FTIR) instrument. The catalyst application was carried out during the kempili pulp hydrolysis process using a microwave with the ratio of catalyst to a pulp of 1:1 (5g:5g), with the power conditions of 300, 400, and 600 watt for 3, 5, and 7 min. The results showed that the sulfonated carbon catalyst had water content, volatile matter, ash content, fixed carbon, iodine adsorption as well as the catalyst acidity as much as 3.48%; 11.70%; 4.21%; 84.62%; 690.88 mg/g; and 6.45 mmol/g, respectively with the highest glucose content of 160.83 ppm. The carbon-based catalyst is expected as an alternative catalyst, can be further developed for hydrolysis reactions, and can serve as a green technology product in the future.

ARTICLE INFO

Article History:
Received 27 Sep 2019
Revised 13 Feb 2020
Accepted 01 Jun 2020
Available online 07 Jun 2020

Keywords:
Catalyst;
Glucose;
Hydrolysis;
Sulfonated carbon.

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1. INTRODUCTION

Researches for energy from renewable resources and environment-friendly technologies have been at the top of agenda of many countries these days. The underlying reason for this growing need is due to the limited conventional energy resources so that energy independence is currently the main priority of governments (Kumar et al., 2015). Biomass is a new energy source that is renewable and has attracted the attention of scientists because of its abundance and it can be further explored to produce biofuels and other chemical materials so that it is promising to be developed further for the future (Radhakumari et al., 2014). The kempili wood (Lithocarpus ewyckii Korth) is an unusual wood originated from West Kalimantan which contains lignin, cellulose, and pentosan like any other woods so that this type of wood can be used as an energy source through hydrolysis reactions with a catalyst assisted.

Generally, the catalyst for a hydrolysis process is the acid catalyst (e.g. sulfuric acid and other types of acids) or with the help of specific enzymes. However, there are several disadvantages in the use of the acid compound; there are difficulties in separating the acid from glucose filtrate, because it has a corrosive property, and it is difficult to reuse the acid (Ormsby et al., 2012; Marzo et al., 2012; Suganuma et al., 2008). The use of enzymes is relatively more expensive, especially for a large scale application due to its low stability and difficulties for reobtaining after the reaction.

Consequently, a catalyst modification was undertaken by combining porous materials such as active carbon with acid chemicals such as H₃PO₄ or H₂SO₄ (Khuluk et al., 2019; Nandiyanto et al., 2017), so that the active carbon surface owns acid function groups which can be utilized effectively as a catalyst in the hydrolysis process.

Active carbon has a high surface area with big pore sizes so that it can bind the SO₃H functional group of sulfuric acid and increase the active site of the catalyst so that the active carbon catalyst will be sulfonated. The modified active carbon using heteropoly acid was established by Kumar et al. (2015) was used to hydrolyze starch into glucose. Therefore, it could result in the 94% of glucose without the generation of side products such as levulinic acid and formic acid. Sun et al. (2015) utilized microwave in the cellulose hydrogel hydrolysis process using an acid catalyst so that it obtained glucose of 59.1%.

Based on references, the utilization of the sulfonated active carbon catalyst in the kempili pulp hydrolysis process with microwave assisted has not been carried out so far. Therefore this study aimed to explain the potency of the sulfonated carbon catalyst from sawdust waste for the hydrolysis process of kempili wood pulp as an alternative method which is considered to be efficient and environment-friendly to be further developed in the near future.

2. MATERIALS AND METHODS

2.1. Tools and materials

This study used several items of equipment, namely a desiccator, a micro pipette, a hot plate, a 100-mesh sieve, a centrifuge, a pyrolysis tool, a falcon tube, glassware, a microwave, an analytical balance, an oven, a furnace, Fourier Transform Infra-Red (FTIR) and a Shimadzu UV-1700 spectrophotometer. The materials used in this study were sawdust from mixed wood waste, kempili wood, sodium sulfate (Merck-Germany), acetic acid (Merck-Germany), sulfate acid (Merck-Germany), sodium hydroxide (Merck-Germany), potassium sodium tartrate (Merck-Germany), phenol (Merck-Germany), alcohol (Merck-Germany), benzene (Smart Lab-Indonesia), sodium hypochlorite (Merck-Germany), hydrochloric acid...
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... (Merck- Germany), potassium iodide (Merck- Germany), ammonia (Merck- Germany), distilled water, and dinitrosalicic acid (DNS) (Sigma Aldrich, US).

2.2. Research metods

2.2.1. The preparation of sulfonated activated carbon (KS)

The production of active carbon was carried out through the pyrolysis process of sawdust waste remains for 4 h at the temperature of 350°C. The pyrolysis was filtered using a 100-mesh filter (coded as K). The carbon sulfonation process was undertaken through the carbon (K) activation using H₂SO₄ 8N at the temperature of 150°C (Amelia et al., 2013) for 4 h (Li et al., 2013). The sulfonation product was then washed until it reached the neutral pH and was dried in the oven at the temperature of 105°C (do Couto Fraga et al., 2015; Li et al., 2013). The dried solid was then calcinated at the temperature of 500°C for 1 h (Anggraeni et al., 2013) and coded as KS, the sample was then ready to be used as a catalyst.

2.2.2. Characterization of a sulfonated carbon catalyst

The obtained catalyst product was characterized for its properties such as its recovery value, water content, volatile matter, ash content, fixed carbon and iodine adsorption capacity based on Indonesian National Standards (SNI) 06-3730-1995, a functional group analysis using FT-IR (Nandiyanto et al., 2019) and the catalyst acidity used an ammonia adsorption so that it is possible to determine the H⁺ (acidity) capacity of the catalyst.

2.2.3. The production of kempili wood pulp

The raw material of kempili wood was cut into the sizes of 2-3 cm in length, 2-2.5 cm in width, and 2-3 mm in thickness. The woodcut was then dried and processed into pulp through the crafting process using a rotary digester. NaOH and Na₂S were used as chemical reagents in the active alkali concoction (16%), sulfide (22.5%), maximum temperature (170°C), the ratio of the wood: liquid of 1:4 with the concoction process for 4 h. The product was analyzed based on the Indonesian National Standards (SNI) 8400:2017, 0492:2008, and 01-1561-1989.

2.2.4. Application of KS catalyst in kempili hydrolysis reaction

The application of the sulfonated active carbon catalyst (KS) potency in the hydrolysis process of the kempili pulp was carried out using a microwave with the power of 300, 400 and 600 watts for 3,5, and 7 min reaction. The ratio of kempili pulp: catalyst was 1: 1 (5 g: 5 g ). The hydrolysis process was carried out by increasing the water as the reaction mediators (Rinaldi et al., 2010) and in each activity test was done two times of replication. The hydrolisate was analyzed using UV Vis spectrophotometry by the use of DNS reactant (Miller, 1959) in the wavelength of 530 nm.

3. RESULTS AND DISCUSSION

3.1. The characteristics of carbon (K) and sulfonated carbon (KS)

The carbon recovery value from the pyrolysis process of 1 kg mixed wood waste approximately reached 31% so we could obtain 310 g sulfonated carbon (Table 1). This process produced a pretty much-obtained carbon because the activation was not carried out using a high temperature yet, only the use of sulfuric acid and the loss of carbon weight occurred following the washing process.

Later on, the water content of K and KS was 1.58% and 3.48% respectively (still adequate the SNI water content requirement <15%) therefore following the sulfonation process the water content was increased.
Table 1. Analysis of carbon (K) and catalyst (KS) based on SNI 06-3730-1995 methods

| Sample          | Characterization analysis |   |   |   |   |
|-----------------|---------------------------|---|---|---|---|
|                 | Recovery value (%)        | Water content (%) | Volatile matter (%) | Ash content (%) | Fixed carbon (%) | Iod adsorption (mg/g) | Ammonia adsorption (mmol/g) |
| Carbon (K)      | 34                        | 1.55                      | 14.08                      | 5.26                        | 80.67                        | 215.27                        | 4.2977                        |
| Sulfonated carbon (KS) | 32                        | 3.48                      | 11.07                      | 4.21                        | 84.62                        | 690.88                        | 6.4502                        |

This occurred because the pores of carbon were able to bind water in the activation and washing process. The water content showed the hygroscopic property of carbon, especially in the cooling down process and due to the flushing process (Sahara et al., 2017; Pari et al., 2006). Water content was expected to be lower since it could interfere with the carbon absorption capability towards gas or liquid compound (Wibowo et al., 2011).

The volatile matter of the carbon (K) and the sulfonated carbon (KS) were 14.08% and 11.17%, respectively. The volatile matter values of K and KS were still normal compared to that of the SNI requirement for the requirement of <25%. This probably occurred due to the presence of interaction such as the one between water vapor and carbon causing it to become volatile. The volatile matter was affected by the high temperature of the carbonization process (Purwanto, 2011).

The ash content was expected to be low since the ash content was the residue which was unable to be burned following the combustion process and it might decrease the carbon quality, such as decreasing the heat value and causing crust or rust on the equipment (Thoha & Fajrin, 2010). It also might decrease the carbon adsorption capacity due to its mineral contents such as K, CA, and Na (Setyawan et al., 2018). In this study, the resulted ash content from both of the carbon (K) and sulfonated carbon ( KS) were 5.26% and 4.21%, respectively, which were still considered to be adequate based on the SNI requirement (<10%). The obtained ash content value decreased due to the evaporation of metal oxides in the carbon activation process.

After being sulfonated, the fixed carbon content increased because the contaminants in the carbon were removed during the activation process and that value corresponded to the SNI requirements (>65%).

Iod adsorption is one of the parameters in SNI while the ammonia adsorption represented the acidity strength of the sulfonated carbon. Drawing upon the iod adsorption analysis, we obtained the adsorption value of 215.27 mg/g for the carbon (K) and 690.88 mg/g for the sulfonated carbon (KS), so the adsorption capacity of sulfonated carbon was still below the SNI requirement (a minimum of 750 mg/g). However, the increase of the adsorption value before and after the sulfonation process showed a significantly high increase. This was probably due to the removal of contaminatnts of the carbon and the opening of new carbon pores in the sulfonated carbon. The acid compound could bind water molecules to dissolve the organic and inorganic substances so the carbon pores could be more opened (Erawati & Fernando, 2018).

This study produced a higher capacity of iod adsorption compared to the result obtained by Lestari et al. (2017) which was generated the iod adsorption of 476.63 mg/g of activated carbon from coconut shells at the temperature of 350°C for 5 h of pyrolysis reactions.
Thus, the carbon adsorption capacity towards ammonia represents a strong capacity of H\textsuperscript{+} or carbon acidity. In the application of the catalyst, the measurement of catalyst acidity is important. This is due to the fact that the higher the acid active sites on the surface of the catalyst, the higher the catalyst activity. From Table 1, we know that the carbon acidity value is 4.2977 mmol/g while the sulfonated carbon acidity is 6.4502 mmol/g.

From Table 2, we observe that there are several absorption differences between carbon before and after the sulfonation process. In the unsulfonated carbon (K), the phenolic OH group was observed in the wave number 3399.59 cm\textsuperscript{-1} while in the sulfonated carbon (KS) was in the wave number of 3400.14 cm\textsuperscript{-1}. CO groups from the COOH appeared on the wavenumber of 1690 cm\textsuperscript{-1} for the KS sample while from the sample K there was no detected absorbance indicating the presence of CO group from the COOH. The sulfonation process using H\textsubscript{2}SO\textsubscript{4} not only formed sulfonic groups but also the other weak acid groups such as COOH.

In the FTIR result of sample KS, several wave numbers were found which appeared to have been caused by the sulfonation process. They were the wavenumbers of 1165.31 and 614.14 cm\textsuperscript{-1} which indicated the presence of O=S and C-S groups, respectively. The C=C group in the sample KS appeared at the wavenumber of 1578.74 cm\textsuperscript{-1}.

The activation process using sulfuric acid might strengthen the acid sites by donating the SO\textsubscript{3}H groups and opening the carbon pores so it could adsorb the base substances better than unsulfonated carbon. The results of the sulfonated carbon (KS) acidity analysis in this study showed a higher result compared to the previous study conducted by Anggoro et al. (2015), which obtained the catalyst acidity value of 2.95 mmol/g and with the acid sites of 2.83 mmol/g (Tong et al., 2013). The contribution of SO\textsubscript{3}H functional group is expected to significantly affect the carbon acid power (Li et al., 2013). Hu et al. (2015) found the vibration related to the O=S=O and SO\textsubscript{3}H groups around the wavenumber of 1383, 1186, and 1038 cm\textsuperscript{-1}.

The presence of OH groups on the catalyst surface might facilitate the cellulose adsorption process and enrich the activity of the catalyst since the OH groups on the surface would serve better for the cellulose fibers by bridging the hydrogen with the existing OH groups (Morales-delaRosa et al., 2018) and OH was related to the β-1,4 glucan adsorption capacity. Shen et al. (2013) found that the phenolic OH groups were proven to facilitate the catalyst adsorption in the cellulose which is associated with the affinity among OH groups and oxygen atoms from the glycosidic bond within the cellulose, and beneficial for the interaction between carbon catalysts and the substrates. The strong interaction between solid acid catalysts and cellulose is the key to obtain a great catalytic performance in the hydrolysis process (Suganuma et al., 2008).

| Sample                  | Characterization analysis (wavenumber cm\textsuperscript{-1}) |
|-------------------------|---------------------------------------------------------------|
|                         | OH     | CO     | O=S    | C-S    | C=C   |
| Carbon (K)              | 3399.59| 1844.22|        |        | 1608.90 |
| Sulfonated carbon (KS)  | 3400.14| 1690   | 1165.31| 614.14 | 1578.74 |
3.2. The chemical components of kempili wood pulp

Bioethanol production from lignocellulose-containing biomass generally needs a preliminary treatment process to destroy cellulose-hemicellulose-lignin complexes (Putra, 2018) so that the cellulose and the hemicellulose could be easily accessed and converted into glucose (Lacerda et al., 2015).

There are two steps of cellulose hydrolysis to produce glucose using the Bronsted acid, the $H^+$ will attack the hydrogen and the β-1,4 glycosidic bond in the cellulose crystalline to form β-1,4 glucan which is dissolved in water and followed by the hydrolysis of β-1,4 glycosidic in the glucan to form glucose. Thus, the process requires a strong interaction between the catalyst and β-1,4 glucan since the catalyst will be difficult to approach the cellulose surface without that interaction (Suganuma et al., 2008).

3.3. Kempili pulp hydrolysis using sulfonated carbon catalyst by the use of microwave

In the hydrolysis process, there were several variations of the reaction condition including the reaction time and the power of the microwave so it is possible figure out the glucose content.

Figure 1 indicates that the obtained glucose content from the hydrolysis result from each reaction condition. The highest glucose content was 160.84 ppm which was obtained through the hydrolysis reaction condition with the power of 300 W for 5 min. This result showed a lower value compared to the study conducted by Goswami et al. (2015) and Anggraeni et al. (2013) which were resulted 262,000 ppm and 15,819 ppm glucose content respectively from the hydrolysis reaction with sulfonated carbon catalyst.

An increase of temperature, acid concentrations, liquid ratios to the solids will enrich the acid penetration into the biomass matrix which later will cut off the crystalline structure and release glucose by destroying the glucose bond (Radhakumari et al., 2014). The cellulose content in the kempili pulp used was 85.84% (Table 3) so the majority of glucose content was probably obtained from the cellulose. The more cellulose used as a reactant, the more the resulted products will increase since the reaction equilibrium moves to the right.

From the data, it is apparent that the glucose content resulted from the hydrolysis process increased with the increase of time reaction from 121.88 ppm into 160.84 ppm (in 3 and 5 min of reaction), subsequently, the glucose content decreased in the time reaction of 7 min. The more time was used in the reaction, the more the opportunity of product generation since the prolonged contact time between the reactants and the catalyst was increased (Qu et al., 2018).

However in a 7-min reaction the result showed a decrease of glucose content. This is probably due to the possibility of a secondary reaction which forms products such as HMF, levulinic acid, and formic acid (Qi et al., 2018).

It turns out that the best utilized microwave power is 300 W. Generally, low power does not cause optimal molecular collision among the reactants and the reactants’ contact with the catalyst since the energy is not adequate. Thus, the obtained results are less. However, in the reaction with the heterogeneous catalyst, there are several factors affecting the product generation, such as adsorption power, if the reaction takes place with extremely high power, it is feared that the product evaporation during the hydrolysis will occur or the possibility of side product production as the side reaction will take place.
Table 3. The analysis results of kempili pulp chemical components

| Sample          | α-cellulose | Holocellulose | Hemicelulose | Lignin | Pentosan |
|-----------------|-------------|---------------|--------------|--------|----------|
| Kempili wood pulp | 85.4        | 96.28         | 10.44        | 5.4    | 18.44    |

![Figure 1. Kempili pulp hydrolysis data using sulfonated carbon catalyst](image)

Table 4. The glucose content in the kempili pulp hydrolysis reaction without a sulfonated carbon catalyst

| Reaction conditions | Glucose (ppm) |
|---------------------|---------------|
| H₂SO₄ (8N)          | 104.18        |
| Carbon (C)          | 112.97        |
| Water               | 114.38        |

According to Shen et al. (2013) and Qi et al. (2018), the acid catalyst owned the SO₃H functional groups will be stable in the organic/ionic solvent, yet it will be not stable in water solvents since that group is able to be rehydrated in water at high temperatures. Generally, the most important factor for catalytic reactions is catalytic sites (such as functional groups) through surface areas and acidity approaches. The other factors needed to be considered in the lignocellulose transformation process into bioenergy or
other chemical products are the involvement of water as a reactant, a product, or a solvent in the reaction process.

From Table 4, the glucose content will decrease without a catalyst. If connected to the acid catalyst property, the more distribution of active sites and catalyst acidity, the easier the catalysis reaction with the reactant occurs. The presence of Bronsted acid significantly affects the cellulose decomposition reaction and without the catalyst, cellulose is difficult to be converted into glucose (Qu et al., 2018). They also stated that the resulted glucose content has a positive correlation with the catalyst acidity. Our study showed that the hydrolysis reaction through the addition of water only also resulted in glucose of 114.38 ppm. Meanwhile, Nata et al. (2015) produced 4.08 mg/mL of glucose content from the starch hydrolysis process at the temperature of 150°C in an 6-h reaction without a catalyst. Thus, from this study, it can be inferred that the heating step using a microwave can positively affect the reaction. An increase in reaction temperatures can increase the reaction rate and the cellulose crystallinity will decrease leading to the hydrolysis process of cellulose (Guo et al., 2012; Chen et al., 2011).

4. CONCLUSION
The sulfonated active carbon catalyst can be synthesized from sawdust waste and resulted in water content, volatile matter, ash content, fixed carbon content, iodine adsorption and the catalyst acidity as much as 3.48%; 11.7%; 4.21%; 84.62%; 690.88 mg/g; and 6.45 mmol/g, respectively. The highest glucose content of 160.83 ppm in the reaction condition of 300 watt for 5 min. The carbon-based catalyst made from wood waste was expected as an alternative substitute of an acid catalyst and can be developed into the lignocellulose biomass transformation reaction process so that this catalyst can serve as a green technology product for the near future.

5. ACKNOWLEDGEMENTS
We would like to thank Prof (R) Gustan Pari for supervising this work and technicians (Saepuloh, Dadang Setiawan, Nela Rahmati Sari and Sucl Aprianty Wati ) for their great work laboratory.

6. AUTHORS’ NOTE
The author(s) declare(s) that there is no conflict of interest and free of plagiarism.

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