Malaysian Journal of Catalysis
http://mjcat.utm.my/
MJCat
Research Article

Characterization and Performance Test of Sulfonated Activated Carbon as a Catalyst in the Levulinic Acid Production Process from Cellulose

Didi Dwi Anggoro[1], Istadi[1], Luqman Buchori[1], Setia Budi Sasongko[1], Novita Susanto[1], Safira Febe Wijaya[1], Brilliant Umara Le Monde[1]

[1]*Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl. Prof. H. Soedarto S.H., Semarang 50275, Indonesia*

**Corresponding Author: dd_anggoro@che.undip.ac.id*

Article history:
Received 02 October 2024
Accepted 23 December 2024

ABSTRACT

The production levulinic acid from cellulose was investigated using activated carbon as catalyst. This research conducted the characterize of activated carbon, sulfonated activated carbon, and nickel impregnation into sulfonated activated carbon. The results showed that the acidity of the activated carbon catalyst is 1233.046 μmol/g, while the Ni/sulfonated activated carbon had the highest catalyst acidity of 6106.512 μmol/g. In addition, the highest acidity of the sulfonated activated carbon catalyst was obtained at a sulfonation temperature variable of 150°C and a H_2SO_4 concentration of 10 N is 5108.332 μmol/g. The results of FTIR analysis show that in the sulfonated activated carbon catalyst, the S-O, S=O, and C-S groups appear at wavelengths of 748-883 cm^{-1}, 1148 cm^{-1}, and around 600 cm^{-1} respectively, which proves that the sulfonic acid group successfully attached to the surface of the sulfonated carbon catalyst. Meanwhile in Ni/sulfonated activated carbon, the Ni^{2+} peak appears at a wavelength of 473 cm^{-1}. XRD patterns of the three variables, indicating that sulfonation does not affect the carbon microstructure. The appearance of a new peak at 43° indicates the presence of NiO species in Ni/sulfonated activated carbon and the sharper peaks in Ni/sulfonated activated carbon indicate that there has been a change in the amorphous area to crystalline. Catalyst performance test show that hydrothermal cellulose without catalyst produces a cellulose conversion of 12% and levulinic acid yield of 1.12% while activated carbon catalyst produces a cellulose conversion of 20% and levulinic acid yield of 1.26%. The results of the catalyst performance test also show that hydrothermal cellulose using sulfonated activated carbon produces a conversion of 30% and levulinic acid yield of 3.95% due to the presence of -COOH, -OH, and $-SO_3H$ functional groups. The highest cellulose conversion of 42% and levulinic acid yield of 4.47% were achieved when using Ni/sulfonated activated carbon.

Keywords: *SAC, hydrothermal, cellulose, levulinic acid, catalyst*

| eISSN 0128-2581 |

1. INTRODUCTION

Biofuel and biochemical production from biomass have the potential to reduce dependence on traditional fossil fuels, reduce greenhouse gases, and increase energy security [1]. Levulinic acid has been identified as one of the most important value-added chemicals derived from biomass. The two functional groups of levulinic acid, namely ketone and carboxylic acid, make it important as a raw material for the production of various biomass-derived commodities [2]. Levulinic acid is known as a platform chemical because it can produce various other compounds, such as 5-bromolevulinic acid, valeric acid, MTHF, methyl pyrrolidone, and others. The potential of levulinic acid as a biofuel is very large because levulinic acid can be converted into γ-valerolactone (GVL), 2-methyltetrahydrofuran, and levulinate esters where these three products are alternative fuels to replace fossil fuels [3]. In addition, levulinic acid can also be used as an additive in the production of cosmetics, plastics, and textiles [4]. Initially, sugars and starches extracted from agricultural crops were highly desirable raw materials for biochemical production. However, this has caused controversy with food producers [5]. Glucose produced from the hydrolysis of cellulose in lignocellulose is an important platform that can be converted into valuable chemicals (e.g. furfural, 5-hydroxymethylfurfural, levulinic acid) and renewable biofuels (e.g. bioethanol, biobutanol, and hydrocarbons) [6]. Several technologies, such as direct combustion, pyrolysis, hydrolysis, and hydrothermal conversion (HTC), have been developed to convert biomass into valuable fuels or chemicals. Among these methods, hydrothermal is a promising method because it can be applied to wet biomass, has a lower temperature than pyrolysis, and has high energy efficiency [7]. During the hydrothermal process, water acts as a reactant and catalyst. In particular, exposure to water at high temperatures and pressures can cause the cellulose crystal structure to become amorphous [8].

In general, the biomass hydrothermal method using an acid catalyst is one of the processes that can be carried out to produce levulinic acid. Consecutively, the cellulose fraction in the biomass will be converted into glucose, then glucose will be dehydrated into hydroxymethylfurfural (HMF) and HMF will undergo rehydration with the help of two water molecules to produce levulinic acid [3]. Glucose can be produced from cellulose by breaking the β-1,4-glycosidic bond between glucose units through hydrolysis catalyzed by acid or enzymes (cellulase). However, currently cellulase is expensive to produce and difficult to recycle. In addition, enzymatic hydrolysis also requires initial processing of lignocellulosic biomass which consumes a lot of energy and costs to produce satisfactory glucose [6]. Meanwhile, reactions with acid catalysts are very important in chemical processes. Acid catalysts have been studied and developed over the past few decades. Homogeneous acid catalysts, such as H_2SO_4, HF, HNO_3, and H_3PO_4 are widely used as homogeneous acid catalyst fluids that show effective catalytic performance even at low temperatures [9]. However, homogeneous acid catalysts cause several problems such as strong protonic acid catalysts easily corrode production equipment during the reaction process, are difficult to separate and recycle if mixed with products after the reaction, and produce acid waste that pollutes the environment [10]. Along with the excitement of green and sustainable development, the application of homogeneous acid catalysts is becoming less popular and is starting to be replaced by the use of heterogeneous catalysts.

To overcome these problems, solid acid catalysts have been gradually developed such as magnetic solid acid catalysts, sulfonated zirconia, sulfonated activated carbon, Amberlyst-15, zeolites, and so on. Among various types of heterogeneous solid catalysts, carbon-based solid acid catalysts show superior catalytic activity [11]. This is due to the high acid density, good thermodynamic stability, excellent surface hydrophobicity, and high chemical stability. In addition, carbon-based solid catalysts can be prepared using cheap and renewable biomass raw materials and their derivatives, thereby reducing production costs [12]. Biomass waste has been used as a carbon precursor for the manufacture of solid acid catalysts such as activated carbon catalysts through carbonization and activation processes. Due to the low catalytic performance of activated carbon for the hydrolysis of cellulose into simple sugars, a sulfonation process is required. Sulfonation is the process of attaching sulfonate groups ($–SO_3H$) to the surface of activated carbon. This process aims to increase acidity and catalytic activity. The sulfonation process is easy to do, cheap, and can be applied in various solid catalysts [13]. Sulfonated activated carbon catalysts have a stable carbon framework and are insoluble in most acidic/basic conditions and organic solvents. In addition, this catalyst can also be separated from the reaction system so that it is easy to recover and reuse [9].

To increase the effectiveness and selectivity of the catalyst, many active sites are needed in sulfonated activated carbon so that the catalytic activity will increase [14]. Acid sites on sulfonated activated carbon can be increased using metal development by impregnation. In addition to producing little waste, the impregnation process is easy to do and has a high success rate [15]. One of the most effective metals used is nickel metal [14]. Ni metal has a low price and has been proven to have good catalytic activity because it has an empty d orbital so that it can increase the acidity of the sulfonated activated carbon catalyst [16]. Therefore, the use of solid acid catalysts based on sulfonated activated carbon impregnated with nickel metal which is easily separated so that the catalyst can be recovered and reused also provides high catalytic activity and selectivity, has been developed.

In this study, the synthesis of sulfonated activated carbon catalysts and sulfonated activated carbon with nickel impregnation will be carried out. Furthermore, the catalysts were characterized and tested for acidity by studying the effect of reaction temperature and H_2SO_4 concentration on the sulfonation process of activated carbon. In addition, the performance of sulfonated activated carbon catalysts and sulfonated activated carbon catalysts impregnated with nickel metal for the production of levulinic acid from cellulose will also be studied.

2. EXPERIMENTS

2.1 Materials

The materials used in this work were activated carbon, sulfuric acid (H_2SO_4, 98%, EMSURE, Merck), cellulose (Aldrich), inert nitrogen gas (N_2) (Aneka Gas), and nickel (II) sulfate hexahydrate ($NiSO_4.6H_2O$, EMSURE, Merck).

2.2 Synthesis of Sulfonated Activated Carbon

Activated carbon is sulfonated by mixing 10 grams of 80 mesh activated carbon into 150 mL of H_2SO_4 solution in various concentrations. Then stirred with a magnetic stirrer and hotplate at a certain temperature for 4 hours. Next, the mixture resulting from the sulfonation process is filtered using Whatman filter paper while washing with distilled water to obtain the sulfonated activated carbon catalyst. After that, the catalyst drying process is carried out in an oven with the aim of removing the remaining distilled water from the washing process. The drying process takes place in an oven at a temperature of 110℃.

2.3 Sulfonated Activated Carbon Acidity Test

The acidity test of the sulfonated activated carbon catalyst was carried out quantitatively using the gravimetric method and ammonia as the adsorbate base. Ammonia gas molecules will diffuse into the sulfonated activated carbon pores and be adsorbed at active sites on the surface. Ammonia adsorption on the sulfonated activated carbon surface can occur physically and chemically. Ammonia is physically adsorbed to the sulfonated activated carbon surface via weak van der Waals forces and chemically adsorbed to the sulfonated activated carbon surface via strong hydrogen bonds. Hydrogen bonds occur between hydrogen atoms of ammonia and oxygen atoms of hydroxyl/carboxyl groups on the surface of sulfonated activated carbon [17]. This method is carried out by placing 1 gram of the catalyst sample in a cup, then placing it in a desiccator which has previously been saturated with ammonia vapor, and leaving it for 24 hours. The acidity level of the catalyst can be calculated using the following equation [18].

$$\text{Ammonia adsorption (mmol/g)} = \left(\frac{W_2-W_1}{W_1-W_0}\times\frac{1}{Mr}\right)\times\frac{1000\ \text{mmol}}{\text{mol}} \qquad (2.1)$$

where:

W_0 = weight of empty cup (g)
W_1 = weight of cup + sample before treatment (g)
W_2 = weight of cup + sample after treatment (g)
Mr = molecular weight of ammonia (g/mol)

2.4 Synthesis of Nickel/Sulfonated Activated Carbon

Sulfonated activated carbon with the highest acidity level is then impregnated with nickel. 5 grams of activated carbon was added to nickel metal contained in a hexahydrate sulfate salt solution ($NiSO_4.6H_2O$) with a concentration of 2.5% wt and dissolved in 20 mL of distilled water. Then cover the mixture with aluminum foil while stirring with a magnetic stirrer at 80°C for 3 hours. Next, the mixture resulting from the impregnation process was filtered using Whatman filter paper while washed with distilled water to obtain the Ni/SAC catalyst and dried in an oven at 105°C for 24 hours. The sulfonated activated carbon impregnated with oven-dried nickel metal is then calcined at a temperature of 400°C for 2 hours.

2.5 Catalyst Characterization

Fourier Transform Infrared (FTIR) analysis aims to determine the functional groups of activated carbon before sulfonation (AC), after sulfonation (SAC), and sulfonated activated carbon after nickel metal impregnation (Ni/SAC). This analysis was carried out at the Physics Laboratory of Negeri Semarang University with a Perkin-Elmer Spotlight 200 at a spectrum range of 400-4000 cm^{-1}. XRD characterization was used with the aim of determining the structure and identification of crystals (crystallinity) in AC, SAC, and Ni/SAC which was carried out at the Physics Laboratory of Negeri Semarang University using Panalytical X'Pert 3 Powder. The crystallinity of the catalyst can be calculated using the following equation:

$$\text{Crystallinity} = \frac{\text{crystalline peak area}}{\text{overall peak area (amorf and crystalline)}}\times 100\% \qquad (2.2)$$

2.6 Production of Levulinic Acid

AC, SAC, and Ni/SAC were used as catalysts in the hydrothermal production process of levulinic acid from cellulose using a 100 mL autoclave reactor. The reactor was filled with 1 gram of cellulose, 12%wt catalyst each, and the volume was adjusted to 60 mL by adding deionized water as a solvent. Then the reactor was injected with inert gas in the form of nitrogen gas (N_2) to remove air in the autoclave. The reactor was heated to the desired reaction temperature of 150°C. When the specified conditions were reached, the reaction was calculated to start for a reaction time of 2.5 hours. After the reaction was complete, the heater was turned off. The reaction mixture was filtered to separate liquid and solid products. The filtrate was analyzed to determine the level of levulinic acid produced using HPLC (High Performance Liquid Chromatography) (Perkin-Elmer Altus). While the remaining cellulose after hydrothermal was dried in an oven at a temperature of 110°C until its weight was constant and then calculated the cellulose conversion with the following equation [19].

$$\text{Conversion of cellulose (\%)} = \frac{\text{initial cellulose weight (g)} - \text{cellulose weight after hydrothermal (g)}}{\text{initial cellulose (g)}}\times 100\% \qquad (2.3)$$

3. RESULTS AND DISCUSSION

3.1 Effect of Sulfonation Temperature on Total Acidity of Sulfonated Activated Carbon Catalyst

One of the factors that affect the total acidity of sulfonated activated carbon catalyst is the sulfonation temperature. In this study, the sulfonation reaction was carried out with 6 N, 8 N, and 10 N H_2SO_4 solutions and stirring at temperatures of 120ºC, 150ºC, and 180ºC. The effect of sulfonation temperature on the total acidity of sulfonated activated carbon catalyst is shown in Fig 1.

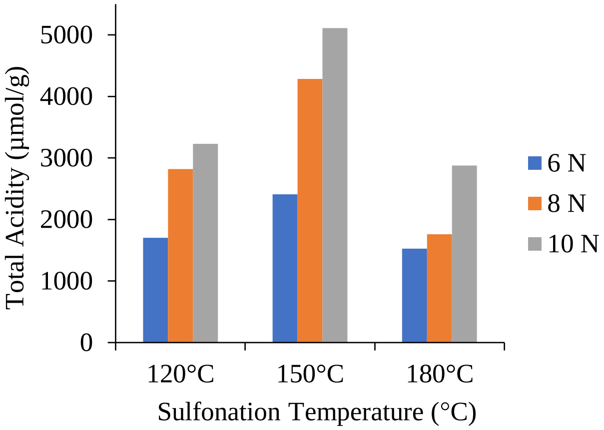

Fig. 1. Effect of sulfonation temperature on the total acidity of the catalyst

Based on Fig 1, it can be seen that the effect of sulfonation temperature on the total acidity of the sulfonated activated carbon produced is fluctuating. At a sulfonation temperature of 120 ºC, the total acidity obtained at H_2SO_4 concentrations of 6 N, 8 N, and 10 N were respectively 1702.777 µmol/g; 2818.390 µmol/g; and 3229.405 µmol/g. At a sulfonation temperature of 150 ºC, the total acidity obtained at H_2SO_4 concentrations of 6 N, 8 N, and 10 N were respectively 2407.375 µmol/g; 4286.301 µmol/g; and 5108.332 µmol/g. Meanwhile, at a sulfonation temperature of 180 ºC, the total acidity obtained at H_2SO_4 concentrations of 6 N, 8 N, and 10 N were respectively 1526.628 µmol/g; 1761.494 µmol/g; and 2877.106 µmol/g. This shows that the highest total acidity was obtained at a sulfonation temperature of 150 ºC with a H_2SO_4 concentration of 10N.

When the sulfonation temperature increases, the acidity of the sulfonated activated carbon catalyst produced will also increase. However, at a sulfonation temperature that is too high, the acidity value of the catalyst decreases. The high temperature applied during the sulfonation process causes the stability of organic molecules to decrease and eventually causes the separation of intermolecular bonds [20]. The acidity of the sulfonated activated carbon catalyst can be measured from the adsorption results on ammonia bases which are linearly correlated with the number of active sites in the catalyst and its catalytic activity. The increase in ammonia adsorption on sulfonated activated carbon indicates that the pores and active sites of the catalyst are increasingly open so that the ammonia adsorption process by sulfonated activated carbon is more optimal [21]. The acidity of all catalysts produced is related to the SO_3H acid sites associated with the oxidation of functional groups such as -OH groups in the catalyst structure. The total acidity of the catalyst is largely influenced by the oxidation of the -OH functional groups on the surface of activated carbon which produces additional carboxyl sites (oxygen functional groups) [22]. At too high sulfonation temperatures, degradation of the -OH functional groups occur so that the acidity of the catalyst decreases. The higher the temperature during the preparation of activated carbon, the lower the amount of hydrogen and oxygen content which is thought to be the main factor in reducing the -OH functional groups [23]. In addition, if the sulfonation temperature is too high, it can damage the pore structure of activated carbon so that the number of active sites decreases and the total acidity of the catalyst decreases [6].

3.2 Effect of H_2SO_4 Concentration on Total Acidity of Sulfonated Activated Carbon Catalyst

Another factor that affects the total acidity of sulfonated activated carbon catalyst is the concentration of sulfuric acid. In this study, the sulfonation reaction was carried out with 6 N, 8 N, and 10 N H_2SO_4 solutions and stirring at temperatures of 120ºC, 150ºC, and 180ºC. The effect of H_2SO_4 concentration on the total acidity of sulfonated activated carbon catalyst is shown in Fig 2.

Based on Fig 2, it can be seen that the effect of H_2SO_4 concentration is directly proportional to the total acidity of the sulfonated activated carbon produced. At a concentration of H_2SO_4 6 N, the total acidity obtained at sulfonation temperatures of 120 ºC, 150 ºC, and 180 ºC were respectively 1702.777 µmol/g; 2407.375 µmol/g; and 1526.628 µmol/g. At a concentration of H_2SO_4 8 N, the total acidity obtained at sulfonation temperatures of 120 ºC, 150 ºC, and 180 ºC were respectively 2818.390 µmol/g; 4286.301 µmol/g; and 1761.494 µmol/g. Meanwhile, at a concentration of 10 N H_2SO_4, the total acidity obtained at sulfonation temperatures of 120 ºC, 150 ºC, and 180 ºC were respectively 3229.405 µmol/g; 5108.332 µmol/g; and 2877.106 µmol/g. This shows that the highest total acidity was obtained at a concentration of 10 N H_2SO_4 with a sulfonation temperature of 150 ºC.

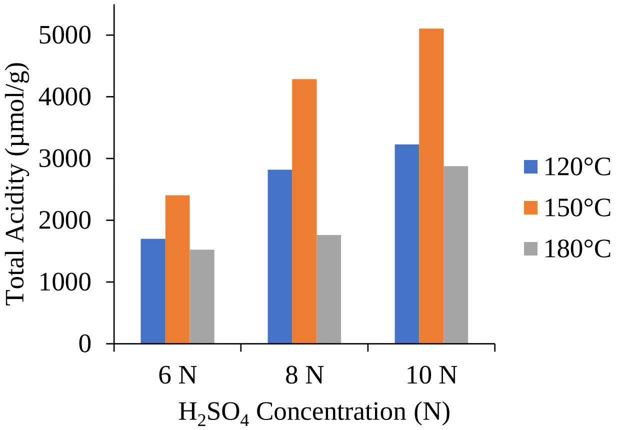

Fig. 2. Effect of H_2SO_4 concentration on the total acidity of the catalyst

The concentration of H_2SO_4 affects the total acidity of sulfonated activated carbon produced from the sulfonation process of activated carbon. The greater the concentration of H_2SO_4 as a sulfonation precursor, the greater the total acidity of the sulfonated activated carbon catalyst. The sulfonation process on activated carbon causes sulfonate groups ($-SO_3H$) to be adsorbed on the pores of the activated carbon. The increasing number of acid sites in the form of adsorbed sulfonate groups will increase the acidity of the activated carbon catalyst [24]. The acidity of the sulfonated activated carbon catalyst tends to increase with the increasing concentration of sulfuric acid as a sulfonation precursor, which means that more sulfonate groups are bound to the surface of the activated carbon. The high acidity of this sulfonated activated carbon catalyst can accelerate the hydrolysis of cellulose into glucose or simple sugars [13]. The acidity of sulfonated activated carbon can be seen from the adsorption results against ammonia base where the increase in acidity occurs due to the more optimal ammonia adsorption process because the catalyst pores are more open [25].

3.3 Catalyst Characterization

3.3.1 Fourier Transform Infrared (FTIR) Analysis

In this study, the FTIR test was used to observe changes in the functional groups of activated carbon before sulfonation (AC), after sulfonation (SAC), and sulfonated activated carbon after nickel metal impregnation (Ni/SAC) which are presented in Fig 3.

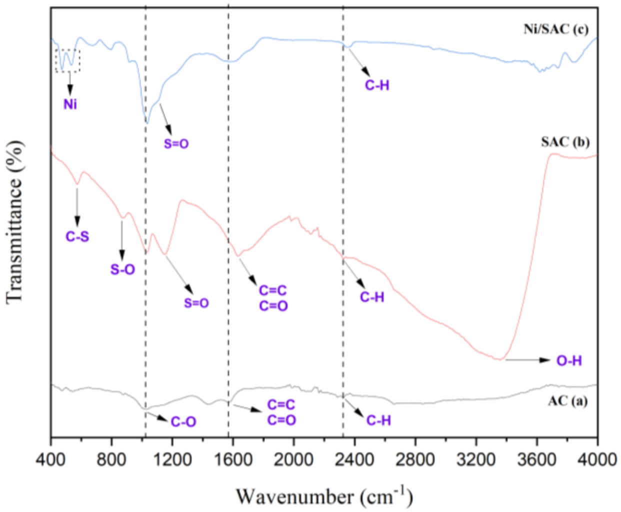

Fig. 3. FTIR spectrum of (a) AC, (b) SAC, and (c) Ni/SAC

Based on Fig 3, in AC, a peak can be seen at 1045 cm^{-1} which indicates the stretching of the C-O group [26]. Absorption at 1593 cm^{-1} indicates the stretching of the C=C and C=O groups while the wavelength of 2366 cm^{-1} indicates the stretching of the C-H aldehyde group [27]. The spectrum in SAC is similar to AC which shows that sulfonation does not change the structure of activated carbon as a catalyst support. In SAC, the stretching of the S-O group appears in the range of 748-883 cm^{-1} [11]. In addition, there is also a peak at 1148 cm^{-1} which is the stretching of the S=O group. The stretching of the C=C and C=O groups of the carbonyl and carboxylate groups is seen to shift at a wavelength of 1647 cm^{-1} and a wavelength of 3290 cm^{-1} refers to the −OH group. The remaining stretching of around 600 cm^{-1} is due to the presence of C–S binding. These results prove that the sulfonic acid group has successfully attached to the surface of the sulfonated carbon catalyst. The sharper C=O group on SAC is due to the oxidation of the -OH functional group on the AC surface which produces additional carboxyl sites [22]. In addition, the C-O peak at a wavelength of 1034 cm^{-1} also looks sharper due to the formation of new C-O bonds such as ether, phenol, and hydroxyl groups [27].

In Figure 3, it can also be seen that the Ni^{2+} peak on Ni/SAC appears at a wavelength of 473 cm^{-1}. This is in accordance with research conducted by [28] which stated that AC-Ni shows its peak around a wavelength of 400–500 cm^{-1} due to stretching of the NiO bond because most metal oxides show this bond in the absorption band between 400 cm^{-1} or 1000 cm^{-1}. However, nickel impregnation into porous activated carbon also causes changes in most functional groups, as seen from the low intensity of the bands that appear on Ni/SAC such as the -SO_3H group. This is because the temperature and impregnation time affect the prepared samples [27].

3.3.2 X-Ray Diffraction (XRD) Analysis

X-Ray Diffraction (XRD) analysis aims to determine the changes in structure and crystallinity that occur in activated carbon (AC), sulfonated activated carbon (SAC), and nickel-impregnated sulfonated activated carbon (Ni/SAC) as presented in Fig 4.

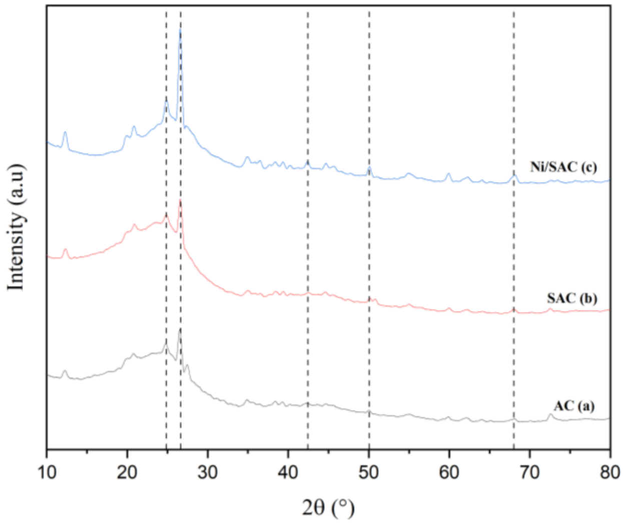

Fig. 4. XRD patterns of (a) AC, (b) SAC, and (c) Ni/SAC

Fig 4 shows the XRD patterns of activated carbon (AC), sulfonated activated carbon catalyst (SAC), and nickel-impregnated sulfonated activated carbon catalyst (Ni/SAC). The crystallinity region is depicted as a narrow and sharp peak capture while the area with a widened peak is an amorphous region [14]. The diffraction peak (2θ) 26.5° shows amorphous carbon consisting of aromatic carbon oriented in a very irregular shape. The diffraction peak (2θ) 24.8° shows a structure between graphite and amorphous carbon which also has an irregular layer [29]. Overall, there is no significant difference in the XRD pattern between activated carbon, sulfonated carbon catalyst, and nickel-impregnated sulfonated activated carbon catalyst indicating that sulfonation does not affect the microstructure of carbon. The emergence of a new peak at 43° indicates the presence of NiO species in Ni/SAC [30]. The increase in peak intensity or increasingly sharp peaks in Ni/SAC indicates that there has been a change from the amorphous region to the crystalline region, which proves that Ni metal is not only attached to the surface of activated carbon, but Ni has entered the structure of activated carbon [14].

Crystallinity can be determined by comparing the intensity or area of one (or a number of) crystalline peaks of a sample with the intensity or area of the entire peak consisting of amorphous and crystalline. Based on the calculation results using Equation 2.2, the crystallinity values of AC, SAC, and Ni/SAC were respectively 46.0989%; 47.3293%; and 66.6073%. According to [31], the increasing crystallinity value means that the carbon structure is more regular and stronger and the better the catalyst synthesis produced. In addition, high crystallinity also indicates that the catalyst has good thermal stability [32].

3.3.3 Catalyst Performance Test for Levulinic Acid Production from Cellulose

Catalyst performance test was conducted to determine the potential of catalyst in the production of levulinic acid from cellulose. The hydrothermal process of cellulose into levulinic acid was carried out by a process without a catalyst, using activated carbon (AC), sulfonated activated carbon (SAC), and nickel-impregnated sulfonated activated carbon (Ni/SAC) catalysts. The amount of cellulose conversion and levulinic acid yield in each variable is presented in Table 1.

Table 1. Cellulose conversion and levulinic acid yield in hydrothermal processes with various catalyst variables

Variable	Cellulose Conversion (%)	Levulinic Acid Yield (%)
Without catalyst	12	1.12
Activated Carbon (AC)	20	1.26
Sulfonated Activated Carbon (SAC)	30	3.95
Nickel Impregnated Sulfonated Activated Carbon (Ni/SAC)	42	4.47

Table 1 shows that the hydrothermal process of cellulose without the use of a catalyst produces the smallest conversion of 12%. Then the conversion increases to 20% when an activated carbon (AC) catalyst is used. In sulfonated activated carbon (SAC), the conversion of cellulose increases to 30% and the highest conversion of 42% is obtained when the hydrothermal process is carried out using a sulfonated activated carbon catalyst impregnated with nickel metal (Ni/SAC).

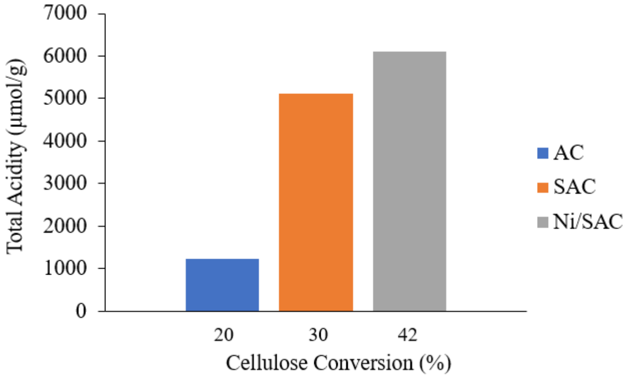

Fig. 5. Effect of total acidity of catalyst on cellulose conversion

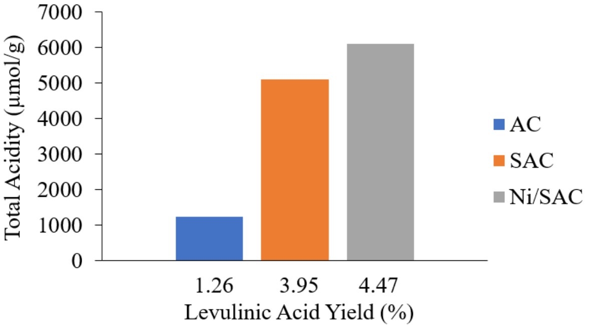

Fig. 6. Effect of total acidity of catalyst on levulinic acid yield

Based on the HPLC results in the standard solution, it can be seen that the peak of levulinic acid appears at a retention time of 9.702. Meanwhile in the other hydrothermal process without a catalyst, using an activated carbon catalyst (AC), sulfonated activated carbon (SAC), and sulfonated activated carbon impregnated with nickel (Ni/SAC), peaks of levulinic acid appears at retention time 9.071, 9.471, 9.189, and 9.058. By using data area of the HPLC results, yield of levulinic acid can be obtained in variables without catalyst, using AC, SAC, and Ni/SAC catalysts respectively at 1.12%, 1.26%, 3.95%, and 4.47%.

Acidity and SO_3H groups affect the activity of the catalyst and the resulting products where the performance of the catalyst is increased along with the increasing acidity value [11]. Fig 5 and Fig 6 show that the conversion of cellulose increases along with the increasing acidity value of AC, SAC, and Ni/SAC which are respectively 1233,046 μmol/g; 5108,332 μmol/g; and 6106,512 μmol/g. The sulfonation process plays an important role in providing SO_3H groups so that sulfonated activated carbon catalysts contain efficient -COOH, -OH, and $-SO_3H$ functional groups for cellulose hydrolysis reactions. The presence of -OH and -COOH functional groups serves to attract the feed compound, namely cellulose, to be closer to the $-SO_3H$ group which acts as a catalytic active site where the α-1,4 and β-1,4 glycosidic bonds of the adsorbed cellulose molecules occur in the hydrolysis process [21]. The $-SO_3H$ group will increase the reactivity of cellulose by protonation so that it will facilitate the breaking of glycosidic bonds in cellulose, thereby increasing cellulose conversion. High total acidity will also increase the accessibility of reactants to active sites on the catalyst surface and provide a better environment for the reaction to take place [33].

The increase in cellulose conversion on the Ni/SAC catalyst is related to the increase in acidity formed by Ni metal bound to the sulfonate group ($-SO_3H$) thereby increasing catalytic activity [34]. In the production of levulinic acid, cellulose is first decomposed into glucose through a hydrolysis reaction. Then the simple sugar is converted into 5-HMF through dehydration and followed by a rehydration reaction into levulinic acid products. However, due to the difficulty of direct dehydration of glucose into 5-HMF, glucose needs to be isomerized first into fructose [35]. Nickel plays a role in the isomerization process of glucose into fructose which contributes to the formation of levulinic acid [36]. The hydrolysis process of cellulose acid into glucose occurs in the sulfonate group. While the isomerization reaction is catalyzed by nickel metal where glucose is converted into fructose. Then the dehydration reaction where fructose is converted to 5-HMF and the hydration reaction where furfural is converted to levulinic acid, both catalyzed by sulfonate groups. The simultaneous hydrolysis of cellulose and isomerization of glucose are what increase the overall efficiency of the catalyst to produce levulinic acid [37].

4. CONCLUSION

The present study shows that the higher sulfonation temperature, the more contaminants are lost and volatile materials are released, so that fixed carbon increases and acidity of the catalyst can be higher. In addition, the acidity of the catalyst tends to increase with increasing H_2SO_4 concentration, which means that more sulfonate groups are bound to the surface of the activated carbon. The highest acidity of the sulfonated activated carbon catalyst was obtained at a sulfonation temperature 150℃ and H_2SO_4 concentration of 10 N. Meanwhile, in the performance test for levulinic acid production, the largest cellulose conversion and levulinic acid yield was obtained in cellulose hydrothermal using Ni/SAC catalyst, which was 42% and 4.47%. Overall, the results of this work can provide preliminary report regarding the potential of sulfonated activated carbon catalysts for the production of levulinic acid.

ACKNOWLEDGEMENTS

This research was financially supported by the Faculty of Engineering, Diponegoro University, Indonesia through Strategic Research Grant 2024.

REFERENCES

[1] M. Rai, A. P. Ingle, R. Pandit, P. Paralikar, J. K. Biswas, S. S. da Silva, (2018), 1–26. DOI:10.1080/01614940.2018.1479503
[2] I. Ogino, Y. Suzuki, S. R. Mukai, (2017). http://dx.doi.org/10.1016/j. cattod.2017.10.001
[3] J. R. H. Panjaitan, (2020), 117-123. https://dx.doi.org/ 10.26578/jrti.v14i2.5327
[4] I. B. Okhlopkova, Z. R. Ismagilov, (2020). DOI: 10.1088/1742-6596/1749/1/012008
[5] N. Sweygers, M. H. Somers, L. Appels, (2018), 95-102. https://doi.org/10. 1016/j.jenvman.2018.04.105
[6] M. Zeng, X. Pan, (2020). DOI: 10.1080/01614940.2020.1819936
[7] X. Cao, X. Peng, S. Sun, L. Zhong, W. Chen, S. Wang, R. C. Sun, (2015), 44-51. http://dx.doi.org/10.1016/j.carbpol. 2014.10.069
[8] D. Beyene, M. Chae, T. Vasanthan, D. C. Bressler, (2020). https://doi.org/10.3389/ fchem.2020.00323
[9] S. Kang, J. Ye, J. Chang, (2013), 133-144.
[10] M. M. Zainol, M. N. F. Rosian, M. Asmadi, N. A. S. Amin, (2021), 1-10. DOI: 10.22146/ajche.59865
[11] A. Kristiani, K. C. Sembiring, Y. Aristiawan, F. Aulia, L. N. Hidayati, H. Abimanyu, (2020), 209-215. https://doi.org/10.14710/ jksa.23.6.209-215
[12] Y. Pi, W. Liu, J. Wang, G. Peng, D. Jiang, R. Guo, D. Yin, (2022). DOI: 10.3389/fchem.2022.944398
[13] T. E. Suharto, C. Wulandari, D. Oktiarni, D. Ratnawati, I. Satar, (2022), 107-113. http://dx.doi. org/10.26555/chemica. v9i2.24511
[14] R.N. Yanti, E. Hambali, G. Pari, A. Suryani, (2020), 129-138. DOI: 10.20886/jphh.2020.38.3.129-138
[15] P. Munnik, E. Petra, P. Krijn, (2015), 6687-6718.
[16] E. H. N. L. Gaol, (2023).
[17] C. Li, S. Zhao, M. Li, Z. Yao, Y. Li, C. Zhu, S. Xu, J. Li, J. Yu, (2023), 1-9. DOI: 10.3389/fenvs.2023.976113
[18] W. Trisunaryanti, I. I. Falah, S. K. Nasi'ah, S. D. Sumbogo, (2023), 463-474. DOI: 10.30495/IJC.2023.1992636.2032
[19] A. Yuksel, (2016), 415-434. DOI:10.17482/uumfd.278150
[20] M. A. Ahmad, N. A. A. Puad, O. S. Bello, (2014), 18-35. https://doi.org/10.1016/j.wri.2014.06.002
[21] L. Efiyanti, D. A. Indrawan, D. Santi, S. Wibowo, G. Pari, (2021), 1998-2005. http://doi.org/10.31788/RJC. 2021.1436276
[22] L.J. Konwar, P. I. Mäki-Arvela, J. P. Mikkola, (2019), 11576-11630.
[23] A. Sandouqa, Z. Al-Hamamre, J. Asfar, (2019), 667-682.
[24] A. Aneu, K. Wijaya, A. Syoufian, (2020), 2265-2270. https://doi.org/10.1007/s12633-020-00741-6
[25] L. Efiyanti, Sutanto, N. Hakimah, D. A. Indrawan, G. Pari, (2019), 67-80. DOI: 10.20886/jphh.2019.37.2.67-80.
[26] A. R. O. Ferreira, J. Silvestre-Albero, M. E. Maier, N. M. P. S. Ricardo, C. L. Cavalcante, F. M. T. Luna, (2020). https://doi.org/ 10.1016/j.mcat.2020.110888
[27] M. Guiza, A. Abdedayem, I. Ghouma, A. Ouederni, (2017), 836-851.
[28] G. I. Danmaliki, T. A. Saleh, A. A. Shamsuddeen, (2017), 993-1003. http://dx.doi.org/10.1016/j.cej.2016.10.141
[29] Z. Liu, Y. Qi, M. Gui, C. Feng, X. Wang, Y. Lei, (2019), 5142-5150. https://doi.org/10.1039/C8RA08685K
[30] R. Ediati, A. Mukminin, N. Mukminin, (2017), 30-36. DOI: 10.22146/ijc.23563
[31] I. G. Lee, A. Nowacka, C. H. Yuan, S. J. Park, J. B. Yang, (2015), 12078-12087. DOI: 10.20886/jphh.2020.38.3.129-138

[32] S. Joshi, A. D. Zodge, K. V. Pandare, B. D. Kulkarni, (2014). DOI: 10.1021/ie5011838

[33] D. D. Kulkarni, Purwanto, Rispiandi, (2014), 126-131.

[34] Q. U. Kulkarni, H. Hasanudin, W R. Asri, A. Mara, R. Maryana, S. Gea, K. Wijaya, (2023), 287-309. https://doi.org/10.1007/s11144-022-02334-3

[35] T. Boonyakarn, P. Wataniyakul, P. Boonnoun, A. T. Quitain, T. Kida, M. Sasaki, N. Laosiripojana, B. Jongsomjit, A. Shotipruk, (2019), 2697-2703. http://dx.doi. org/10.1021/acs.iecr.8b05332

[36] Y. Wu, H. Wang, J. Peng, M. Ding, (2023), 92-110. https://doi.org/10.1016/j.cattod.2022.08.012

[37] F. Perveen, M. Farooq, A. Ramli, A. Naeem, I. W. Khan, T. Saeed, J. Khan, (2023), 333-345. https://doi.org/10.1021/ acsomega.2c04545