

Facile Strategy for Surface Functionalization of Corn Cob to Biocarbon and Its Catalytic Performance on Banana Peel Starch Hydrolysis

Iryanti Fatyasari Nata[#], Meilana Dharma Putra[#], Desi Nurandini[#], Chairul Irawan[#]

[#]Department of Chemical Engineering, University of Lambung Mangkurat,
Jl. A. Yani Km. 36, Banjarbaru, South Kalimantan, Indonesia 70714

E-mail: ifnata@unlam.ac.id, mdputra@unlam.ac.id, desi.nurandini@unlam.ac.id, cirawan@unlam.ac.id

Abstract— The sulphonated biocarbon (C-SO₃H) has been prepared from carbonization of corn cob and followed by one-step hydrothermal treatment. This research focuses on characterization of C-SO₃H and evaluate the capability of C-SO₃H for hydrolyzed banana peel starch, and also investigate the optimum concentrations of substrate and the reaction time for hydrolysis. The C-SO₃H was produced from corn cob ($\pm 60 \mu\text{m}$ mesh); it was carbonized at 400 °C for 1 hour. The resulting carbon was sulphonated by hydroxy ethyl sulphonic acid at 180 °C for 4 hours, and then washed with 50% methanol and water, and then resulting biocarbon was dried at 80 °C for 6 hours in the oven. Based on Scanning Electron Microscopy (SEM) observation, structure morphology of corn cob was changed due to carbonization process. The C-SO₃H after sulphonation has random pores with diameter around 3 μm –10 μm . The X-Ray Diffraction (XRD) showed increased of the crystalline index of corn cob about 133% after carbonization. Analysis of EDX result for S component on C-SO₃H is 3.79% w/w and capacity of H⁺ is 1.447 mmol/g. The apparent peaks of -SO₃H functional groups (1207 cm⁻¹ and 1720 cm⁻¹) on C-SO₃H were indicated the by Fourier Transform Infra Red (FTIR). Optimum hydrolysis concentration of banana peel starch is 7% w/v for 60 min at 100°C which Total Reducing Sugar (TRS) concentration about 0.688 mg/mL. Reusability of C-SO₃H for 4 repeated used which showed a good performance that only 6% of decreasing activity of C-SO₃H. The utilization of corn cob can be enhanced of corn cob and also it can be utilized as a heterogeneous catalyst.

Keywords— corn cob; C-SO₃H; sulphonated; biocarbon; glucose; hydrolysis; banana peel starch

I. INTRODUCTION

The preparation of materials using natural resources waste is potentially expected in the long term, renewable, and does not have negative effects on the environment. South Kalimantan, Indonesia, has natural resources that could be used and developed in a balanced, sustainable, and beneficial to society. The process is a manifestation of green technology concept which provides a clear direction of how to synthesis process can become more sustainable and reduce the impact on the environment. Corn cob is one agricultural waste containing lignocelluloses which abundant in South Kalimantan. Corn cob is containing approximately 36.4% of cellulose, 34.9% of hemicelluloses and 14.8% of lignin [1]. Recently, some peoples tend to use only corn cob waste as animal feed, fuel or waste. To overcome this problem, the utilization of corn cob needs to develop such as carbon material and as a resource for catalyst have been investigated and good ability as a activated carbon, preparation of cellulose gel, conversion of cellulose to

glucose, synthesis for biodiesel, formic and acetic acid production [2]-[7].

The heterogeneous catalyst is an alternative catalyst for recyclable replacements for unrecyclable liquid ones. The advantages of heterogeneous catalyst are that it can be directly separated from the mixture by decantation or filtration, and also it can be used for several times without neutralization, stable, minimum energy consumption, and there is no waste generation. The heterogeneous catalysis is one of the economically and efficiency material in catalyst field.

Activated carbon is a material produced by pyrolysis at a temperature of 600-900°C. Nearly 70% of active carbon used for the purification in the industry of sugar, coconut oil, pharmaceutical and chemical [8], [9]. There are physical and chemical modifications methods to prepare for activated carbon. The physical modification through carbonization of raw material below 1073 K in an inert atmosphere followed by mild oxidation with an activating agent such as steam, air, and CO₂ at high temperatures about 800-1000°C [10]. Chemical modification through impregnation of the raw

material with dehydrating chemical agents such as phosphoric acid, sulphuric acid and potassium hydroxide in an inert atmosphere [11], [12].

In recent years, there has been an increasing interest in sulphonated carbonaceous material for their potential properties to replace homogeneous acid catalysts. Sulphonated carbonaceous is made by reacting carbon material with sulphuric acid, the sulphonate group and H^+ ion are expected to attach on the surface of the carbon. The conventional process of sulphonation is using concentrated H_2SO_4 and heating at $150^\circ C$ for 12-15 hours [13]. The simple reaction was introduced for sulphonation process using citric acid and hydroxyl ethyl sulphonic acid by hydrothermal treatment for $180^\circ C$, 4 hours which using carbohydrate as carbon precursor [14]. The sulphonation by hydrothermal treatment is an efficient and environmentally friendly process. The sulphonated carbon material is one alternative that can be used in the process of hydrolysis of glucose [2] beside use liquid acids or enzymes and biodiesel production [15]. Starch is an attractive feedstock for the chemical industry, pharmaceutical, as raw materials for bioethanol and other agro-industry. There was studied about the investigation of cassava starch which has antioxidant activity [16] and edible film production [17]. Banana peel starch was used on this work, the advantages of this material are to reduce food waste and make it more valuable. This study was conducted to determine the potential and ability of corn cob as sulphonated biocarbon catalyst that can be developed into new candidate as heterogeneous catalysts. The performance of catalyst on banana peel hydrolysis was also investigated. The utilization of corn cob can be enhanced of corn cob, it is not just a waste or animal feed but can be utilized as a heterogeneous catalyst as a solid acid catalyst.

II. MATERIAL AND METHOD

A. Material

Corn cob was collected as agriculture by product from local farmland at Pelaihari, South Kalimantan, Indonesia. The newly harvested corn cobs are dried under the sun for reducing moisture content. The sufficient dried cobs are sealed in the plastic bag. The corn cobs are dried at $110^\circ C$ for 24 hours, ground and could pass through 60 mesh screen. The banana peel was collected from the traditional market at Banjarbaru. They were cut into small piece (1 cm x 1 cm), washed thoroughly with tap water and ground into fine powder by a high-speed blender. The precipitated materials are filtered and dried at $80^\circ C$ for 12 hours and starch of banana peel was obtained. The banana peel starch was used as a substrate for hydrolysis experiment. Another chemical were used such as oxalic acid ($H_2C_2O_4$), hydroxyl ethyl sulphonic acid ($C_2H_6O_4S$), citric acid ($C_6H_8O_7$), sodium hydroxide (NaOH), sodium chloride (NaCl), chloric acid (HCl), phenolphthalein, methanol (CH_3OH), 3,5 dinitrosalicylic acid ($C_7H_4N_2O_7$), and potassium tartrate ($K_2C_4H_4O_6$).

B. Synthesis of Sulfonated Biocarbon from Corn Cob

The corn cob (60 mesh, 500 g) was carbonized at $400^\circ C$ for 1 hour. The resulting carbon (1 g) was mixed with

hydroxyl ethyl sulphonic acid (1.8 mL) and citric acid (1.5 g) in distilled water (30 mL) and then put in 50 mL Teflon autoclave. Next step, heated in oven for 4 hours at $180^\circ C$. The modify biocarbon was separated by filtration and washed with deionized (DI) water, methanol and DI water again for removed the remaining chemical which it is not reacted, and dried in an oven at for 6 hours at $80^\circ C$. The product called sulphonated biocarbon ($C-SO_3H$).

C. Hydrolysis of Banana Peel Starch over Sulphonated Biocarbon ($C-SO_3H$)

The performance of $C-SO_3H$ was investigated by hydrolysis of banana peel starch. The hydrolysis was conducted in three bottle neck containing solid acid catalyst (0.25 g) and distilled water (50 mL) at various concentrations of banana peel starch (1%, 3%, 5%, 7% and 10%, w/v) and time for reaction (15, 30, 45, 60, 75, 90, and 120 minutes) at $100^\circ C$. Furthermore, the product obtained by filtration was analysed by 3,5-dinitrosalicylic acid (DNS) method for detecting total reducing sugar (TRS) concentration [18].

D. Characterization and Analysis

The Brønsted acid sites on sulphonated biocarbon were calculated by neutralization titration method [19]. The 1 M NaCl (40 mL) and the amount of $C-SO_3H$ (80 mg) were added to the solution. The mixture was sonicated for 20 min and stirred at 100 rpm for 24 h at room temperature. The supernatant of the mixture, which collected by filtration, was titrated with 0.01 N NaOH using phenolphthalein as an indicator. The volume of NaOH solution which used for titration is equivalent to H^+ ion containing on sulphonated biocarbon. As a control, the original biocarbon also investigated for H^+ concentration. The Scanning electron microscopy (SEM) images were observed using scanning electron microscope machine (JEOL, JSM-6500 LV) at 20 kV. The Rigaku D/MAX-B X-ray diffractometer machine which using Copper K-alpha (Cu Ka) radiation with 2θ in the range from 5 to 40° at a scan rate of 2° min^{-1} for investigated X-ray diffraction (XRD) measurement. The operation voltage and current were kept at 40 kV and 100 mA, respectively.

The crystalline index (CrI) value of samples is calculated by:

$$CrI_{110} = \left(\frac{I_{110} - I_{am}}{I_{110}} \right) \times 100\% \quad (1)$$

Where:

I_{110} = maximum intensity of cellulose (diffraction at 22.4°)

I_{am} = specific diffraction of amorphous intensity of sample (18.7°)

Fourier transform infrared spectrometry (FTIR, Bio-rad, Digilab FTS-3500) was used for functional groups identification of the on the carbon surface. UV-Vis spectroscopy (V-550-JASCO) was used for measuring the absorbance for TRS [18] assay. All data presented were obtained from duplicate experiments.

III. RESULTS AND DISCUSSION

A. Characterization of Sulphonated Biocarbon from Corn Cob

The sulphonated biocarbon was prepared by one-step hydrothermal treatment. The biocarbon material was prepared by carbonization of corn cob followed by sulphonation. The schematically preparation of sulphonated biocarbon is shown in Fig. 1. In the first stage of carbonization (A), the corn cob as lignocelluloses is introduced to heat and the material start to pyrolyzed, accompanied by dehydration and dissociation of $-C-O-C-$, then leading to the formation of polycyclic aromatic carbon rings at a higher temperature and carbon structure (B). The $-SO_3H$ functional group is then introduced into the aromatic carbon rings by hydrothermal treatment in the present of hydroethyl sulphonic acid and citric acid (C). The sulphonated biocarbon after carbonization is expected to

have an amorphous carbon structure composed of polycyclic aromatic carbon sheets with $-SO_3H$, $-COOH$, and phenolic OH groups.

The biocarbon materials become harder with increasing temperature during carbonization due to plane growth and stacking of the carbon sheets. The materials are carbonized at lower temperatures have smaller carbon sheets and therefore have higher $-SO_3H$ densities because the SO_3H groups are attached only to the edges of the carbon sheet [13]. Fine black carbon was produced after sulphonation. The surface morphology of corn cob (CC) was presented in Fig. 2 (a). The original structure of corn cob is a rude surface which contains lignin, hemicelluloses, and cellulose. After carbonization, the biocarbon (C) was obtained (Fig. 2 b). The surface of biocarbon was smoother compared the original one; it can be happened because during the carbonization process lignin and another component which staked on the surface of corn cob were removed.

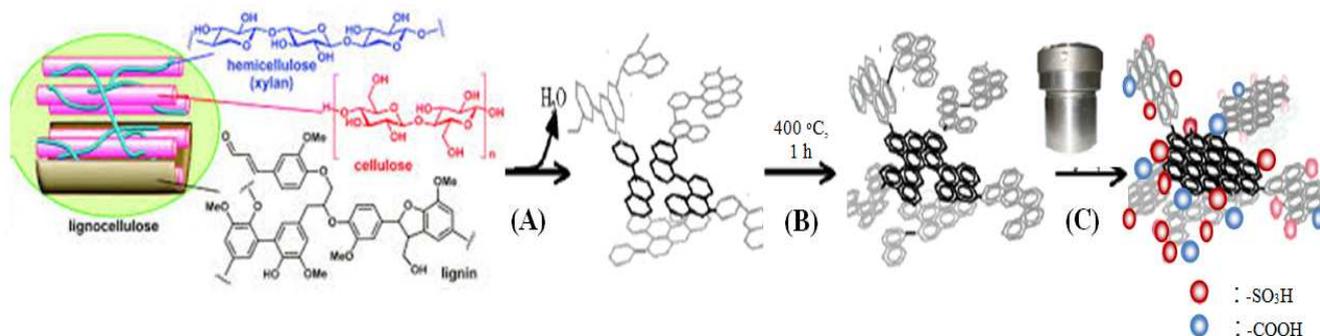


Fig. 1 Preparation of sulphonated biocarbon from corn cob, (A) pyrolysis, (B) carbonization, and (C) sulphonation by hydrothermal treatment

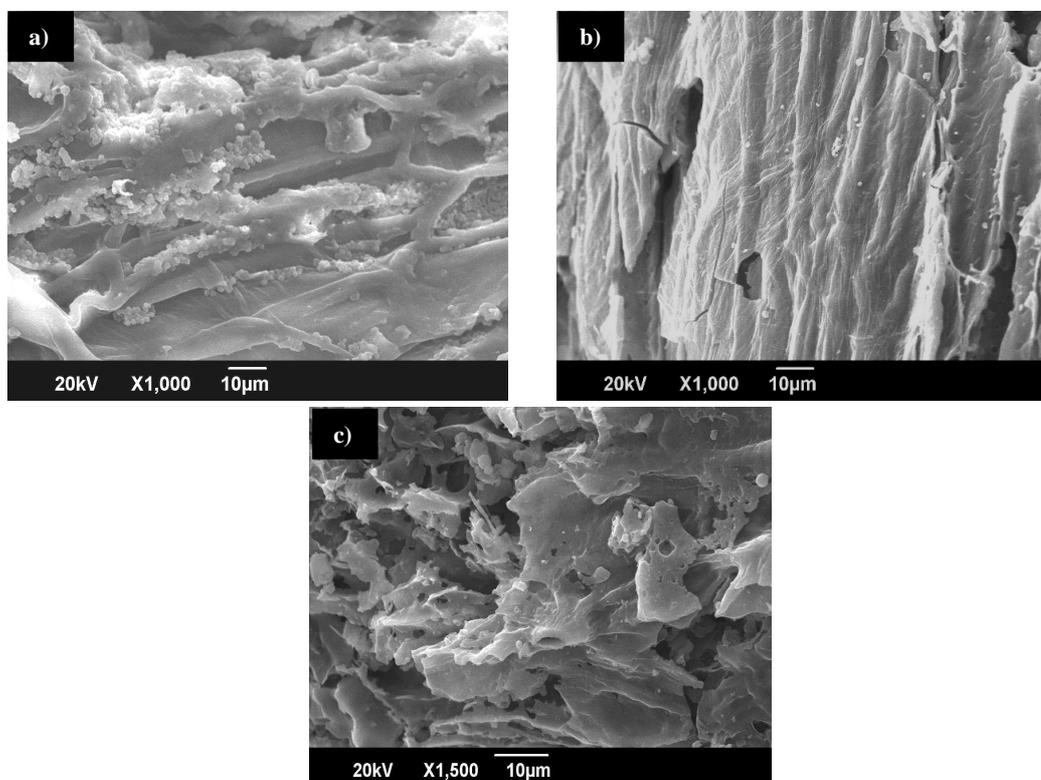


Fig. 2 SEM micrographs of (a) corn cob (CC); (b) biocarbon (C); (c) sulphonated biocarbon (C- SO_3H)

Surface morphology of sulphonated biocarbon (C-SO₃H) was different after hydrothermal treatment which was shown in Fig. 2 (c). Hydrothermal treatment by hydroethyl sulphonic acid and citric acid were reconstructed surface morphology of biocarbon. The post-sulphonation treatment for 4 h at 180 °C, enlarges the pores on the surface and it was founded random pore with diameter size around 3 μm–10 μm could be found on the surface of sulphonated biocarbon. The pore form on biocarbon is provided an opportunity to functional groups (–SO₃H and –OH) attach and also provide an electrochemical reaction site for further application. The images of sulphonated biocarbon are similar morphology which produced by pyrolysis of corn cob which has pore and random size [20]. For the preparation of sulphonated biocarbon, citric acid was employed to participation the acidity formation on the surface of biocarbon. The acidity of sulphonated biocarbon was significantly increased about 6.6-folds than that original one. The original value of acidity was 0.22 mmol/g and after treatment become 1.447 mmol/g. In order to investigate the components of all samples and also the formation of the new structure of the material, all samples were analysed by energy dispersive X-ray (EDX) and the results as shown in Table 1.

TABLE I
THE COMPONENTS OF CORN COB, BIOCARBON, AND SULFONATED BIOCARBON

No	Component	Concentration (weight, %)		
		Corn Cob (CC)	Biocarbon (C)	Sulfonated biocarbon (C-SO ₃ H)
1	C	57.11	79.45	82.39
2	O	42.79	20.55	13.82
3	S	-	-	3.79

The original corn cob consists of carbon and oxygen, after carbonization the concentration of carbon was increased up to 79.45%. In the other hand, the concentration of oxygen was decreased, the oxygen will be removed from the structure of corn cob because of the formation of carbon by carbonization. After sulphonation, there is only sulphonate was founded on C-SO₃H, approximately 3.79% of S content was detected on sulphonated biocarbon.

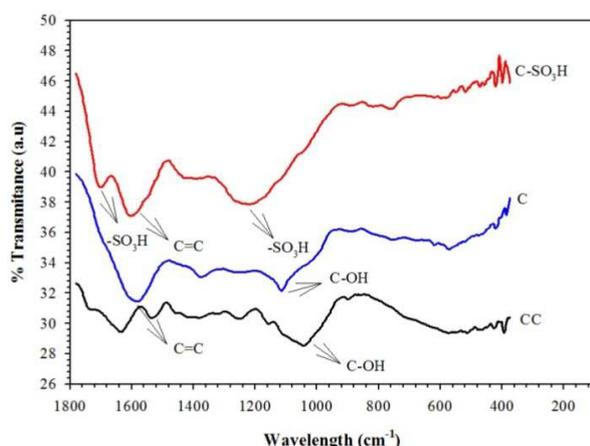


Fig. 3 FTIR spectra of (a) corn cob (CC); (b) biocarbon (C); (c) sulphonated biocarbon (C-SO₃H)

The FTIR spectra of all samples are shown in Fig. 3, the apparent –SO₃H peaks at 1730 cm⁻¹ and 1210 cm⁻¹ were indicated for C-SO₃H. These peaks prove that the biocarbon was sulphonated by hydroxyethylsulfonic acid. Another absorption peak at 1610 cm⁻¹ be assigned to C=C double bonds stretching which identified for the aromatic ring in lignin and the product of carbonization was has aromatized and carbonized material from carbohydrate ring dehydration and cyclisation [21].

The C=C stretching only fronded on C and C-SO₃H. The C-OH stretching and -OH bending vibrations at 1000-1300 cm⁻¹ were also identified for C, CC, and C-SO₃H which indicates the structure of sample was carbon material. A similar result has been reported by another researcher that showed FTIR spectra of sulphonated carbonaceous particle [2].

The X-ray diffraction patterns of corn cob biocarbon are displayed in Fig. 4. For CC and C sample had analogous diffractogram patterns. The C-SO₃H some slight differences were noted among the samples, a weak and broad on C-SO₃H (002) at diffraction peak (2θ = 20°-30°) was observed which could be the amorphous structure of carbon [13]. Base on characteristic peak of cellulose at 2θ = 18,7° (cellulose I, amorphous) and 2θ = 22,4° (cellulose II, crystal) [22], the crystalline structure of corn cob was increased from 18.30% to 42.64% which indicated the higher crystalline structure of C due to carbonization process was removed volatile matter and another component of lignocelluloses content in corn cob and then carbon sheet was formed.

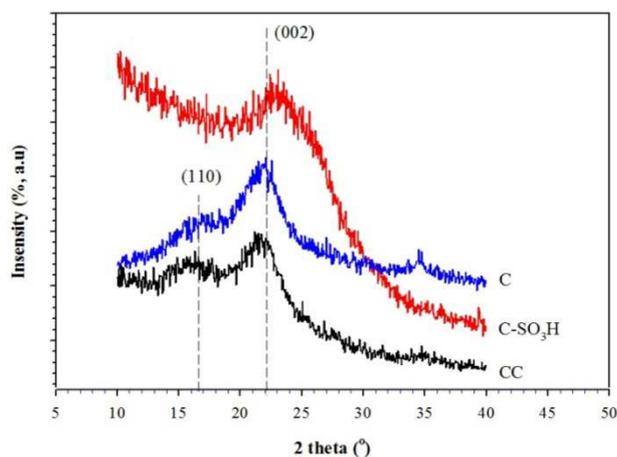


Fig. 4 XRD pattern of (a) corn cob (CC); (b) biocarbon (C); (c) sulphonated biocarbon (C-SO₃H)

B. Banana Peel Starch Hydrolysis over Sulphonated Biocarbon

The banana peel starch produced from local banana which consists of some components is shown in Table 2.

TABLE III
THE COMPONENTS OF BANANA PEEL STARCH

No	Component	Concentration (%)
1	Water	18.26
2	Ash	9.43
3	Protein	8.67
4	Fat	6.69
5	Carbohydrate	56.95

Based on observation, the banana peel starch consists of 56.95% of carbohydrate. This material has the opportunity to develop a new product based on carbohydrate. One of the interesting values, carbohydrate is a potential substrate for glucose production. It is well known that the carbohydrate could be converted to glucose by hydrolysis over the heterogeneous or homogeneous catalyst and enzymatic reaction. Enzymes such as α amylase and amyloglucosidase, are capable of digesting these glycosidic linkages in starches [23]. The carbon-based solid acid catalyst could be hydrolysed pure crystalline cellulose and natural lignocellulosic materials. So that, the starch of banana peel is used in this experiment. It is well known that starch is consisting of amylose and amylopectin. Amylose is glucose

linked chain polymer mainly by α -(1,4)-glycosidic bonds and amylopectin is a highly branched polymer of glucose linked by α -(1,6)- and α -(1,4)-glycosidic bonds. The starch hydrolysis was carried out in the reactor by variation of concentration of substrate (banana peel starch). The amount of total reducing sugar in the supernatant was considered as the hydrolysis product catalyzed by C-SO₃H. The sulfonated biocarbon catalyst breaks the α -(1,6)- and α -(1,4)-glycosidic bonds on the starch chain and oligomers of glucose were produced. The schematic diagram of starch hydrolysis by C-SO₃H is shown in Fig. 5.

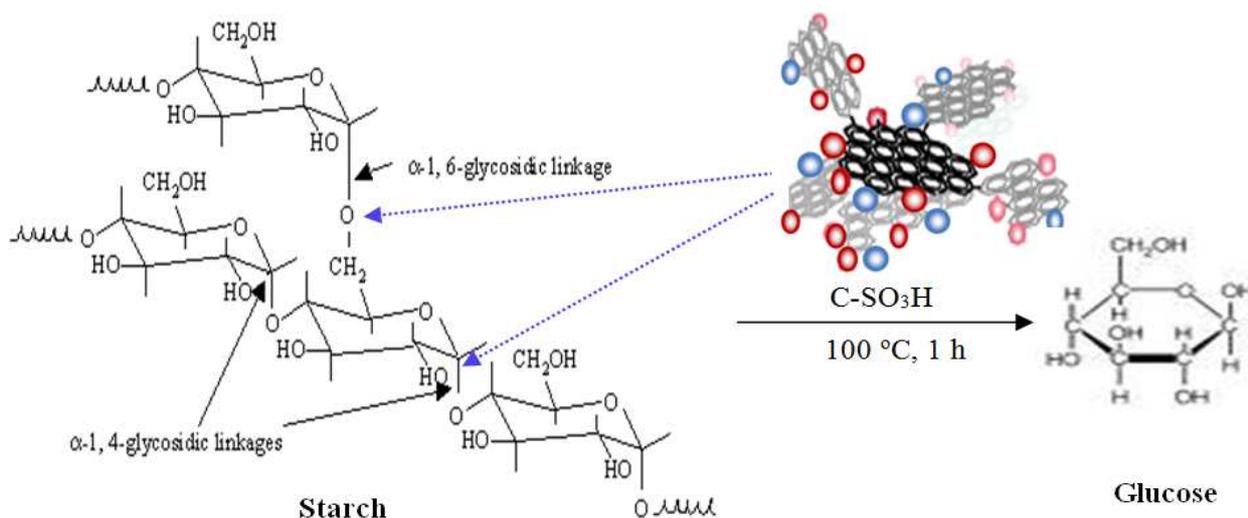


Fig. 5 Schematic diagram of banana peel starch hydrolysis over C-SO₃H as catalyst

As shown in Fig. 6, TRS concentration for hydrolysis product was increased up to 0.689 mg/mL using catalyst C-SO₃H. TRS produced by C-SO₃H at the variation of banana peel starch concentration in the range of 0.5–10% (w/v), the TRS significantly increased when the substrate concentration up to 5%, after that the increasing TRS relative slow until 10% concentration of substrate. The capability of C-SO₃H was limited to break starch chains linked when the concentration of banana peel starch about 7%. It means the capability of catalyst was reached to maximum condition on that condition. The colour intensity is developed by DNS assay which indicates more reducing sugars was produced with increasing concentration of substrate (Fig. 6, inset). The colour of solution became darker when high TRS concentration. Based on the concentration of TRS, efficiency of energy and operational cost, the concentration 7% of banana peel starch is optimum in this reaction condition.

Fig. 7 shows the effects of reaction time to TRS concentration by hydrolysis at 100 °C using C-SO₃H. The TRS increased linearly up to 0.688 mg/mL after 60 minutes reaction and the primary products are oligomers. By increasing banana peel concentration, it followed by increasing of TRS concentration. After 60 minutes reaction, the TRS start decreased until level off to 0.639 mg/mL for 120 minutes. By prolonging reaction time, the decreasing of

TRS was probably due to sugar degradation. It is known that longer reaction time, sugar will dehydrate through an intermolecular condensation reaction that leads to furan-like molecules (furfural aldehyde and/or 5-(hydroxymethyl)-2-furaldehyde) formation [24].

In order to investigate the reusability of C-SO₃H, the recovered catalyst was washed three times with warm DI water by vigorous stirring at 100 rpm for 30 minutes and collected by centrifugation and dried. The catalytic activity of recovered catalyst was slightly lower than that observed in the first reaction. After 4 repeated uses, there is only 6% TRS decrease was observed, it was shown at Fig. 8.

It is interesting to investigate the concentrate H₂SO₄ (>96%) and the original biocarbon for hydrolysis reaction. The H⁺ concentration of H₂SO₄ should same concentration with H⁺ on C-SO₃H. The biocarbon without treatment was used as a control. As shown in Fig. 9, the concentration of TRS about 0.26 mg/mL could be obtained when using biocarbon without treatment. The TRS was produced by using C-SO₃H about 1.65 folds than that original biocarbon (C). It means catalytic activity of C-SO₃H increased due to surface functionalization of biocarbon. In order hand, when using liquid catalyst the production of TRS was 0.78 mg/mL. The highest number of TRS is due to the accessibility of catalyst easier to attach carbohydrate linkage in the

homogenous phase. This shows that this one-step prepared sulphonated biocarbon not only has the merit of non-toxic materials, eco-friendly, recyclable but also has good catalytic activity for hydrolysis reaction.

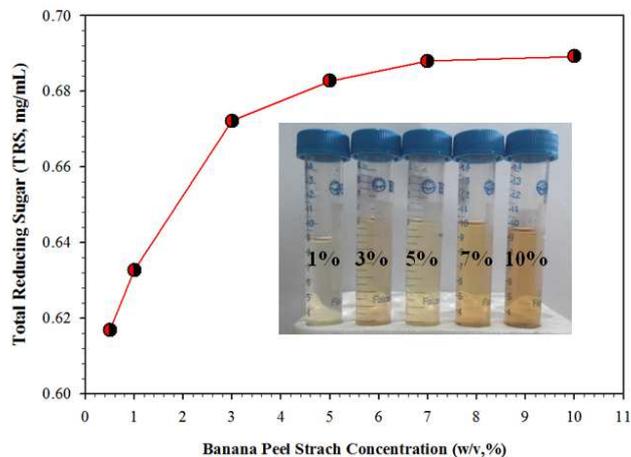


Fig. 6 Total reducing the sugar for banana peel starch (hydrolysis by variation of the substrate). Reaction condition: 0.25 g of C-SO₃H, 50 mL aquadest, 100 °C, 1 h

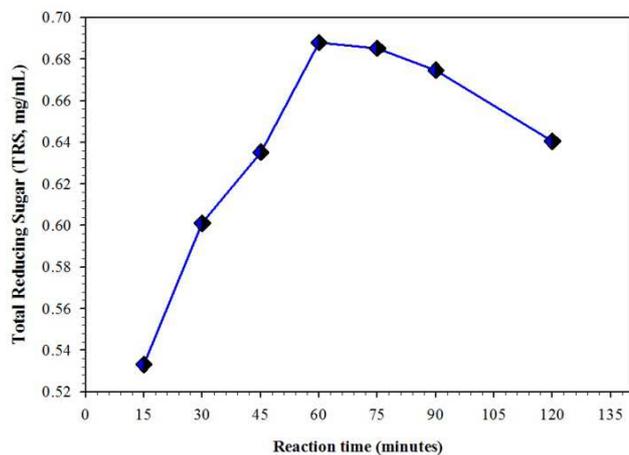


Fig. 7 Total reducing sugar for banana peel starch (hydrolysis by variation of reaction time). Reaction condition: 0.25 g of C-SO₃H, 7% (w/v) banana peel starch, 50 mL aquadest, 100 °C.

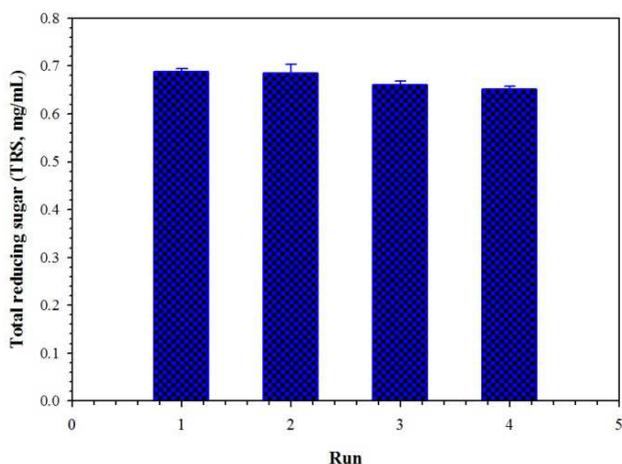


Fig. 8 Catalytic activity of C-SO₃H during 4 repeated used for banana peel starch hydrolysis. Reaction condition: 0.25 g C-SO₃H, 7% (w/v) banana peel starch, 50 mL aquadest, 100 °C, 1 h

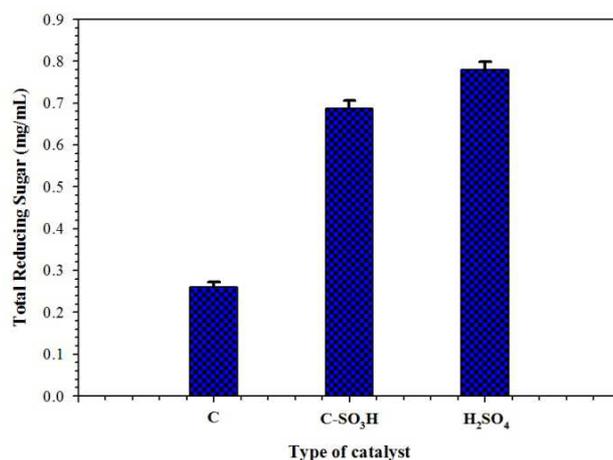


Fig. 9 Total reducing sugar (TRS) for banana peel starch hydrolysis using a different type of catalyst. Reaction condition: acidity of catalyst 0.362 mmol, 7% (w/v) banana peel starch, 50 mL aquadest, 100 °C, 1 h.

IV. CONCLUSIONS

The sulphonated biocarbon from corn cob with rich content of sulphonate group and high acidity could be synthesized by one-step hydrothermal treatment. Sulphonate and hydroxyl groups are attack on the edge of carbon sheet. The sulphonated biocarbon could be used as solid acid catalyst; it has good capability to hydrolyse banana peel starch. It is not only possesses good for reusable material and high acidity content but also has the similar catalytic activity as concentrated H₂SO₄. The raw material for preparation biocarbon and substrate for this research are using waste material that can solve the environmental problem.

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