

One-step Synthesis to Enhance the Acidity of Biocarbon-Based Sulfonated Solid Acid Catalyst

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ONE-STEP SYNTHESIS TO ENHANCE THE ACIDITY OF BIOCARBON-BASED SULFONATED SOLID ACID CATALYST

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ABSTRACT

Biocarbon based sulfonated catalyst was prepared by carbonization of palm empty fruit bunch (PEFB) then followed by sulfonation. In order to enhance the acidity of biocarbon, the hydroxyethylsulfonic acid in difference concentration was added into solution during sulfonation at 180 °C for 4 h in Teflon stainless steel autoclave. The H⁺ ion capacity of biocarbon sulfonated acid catalyst (BC-SO₃H) was increased 2 folds (3.569 mmol/g) in the presence 10% of hydroxyethylsulfonic acid and 10% of acrylic acid. The X-Ray Fluorescence (XRF) analysis shows the BC-SO₃H contained of 38% of S. The original structure of PEFB after carbonization disintegrates from the fibrous materials onto porous carbon. The crystalline index (CrI) of PEFB significantly decreased about 32% and a wide broad peak of X-Ray Diffraction (XRD) pattern around 20-30° which shows amorphous biocarbon structure was identified. Fourier Transform Infra-Red (FT-IR) analysis proves that the -SO₃H, COOH and -OH functional group were deposited on the carbon due to specific peaks around 1180 cm⁻¹, 1724 cm⁻¹ and 3431 cm⁻¹, respectively. The decomposition of sulfonic group on biocarbon sulfonated solid catalyst was observed start at 227.9 °C which observed by thermal gravimetric analysis (TGA).

Keywords: Acid Catalyst; Biocarbon; Sulfonation; Sulfonated; Palm Empty Bunch Fruit

1. INTRODUCTION

Palm is one of the most important commodities in Indonesia due to its rapid development. The major product from palm industry is Crude Palm Oil (CPO) and along with the increasing production of CPO, the waste that takes form of empty fruit bunch increased. Nowadays biomass and industrial waste become highly interesting issues as utilized object in catalyst development both in research and technical point of view due to its valuable merit (Guerrero-Pérez et al., 2006). Biomass energy is an ideal clean and renewable energy source with characteristics of wide sources, low prices, strong reproducibility and less pollution (Wenjing et al., 2018).

Solid acid catalyst in the utilization is easily and efficient when separated from their products, reusable and it is possible to apply in wide of applications, but mostly solid acid catalyst reported is expensive and quite difficult in preparation (Okuhara, 2002).

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Recently, work on sulfonated solid acid catalyst is the highlight of attention from researcher for hydrolysis reaction of cornstarch (Nata et al., 2015) banana starch utilized corn cob as biocarbon (Nata et al., 2017b) and biodiesel production from waste cooking oil (Zong et al., 2007; Nata et al., 2017a). The performance in the reaction of carbon-derived catalysts depends on the precursor as materials for carbon production and treatment process (Tao et al., 2015). In view of “green chemistry” issue, the sulfonated carbon catalyst has emerged as promising solid acid catalyst (Jiang et al., 2012).

Theoretically, at low carbonization (400 – 600 °C), the biomass generate highly cross-linked, multi-ringed, aromatic structure anchored to lignin that could be easily functionalized with catalytically active acidic groups by slow pyrolysis (Kastner et al., 2012). Generally, there is two steps process for production of sulfonated carbonaceous materials. Saccharide was incomplete carbonized at temperature >400 °C for >15 h under an inert atmosphere. The large amount of sulphuric acid was used in sulfonation process at high temperature for inactive surface of carbonaceous material (Zong et al., 2007). This process was used hazard material and and large amount of harmful wastes produced, moreover the carbon in concentrate sulphuric was also need special work for separation and treatment.

Hydrothermal carbonization (HTC) is thermo chemical process that capable for converting wet biomass into carbon-enriched solid as hydro char. The HTC process consists of several reactions conducting both in series and in parallel: hydrolysis, dehydration, decarboxylation, condensation, aromatization and others (Muzari et al., 2018). HTC is process which including various of carbohydrates decomposition in aqueous solution at 180 °C. This method being cheap, mild, and environmental friendly as it no organic solvents, catalyst or surfactants used (Titirici et al., 2007). However, the product of HTC still owned little of functional groups, hence to generate carbonaceous material loaded with carboxylic groups and acrylic acid were added (Bautista-Toledo et al., 2005). This work is focus on effect of hydroxyethylsulfonic acid concentration and addition of acrylic acid during hydrothermal process. Therefore the characterization of materials such as acidity, morphology structure, crystalline structure, functional groups and thermal gravimetric analysis were investigated.

2. METHODS

2.1. Materials

The raw material as a carbon source for catalyst is palm empty fruit bunch, it was collected from PT. Perkebunan Nusantara XIII, South Kalimantan, Indonesia. Citric acid ($C_6H_5Na_3O_7 \cdot 2H_2O$), acrylic acid ($C_3H_4O_2$), hydroxyethylsulfonic acid ($C_2H_6O_4S$), sodium chloride (NaCl), sodium hydroxide (NaOH), oxalic acid ($H_2C_2O_4$), chloride acid (HCl), , methanol (CH_3OH), phenolphthalein were purchased from Sigma-Aldrich.

2.2. Synthesis of Biocarbon Sulfonated Solid Acid Catalyst

Biocarbon sulfonated solid acid catalyst was carried out according by Xiao et al. (2010) with some modification, thorough one-step hydrothermal treatment. Empty fruit bunch was heated in a furnace at 350 °C for 1 h, then producing carbon mashed up to 60 mesh. The obtained carbon material was mixed with hydroxyethylsulfoic acid in concentration of 10, 20 and 30 % v/v. 5 g of citric acid, 1.5 mL of acrylic acid and 30 mL of deionized (DI) water that poured in a 50 mL Teflon-lined stainless steel autoclave, then heated for 4 h at 180 °C. Black carbon material produced then washed with DI water and 50% of methanol for twice. The biocarbon sulfonated solid acid catalyst (BC-SO₃H) was obtained after dried at 80 °C for 6 h in an oven. Four different type of carbon particles produced were the carbon without sulfonation, carbon with

sulfonation contains 10%, 20% and 30% of hydroxyethylsulfonic acid which namely BC, BC-SO₃H-1, BC-SO₃H-2, and BC-SO₃H-3, respectively.

2.3. Calculation of Acid Contents

The Brønsted acid acid content in sample was measure by by neutralization titration (Onda et al., 2008). Carbon material (50 mg) was added into 2 M NaCl (25 mL) solution at room temperature and stirred for 5 h . Afterwards, the filtered and supernatant obtained clear solution was added with phenolphthalein then titrated with 0.1 M NaOH to determine the acid contents.

2.4. Characterization

The observation of morphology structure image was obtained by scanning electron microscope (SEM) using JEOL, JSM-6500 LV equipment. The functional groups on the surface of material were detected by Fourier transform infrared spectrometry (FT-IR, Bio-rad, Digilab FTS-3500) at wavelength range 4000-400 cm⁻¹ with scan rate 8. The X-ray diffraction (XRD) analysis was carried out on X-ray diffractometer by using Cu K α radiation (Rigaku D/MAX-B) with 2 θ (10-40 °) at a scan rate of 2° min⁻¹ and work on voltage and current at 40 kV and 100 mA, respectively. Thermal gravimetric analysis (TGA) performance using Perkin Elmer, Diamond TG/DTA was conducted from 30 °C-600 °C under nitrogen atmosphere by heating rate of 10 °C/min. The remaining material content in sample was calculated by mass change from the corresponding TGA curves.

3. RESULTS AND DISCUSSION

The PEFB in its original form was turning to black carbon after carbonization. The producing carbon was followed by sulfonation via hydrothermal treatment. Hydrothermal carbonization is method which an attractive mild preparation of carbons with special properties. The accessible external surface densely functionalized with polar groups, such as carboxylic and hydroxyl, confers them high hydrophilicity and susceptibility to chemical modification (Frail et al., 2012). The treatment of carbon materials under HTC increases or changes their solubility, melts crystalline parts, accelerates the physical and chemical interaction between reagents and the solvents, facilitating the ionic and acid reactions, and leads to the carbonaceous structure formation (Hu et al., 2010). Schematic diagram preparation of biocarbon sulfonated solid acid catalyst is shown in Figure 1.

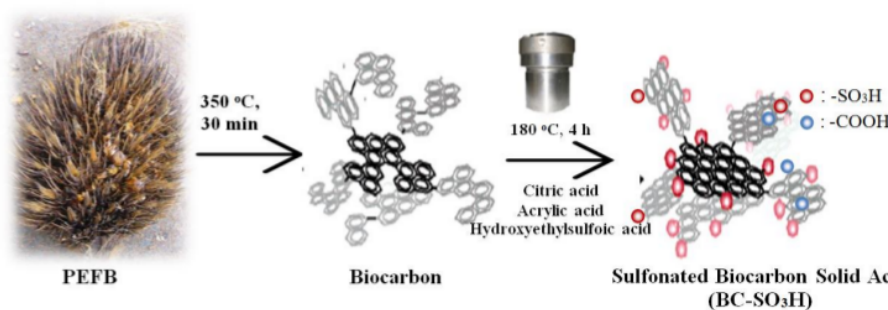


Figure 1 Schematic diagram preparation of biocarbon sulfonated solid acid catalyst from PEFB

It's known that during carbonization process, lignin would breaks in to partial decomposition, then hemicellulose and cellulose would through of thermal homolysis, hydrolysis, dehydration,

and rearrangement of molecular reactions to form a polymerized aromatic structure. The process of bounded sulfonic groups to biocarbon materials during hydrothermal treatment. The arrangement of biocarbon material involves the biocarbon dehydration, hydroxyethylsulfonic, citric and, acrylic acid in the first step then allowed sulfonic and carboxylic acid groups induced on carbon materials and subsequently provide hydroxyl functional groups for intermolecular dehydration. Here, hydroxyethylsulfonic acid was used as functional molecule to introduce sulfonic groups to the biocarbon material and carbonyl groups were supplied by citric acid that help obtained the carbon with high acidity (Xiao et al., 2010).

Moreover, the addition of acrylic acid as a co-monomer in hydrothermal treatment causes the escalation of catalyst acidity. The acrylic acid induction for hydrothermal carbonization process could achieved for product rich of carboxylic group on the surface, which was known that the more active on reaction is carboxylic acid group than sulfonic acid groups and participate the reaction instead of sulfonic acid groups (Demir-Cakan et al., 2009). The apparent of sulfonic acid groups is reached by the reaction of sulfonating agent and the polysyclic aromatic rings of biocarbon that make up the new structure, through electrophilic substitution (Aldana-Pérez et al., 2012). It was reported that sulfonated carbon catalysts had great stability in reaction condition (Lokman et al., 2016).

Table 1 is shown the acidity and S content base on X-Ray Fluorescence for different types of biocarbon sulfonated solid acid catalyst. The addition of 10% of hydroxyethylsulfonic acid has increasing number of S content about 30%, however the acidity of biocarbon turn to decreased when hydroxyethylsulfonic acid was added >10%. This is probably due to competitiveness of each functional group when taking place and binding with carbon during hydrothermal treatment. The more hydroxyethylsulfonic acid used in sulfonation process, the higher S content accommodated on the carbonaceous materials which resulting more acidic groups such as carboxyl, carbonyl and hydroxyl group cannot bind with the carbon, whereas these acid groups acted as the supplier of H⁺ ion that help produced carbon with high acidity. This explained the decreased of acid capacity for BC-SO₃H-2 and BC-SO₃H-3 compared to BC-SO₃H-1.

Table 1 The acidity and S content of different type of biocarbon solid acid catalyst

Sample	Acidity (mmol/g)	S content (%)
BC	0.209	-
BC-SO ₃ H-1	3.569	38
BC-SO ₃ H-2	2.380	46.8
BC-SO ₃ H-3	2.712	54.4

The biocarbon morphology characterization of solid acid catalyst was carried out in order to prediction of physical and chemical properties of material. As shown in Figure 2(a), the PEFB had fibrous shape with smooth surface and 2(b) show the structure after carbonization. In comparison, Figure 2(c), 2(d) and 2(e) was generated in the presence of hydroxyethylsulfonic and acrylic acid, form scattered shape but more aggregated. Presumably, hydroxyethylsulfonic acid acted as agent that disintegrates the fibrous materials onto porous carbon which allow sulfonate groups attached in the surface of carbon. In addition, more particles formed with a smaller sized during dehydration and polymerization causes surface of material is no longer smooth due to change in the material morphology induced by the addition of hydroethylsulfonic and acrylic acid.

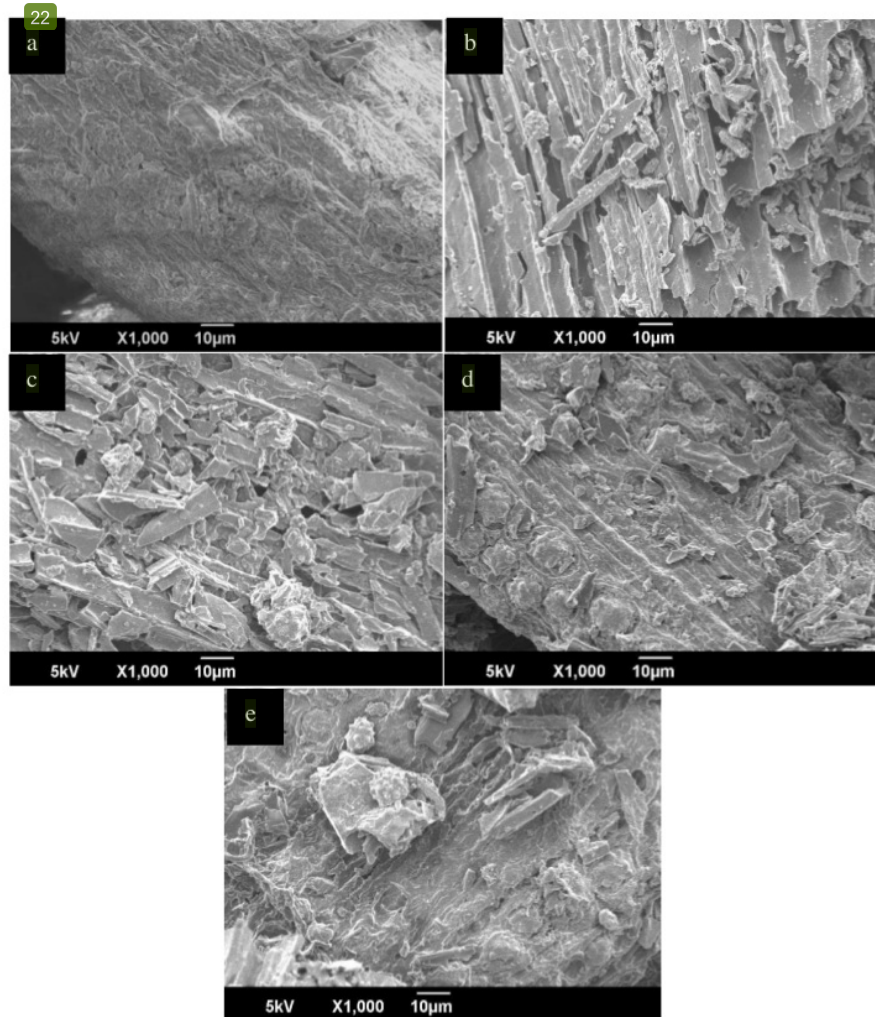


Figure 2 SEM micrographs of (a) PEFB; (b) BC; (c) BC-SO₃H-1; (d) BC-SO₃H-2, (e) BC-SO₃H-3

Figure 3 shown XRD pattern for material which the crystalline index of PEFB significantly decreased about 22,38% and material for BC, BC-SO₃H-1; BC-SO₃H-2; BC-SO₃H-3 form a wide-broad peak pattern around $2\theta = 20-30^\circ$, that shows the amorphous structure of carbon (Okamura et al. 2006). The reduction in crystalline index (CrI) indicates the crystalline structure transform onto carbon due to carbonization process which involves degradation of lignin, hemicelluloses and cellulose. FT-IR measurement was applied to identify functional groups on material. The absorption bands of -OH stretching at 3450 cm^{-1} and -OH bending at $1000-1300\text{ cm}^{-1}$ and C=C double bonds at 1608 cm^{-1} were found for all the samples (Zong et al., 2007). The presence of sulfonate absorption band at 1207 cm^{-1} and C=O double bonds at 1720 cm^{-1} which indicate carboxylic groups was identified for BC-SO₃H-1, BC-SO₃H-2, BC-SO₃H-3, as shown in Figure 4. The difference concentration of hydroxyethylsulfonic acid gives difference intensity peaks for sulfonate group, the higher the concentration, the sharper peaks were formed. This observation is related with XRF result. Furthermore, FT-IR analysis proved that

the biocarbon materials were successfully sulfonated during hydrothermal process in the addition of hydroxyethylsulfonic acid. The presence of sulfonic acid groups (-SO₃H) on carbon will be changes the pH of the surface, therefore it also impact to changing the adsorption characteristics and making these carbons suitable for the applications of heterogeneous solid acid catalyst (Fraga et al., 2016).

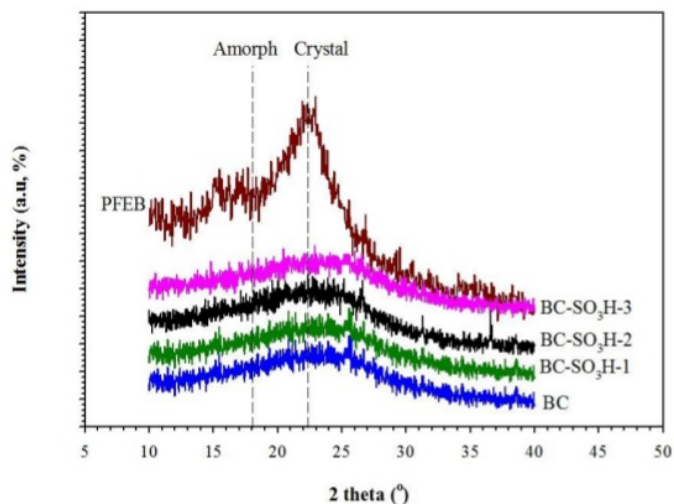


Figure 3 XRD patterns of PEFB, BC, BC-SO₃H-1, BC-SO₃H-2, and BC-SO₃H-3

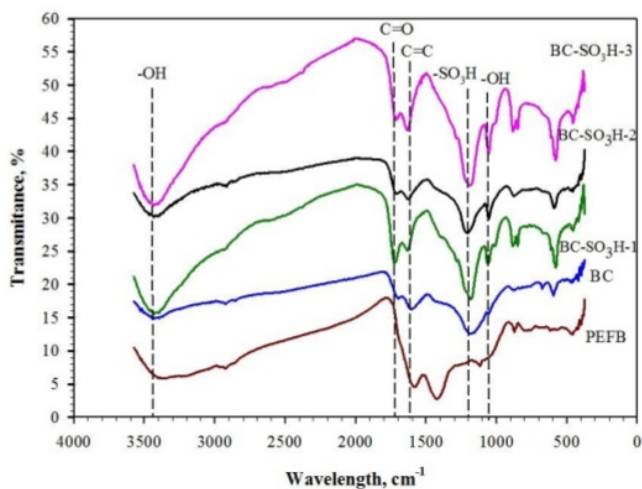


Figure 4 FT-IR spectra of PEFB, BC, BC-SO₃H-1, BC-SO₃H-2, and BC-SO₃H-3

In order to understand the typical degradation of PEFB and impact of sulfonation on the thermal stability of biocarbon sulfonated solid acid catalysts, thermal gravimetric analysis was investigated. In Figure 5, the gravimetric analysis of all materials carbonized until 600 °C were shown, the PEFB start the dehydration of water at 74.4 °C and then followed by decomposition of lignin and hemicellulose at 332.5 °C. The decomposition of carbon material including sulfonated solid catalyst was observed start at 227.9 °C for sulfonic group (Kastner et al.,

2012). The higher concentration of sulfonic acid will give more mass loss on TGA curve as for BC-SO₃H-1, BC-SO₃H-2, and BC-SO₃H-3 about 40%, 50, 67% respectively. This phenomenon is related with amount of sulfonic group which obtained by XRF result.

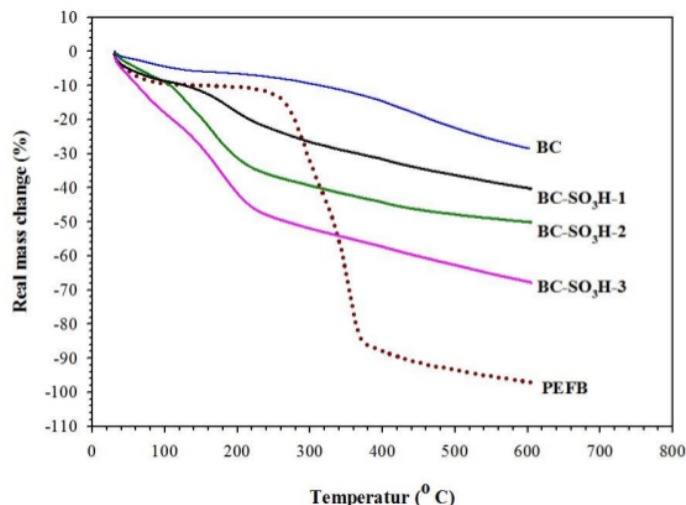


Figure 4 TGA curve of PEFB, BC, BC-SO₃H-1, BC-SO₃H-2, BC-SO₃H-3

4. CONCLUSION

The strong acid, rich of sulfonic and biocarbon carboxylic groups of biocarbon materials could be easily synthesized by one-step hydrothermal process using biocarbon from incompletely carbonized of PEFB, hydroxyethylsulfonic, acrylic and citric acid under mild condition. The simplicity of operation, high activity and stability, low cost raw materials and reusable are the point features the novelty of biocarbon-based sulfonated solid acid catalyst, which signify that biocarbon holds great potential for green process in various catalytic applications.

5. ACKNOWLEDGEMENT

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