



Iryanti Fatyasari Nata <ifnata@ulm.ac.id>

Decision on submission to RSC Advances - RA-ART-12-2020-010163

1 message

RSC Advances <onbehalf@manuscriptcentral.com>

Thu, Dec 24, 2020 at 8:40 AM

Reply-To: advances@rsc.org

To: ifnata@ulm.ac.id, yanti_tkunlam@yahoo.com

24-Dec-2020

Dear Professor Nata:

Manuscript ID: RA-ART-12-2020-010163

TITLE: A green synthesis of palm empty fruit bunch-derived sulfonated carbon acid catalyst and its performance for cassava peel starch hydrolysis

Thank you for your submission to RSC Advances, published by the Royal Society of Chemistry. I sent your manuscript to reviewers and I have now received their reports which are copied below.

After careful evaluation of the manuscript and reviewers' comments, I regret to inform you that I do not find your manuscript suitable for publication and therefore it has been rejected in its current form.

However, if you are able to fully address the concerns raised by the reviewers in the reports below, I will consider a substantially rewritten manuscript which takes into account all of the reviewers' comments. If you choose to resubmit your manuscript, please include a point by point response to the reviewers' comments and highlight the changes you have made.

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I look forward to receiving your re-submission.

Yours sincerely,
Professor Yongjun Liu

Associate Editor, RSC Advances

REVIEWER REPORT(S):

Referee: 1

Recommendation: Major revisions

Comments:

This revision is the manuscript entitled "A green synthesis of palm empty fruit bunch-derived sulfonated carbon acid catalyst and its performance for cassava peel starch hydrolysis" (RA-ART-12-2020-010163). The purpose of the manuscript is to synthesize and evaluate the catalytic performance of sulfonated carbon in hydrolysis reaction of cassava peel starch.

The abstract and Introduction are well written with essential and concise information. Other information should be included in the study, such as some discussions of structural characterization results, in order to better evaluate the properties of the catalyst, as well as on the reuse of the catalyst. The information provided on materials and methods requires minor adjustments. Therefore, considering the relevance and importance of this journal, I recommend that manuscript be accepted after major revision. Some suggestions are given below:

Materials and Methods:

- In carbonization process, I suggest the authors to specify the type of gas and furnace used. In addition, the authors should cite the reference used for the carbonization process that specifies both the temperature and time used.
- After the sulfonation process, the catalyst has been washed until the washing water has a pH ~7? Please grant this information. This is crucial to understanding catalytic activity.
- In hydrolysis process, what kind of reactor was used? steel reactor with closed system, or open reactor?
- Is the amount of water used (50 mL) equal to the total volume of the reactor? Please provide these details in this description.
- The authors must specify in the topic materials and methods how the catalyst recovery process was performed after the catalytic test was completed. Was the catalyst was washed? With water or organic solvent? How many times? Was it dried at what temperature? For how long? This information should be in the methodology and not in the results and discussion.
- In characterizing the catalyst, the authors must specify the range of operation of the FTIR spectra collection, as well as the number of scans and resolution used. For TG analysis, the authors must inform the gas flow and the type of crucible used.

Results and Discussion:

- I do not recommend using SEM micrography to state that the catalyst has pores of diameters of 3-6 μm , because only by a micrography there is no confirmation of the homogeneity of the material, in other words, it is not a precise image of the representation of the entire material. For this, it would require a more extensive study, which is not the case presented. In order to provide this affirmation with more precision, it is recommended to determine the average pore size by the BJH method. Furthermore, I understand that there is not enough data, only by SEM analysis, that can state that the catalyst contains in its composition sulfonic and carboxylic groups. For this, one should associate to SEM, the analysis of elemental mapping by EDS in order to determine the presence, for example of sulfur for association to sulfonic groups.
- I recommend adding the DTG curves to the TG graph (Fig. 6) in order to facilitate the visualization of the events of loss of mass of TG curves. It is common to associate a mass loss event to sulfonic groups in sulfonated carbons in the temperature range of ~ 210 $^{\circ}\text{C}$ to 290 $^{\circ}\text{C}$. This is not evident or is not detected in the graph presented in Fig. 6. I suggest that the authors characterize this loss of mass with respect to this sulfonic group, as I understand that this information is essential for the elucidation of the properties of the catalyst.
- Why did the catalyst reuse study not continue until the catalyst showed significant loss of activity?
- What is the mass percentage of catalyst recovery?
- The reaction condition fixed at 100 $^{\circ}\text{C}$ for 1h, can't be underestimating the potentiality of the catalyst? Is there evidence of increased or decreased catalytic efficiency when promoting increased or decreased temperature or reaction times?
- I suggest that the catalyst be characterized by FTIR and surface acidity after use in the catalytic test, i.e. after the study of the reaction cycles, in order to evidence the maintenance of the active sites responsible for the catalytic activity.

Additional Questions:

Does the work significantly advance the understanding or development in this field?: Yes

Is this work of relevance to the chemistry community?: Yes

Are the conclusions of the work convincing and sufficiently supported by experimental evidence?: Yes

Is the experimental section sufficiently detailed to allow others to reproduce the work?: Yes

Are the reported claims adequately discussed in the context of the literature?: Yes

Are the number of tables and figures in the manuscript appropriate and clear?: Yes

Referee: 2

Recommendation: Reject

Comments:

1. If it's simple carbon from plant material then why describe many the process?
2. Why Citric acid added? When the SO₃H is bind with Carbon prepared from PEFB fiber?
3. What is the role of Citric acid?
4. If only carbon need then why not charcoal or graphite used?
5. No reaction, mechanism or catalytic effect shown for the hydrolysis of carbohydrate?
6. Where is Mass and NMR spectra?
7. SO₃H is bind with what?
8. It is just like well drafted manuscript but no scientific voice.

Additional Questions:

Does the work significantly advance the understanding or development in this field?: No

Is this work of relevance to the chemistry community?: No

Are the conclusions of the work convincing and sufficiently supported by experimental evidence?: No

Is the experimental section sufficiently detailed to allow others to reproduce the work?: No

Are the reported claims adequately discussed in the context of the literature?: Yes

Are the number of tables and figures in the manuscript appropriate and clear?: No

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Decision on submission to RSC Advances - RA-ART-01-2021-000019

1 message

RSC Advances <onbehalf@manuscriptcentral.com>

Sat, Jan 23, 2021 at 5:45 PM

Reply-To: advances@rsc.org

To: ifnata@ulm.ac.id, yanti_tkunlam@yahoo.com

23-Jan-2021

Dear Professor Nata:

Manuscript ID: RA-ART-01-2021-000019

TITLE: A green synthesis of palm empty fruit bunch-derived sulfonated carbon acid catalyst and its performance for cassava peel starch hydrolysis

Thank you for submitting your revised manuscript to RSC Advances. After considering the changes you have made, I am pleased to accept your manuscript for publication in its current form. I have copied any final comments from the reviewer(s) below.

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With best wishes,

Professor Yongjun Liu
Associate Editor, RSC Advances

REVIEWER REPORT(S):
Referee: 2

Recommendation: Accept

Comments:
Still answer of some queries are missing.

Additional Questions:
Does the work significantly advance the understanding or development in this field?: Yes

Is this work of relevance to the chemistry community?: Yes

Are the conclusions of the work convincing and sufficiently supported by experimental evidence?: Yes

Does the data provided fulfil the journal's data requirements?

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Is the experimental section sufficiently detailed to allow others to reproduce the work?: Yes

Are the reported claims adequately discussed in the context of the literature?: Yes

Are the number of tables and figures in the manuscript appropriate and clear?: Yes

Referee: 1

Recommendation: Accept

Comments:
Through corrections and justifications presented by the authors, I am convinced that the manuscript has quality and robustness in the data presented to be published in this journal. Thus, I am favorable to the publication of the manuscript.

Additional Questions:
Does the work significantly advance the understanding or development in this field?: Yes

Is this work of relevance to the chemistry community?: Yes

Are the conclusions of the work convincing and sufficiently supported by experimental evidence?: Yes

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The green synthesis of a palm empty fruit bunch-derived sulfonated carbon acid catalyst and its performance for cassava peel starch hydrolysis


 Author and affiliation details can be edited in the panel that appears to the right when you click on the author list.

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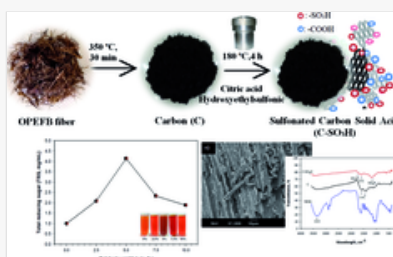
Funding Information

 We have combined the funding information you gave us on submission with the information in your acknowledgements. This will help ensure the funding information is as complete as possible and matches funders listed in the Crossref Funder Registry. Please check that the funder names and award numbers are correct. For more information on acknowledging funders, visit our <http://www.rsc.org/journals-books-databases/journal-authors-reviewers/author-responsibilities/#funding>.

Funder Name :	Direktorat Jenderal Pendidikan Tinggi
Funder's main country of origin :	Indonesia
Funder ID :	10.13039/501100005981
Award/grant Number :	122.9/UN8.2/PL/2019

Funder Name :	Kementerian Riset Teknologi Dan Pendidikan Tinggi Republik Indonesia
Funder's main country of origin :	Indonesia
Funder ID :	10.13039/5011000009509
Award/grant Number :	Unassigned

Table of Contents Entry



Abstract

A sulfonated carbon acid catalyst (C-SO₃H) was successfully generated from palm empty fruit bunch (PEFB) carbon *via* hydrothermal sulfonation *via* the addition of hydroxyethylsulfonic acid and citric acid. The C-SO₃H catalyst was identified as containing 1.75 mmol g⁻¹ of acid and 40.2% sulphur. The surface morphology of C-SO₃H shows pores on its surface and the crystalline index (CrI) of PEFB was decreased to 63.8% due to the change structure as it became carbon. The surface area of the carbon was increased significantly from 11.5 to 239.65 m² g⁻¹ after sulfonation *via* hydrothermal treatment. The identification of -SO₃H, COOH and -OH functional groups was achieved using Fourier-transform infrared spectroscopy. The optimal catalytic activity of C-SO₃H was achieved *via* hydrolysis reaction with a yield of 60.4% of total reducing sugar (TRS) using concentrations of 5% (w/v) of both C-SO₃H and cassava peel starch at 100 °C for 1 h. The stability of C-SO₃H shows good performance over five repeated uses, making it a good potential candidate as a green and sulfonated solid acid catalyst for use in a wide range of applications.

Introduction

In recent years, the interest in the bioconversion of lignocellulosic waste materials to chemicals and fuels has been steadily increasing because of their abundance, low cost, and sustainability.^{1,2} One of the most highly produced vegetable oils worldwide is crude palm oil, with 6.93.107 tons produced in 2017.³ Palm Empty Fruit Bunches (PEFB) are one of the main waste products obtained from the oil palm industry and a main cause of pollution. Concerns about environmental protection have increased over the years from a global point of view. The oil palm industry generates large amounts of solid waste, *i.e.*, PEFB, which is utilized as mulch for preventing erosion and maintaining soil moisture, fertilizer and compost. However, PEFB has little commercial value and is even a disposable problem due to its low bulk density and it thus needing a large storage volume. PEFB is usually used as a fuel in the factory, in which every ton of palm fruit bunch (PFB) processed in the mills consists of 23% of PEFB, 12% of mesocarp fiber, and 5% of shell.⁴

PEFB consists of potential components such as 44.4% of cellulose, 30.9% of hemicelluloses, and 14.2% of lignin, which could be utilized for more useful products.^{5,6} Due to the high content of lignocellulosic materials, many researchers have investigated the utilization of PEFB in biodiesel,⁷ biogas,⁸ ethanol, nanocomposites⁹ and other value-added products.^{6,10,11} However, there is an increasing need to utilize PEFB at low cost.

Many researchers have tried to produce low-cost activated carbon as an adsorbent using oil palm shell,¹² palm fiber¹³ and other carbon.¹⁴ The surface functionalization of carbon can be achieved *via* a hydrothermal method by modifying the carbon surface through a one-step reaction.^{11,15} In addition, no research has been found to utilize PEFB in terms of their conversion to a solid acid catalyst. Solid acid catalysts are a type of catalyst that can be economically and ecologically applied in catalysis. These catalysts have many advantages compared to common liquid acid catalysts, such as fewer disposal problems, they are non-corrosive, reusable, environmentally benign and easy to handle. Recently, incomplete carbonization of sugars during the preparation of sulfonated carbon was reported, in which the process resulted in better catalytic activity in the synthesis of biodiesel compared with other solid acid catalysts, including sulfonated zirconia, Nafion, and niobic acid.¹⁶ Catalytic reactions based on solid acid catalysts using reactants such as glycerol,¹⁷ cellulose,¹⁸ hemicelluloses¹⁹ and starch²⁰ have been confirmed as effective. However, the acid content of the catalyst depends on the carbon structure used as a template for modification. In order to increase the catalyst performance, the surface functionalization or depositing of functional groups on the carbon structure of PEFB can be achieved due to it being porous.

Based on our knowledge, no research has been reported on the synthesis of sulfonated carbon solid acid catalysts from PEFB as a carbon source *via* hydrothermal treatment. Herein, a green process of producing a sulfonated carbon acid catalyst (C-SO₃H) from PEFB was conducted. The carbon formation and sulfonation process were expected to produce a high acid content, with sulfonate and carboxyl groups on the catalyst. In this work, the effect of the sulfonation process on the structure of the carbon was evaluated. The physical properties of the original material,

carbon, and C-SO₃H, such as their surface morphology, crystalline structure, surface functional groups, and surface area were characterized. C-SO₃H was applied in cassava peel starch hydrolysis. Furthermore, the utilization of cassava peel starch as a substrate is also one strategy for making value-added products from food waste. The reusability of C-SO₃H was also investigated to evaluate the catalyst performance. The results of this research could be useful in the field of catalysis and also relevant to the environment, especially in the utilization of waste biomass.

Experimental methods

Chemicals

PEFB and cassava peel were collected from PT. Pola Kahuripan Inti Sawit, Kintapura, South Kalimantan, Indonesia and a traditional local market, respectively. D-Glucose (C₆H₁₂O₆), citric acid (C₆H₅Na₃O₇·2H₂O), 3,5-dinitrosalicylic acid (C₇H₄N₂O₇), hydroxyethylsulfonic acid (C₂H₆O₄S), phenolphthalein (C₂₀H₁₄O₄), sodium hydroxide (NaOH), methanol (CH₃OH), sodium chloride (NaCl), chloride acid (HCl), sulfuric acid (H₂SO₄) and oxalic acid (H₂C₂O₄) were purchased from Sigma-Aldrich.

Preparation of the sulfonated carbon solid acid catalyst

The PEFB was washed with tap water and further dried in an oven at 100 °C, then ground into a powder using a high speed blender to gain a material with a size that passes through a 60 mesh sieve. The PEFB (500 g) was heated in a furnace (muffle furnace, Hema scientific instruments) at 350 °C for 30 min under an inert atmosphere.²¹ The obtained carbon (C) was sulfonated *via* a hydrothermal treatment according to procedure reported in the literature,²² with slight modification. Briefly, 1.5 g of citric acid, 2.5 g of hydroxyethylsulfonic acid and 30 g of carbon were added to 40 mL of deionized (DI) water, and this solution was then placed in a Teflon-lined stainless steel autoclave (50 mL). The reaction was then carried out at 180 °C for 4 h in an oven. The carbon material was obtained after filtration and sequential washing of the reaction product using DI water, methanol and then DI water. The C-SO₃H product was then dried in an oven at 80 °C overnight.

Preparation of the cassava peel starch and hydrolysis reaction

Cassava peel (2 × 2 cm) was blended in the presence of DI water, with a cassava peel ratio of 1 : 4. After filtration, the precipitate was dried for 24 h at 90 °C in an oven and then sieved to pass through a 40 mesh. The hydrolysis of the cassava peel starch (2.5%; 5.0%; 7.5%; 10%, w v⁻¹) was conducted in a three-necked glass flask reactor (100 mL) in a close system with the addition of C-SO₃H (2.5%; 5.0%; 7.5%; 10%, w v⁻¹) and DI water (50 mL) at 100 °C for 60 min. The hydrolysed product was obtained *via* centrifugation and analysis of an aliquot of the solution was conducted using the 3,5-dinitrosalicylic acid (DNS) method to measure the total reducing sugar (TRS).²³ To examine the catalyst performance, concentrated sulfuric acid as a common homogeneous catalyst and the carbon from the PEFB as a general heterogeneous catalyst were also tested in the hydrolysis reaction. All data are presented as averages of experimental results that were carried out in triplicate.

C-SO₃H was treated to allow its repeated use, where the recovered C-SO₃H was rinsed three times by stirring it in DI water for 45 min each time and was then collected when the filtrate was ~pH 7. After separation from the liquid, it was then dried at 80 °C overnight in an oven.

Characterization

A neutralization titration method was used to calculate the Brønsted acid sites on C and C-SO₃H.²⁴ Briefly, the carbon materials (80 mg) and a solution of 1 M NaCl (40 mL) were mixed with stirring for 6 h at room temperature. After centrifugation, the supernatants were obtained and then titrated using 0.01 N NaOH with phenolphthalein as an indicator. X-ray fluorescence (XRF) measurements were used to detect elements in the samples using a PANalytical/Minipal machine. The surface areas of the materials were calculated *via* Brunauer–Emmett–Teller (BET) characterization using a nitrogen adsorption–desorption type Quantachrome Autosorb-1 instrument. Scanning Electron Microscope (SEM) measurements were carried out using a JEOL JSM-6500 LV microscope to analyze the surface morphologies of the samples. A Rigaku D/MAX-B X-ray diffractometer equipped with a copper K-alpha (Cu Kα) radiation source was used in the X-ray diffraction (XRD) measurements at a voltage of 40 kV and current of 100 mA. Fourier-transform infrared spectroscopy (FT-IR, Bio-rad, Digilab FTS-3500) was utilized to analyze the functional

groups on the carbon surface in the wavelength range of 4000–400 cm^{-1} at a scan rate of 8. Thermogravimetric analysis (TGA) was conducted to identify the weight loss of the samples using a platinum crucible over the temperature range of 30 to 600 $^{\circ}\text{C}$ under a flow of nitrogen at a specific heating rate of 10 $^{\circ}\text{C min}^{-1}$ (PerkinElmer, Diamond TG/DTA). The carbon content of the particles and degradation of the components were calculated from the weight loss percentages of the TGA curves. The TRS was analyzed using the DNS method²³ and analyzed by UV-vis spectroscopy with a V-550-JASCO spectrometer.

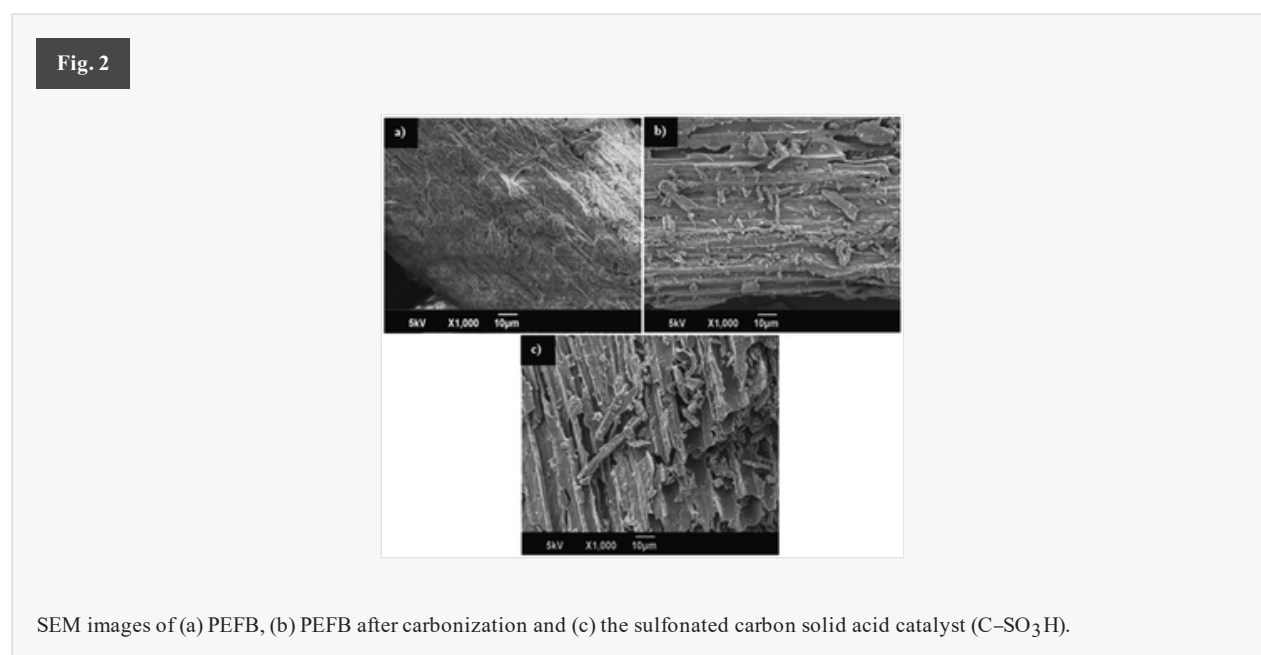
Results and discussion

Characterization of the sulfonated solid acid catalyst

The formation of the $\text{C-SO}_3\text{H}$ catalyst was conducted *via* a two-step reaction. First, PEFB fiber was carbonized to produce carbon. The second step involved the sulfonation of the carbon *via* hydrothermal treatment. All of the preparation steps of the generation of $\text{C-SO}_3\text{H}$ from PEFB are presented in Fig. 1.



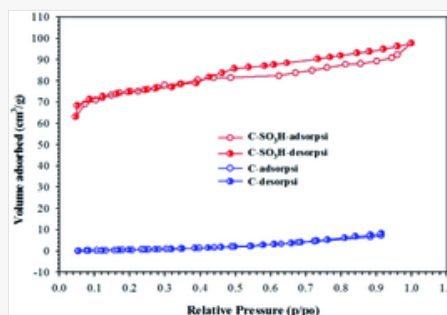
Materials changes of the surface morphology of PEFB were observed by SEM (Fig. 2), where from the SEM images it can be seen that the original structure of the PEFB fibers was fibrous with a smooth surface. The PEFB consists of cellulose, hemicelluloses and lignin that still bind to each other (Fig. 2a). The PEFB is pyrolyzed, dehydrated $-\text{C-O-C}-$ dissociation occurs and then the final step is polycyclic aromatic carbon ring formation at 350 $^{\circ}\text{C}$ to form the carbon structure.^{25,26} After carbonization, the surface structure of the PEFB is coarse and porous. This is possibly due to the heating process during carbonization causing the cellulose, hemicelluloses and lignin compounds to break down into three main components of carbon, tar and gas (volatile matter) (Fig. 2b). The sulfonation process *via* the hydrothermal treatment leads to the surface of the carbon becoming more porous (Fig. 2c). Hydroxyethylsulfonic and citric acids were added to the hydrothermal treatment as coupling agents to functionalize the carbon with sulfonate and carboxylic groups, respectively.



A hydrothermal (HT) system is a spontaneous and exothermic reaction, the way in which the vast majority of carbon is produced. Relatively low temperatures of over 100 $^{\circ}\text{C}$ are widely found in HT systems in nature because many minerals are formed under these conditions. Materials that are formed under vacuum *via* hydrothermal conditions have

increased solubility, which facilitates the physical and chemical interactions between reagents and solvent and also ionic and acidic reactions.²⁷ The HT process enhances the acidity level of the C-SO₃H by up to 7.3-fold compared to the level of C. Compared to C, the surface area of C-SO₃H is also significantly increased from 11.5 to 239.65 m² g⁻¹. Upon going from C to C-SO₃H, the pore volume increased from 0.018 to 0.137 cm³ g⁻¹. The nitrogen adsorption-desorption isotherms for C and C-SO₃H are illustrated in Fig. 3. The carbon material exhibits a type IV isotherm with a H3-type hysteresis loop, which indicates the mesoporous structure of C-SO₃H. Besides this, C-SO₃H is more stable and water-tolerant to hydrothermal conditions than other solid acid catalysts.²⁴

Fig. 3



The nitrogen adsorption-desorption isotherm of PEFB after carbonization (C) and the sulfonated carbon solid acid catalyst (C-SO₃H).

The sulfonic acid groups were formed on the catalyst through the reaction of a sulfonating agent with the aromatic rings of the carbon *via* electrophilic substitution.^{28,29} It was reported that the surface functionalization of the polycyclic aromatic carbon rings with sulfonate groups generates a large number of thermally stable acid sites, and furthermore, leads to the stacking of sulfonate groups at the edges of the carbon rings.³⁰ XRF analysis shows the sulphur content on the carbon to be around 40.2%, which indicates that sulfonation of the carbon was achieved to form an amorphous structure, with this type of structure being composed of polycyclic aromatic carbon sheets with sulfonate and carboxylic groups. The detailed results of the characterization of PEFB, C, and C-SO₃H are presented in Table 1.

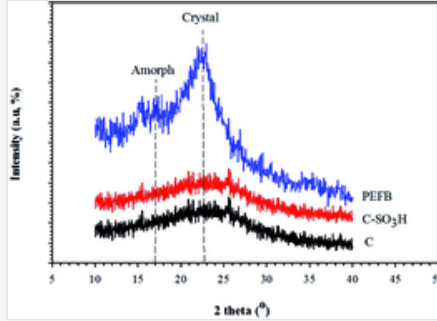
Table 1

The characterization of the PEFB fiber, C, and C-SO₃H

Sample	Sulphur content (%)	Acidity (mmol g ⁻¹)	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
PEFB fiber	—	—	0.171	—
C	—	0.21	11.55	0.018
C-SO ₃ H	40.2	1.75	239.65	0.137

The crystalline index (CrI) is a measure of the regularity of the crystal structure of a material. The breaking of the structure of PEFB led to a decrease in its crystalline index of 63.8% (Fig. 4). The XRD pattern shows the changes in the intensity of an amorphous area at $2\theta = 17^\circ$ and cellulose crystals at $2\theta = 22.8^\circ$.³¹ The decrease in the CrI values occurs because the crystallinity of the structure is lost as the material is converted into carbon during carbonization. Only high intensity of the cellulose crystal area was observed for PEFB. Similar results for the carbon and sulfonated solid acid catalysts were observed, indicating that no structural changes occurred during the sulfonation treatment.

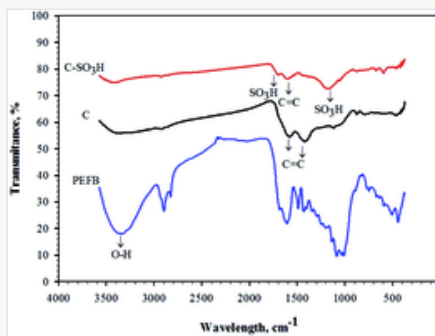
Fig. 4



XRD patterns of PEFB, C and C-SO₃H.

After the sulfonation process, the appearance of bands at 1207 and 1720 cm⁻¹ was recorded due to sulfonate group (Fig. 5); with the presence of sulfonate groups also confirmed elsewhere in the literature.³² The band observed at 3400 cm⁻¹ can be attributed to the -OH in carboxylic acid groups; which indicates that the sulfonation process not only creates sulfonate groups but also forms other functional groups because of oxidization reactions.³³ Polyaromatic C=C bond peaks were observed at 1608 cm⁻¹, assigned as a carbon material.

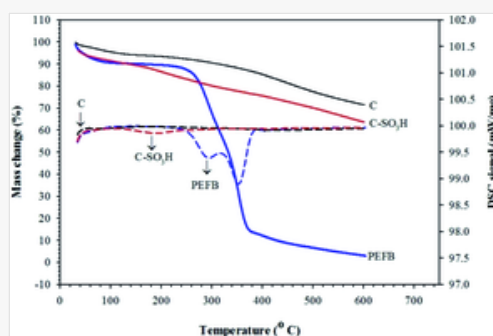
Fig. 5



FT-IR spectra of PEFB, C and C-SO₃H.

TGA was conducted to study the type of thermal degradation of the material and impact of sulfonation on C-SO₃H. Fig. 6 shows the TGA of the materials carbonized up to 600 °C. The dehydration of the water of the PEFB sample began at 74.4 °C, continued upon the decomposition of cellulose and hemicellulose in the range of 240–320 °C, and the next degradation in this was that of lignin at 320–380 °C. For both materials, the reduction in mass was due to the decomposition of carbon and the thermal process also enhanced the oxidized structure, thus reducing its thermal stability.²⁵ The TGA curves also show that the mass loss trend of C-SO₃H is around 8% more than that of C. At temperatures in the range of 140–240 °C, the material is rapidly degraded in the case of C-SO₃H, possibly related to the number of sulfonate groups present on the carbon. As reported, C-SO₃H sulfonated by sulfonate groups has a weak structure and is unstable compared to the original carbon.²¹

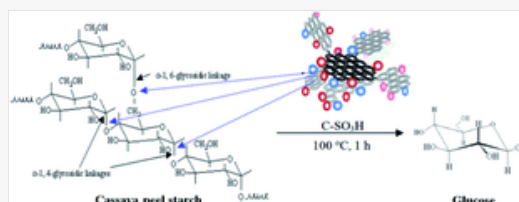
Fig. 6



Hydrolysis of cassava peel starch over the sulfonated carbon solid acid catalyst

One of the potential raw materials for glucose production is carbohydrate, as it can be converted into glucose *via* a hydrolysis reaction using a heterogeneous/homogeneous catalyst and an enzymatic reaction. The cassava peel starch used in this research consists of 80.2% carbohydrate. The C-SO₃H breaks the α -(1,6)- and α -(1,4)-glycosidic bonds in the starch chain to produce an oligomer of glucose. The schematic diagram of the hydrolysis of cassava peel starch by C-SO₃H is shown in Fig. 7.

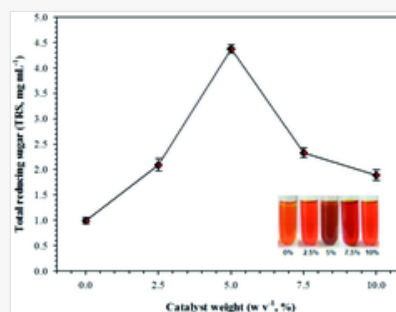
Fig. 7



Schematic diagram of the hydrolysis of cassava peel starch by C-SO₃H.

The hydrolysis performance with a variation of catalyst concentration is presented in Fig. 8. The TRS as a hydrolysis product was increased when the weight of C-SO₃H was increased up to 5%, with a TRS produced of 4.375 mg mL⁻¹. The presence of C-SO₃H as a catalyst in cassava peel starch hydrolysis significantly increased the amount of product produced by around 4.4-fold compared to hydrolysis without a catalyst. This means that the catalytic performance of C-SO₃H increases due to it being modified *via* surface functionalization. The concentration of TRS regularly decreased at higher C-SO₃H concentration (>5%) because the formed sugar compounds degraded into furfural.³⁴ This reason also becomes a key point in hydrolysis in terms of high temperature and prolonged time.³⁵ The hydrolysis performance of C-SO₃H was also observed to show TRS compared with sulfonated catalysts that use corn on the cob as a carbon precursor.³⁶

Fig. 8



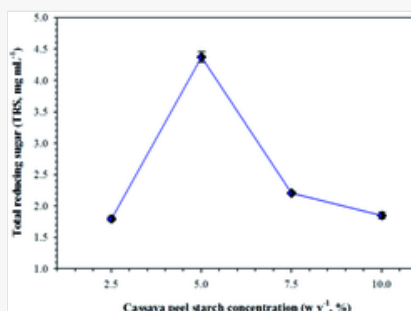
Total reducing sugar (TRS) of cassava peel starch hydrolysis in terms of the variation in the weight of the C-SO₃H catalyst. Reaction conditions: 5% (w v⁻¹) of cassava peel starch, 100 °C, 1 h.

The TRS produced was indicated by color intensity, and the DNS assay was used to evaluate this intensity. The color of the solution obtained was more orange and a higher color intensity showed the presence of a higher concentration of TRS (Fig. 8, inset).

The high TRS concentration was obtained because the catalyst has access and can easily attach to the carbohydrate linkage. Furthermore, the concentration of the cassava peel starch as a substrate is at its optimal at 5% in terms of producing TRS (Fig. 9). A higher concentration of starch leads to a more viscous solution due to the swelling and gelatinization of starch in the presence of water. Thus, these conditions make it more difficult for C-SO₃H to access the carbohydrate linkage, hence resulting in a lower TRS. Based on the energy efficiency and consumption costs of the

hydrolysis reaction, a concentration of 5% cassava peel starch using 5% C-SO₃H was selected as the optimal conditions.

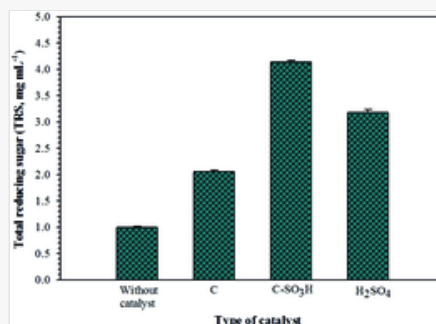
Fig. 9



Total reducing sugar (TRS) of the cassava peel starch hydrolysis in terms of the variation in cassava peel starch concentration. Reaction condition: 5% (w v⁻¹) C-SO₃H, 100 °C, 1 h.

In order to determine the reactivity of C-SO₃H, it is interesting to investigate the performance of C and H₂SO₄ as heterogeneous and homogeneous catalysts, respectively. C was used as a control, whereas the H⁺ ion concentration of H₂SO₄ used was the same concentration as the H⁺ ion content of C-SO₃H. As shown in Fig. 10, TRS values of around 2.05 and 3.18 mg mL⁻¹ were obtained using C and H₂SO₄ as catalysts, respectively. The reaction using the C-SO₃H catalyst has a higher TRS value of around 1.02-fold than that using C. However, the common liquid catalyst (H₂SO₄) showed lower performance (TRS value of 3.18 mg mL⁻¹) compared to C-SO₃H. This is probably due to the presence of -SO₃H and -COOH groups that functionalize the carbon. Furthermore, H₂SO₄ only has H⁺ ions in the homogenous phase and it should be easy for the catalyst to access and attach to a carbohydrate linkage.

Fig. 10



Total reducing sugar (TRS) of cassava peel starch hydrolysis over different types of catalysts. Reaction condition: 5% (w v⁻¹) of cassava peel starch and C-SO₃H, 100 °C, 1 h.

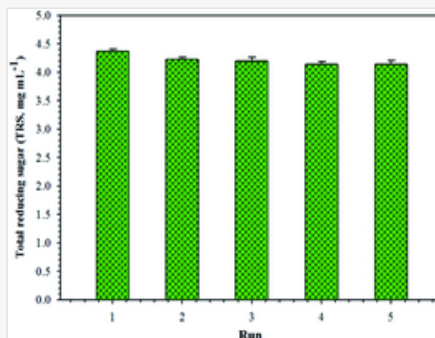
Table 2 shows that the sulfonated carbon acid catalyst prepared in this work is more efficient and has higher hydrolysis activity than other sulfonated solid catalysts, even those prepared using difficult methods in ionic liquids or water using HT and microwave methods. In order to investigate the activity of the catalyst for repeated uses, the recovered C-SO₃H was used in another cycle of hydrolysis. The recovered catalyst performance was observed to be slightly lower than that achieved in the 1st reaction. The decrease in TRS was observed to be only 5.3% after five repeated uses until the TRS result was fairly constant (Fig. 11). The decrease in activity is due to the loss of active sites from catalyst during washing, decreasing the acidity of C-SO₃H to around 5.14%. In addition, the sulfonated carbon solid catalyst is easy to handle and almost 98% was recovered. This proves that C-SO₃H provides effective hydrolysis of starch into glucose. This result also shows that the prepared C-SO₃H not only is a non-toxic material, prepared *via* a green process and is easy to handle, but also shows good catalytic performance for hydrolysis reactions.

Table 2

The catalytic activity of sulfonated acid catalysts in hydrolysis

Catalyst	Acidity (mmol g ⁻¹)	Solvent	Method	Temp (K)/time (h)	TRS yield (%)	Ref.
30-CCSA	0.86	H ₂ O	HT	423/6	44.52	37
PCPs-SO ₃ H	1.80	H ₂ O	—	393/3	5.30	38
CM-SO ₃ H	4.22	[BMIM][Cl]	—	303/3	59.4	39
CSA-SO ₃ H	1.76	H ₂ O	Microwave	403/1	34.6	40
C-SO ₃ H	1.75	H ₂ O	—	373/1	64.0	This work

Fig. 11



Catalytic performance of C-SO₃H during its fifth repeated use in cassava peel starch hydrolysis. Reaction conditions: 5% (w v⁻¹) of cassava peel starch and C-SO₃H, 100 °C, 1 h.

Conclusions

Carbon with a high acid content, rich in sulfonate and carboxyl groups, was prepared from PEFB by sulfonation *via* a hydrothermal treatment. Hydroxyethylsulfonic and citric acids were used as sources for the sulfonate and carbonyl groups, respectively. Good performance and stability of the sulfonated acid catalyst in cassava peel starch hydrolysis were shown after five repeated uses. Simple operation, high catalytic activity and utilization of waste materials are the important advantages in the development of this sulfonated solid acid catalyst. The synthesized catalyst has great potential to be developed for use in green process and also various catalyst applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors wish to thank the Directorate General of Research and Community Services, Ministry of Research, Technology and Higher Education, Republic of Indonesia, who provided the research grant (contract No. 122.9/UN8.2/PL/2019).

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i References can be edited in the panel that appears to the right when you click on a reference.

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Queries and Answers

Q1

Query: Have all of the author names been spelled and formatted correctly? Names will be indexed and cited as shown on the proof, so these must be correct. No late corrections can be made.

Answer: Please add the ORCID ID for author

Chairul Irawan: <https://orcid.org/0000-0002-6099-4655>; Meilana Dharma Putra: <https://orcid.org/0000-0002-7923-1818>

Q2

Query: In the graphical abstract image, the word ‘Transmittance’ is spelled incorrectly. Please supply a corrected version of the image with your proof corrections, preferably as a TIF file at a resolution of 600 dpi.

Answer: Please find our new graphical abstract file in TIGF file

Q3

Query: Is the inserted Graphical Abstract text suitable? If you provide replacement text, please ensure that it is no longer than 250 characters (including spaces).

Answer: Yes

Q4

Query: The sentence beginning “In order to increase the catalyst performance...” has been altered for clarity, please check that the meaning is correct.

Answer: The sentence can be replace:

In order to increase the catalyst performance, surface functionalization on carbon structure can be achieved due to porous structure of PEFB.

Q5

Query: The sentence beginning “The PEFB was washed...” has been altered for clarity, please check that the meaning is correct.

Answer: The sentence can change become:

The PEFB was washed with tap water and then dried in an oven at 100 °C.

Q6

Query: The sentence beginning “C–SO₃H was treated to allow...” has been altered for clarity, please check that the meaning is correct.

Answer: Sentences can change to:

C–SO₃H was treated to allow for its repeated use. The recovered C–SO₃H was rinsed three times by stirring in DI water for 45 min and then collected when the filtrate was ~pH 7.

Q7

Query: In the sentence beginning “Fourier-transform infrared spectroscopy...”, please check if ‘a scan rate of 8’ is associated with any units and specify if any changes are required here.

Answer: The sentence is correct, there is no unit for scan rate

Q8

Query: The sentence beginning “A hydrothermal (HT) system...” has been altered for clarity, please check that the meaning is correct.

Answer: The sentence can change to:

A hydrothermal (HT) system is a spontaneous and exothermic reaction, the majority product of this system is carbon.

Q9

Query: The sentence beginning “Relatively low temperatures...” has been altered for clarity, please check that the meaning is correct.

Answer: The sentence can change:

The operating temperatures of HTC widely found over 100 °C in nature because many minerals are formed under these conditions.

Q10

Query: The sentence beginning “Materials that are formed...” has been altered for clarity, please check that the meaning is correct.

Answer: Sentence can change:

Materials are formed under vacuum *via* hydrothermal conditions have increased solubility, which facilitates the physical and chemical interactions between reagents and solvent and also ionic and acidic reactions.

Q11

Query: In the Fig. 3 graphic, the words ‘adsorption’ and ‘desorption’ are spelled incorrectly in four places. Please supply a corrected version of the image with your proof corrections, preferably as a TIF file at a resolution of 600 dpi.

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Query: In the Fig. 4 graphic, the words ‘amorphous’ and ‘crystalline’ are presented incorrectly. Please supply a corrected version of the image with your proof corrections, preferably as a TIF file at a resolution of 600 dpi.

Answer: Please find our new file

Q13

Query: In the sentence beginning “Polyaromatic C=C bond peaks...”, the meaning of ‘assigned as a carbon material’ is not entirely clear. Please check this and specify the changes required here.

Answer:

The sentence can change become:

Polyaromatic C=C bond peaks were observed at 1608 cm^{-1} , which signed as a carbon material.

Q14

Query: In the Fig. 5 graphic, the word ‘Transmittance’ is spelled incorrectly. Please supply a corrected version of the image with your proof corrections, preferably as a TIF file at a resolution of 600 dpi.

Answer: Please find our new file

Q15

Query: In the sentence beginning “For both materials...” should ‘the oxidized structure, thus reducing its thermal stability’ be changed to ‘their oxidized structures, thus reducing their thermal stability’?

Answer: For both materials, the reduction in mass was due to the decomposition of carbon and the thermal process also enhanced their oxidized structure, thus reducing their thermal stability.

Q16

Query: The meaning of the sentence beginning “This reason also becomes...” is not clear in the context of its surrounding sentences. Please check this and specify the changes required here.

Answer: The sentence change to:

Its also becomes a key point in hydrolysis in terms of high temperature and prolonged time.

Q17

Query: In the sentence beginning “Good performance and stability...”, ‘4th repeated used’ has been changed to ‘five repeated uses’ to match the information given in the text. Please check that this change is correct.

Answer: Yes, it is correct.

Q18

Query: Have all of the funders of your work been fully and accurately acknowledged?

Answer: Yes