Hydrothermal sulfonation of palm empty fruit bunch carbon as solid acid catalyst and its hydrolysis catalytic activity

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Research

Abstract

The sulfonated carbon solid acid catalyst (C-SO_3H) was successfully generated from palm empty fruit bunch (PEFB) carbon via hydrothermal sulfonation by addition of hydroxyethylsulfonic acid and citric acid. The C-SO_3H was identified contain of 1.75 mmol/g of acidity and 40.2% of sulphur. The surface morphology of C-SO_3H showed pores with diameters of 3-6 μm and crystalline index (CrI) of material was decreased to 63.8% due to changed structure become carbon. The surface area of carbon was increased significantly from 11.5 to 239.65 $m^2\,g^{-1}$ after hydrothermal treatment. The identification of functional groups of -SO_3H, COOH and -OH were detected by Fourier Transform Infra-Red (FT-IR). The optimum catalytic activity of C-SO_3H was achieved via hydrolysis reaction with 60.4% of total reducing sugar (TRS) yield. The both concentrations of C-SO_3H and cassava peel starch are 5% (w v^{-1}) at 100 ^oC for 1 h. Stability of C-SO_3H showed good performance for 4th repeated used; it showed insignificant of activity that decreased only of 6%. Thus, the C-SO_3H is a candidate for green and potential sulfonated solid acid catalyst for wide range applications.

1. Introduction

In recent years, the interest in 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 worldwide highest production of vegetable oil is crude palm oil with the amount of $6.93.10^7$ tons on 2017 (3). Palm empty fruit bunch (PEFB) is one of the main waste products obtained from oil palm industry and it's mainly causing of pollution. Concern about environmental protection has increased over the year from a global viewpoint. The utilization of oil palm industry leads to generate large amount of solids wastes i.e., PEFBs; these are utilized as mulch for preventing erosion maintain soil moisture, fertilizer and compost. On the other hand, the PEFB has a little commercial value and even became a disposable problem due to the low bulk density thus needing large storage volume. The PEFB is usually used as a fuel in the factory in which every ton of FFBs processed in the mills consist of 23% of PEFB, 12% of mesocarp fiber, and 5% of shell 5% (4).

PEFB consist potential component of 44.4% of cellulose; 30.9% of hemicelluloses, and 14.2% of lignin that could be utilized for more useful products (5, 6). Due to the high content of biomass, many researchers have investigated the utilization of PEFB such as biodiesel (7), biogas (8), ethanol and nanocomposites (9) and other value-added products (6, 10, 11). However, there is increasing concern to utilize PEFBs with low cost of process.

Many researchers have tried to produce low cost activated carbons as adsorbent using oil palm shell (12), palm fiber (13) and other carbon (14). Enrich-solid carbon could be produced via hydrothermal method by modifying the carbon surface through one-step reaction (11, 15). In addition, no research has been found that utilized the PEFBs in term of its conversion to solid acid catalyst. Solid acid catalysis is type of catalyst which is economically and ecologically applied in catalysis. The catalyst has many

advantages compared to the common liquid acid catalysts such as fewer disposal problems, non-corrosive, reusable, environmentally benign and easy handling. Newly, incomplete carbonization of sugars during preparation of sulfonated carbon was reported; the process resulted in a better catalytic activity on synthesis of biodiesel compared with other solid acid catalyst, including sulfonated zirconia, nafion, and niobic acid (16). Catalytic reactions based on solid acid catalyst by using reactant such as glycerol (17), cellulose (18), hemicelluloses (19) and starch (20) have been confirmed as an effective catalyst. On the other hand, the acid content on the catalysts depend on the carbon structure as precursor which effect to performance in catalytic reaction. To increase the performance, it is likely to sulfonate functionalization or deposit other functional group on the carbon chains due to morphology structure of PFEB is having pore along the fibers.

Based on our knowledge, no research has been reported for preparation of high sulfonated carbon solid acid catalyst from carbonized of PEFB via hydrothermal treatment. Herein, the facile preparation of sulfonated solid acid catalyst based on PEFB was conducted. Formation of carbon materials and the sulfonation process are expected to result in high acid content. In this work, the effect of sulfonation process on the structure of carbon was evaluated. Physical properties of functionalization of biocarbon (C-SO$_3$H) such as the morphology, crystalline structure, surface functionalization, and surface area were characterized. The C-SO$_3$H formed catalyst was applied for hydrolysis of cassava peel starch. Moreover, the utilization of cassava peel as substrate is also one of strategy to cover the problem of waste food becoming value-added. The reusability of C-SO$_3$H was also investigated to evaluate the catalyst performance. This research can be useful in the catalyst field and more take attention on environmental benign; especially using waste biomass material.

2. Materials And Methods

2.1 Material

Palm empty fruit bunch and cassava peel were collected from PT. Pola Kahuripan Inti Sawit, Kintapura, South Kalimantan, Indonesia and from traditional local market, respectively. The D-glucose (C$_6$H$_{12}$O$_6$), citric acid (C$_6$H$_5$Na$_3$O$_7$.2H$_2$O), 3,5-dinitrosalicylic acid (C$_7$H$_4$N$_2$O$_7$), hydroxyethylsulfonic acid (C$_2$H$_6$O$_4$S), phenolphthalein (C$_{20}$H$_{14}$O$_4$), sodium hydroxide (NaOH), methanol (CH$_3$OH), sodium chloride (NaCl), chloride acid (HCl), sulfuric acid (H$_2$SO$_4$) and oxalic acid (H$_2$C$_2$O$_4$) were purchased from Sigma-Aldrich.

2.2 Preparation of sulfonated carbon solid acid catalyst

The PEFB was washed with tape water and further dried in oven at 100 °C, then grounded into powder by a high speed blender to gain a size material pass off sieve 60 mesh. PEFB (500 g) was heated in the furnace at 350 °C for 30 min. The obtain carbon (C) was through the sulfonation process by hydrothermal treatment according to the procedure (21) with a little modification. Briefly, 1.5 g of citric acid, 2.5 g of hydroxyethylsulfonic acid and 30 g of carbon were poured into 40 mL of deionized water; this solution was then placed in Teflon-lined Stainless Steel autoclave (50 mL). Reaction took place at

180 °C for 4 h in an oven. The carbon materials were obtained after filtration process and consecutive washing process of using DI water, methanol and DI water. The product (C-SO$_3$H) continued to dry at 80 °C overnight in an oven.

2.3 Preparation of cassava peel starch and hydrolysis reaction

Cassava peel starch was prepared by blended small size of cassava peel (2x2 cm) after cleaning process was conducted with tape water in the presence of DI water (ratio 1:4). After filtration, the precipitate was dried for 24 h at 90 °C in oven and then sieved to pass 40 mesh. The hydrolysis of cassava peel starch (2.5; 5.0; 7.5; 10 %, w/v) was conducted in reactor (50 mL) with the addition of C-SO$_3$H (2.5; 5.0; 7.5; 10 %, w/v) and distilled water (50 mL) at 100 °C for 60 min. Hydrolysis product was obtained by centrifugation; the analysis of an aliquot of solution was conducted by using DNS method with 3,5-dinitrosalicylic acid to measure total reducing sugar (22). To examine the catalyst performance, the concentrated sulfuric acid as common homogeneous catalyst and the carbon without sulfonation process as general heterogeneous catalyst were also tested for catalytic reaction. All data are presented in averages of experiments results in triplicate.

2.4 Characterizations

Neutralization titration method was used to calculate Brønsted acid sites on C-SO$_3$H (23). Briefly, carbon (80 mg) and solution of 1 M NaCl (40 mL) was mixed with stirring for 6 h and at room temperature. After centrifugation process and then titrated by 0.01N NaOH, the supernatant was obtained. Phenolphthalein was utilized as an indicator. The X-Ray Fluorescence (XRF) observation was used for detecting element in the sample by PANalytical/Minipal machine. Surface area of materials was calculated using Brunauer–Emmet–Teller (BET) characterization by Quantachrome, Autosorb-1 instrument with nitrogen adsorption–desorption type. The scanning electron microscope with type of JEOL, JSM-6500 LV was utilized to analyze the surface morphology. The X-ray diffractometer with Rigaku D/MAX-B model equipped with Copper K-alpha (Cu Ka) radiation machine was used for X-ray diffraction (XRD) measurement. The number of 40 kV and 100 mA were used for operation of voltage and current, respectively. The Fourier transform infrared spectrometry (FT-IR, Bio-rad, Digilab FTS-3500) was utilized for analyzing the functional groups on carbon surface. The thermal gravimetric analysis (TGA) was conducted to monitor the weight loss of the samples at temperature range of 30 °C to 600 °C; this process was flowed with nitrogen at the specific heating rate of 10 °C min^{-1} (Perkin Elmer, Diamond TG/DTA). The carbon content in the particles and degradation of component were calculated by weight loss percentage from TGA curves. Total reducing sugar (TRS) was analyzed by using 3,5-dinitrosalicylic acid (DNS) method (22) by using UV-Vis spectroscopy with type V-550-JASCO.

3. Results And Discussion

3.1 Characterization of sulfonated solid acid catalyst

The formation of C-SO$_3$H catalyst was conducted through two steps reaction. First, fibre of PEFB was carbonized to produce black carbon. Second step is sulfonation of carbon by hydrothermal treatment. The all preparation steps of C-SO$_3$H generated from PEFB are presented in Figure 1.

Material changes of morphology structures were observed by SEM (Figure 2); it can be seen that the original structure of PEFB fibre was fibrous and smooth surface. The PEFB consisted of cellulose, hemicelluloses and lignin that still bind to each other (Figure 2a). The PEFB started to be pyrolyzed, continued by dehydration and dissociation process of -C-O-C-; then last step is polycyclic aromatic carbon rings formation at 350 °C and finally form carbon structure [24, 25]. After carbonization, surface structure was coarse and porous. This was possible due to the heating process during carbonization causing the cellulose, hemicelluloses and lignin compounds to break into 3 main components of carbon, tar and gas (volatile matter) (Figure 2 b). The sulfonation process by hydrothermal carbonization (HTC) treatment has led to the surface of carbon becoming more porous with diameters of 3-6 μm (Figure 2c); this contained of sulfonate and carboxylic group.

HTC system is spontaneous process and an exothermic reaction with vast majority of the carbon. A low temperature of HTC operated at over 100 °C is widely found in nature because many minerals formed under these circumstances. The process to form carbon materials via hydrothermal condition led to the increased solubility, facilitating the physical and chemical interaction between reagents and solvent and also ionic and acid reaction to form structure of carbonaceous [26]. The HTC process enhanced the acidity level of the C-SO$_3$H up to 7.3-fold than its level of C. Compared to C, the surface area of C-SO$_3$H was also significantly increased from 11.5 to 239.65 m^2 g^{-1}. The nitrogen adsorption-desorption isotherms for C and C-SO$_3$H was illustrated in Figure 3. The carbon material exhibited type IV isotherm with H3-type hysteresis loop, which was indicating the mesoporous structure of the C-SO$_3$H. Besides, the C-SO$_3$H more stable and water-tolerant in hydrothermal conditions than other solid acid catalyst [23].

The sulfonic acid group was reached through a reaction of sulfonating agent and aromatic rings resulting in a structure of carbon with the electrophilic substitution [27, 28]. It was reported that the surface functionalization by sulfonate group on polycyclic aromatic carbon rings would generate a large amount of acid sites with form of thermally stable; furthermore, the sulfonic groups was stacked at the edge of carbon ring [29]. The XRF analysis detected the sulphur content on carbon about 40.2%. The sulfonated carbon solid acid catalyst was successfully to form amorphous structure; this type of structure was composed of polycyclic aromatic carbon sheets with sulfonate and carboxylic group. The detail result of characterization of PEFB, C, and C-SO$_3$H are presented in Table 1.

Table 1. The characterization of PFEB fiber, C, and C-SO$_3$H

Sample	Component (%)				Acidity	Surface area
	Ca	K	Si	S	(mmol g^{-1})	(m^2 g^{-1})
PEFB fiber	36.0	46.9	6.5	-	-	0.171
C	30.1	53.9	4.8	-	0.21	11.55
C-SO$_3$H	13.3	7.16	10.0	40.2	1.75	239.65

The crystalline index is the level of regularity of the crystal structure of a material; the breaking structure of PEFB was also proven by a decrease of crystalline index of 63.8% (Figure 4). The XRD pattern shows the changes of intensity on amorph area at 2θ = 17 ° and cellulose crystals at 2θ = 22.8° (30). The decrease in the CrI number because the crystal structure has been lost and converted into carbon structure during carbonization process. The high intensity of cellulose crystal area was only found for PEFB. The similar results in the carbon and sulfonated solid acid catalyst were observed indicating no structure change during sulfonation treatment.

Figure 5 presents the spectra of FT-IR for PEFB, C, and C-SO$_3$H. After sulfonation process, the appearance of bands at 1207 cm^{-1} and 1720 cm^{-1} were recorded due to sulfonic group; the presence of sulfonation was also confirmed elsewhere (31). The band observed at 3400 cm^{-1} was attributed to -OH in carboxylic acids; this indicated that the sulfonation process not only created sulfonic groups but also formed other functional groups because of oxidizing reaction (32). The C=C bond in polyaromatic compounds was observed at 1608 cm^{-1} that was assigned as carbonized material.

Thermal gravimetric analysis was conducted to study the thermal degradation type of material and impact of sulfonation on C-SO$_3$H. Figure 6 showed the thermal gravimitric of materials carbonized up to 600 °C. The dehydration of water for PEFB sample was started at 74.4 °C, continued by decomposition of hemicellulose and lignin at 332.5 °C. For both materials, the reduction of mass was due to the decomposition of carbon and thermal process also enhanced the oxidized structure thus thermal stability was reduced (24). TGA curve also shows the mass loss trend of C-SO$_3$H about more 8% than that of C. At higher temperature, the material was rapidly degradated especially for C-SO$_3$H; this is possible related to the amount of sulfonate group on carbon. As reported, the C-SO$_3$H sulfonated by sulfonate group have a weak structure and unstable condition on range of temperature compared to original carbon (33).

3.2. Hydrolysis of cassava peel starch over sulfonated carbon solid acid catalyst

One of potential material for glucose production is carbohydrate; it could be converted to glucose by hydrolysis reaction using heterogeneous or homogeneous catalyst and enzymatic reaction. The cassava peel starch which was used in this research consists of 80.2% of carbohydrate. The hydrolysis

performance with variation of catalyst concentration was presented in Figure 6. The TRS as hydrolysis product was increased when C-SO$_3$H weight increased up to 5% with TRS of 4.139 mg mL^{-1}. The presence of C-SO$_3$H as catalyst on cassava peel starch hydrolysis significantly increased the product about 316.7% compared than hydrolysis without catalyst. It means that the catalytic performance of C-SO$_3$H increased due to modified surface functionalization. The concentration of TRS regularly decreased at higher C-SO$_3$H concentration (>5%); it was because the formed sugar compounds was degraded become to furfural compounds (34). The performance of C-SO$_3$H in hydrolysis was observed to be higher TRS compared with those sulfonated catalyst about 0.639 mg mL^{-1} (35). The TRS produced was also indicated by color intensity; the DNS assay was used to evaluate the intensity. The color of solution was obtained to more orange and higher color intensity showed higher concentration of TRS detected (Figure 7, inset).

The highest TRS concentration was obtained because catalyst have access and easily to attach the carbohydrate linkage. Furthermore, concentration of cassava peel starch as substrate also has optimum condition at 5% to produce TRS (Figure 8). Higher concentration of starch would lead to more viscous solution due to swelling and gelatinization of starch in the presence of water. Thus, this condition caused the C-SO$_3$H more difficult to access the carbohydrate linkage; hence, lower TRS was produced. Based on energy efficiency and consumption cost for hydrolysis reaction, the concentration 5% of cassava peel starch using 5% of C-SO$_3$H was selected as optimum condition.

In order to know the reactivity of C-SO$_3$H, it is interesting to investigate the C and H$_2$SO$_4$ performance as heterogeneous and homogeneous catalyst, respectively. The C was used as a control; whereas, the H$^+$ ions concentration on H$_2$SO$_4$ used was the same concentration with the H$^+$ ion content on C-SO$_3$H. As shown in Figure 9, the TRS about 2.05 mg/mL and 3.18 mg/mL were obtained when using C dan H$_2$SO$_4$ as catalyst, respectively. The process using C-SO$_3$H catalyst had higher value of TSR about 1.02-fold than that using C. On the other hand, the common liquid catalyst (H$_2$SO$_4$) showed lower performance (TRS value of 3.18 mg/mL) compared to C-SO$_3$H. It is probably due to presence of −SO$_3$H and -COOH groups that were functionalized on carbon. Furthermore, the H$_2$SO$_4$ only have H$^+$ ions in homogenous phase and the catalyst accessibility should be easier to attach carbohydrate linkage.

Table 2 shows that the sulfonated carbon solid acid catalyst prepared in this work is more efficient and had higher hydrolysis activity than other sulfonated solid catalysts; even, they used difficult method of ionic liquid or water with HTC and microwave method.

Table 2. Sulfonated solid acid on hydrolysis catalytic activity

Catalyst	Acidity (mmol g^{-1})	Solvent	Method	Temp (K)/Time (h)	TRS yield (%)	Ref.
30-CCSA	0.86	H_2O	HTC	423/6	44.52	(36)
PCPs-SO$_3$H	1.80	H_2O	-	393/3	5.30	(37)
CM-SO$_3$H	4.22	[BMIM][Cl]	-	303/3	59.4	(38)
CSA-SO$_3$H	1.76	H_2O	Microwave	403/1	34.6	(39)
C-SO$_3$H	1.75	H_2O	-	373/1	64.0	This work

In order to investigate the activity of catalyst in repeated uses, the recovered C-SO$_3$H was rinsed 3rd times with DI water by stirred for 45 min and collected after separation with liquid and then dried. The recovered catalyst performance was observed to be slight lower than that was obtained in the 1st reaction. TRS decrease was observed only 6% after 4th repeated uses (Figure 10). This proves that the C-SO$_3$H provide effectively to hydrolyze the starch into glucose. This result also shows that the prepared C-SO$_3$H not only provide non-toxic materials, green process and easy handling, but also has good catalytic performance for hydrolysis reaction.

Conclusions

The high content of acidity, rich in sulfonate and carboxyl group on carbon materials could be synthesized by hydrothermal treatment by addition of hydroxyethylsulfonic and citric acid. The good performance on hydrolysis and stability reaction were shown after 4th repeated used. Simple operation, high catalytic activity and waste materials as precursor are the important key for development of sulfonated solid acid catalyst. The synthesized catalyst has high potential to be developed for green process in various catalytic applications.

Declarations

Availability of data and materials

All data used to support the findings of this study are available from the corresponding author.

Competing interests

The authors declare they have no competing interests.

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Figures
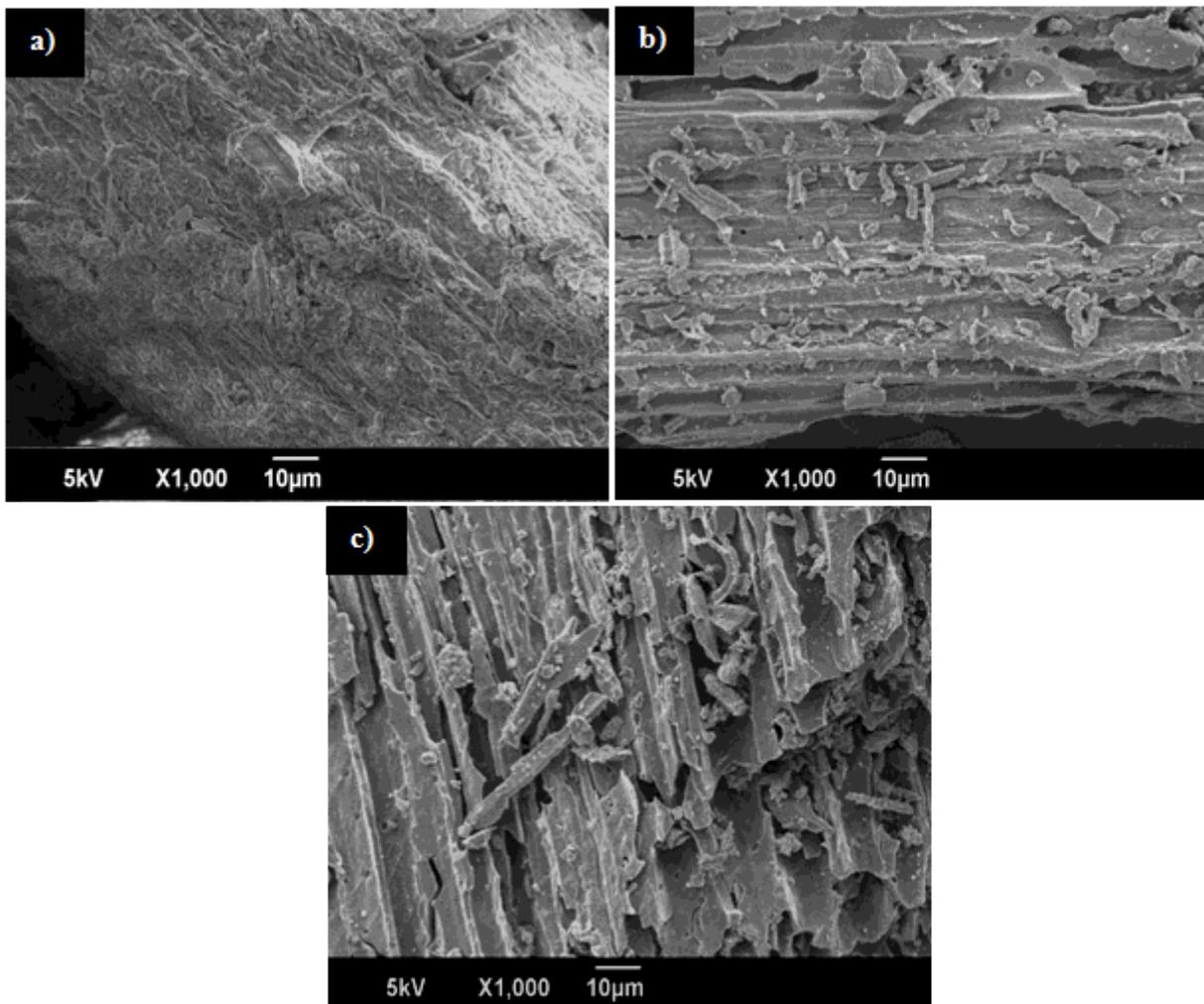

Figure 1

Preparation steps of C-SO3H generated from PEFB

Figure 2

SEM images of (a) palm empty fruit bunch (PEFB); (b) PEFB after carbonization and (c) sulfonated carbon solid acid catalyst (C-SO3H).
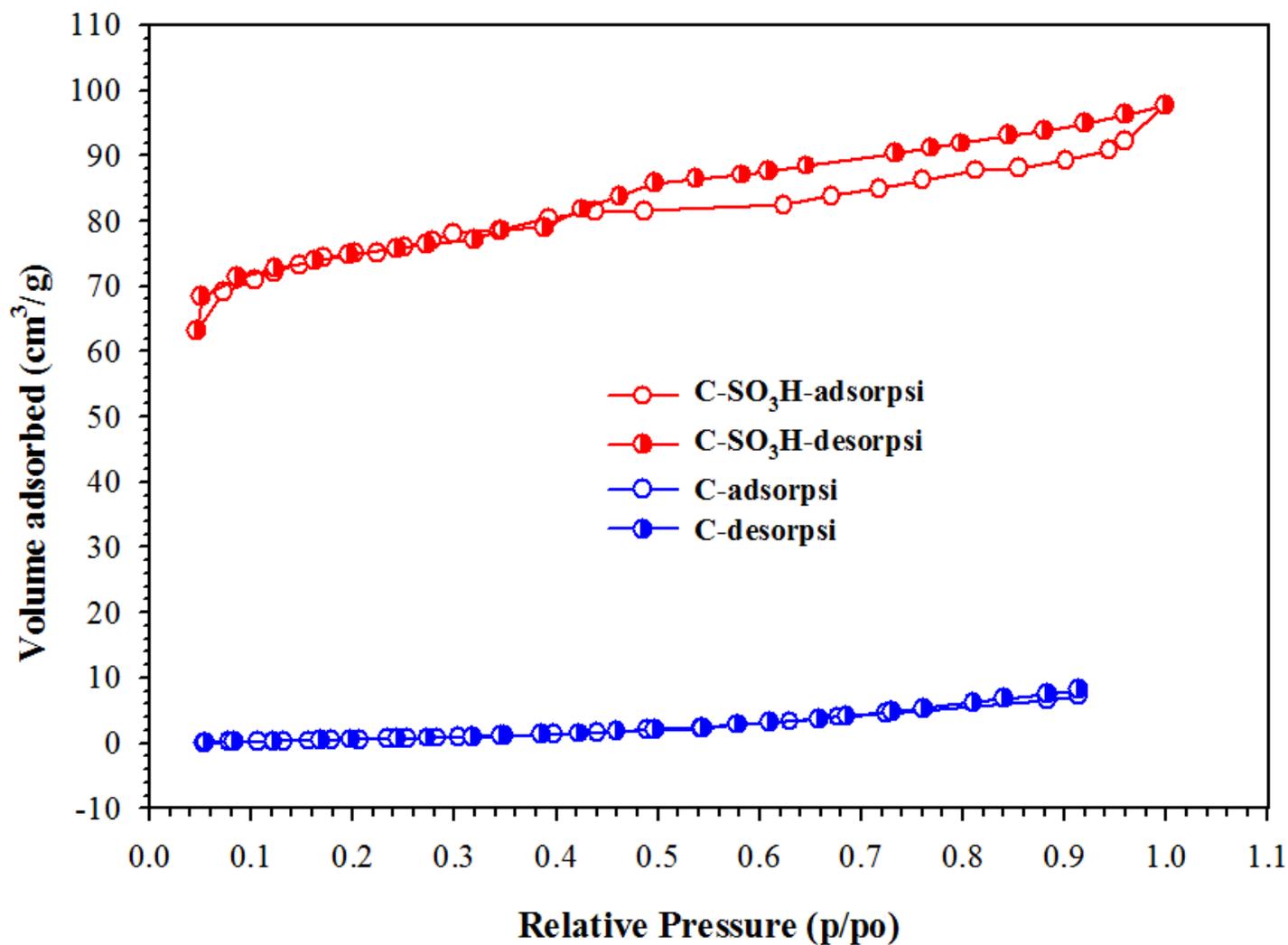
Figure 3

The nitrogen adsorption-desorption isotherm of PEFB after carbonization (C) and sulfonated carbon solid acid catalyst (C-SO3H).
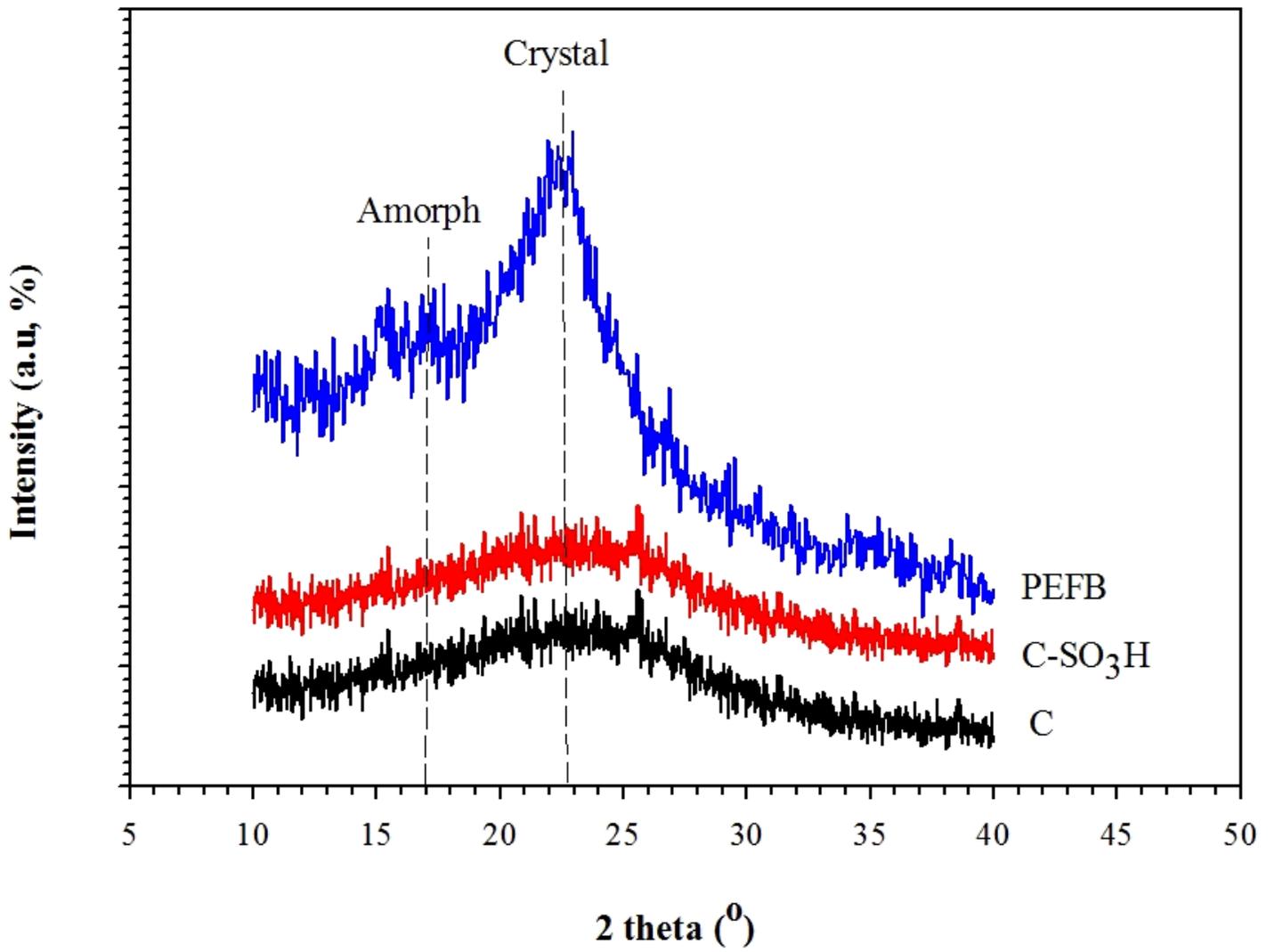
Figure 4

XRD pattern of PEFB, C and C-SO3H
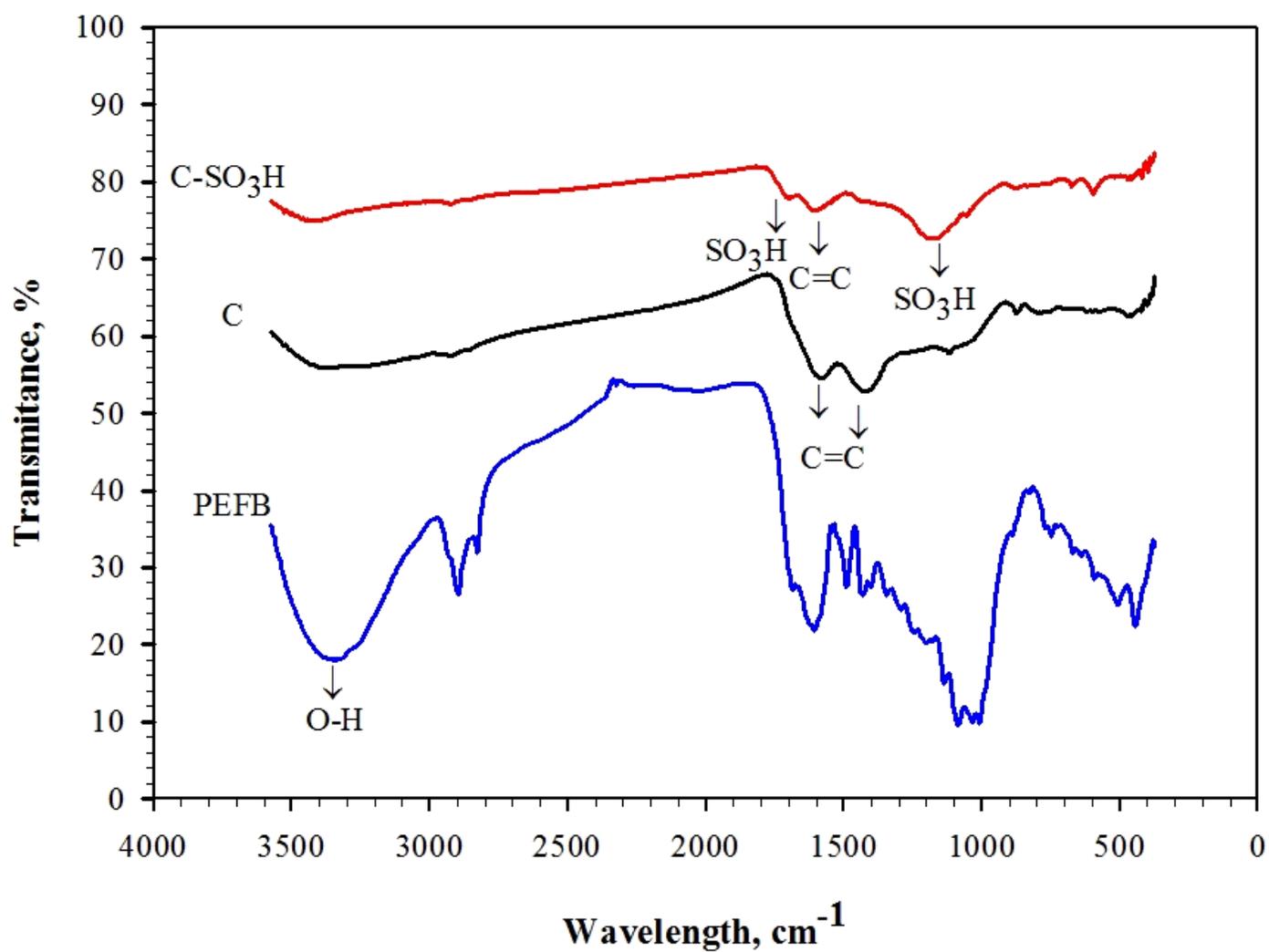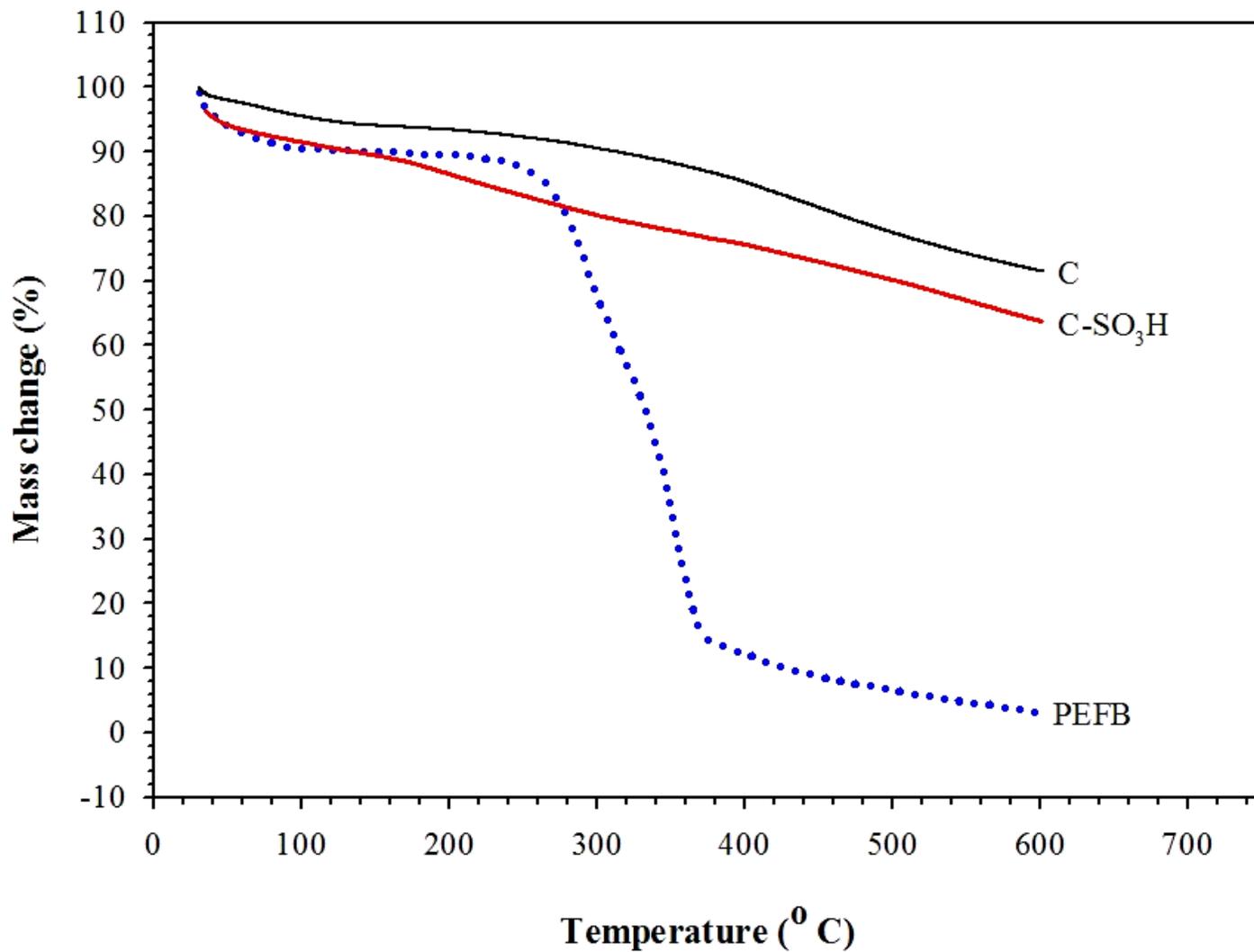
Figure 5

FT-IR spectra of PEFB, C and C-SO3H

Figure 6
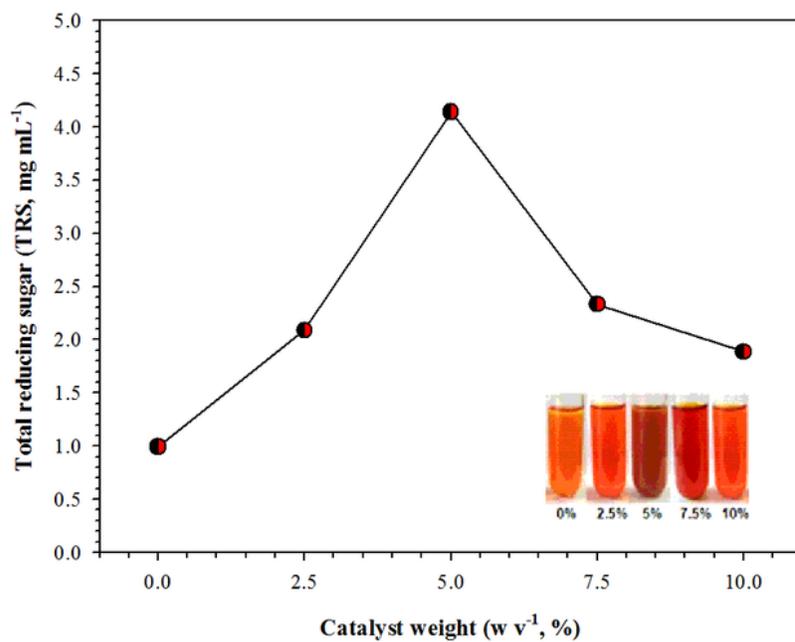
Thermal gravimetric analysis curve of PEFB, C, and C-SO3H

Figure 7

Total reducing sugar (TRS) of cassava peels starch hydrolysis on variation of C-SO3H as catalyst weight. Reaction condition: 5% (w/v) of cassava peel starch, 100 oC, 1 h.
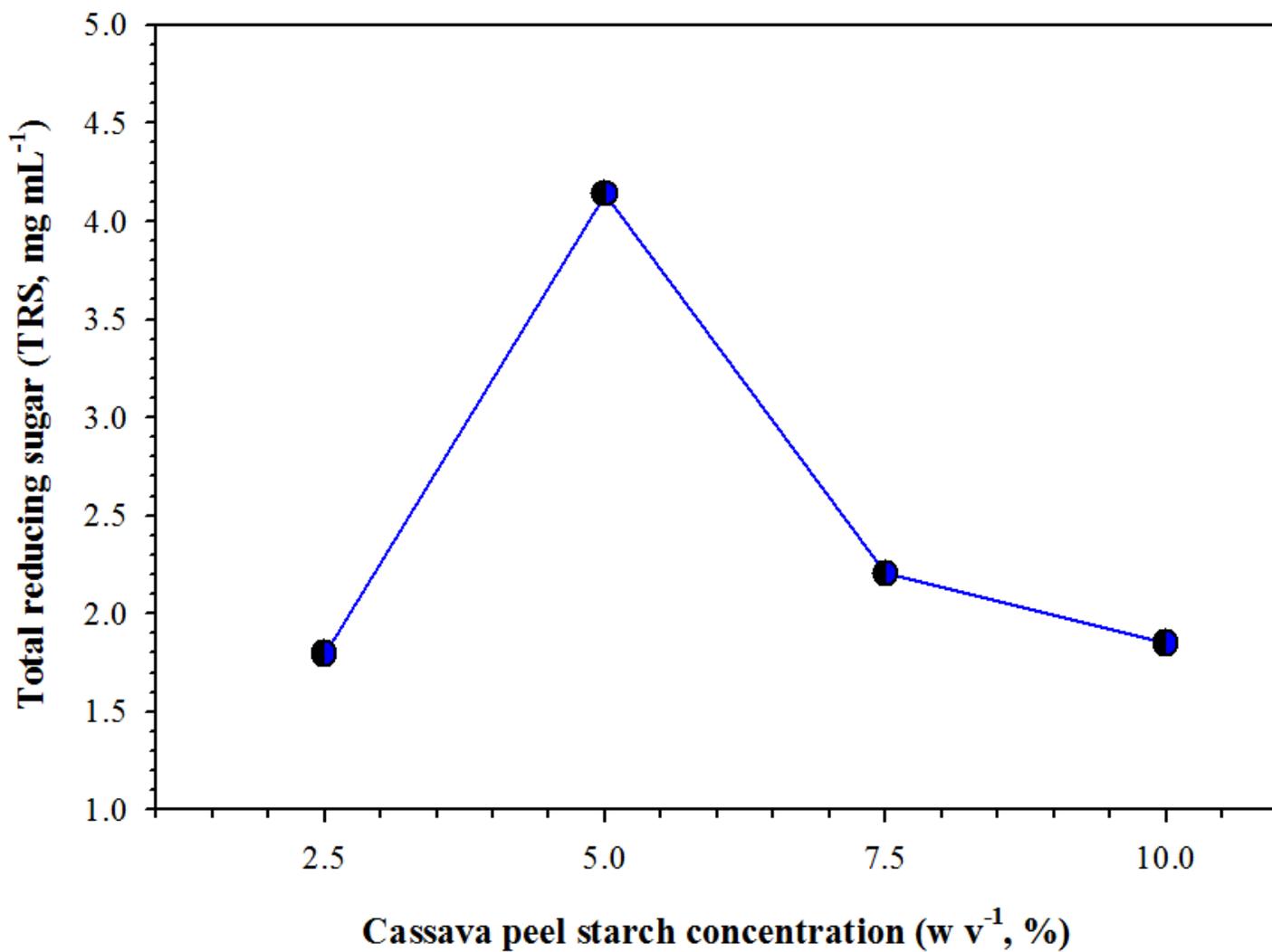
Figure 8

Total reducing sugar (TRS) of cassava peels starch hydrolysis on variation of cassava peel starch concentrations. Reaction condition: 5% (w/v) of C-SO3H, 100 oC, 1 h.
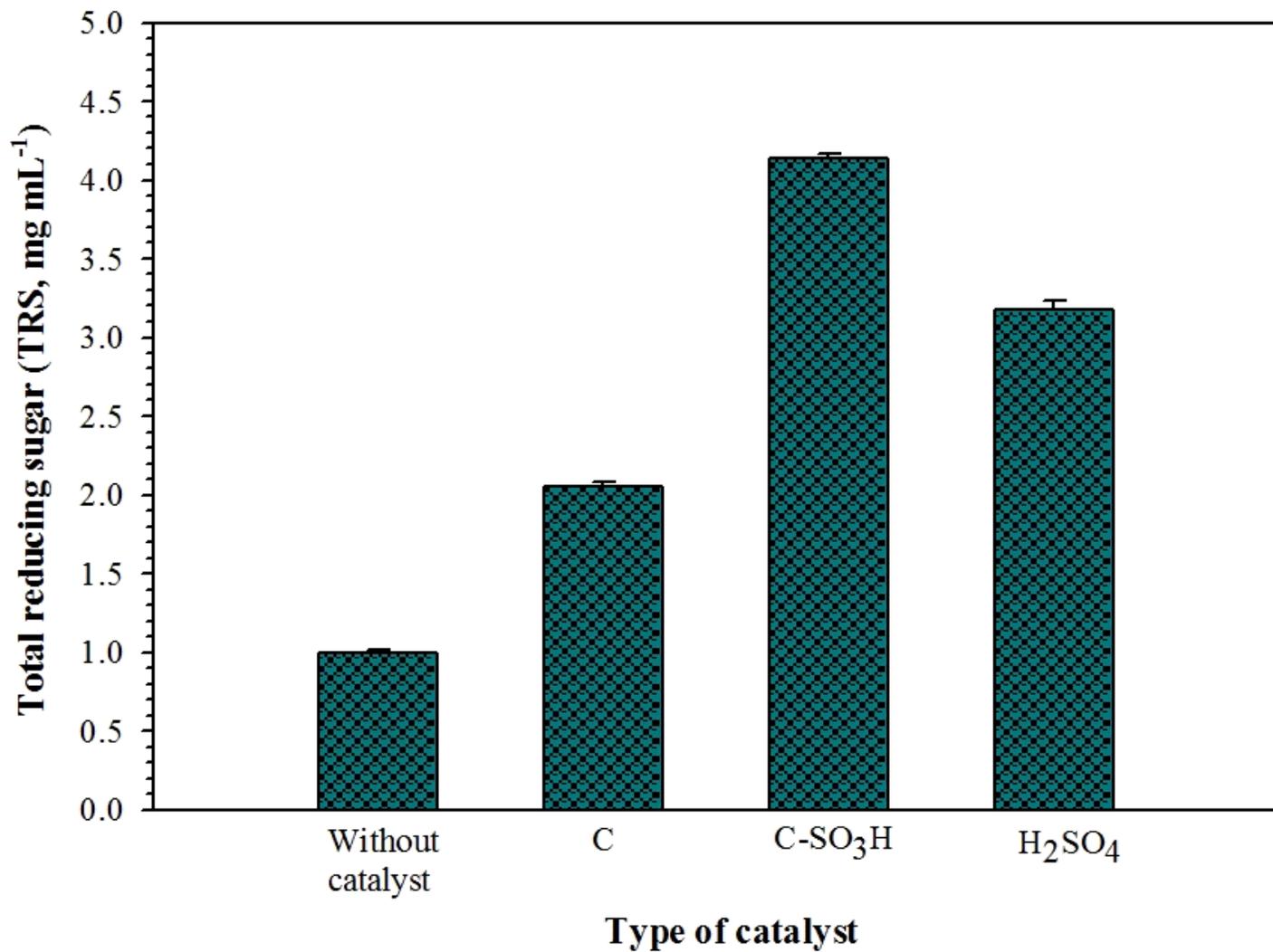
Figure 9

Total reducing sugar (TRS) of cassava peels starch hydrolysis over different catalyst type. Reaction condition: 5% (w/v) of cassava peel starch and C SO3H , 100 oC, 1 h.
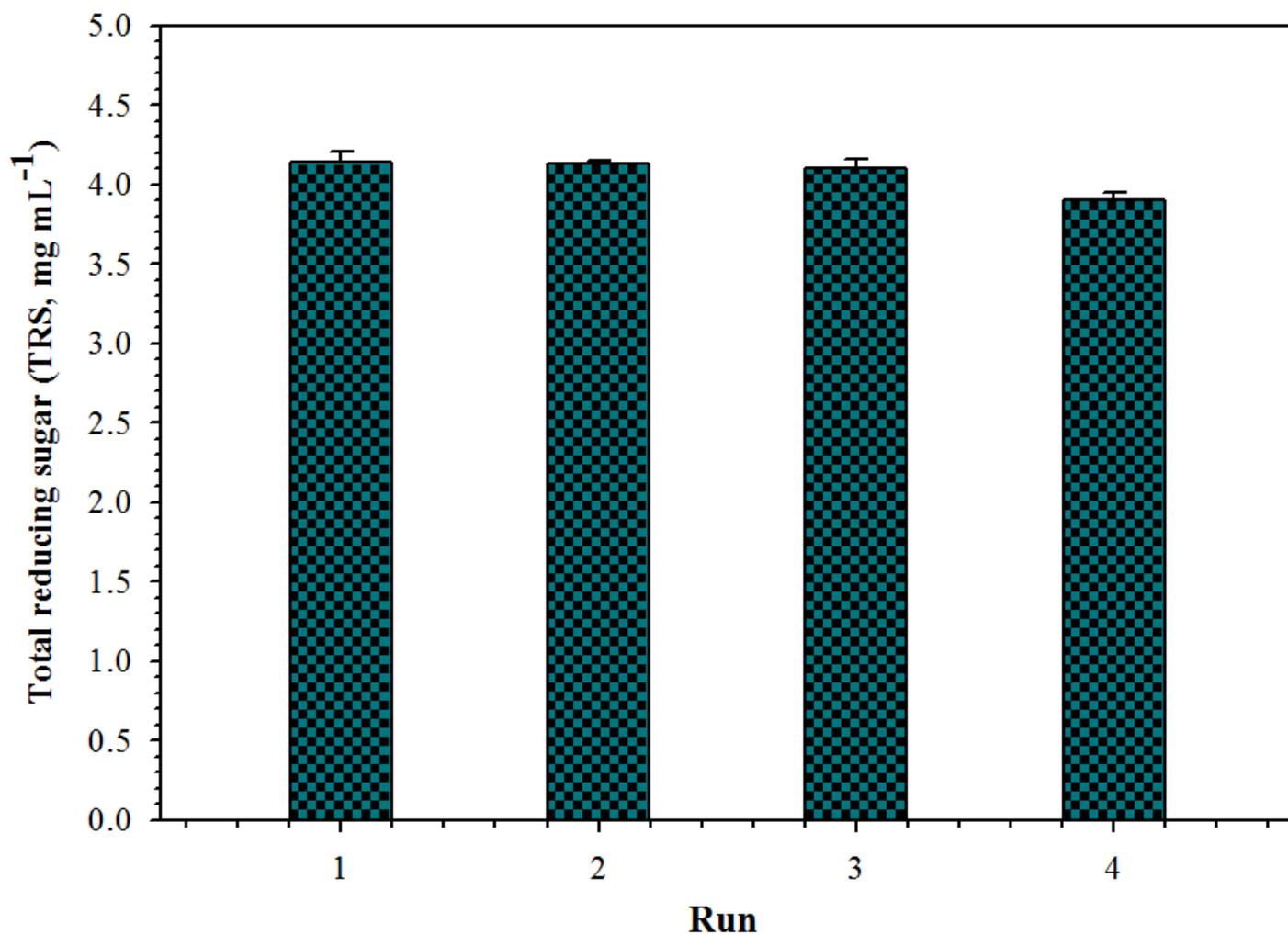
Figure 10

Catalytic performance of C-SO3H during 4th repeated used of cassava peel starch hydrolysis. Reaction condition: 5% (w/v) of cassava peel starch and C-SO3H, 100 oC, 1 h.