

BIOMASS CHAR SULFONIC ACIDS (BC-SO₃H)-CATALYZED HYDROLYSIS OF BAMBOO UNDER MICROWAVE IRRADIATION

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A heterogeneous process for the hydrolysis of bamboo into reducing sugars, a process catalyzed by biomass char sulfonic acids (BC-SO₃Hs), was carried out under microwave irradiation. This transformation technology was nearly ineffective with regards to the hydrolysis of fresh bamboo because of the impeding lignin that was wrapped around the cellulose, but the hydrolysis proceeded efficiently when the hemicellulose, and especially the lignin in bamboo, were partly removed through pretreatment with an aqueous ZnCl₂ solution under microwave irradiation. The BC-SO₃H catalyst bearing -SO₃H, OH, and COOH groups showed much higher turnover numbers (TON, 0.64 to 1.07) for the hydrolysis of the pretreated bamboo than did the dilute H₂SO₄ solution (TON, 0.08). This is likely due to its strong affinity for β-1,4-glycosidic bonds of cellulose. The microwave irradiation resulted in much higher hydrolytic efficiency than did conventional heating. This likely resulted from the microwave irradiation's unique role in activating the cellulose molecules and heightening particle collisions, effects that can remarkably accelerate this process of heterogeneous catalysis.

Keywords: Biomass; Carbon sulfonic acid; Hydrolysis of lignocellulose; Reducing sugars; Microwave irradiation

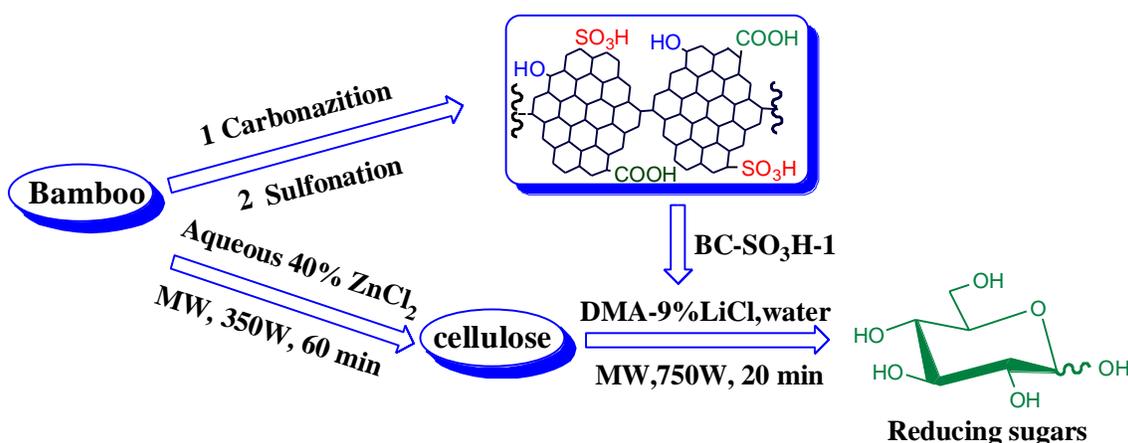
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INTRODUCTION

Cellulosic biomass is an abundant renewable resource on earth, consisting of various agricultural residues, fruit and vegetable waste, woods, municipal solid waste, waste from the pulp and paper industry, and herbaceous energy crops (Ragauskas *et al.* 2006). The degradation of cellulosic materials has gained increasing research attention due to their worldwide availability and their immense potential for conversion into sugars, alternative fuels, and chemical feedstocks (Zhang 2008). The hydrolysis of lignocellulose into fermentable sugars is an essential step in any practical cellulosic-ethanol process. Usually, the conversion of lignocellulose into reducing sugar includes two sub-processes: pretreatment and saccharification. There are many efficient methods for pretreating lignocellulose biomass, including steam explosion (McMillan 1994), ammonia fiber explosion (AFEX) (Mes-Hartree 1988), ozonolysis (Ben-Ghedalia and Miron 1981), oxidative delignification (Azzam 1989), and so on, but these processes have various shortcomings, such as the necessary use of high pressure vessels and severe pretreatment, as well as high operating costs and the risk of producing various environmental contaminants. To solve these problems, some efficient processes for the hydrolysis of lignocellulose biomass have been developed that eliminate the need for pretreatment. For example, the hydrolysis of lignocellulose can be achieved by acid or

enzyme catalysis in the aqueous phase (Hamelinck *et al.* 2005; Huber *et al.* 2006; Sun and Cheng 2002) and in ionic liquids (Li *et al.* 2008; Sievers *et al.* 2009). A high selectivity for monosaccharides is obtained in enzyme-catalyzed processes, but such processes typically require several days to achieve the desired conversion. Moreover, its commercialization is hindered by the prohibitive high cost of the currently available enzyme preparations, the harsh conditions of enzyme reaction, and the trouble of enzyme separation (Broll *et al.* 1999; Hamelinck *et al.* 2005). A faster conversion of the lignocellulose can be achieved via acid-catalyzed hydrolysis, but this usually proceeds at high pressure and temperature in order to disrupt the strong network of hydrogen bonds before hydrolysis, conditions that leads to low selectivity, high operating costs, and the production of various environmental contaminants (Calvini *et al.* 2008; Mok *et al.* 1992). To address these problems, some researchers (Onda *et al.* 2008; Suganuma *et al.* 2008; Toda *et al.* 2005) have developed a process in which the hydrolysis of cellulose is catalyzed by some solid acids; however, this heterogeneously catalytic process shows poor hydrolytic efficiency due to a mass transfer resistance between the solid acids and the insoluble cellulose in water. Therefore, there is an urgent demand for simpler and more efficient technologies aimed at the degradation of cellulose, and especially lignocellulose, for the production of various biomass products.

In the last decade, the use of microwave irradiation to accelerate organic reactions has been of growing interest as a type of environmentally friendly process, particularly when it is carried out under solvent-free conditions. Microwave irradiation produces efficient internal heating or in-core volumetric heating by way of the direct coupling of microwave energy with the molecules, whether solvents, reagents, or catalysts, that are present in the reaction mixture (Dallinger and Kappe 2007). This method has been successfully applied to the dilute alkali- (Yu *et al.* 1996) or dilute acid- (Zhu *et al.* 2006) catalyzed hydrolysis of various lignocellulosic materials as well as to the heterogeneous hydrolysis of cellulose catalyzed by Lewis Acid (Wu *et al.* 2010b), in which it usually affords a high yield of reducing sugars or 5-hydroxymethylfurfural in a short reaction time.



Scheme 1. Graphical representation of the pretreatment of bamboo and its subsequent hydrolysis into reducing sugars upon catalysis by the BC-SO₃H-1 prepared from bamboo under MW irradiation. DMA is the abbreviation of N,N-dimethylacetamide.

Biomass char sulfonic acid (BC-SO₃H) is a novel, recoverable, and renewable solid acid (Xu *et al.* 2008). The development of an efficient process for the hydrolysis of

cellulose catalyzed by a biomass char sulfonic acid was achieved under microwave irradiation. The BC-SO₃H catalysts that were prepared from natural bamboo, cotton, and starch showed a much higher turnover number (TON, 1.33 to 1.73) for this reaction than did a dilute H₂SO₄ solution (TON, 0.02) (Wu *et al.* 2010a).

This paper introduces an efficient process for the pretreatment and then hydrolysis of lignocellulose into reducing sugars using the BC-sulfonic acid catalyst under microwave irradiation. The relevant technical route is shown in Scheme 1.

EXPERIMENTAL

Lignocellulose Materials and Reagents

Raw bamboo was obtained from local farmers in Changsha, Hunan province, PR China. Before any pretreatment, the bamboo was cut into 1 to 2 cm lengths and washed thoroughly with tap water until the rinsate was clear. It was then dried at 120 °C for 4 hours. The dried materials was ground and sieved to obtain the 100 mesh fraction of bamboo sawdust. The main composition of this bamboo sawdust was as follows: cellulose, 40.5 ± 0.5%; lignin, 21.8 ± 0.4%; hemicellulose, 15.6 ± 0.5%; and moisture, 21.1 ± 0.5%. All other chemical reagents used in this study were of analytical grade.

Methods

Preparation of biomass char sulfonic acids

The biomass char sulfonic acid (BC-SO₃H) catalyst was prepared following a published procedure with a little modification (Wu *et al.* 2010a; Xu *et al.* 2008). As shown in Scheme 1, the pulverized bamboo powder was effectively delignified by an aqueous ZnCl₂ solution under microwave irradiation. Then, the biomass char sulfonic acids (BC-SO₃H) were prepared from bamboo, cotton, and starch. The number of acid sites on the catalysts was determined via titration (Wu *et al.* 2010a).

Microwave-assisted pretreatment of bamboo sawdust with metal halogenosalts

In a typical procedure, 20 g of raw bamboo sawdust was suspended in an 40% aqueous solution of metal halogenosalt (80 mL) in a 250 mL round-bottom flask equipped with a reflux device. Then, the flask was positioned at the center of an experimental microwave oven (JQ NANJING Model NJL07-3, with frequency 2.45 GHz, power from 0 to 1000 W, and IR remote sensing temperature controller) and irradiated for 1 hour at 120 °C with a microwave power of 350 W. The residue was collected, washed, and dried prior to use. The cellulose, hemicellulose, and lignin contents of the bamboo sawdust before and after pretreatment were measured following a published method (Liu 2004). The moisture was measured as the weight loss of 1g of raw bamboo sawdust at 100 °C for 24 hours.

Typical procedure for lignocellulose hydrolysis

The treated lignocellulose (0.1 g) and the catalyst (0.1 g) were mixed with 10 mL DMA-LiCl (9%), and then the reaction mixture was removed to a Pyrex reactor, upon which distilled water (5 mL) was added. The sealed reactor was placed in the aforementioned microwave oven and irradiated at a specified microwave power for an appropriate time. After the desired reaction time had elapsed, the reaction mixture was immediately quenched with cold water, neutralized with a 0.5 mol/L NaOH solution, and

filtered. The aqueous solution was collected and subjected to an analysis of total reducing sugars (RSs) in accordance with an established method that used 3,5-dinitrosalicylic acid (DNS method) (Li *et al.* 2008; Miller 1959). The mixture of the DNS reagent (0.15 mL) and the reaction sample (0.2 mL) was heated for 5 min at 100 °C, then cooled to room temperature and diluted to 50 mL. The absorbance of the diluted solution was measured on an Agilent 8453 spectrophotometer at 520 nm, and the concentration of RSs was calculated based on a standard curve obtained with glucose. The turnover number was evaluated on the basis of the molar amount of converted substrate (glucose as substrate, and one water eliminated from the glucose as model reaction) per mole of effective acid sites (SO₃H) (mol. mol⁻¹) (Wu *et al.* 2010a). Each experiment was repeated in duplicate, and the data deviation between two parallel experiments was lower than *ca.* 5%.

RESULTS AND DISCUSSION

Table 1 lists the contents of the cellulose, hemicellulose, and lignin in bamboo before and after pretreatment with an aqueous solution of various metal halogenosalts under microwave irradiation (salt-MW) or conventional heating (salt-CH). In comparison to entry 1, entries 2 through 7 show that the salt-MW or salt-CH pretreatment process both caused a decrease in the content of the three components, to some extent. Among the metal halogenosalts examined, ZnCl₂ was found to be the most effective in the removal of lignin, as about half the lignin was eliminated by the ZnCl₂-MW treatment (entry 6), while a very poor removal of lignin was obtained using the ZnCl₂-CH method (entry 7). The reason that the ZnCl₂-MW treatment can provide a much higher efficiency than the ZnCl₂-CH treatment is likely because microwave irradiation produces efficient internal heating or in-core volumetric heating by way of the direct coupling of microwave energy with the reaction molecules, thus resulting in an obvious acceleration of reaction (Dallinger and Kappe 2007; Taherzadeh and Karimi 2008).

Table 1. Various Halogenosalts Used for the Pretreatment of Lignocellulosic Biomass

Entry	Additive, wt%		MW Power (W)	Content of component ^a (wt%)		
				cellulose	hemicellulose	lignin
1	--	--	--	40.52	15.63	21.76
2	CrCl ₂ ,	40	350	39.90	14.80	20.70
3	CuCl ₂ ,	40	350	38.10	13.42	20.30
4	NaBr,	40	350	36.18	12.14	18.52
5	KI,	40	350	37.90	11.52	19.55
6	ZnCl ₂ ,	40	350	34.50	10.41	10.90
7 ^b	ZnCl ₂ ,	40	--	38.64	10.58	20.45

^a Not expressed in units of percentage are moisture; ^bWith oil bath at 120 °C for 1 h.

Figure 1 shows the X-ray diffraction patterns of fresh bamboo, MW-treated bamboo, and ZnCl₂-MW-treated bamboo, in which the characteristic peaks observed at 2θ=16.5° and 22.5° were assigned to those of cellulose crystal, and a broad peak between 16.5° and 22.5° represents the hemicellulose (Kobayashi *et al.* 2009). Furthermore, another strong and sharp peak appearing at 31.5° was noticed in these samples, and its assignment is still unknown. Notably, the intensity of the two peaks at 2θ=16.5° and 22.5° decreased to some extent after the fresh bamboo sawdust was treated by MW and

especially ZnCl_2 -MW irradiation. This is likely due to the partial demolition of the crystal structure of the cellulose, as depicted by Wu *et al.* (2010a) for the XRD characterization of the cellulose before the microwave irradiation.

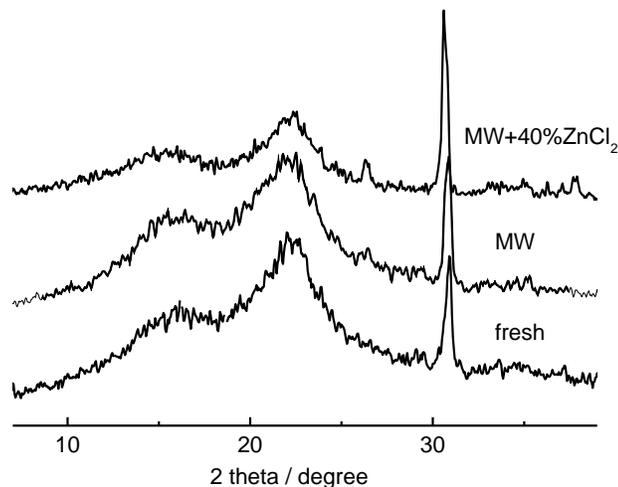


Fig. 1. X-ray diffraction patterns of bamboo before and after ZnCl_2 pretreatment under microwave irradiation

The mediation effect of the solvent on the hydrolysis of the bamboo treated with ZnCl_2 -MW was examined with a BC-SO₃H-1 catalyst under MW irradiation. The results are shown in Table 2. As shown in entries 1 through 3, this hydrolysis was able to occur in the presence of N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and N,N-dimethylacetamide (DMA), but only provided a relatively low RSs yield (3.4 to 9.4%). This is likely due to the poor solubility of the lignocellulosic material in these solvents. Entry 4 shows that the hydrolysis proceeded efficiently in an ionic liquid 1-butyl-3-methylimidazolium chloride [BMIM]Cl medium due to its good ability to solubilize lignocellulose (Remsing *et al.* 2006; Swatloski *et al.* 2002), providing about a 15.8% RSs yield. Notably, when 9% LiCl was added to the DMF, DMSO, or especially DMA solvent, the hydrolytic efficiency improved drastically (Entries 5 through 7). For example, the yield of RSs in DMA-9wt% LiCl was about 32.4% (entry 5), which was 8.5 times higher than it was in DMA. The favorable effect of the DMA-LiCl media was most likely due to the media's good ability to solubilize lignocellulose (Binder and Raines (2009); McCormick *et al.* 1985; Potthast *et al.* 2002). Entry 8 shows that the hydrolysis that was carried out under conventional heating (at 110 °C with oil bath) produced a far lower RSs yield (1.8%) than it had under MW irradiation (entry 5). This is most likely because MW irradiation plays a unique role in activating lignocellulose and in improving the opportunities for collision between solid lignocellulose and catalyst particles, as has been reported (Wu *et al.* 2010a,b). The BC-SO₃H-1-catalyzed hydrolysis of the fresh bamboo in DMA-LiCl only produced a 2.5% RSs yield under MW irradiation (entry 9), reflecting what was most likely inhibition by the lignin that was wrapped around the cellulose in the fresh bamboo. Entry 10 shows that when the pretreatment and hydrolysis of the fresh bamboo were carried out simultaneously in DMA-LiCl containing aqueous ZnCl_2 solution, the yield of RSs in this one-step process was much lower than that in the above two-step process (entry 5).

The effects of microwave power and irradiation time on the BC-SO₃H-1-catalyzed hydrolysis of the bamboo pretreated with ZnCl₂-MW were further investigated with the DMA-LiCl media. The results of the investigation into the effects of microwave power and irradiation time are summarized in Figs. 2 and 3, respectively. It can be seen in Fig. 2 that RSs yield increased gradually with the increase in power in the range of the examined MW power. Figure 3 illustrates that the curve of RSs yield climbed sharply with time until it achieved a maximum at 20 min, after which it fell rapidly. This was because the RSs were easily degraded to 5-hydroxymethylfurfural (5-HMF) and organic acids (Yin *et al.* 2011). Here, The content of 5-HMF and organic acids in a hydrolysis solution after 80 min of irradiation time was measured by UV-Vis spectrophotometer at 287 nm and chemical titration, respectively. The results indicated that 2.86 % of 5-HMF and 4.66% of organic acids were detected in the hydrolysis solution.

Table 2. Influence of Solvent on the Hydrolysis of Bamboo Catalyzed by BC-SO₃H-1 under Microwave Irradiation^a

Entry	Solvent	RSs yield (%)	Entry	Solvent ^b	RSs yield (%)
1	DMA	3.4	6	DMF-LiCl	8.8
2	DMF	6.8	7	DMSO-LiCl	16.8
3	DMSO	9.4	8 ^d	DMA-LiCl	1.8
4 ^c	[BMIM]Cl	15.8	9 ^e	DMA-LiCl	2.5
5	DMA-LiCl	32.4	10 ^f	DMA-LiCl	4.6

^aReaction Conditions unless otherwise specified: bamboo, 0.1 g; solvent, 10 mL; catalyst, 0.1 g; and distilled water, 5 mL. The reaction mixture was heated for 20 min at 110 °C under microwave irradiation with a power of 750 W. ^bThe media composition is indicated by 9wt% of LiCl relative to the solvent. ^cUsing 5 mL of [BMIM]Cl. ^dThe reaction mixture was heated for 20 min at 110 °C with oil bath. ^eUsing bamboo without any pretreatment. ^fUsing fresh bamboo as raw material, 0.1 g, 5 mL of water containing 40% ZnCl₂.

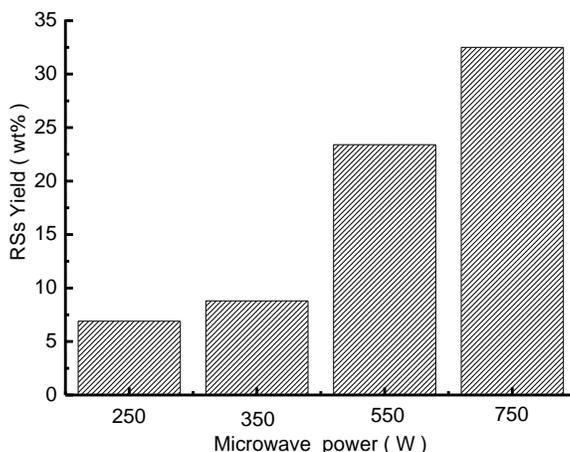


Fig. 2. Microwave power-dependence of RSs yield for BC-SO₃H-1-catalyzed hydrolysis of the bamboo pretreated in DMA-LiCl media (irradiation time, 20 min)

The catalytic performance of other BC-SO₃Hs was examined by means of the microwave-assisted hydrolysis of the bamboo under the optimal conditions, and the results were compared with those of a commercial Amberlyst-15 with single -SO₃H group and a dilute H₂SO₄ solution.

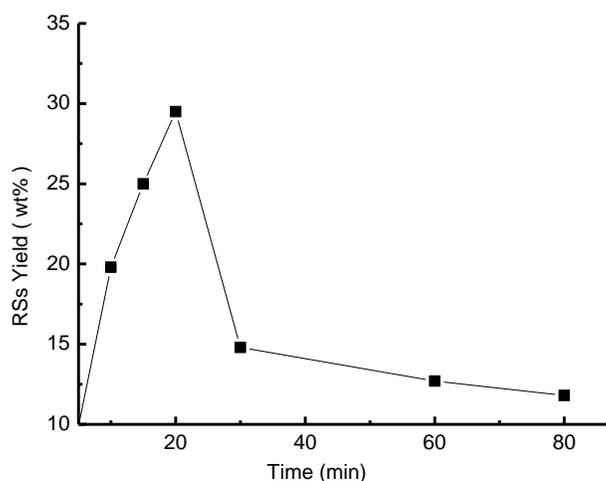


Fig. 3. Irradiation time-dependence of RSs yield for BC-SO₃H-1-catalyzed hydrolysis of the bamboo pretreated in DMA-LiCl media (MW power, 750 W).

As shown in Table 3, both catalysts BC-SO₃H-2 and BC-SO₃H-3, like BC-SO₃H-1, were active for the reaction, affording RSs yields of 28.1 and 11.8%, respectively (entries 1 and 3). Moreover, the turnover number (TON) of these BC-SO₃Hs was much higher than it was with a dilute H₂SO₄ solution (entry 4). Notably, a typical Amberlyst-15 catalyst with a higher acid density could not catalyze this reaction at all (entry 5). The high TON of the BC-SO₃Hs was likely due to the strong hydrogen bond interaction of their phenolic OH groups with the oxygen atoms in the β-1,4 glycosidic bonds of the cellulose, as previously reported by Suganuma and co-workers (2008).

Table 3. MW-assisted Hydrolysis of Lignocellulose by Various Catalysts^a

Entry	Catalyst	Density ^b (mmol/g)	RSs Yield (%)	TON ^c
1	BC-SO ₃ H-1	1.8750	32.4	1.07
2	BC-SO ₃ H-2	1.9886	28.1	0.87
3	BC-SO ₃ H-3	1.1357	11.8	0.64
4	H ₂ SO ₄ ^d	0.0125	2.4	0.08
5	Amberlyst-15 ^e	4.7	----	----

^aUnless otherwise specified, reaction conditions were: treated bamboo material, 0.1 g; catalyst, 0.1 g; microwave power, 750W; DMA-9% LiCl, 10 ml; H₂O, 5 mL; temperature, 110°C; irradiation time, 20 min. ^bThe number of acid sites on the catalysts was determined via titration. ^cThe turnover number was evaluated on the basis of the molar amount of converted substrate (glucose as substrate, and one water eliminated from the glucose as model reaction) per mole of effective acid sites (SO₃H) (mol. mol⁻¹). ^dUsing 0.0125 M of H₂SO₄ (15 mL) as a catalyst. ^eAmberlyst-15 (polystyrene-based cation exchangeable resin with ca. 4.7 mmol.g⁻¹ of SO₃H, 38 m².g⁻¹ of specific surface area and 30 nm of porous diameter).

Finally, the catalyst's potential for reuse was checked using the BC-SO₃H-1 as an example. After the first reaction was carried out at 110 °C for 20 min under microwave irradiation, the solid residue containing the catalyst and bamboo was separated and recovered from the hydrolytic solution via filtering and washing with water. After some pretreated bamboo was dried and supplemented, the ground residue was used directly for the hydrolytic reaction under the same conditions. This recycling process proceeded four

times. The results of the recycling indicated that the catalytic activity decreased gradually with each additional reuse, but its decrease between the 1st and 3rd recycling run was not very serious compared to the decrease during the first run (fresh) (see Fig. 4). The following two factors are responsible for the loss activity in the catalyst: i) a slight loss of catalytic mass is inevitable in each recycling run and ii) a part of the SO₃H groups are probably shed from the catalyst's surface in each recycling run, as supported by the recorded observation that the content of the -SO₃H groups on the catalyst decreased after the 3rd run from 1.875 to 1.283 mmol/g.

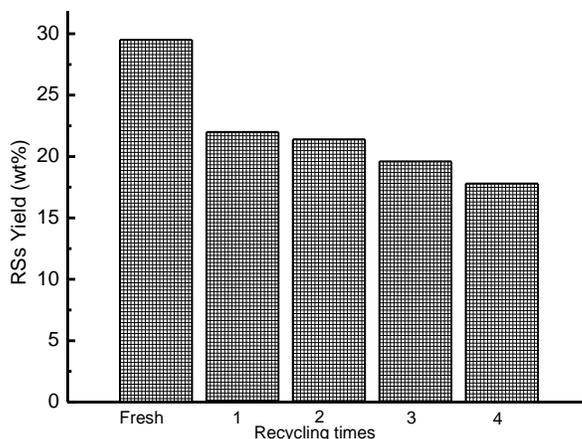


Fig. 4. Results of recycling for the BC-SO₃H-1-catalyzed hydrolysis of bamboo under the optimum conditions

CONCLUSIONS

In summary, we have developed a simple and efficient method for the pretreatment and then hydrolysis of lignocellulose into reducing sugars, a process catalyzed by biomass char sulfonic acids (BC-SO₃Hs) under microwave irradiation. Such a method has the following advantages: (i) the use of the recoverable and renewable BC-SO₃Hs as the catalyst; (ii) the use of microwave irradiation to efficiently preactivate the lignocellulose and thereby accelerate its hydrolysis; (iii) and high catalytic efficiency and good stability. This transformation technology is expected to be of competitive potential if its hydrolytic efficiency and catalytic stability are further improved.

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