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Cellulose hydrolysis reactor incorporating stirring apparatus for use with carbon-based solid acid catalyst

Daizo Yamaguchi

National Institute of Technology, Tsuyama College, 624-1, Numa, Tsuyama-City, Okayama 708-8509, Japan

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ABSTRACT

A highly efficient reactor with a stirring device was specially designed with the intent of performing the hydrolysis of pure crystalline cellulose using a carbon-based solid acid catalyst. This catalyst comprised an amorphous carbon-based material bearing –SO_3H, –COOH and –OH groups. The stirring apparatus had seven blades coated with polytetrafluoroethylene and arranged axially at regular intervals with a 60° offset. This design proved highly effective, providing double the glucose yield compared with conventional stirring systems. The basic properties of this novel reactor were investigated and analyzed and are discussed herein.

1. Introduction

Cellulosic biomass is an attractive fuel source and the most sustainable carbon-neutral energy resource [1,2]. Important chemicals, including ethanol, various hydrocarbons and starting materials for polymers linked by β-1,4 glycosidic bonds, can also be produced from sugars obtained from cellulose [3,4]. The hydrolysis of cellulose to generate these compounds is typically catalyzed by sulfuric acid, although substantial effort has been devoted to developing other methods. These have included catalysis by mineral acids [5–7] and the use of cellulase enzymes [8,9], subcritical or supercritical water [10–13], carbon-based solid acid catalysts [14–16], magnetic mesoporous carbon-based solid acid catalysts [17] and cellulase-mimetic solid catalysts [18,19]. Techniques employing sulfuric acid require a costly neutralization step and the removal of this catalyst from the homogeneous reaction mixture is inefficient and also generates non-recyclable sulfate waste. The requirement to develop more environmentally friendly approaches to cellulose processing has led to the use of recyclable yet strong solid acids as alternatives to sulfuric acid [15,17,20–29].

An amorphous carbon-based material bearing –SO_3H, –COOH and –OH groups has been reported to function as an efficient solid acid catalyst for the hydrolysis of cellulose at 343–373 K. This material can also be reused without loss of activity and with minimum energy consumption [14]. The use of such heterogeneous catalysts also provides an environmentally benign option that does not involve toxic chemicals [16]. Similar to mineral acid catalysts, this solid acid is able to promote the hydrolysis of pure crystalline cellulose as well as that of naturally occurring lignocellulosic materials such as eucalyptus and straw tips. Through this process, water-soluble β-1,4-glucans (that is, linear polysaccharides composed of glucose monomers linked by β-1,4-glycosidic bonds) are generated and, in turn, are hydrolyzed to produce glucose. This type of carbon-based catalyst has been shown to readily attach to cellulose and to the water-soluble β-1,4-glucan products of cellulose hydrolysis via hydrogen bonding involving –OH groups on the catalyst surfaces [14,30]. In addition, the highly acidic –SO_3H groups on the catalyst surfaces act to disrupt hydrogen bonding within the cellulose while promoting the hydrolysis of β-1,4 glycosidic bonds, such that cellulose is efficiently transformed into glucose [14, 30]. These effects are ascribed to swelling of the bulk carbon catalyst as a consequence of the absorption of significant quantities of

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E-mail address: tnt_yama@tsuyama-ct.ac.jp.

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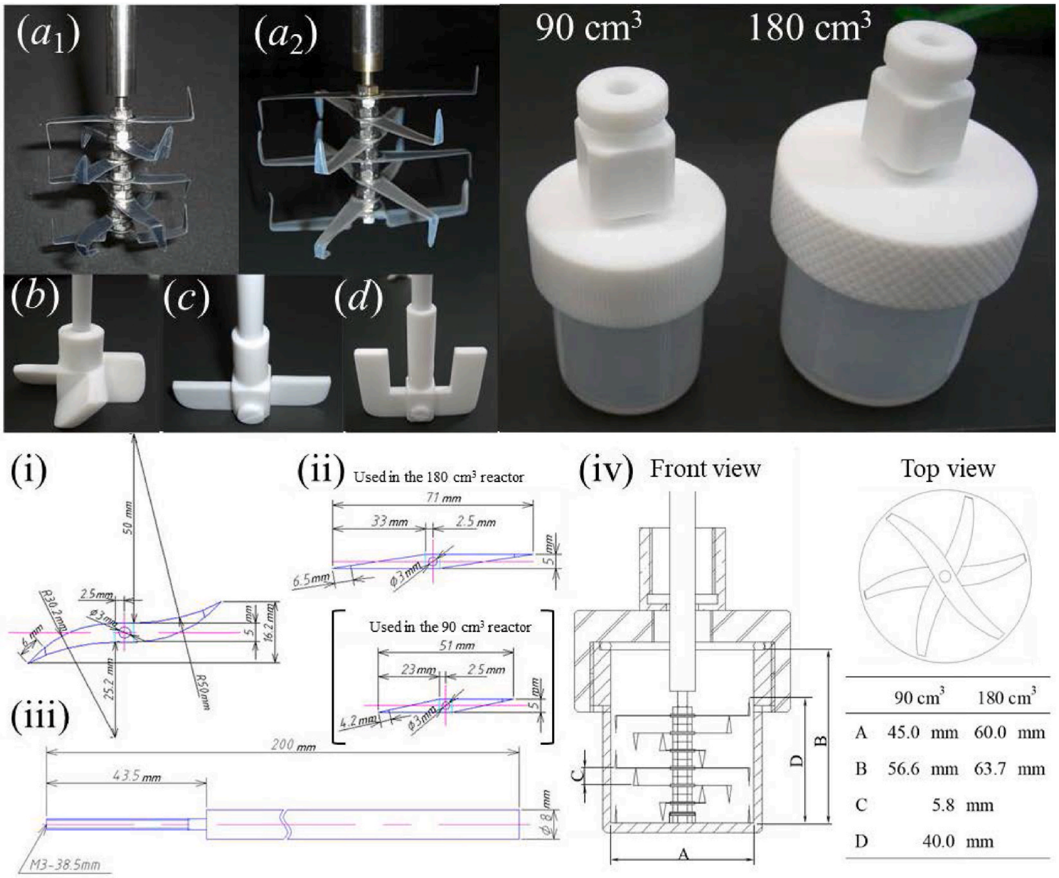

	90 cm³	180 cm³
A	45.0 mm	60.0 mm
B	56.6 mm	63.7 mm
C	5.8 mm	
D	40.0 mm	

Fig. 1. The new stirring apparatus developed in this work and the designs of conventional PTFE stirring devices. (a_1) The curved blades used in the 90 cm^3 reactor (width, 43 mm, active height, 40 mm, blade thickness, 0.3 mm, see diagrams (i), (iii) and (iv)) and (a_2) the rhombic blades used in the 180 cm^3 reactor (width, 58 mm, active height, 40 mm, blade thickness, 0.3 mm, see diagrams (ii), (iii) and (iv)). The rhombic blades used in the 90 cm^3 reactor (width, 43 mm, active height, 40 mm, blade thickness, 0.3 mm. The two ends of each blade (6, 6.5 or 4.2 mm) were bent to ensure removal of any materials adhering to the reactor wall. (*b*) The screw-type, four-wing stirrer (width, 59 mm; active height, 15 mm), (*c*) the two-wing stirrer (width, 59 mm; active height, 15 mm) and (*d*) the W-type stirring wing device (width, 59 mm; active height, 40 mm). Upper right: Cylindrical PTFE reactors, each with a PTFE cap and PTFE stirring seal.

water. Analyses based on water vapor adsorption isotherms acquired at 293 K have demonstrated that, prior to sulfonation, partially carbonized cellulose exhibits minimal water adsorption. In contrast, sulfonated carbon-based specimens having surface –SO_3H, –COOH and –OH groups have been found to show significant water adsorption [30]. In addition, these solid acid catalysts have been demonstrated to have a high surface area of 580 m^2 g^{-1} when applied to hydrolysis in conjunction with an excess of water. This value is much greater than the Brunauer–Emmett–Teller (BET) surface area of 2 m^2 g^{-1} observed following the removal of water from this material [30]. This is attributable to the high density of hydrophilic functional groups on graphene clusters in the catalyst. These groups permit dissolved reactants to easily reach –SO_3H active sites in the bulk of the carbon-based material, thus increasing catalytic activity even in the case of a low specific surface area [30].

The hydrolysis of crystalline cellulose by a carbon-based solid acid catalyst was previously investigated using an artificial neural network together with response surface methodology [31–37]. These analyses established that the catalytic hydrolysis of cellulose in the presence of amorphous carbon bearing –SO_3H, –OH and –COOH groups proceeds via the same mechanism as cellulose saccharification using concentrated sulfuric acid. As such, the reaction is greatly affected by the amount of water that is available. Specifically, the glucose yield reaches a maximum in the case that equal masses of water and solid catalyst are supplied. Because the catalyst is highly acidic, an amount of water that is less than optimal tends to favor the decomposition of β-1,4 glycosidic bonds and the disruption of strong hydrogen bonds in the cellulose to give water-soluble β-1,4-glucans. However, based on kinetic and equilibration factors, this scenario does not promote the hydrolysis of such products to produce glucose [37].

Following water adsorption, the Carr index for the catalyst (an indication of flowability) was determined to be extremely low, such that a specially-designed reactor had to be employed to perform cellulose hydrolysis trials [38]. In contrast, subsequent to water adsorption, this material was determined to be "non-floodable" according to the Carr system and so no special provisions were necessary [38]. Hydrolysis trials using this catalyst together with crystalline cellulose were performed with an adherence pressure on the order of *ca.* 3 kPa, as determined using the internal fraction angle associated with the Mohr stress circle [38]. The water concentration providing the *ca.* 3 kPa adherence was in the range of 50 %–100 % of the catalyst weight and so was equal to the range required for cellulose hydrolysis [38]. During cellulose hydrolysis using this type of solid acid, it is important to keep the temperature below 423 K so as to avoid carbonization of the cellulose. Such reactions are typically carried out in closed reactors with stirring to ensure that reactions progress at solid-solid interfaces in conjunction with an optimal concentration of water. It should be noted that the progress of this reaction can be limited in the case that a high amount of water or of gases are present or if the reactor undergoes corrosion. Consequently, slurry-based methods (including bubble columns and stirred tanks), fixed-bed processes (such as trickle beds), micrometer-scale channel reactors, jet loops, monolithic honeycomb-type catalysts and magnetic stirring are not advisable [39–41]. Hence, specially-designed reactors are required to mitigate the various challenges associated with these reactions.

The present work demonstrates a unique reactor design incorporating a stirring device specially designed for use with heterogeneous catalytic reactions. The hydrolysis of pure crystalline cellulose promoted by a solid acid catalyst was performed in this reactor and the reaction efficiency was compared with those obtained using conventional stirring devices. The development of a reactor for the mixing of a carbon-based material and crystalline cellulose so as to promote reactions at solid-solid interfaces in the presence of water that is primarily adsorbed into the carbon material is challenging. In fact, far more effort has been devoted to the design of stirred liquid phase or solid-liquid phase mixing reactors with stirring units [42–44].

2. Materials and methods

2.1. Reactor with stirring device

A stirring apparatus was developed comprising seven thin polytetrafluoroethylene (PTFE)-coated, curved (Fig. 1a_1) or rhombic (Fig. 1a_2) stainless steel blades arranged axially at regular intervals in conjunction with a 60° offset. The steel shaft and spacers between the blades were also coated with PTFE such that the entire unit was resistant to acids. The two ends of each blade were bent to ensure removal of any reactants adhering to the reactor walls. Trials were also performed using a number of conventional PTFE-based stirring apparatuses for comparison purposes. These included a screw-type four-wing stirrer (Fig. 1*b*), a two-wing stirrer (Fig. 1*c*) and a W-type stirring wing device (Fig. 1*d*). Cylindrical PTFE reactors having volumes of 90 cm^3 for the curved blades or 180 cm^3 for the rhombic blades, each equipped with a PTFE cap and a stirring seal (Fig. 1), were used during these experiments. Prior to each trial, the reactor being used was loaded with a mixture of cellulose, water and the carbon-based solid acid. Following this, a stirring apparatus attached to a PTFE-coated rod passed through the stirring seal was employed to stir the mixture. The clearance between the blades and the inner walls of the reactor was 1 mm and the lowest blade of the stirring apparatus was positioned so as to make contact with the inner bottom surface of the reactor.

2.2. Cellulose saccharification

A carbon-based solid acid catalyst bearing $–SO_3H$, –COOH and –OH groups was prepared via the sulfonation of partially-carbonized crystalline cellulose having particle sizes in the range of 2–200 μm. This process has been previously described in the literature [14,29,45]. The black powder obtained from this synthesis was determined to have a BET surface area of 2 $m^2\ g^{-1}$ together with a true density of 1.66 g mL^{-1}. This material comprised amorphous carbon made of phenolic nanographene sheets having thicknesses on the order of 1 nm and an essentially random distribution. The formula for this material was determined to be $CH_{0.622}O_{0.540}S_{0.048}$ while the concentrations of $–SO_3H$, –COOH and phenolic –OH functional groups attached to the graphene nanosheets were found to be 1.6, 0.8 and 5.0 mmol g^{-1}, respectively.

Hydrolysis of pure crystalline cellulose (Avicel®; particle size, 0.5–300 μm; crystallinity, 80%; degree of polymerization, 200–300) was performed in the presence of this solid acid while heating the reactor in an oil bath. Following each reaction, the quantities of glucose and water-soluble β-1,4-glucans that were generated were estimated. These analyses were performed using a previously reported method [37].

The catalytic activities obtained with various mixing modes were assessed. These modes consisted of: (*1*) mixing with the stirring apparatus throughout the entire reaction using the curved blades [37], (*2*) mixing manually for 5 min prior to the reaction with no mixing during the reaction, (*3*) mixing with the stirring apparatus at 400 rpm for 15 min before the reaction at room temperature with no mixing during the reaction and (*4*) no mixing before or during the reaction. The conditions applied during cellulose saccharification included a temperature of 373 K, reaction time of 3 h, a solid acid catalyst loading of 3 g, a cellulose loading of 3 g, a water loading of 2.5 mL, a stirring rate of 400 rpm and a reactor size of 90 cm^3 [37]. These conditions were previously determined to be optimal for this hydrolysis reaction based on assessments using an artificial neural network with response surface methodology using the curved blades [37]. All experiments were repeated five times using the same conditions, and differences between replicate trials were evaluated using Student's *t*-test (alpha is 0.01) [46]. The time course of glucose yields obtained with a reaction temperature of 373 K, a catalyst loading of 3 g, a cellulose loading of 0.9 g, a water loading of 1.6, 2.5 or 3.75 g, a stirring rate of 370 rpm and a reactor size of 90 cm^3 with the curved blade stirring apparatus were evaluated while repeating each experiment twice.

The catalytic activity and efficiency associated with the rhombic blade stirring apparatus were also assessed and compared with those of the conventional stirring devices. The conditions employed during cellulose saccharification included a temperature of 373 K, a reaction time of 3 h, a solid acid catalyst loading of 6 g, a cellulose loading of 6 g, a water loading of 5 mL, a stirring rate of 400 rpm and a reactor size of 180 cm^3. The amounts of catalyst, cellulose and water in these trials were double the optimal values noted above because the size of the reactor was doubled. Experiments were repeated twice under the same conditions.

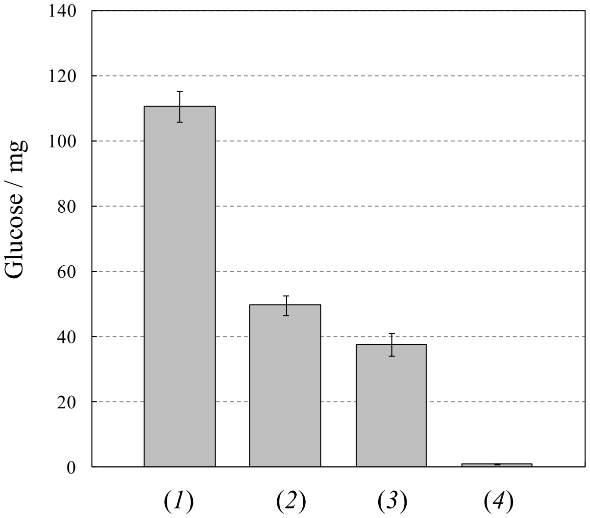

Fig. 2. Comparison of catalytic activities obtained using different mixing modes in conjunction with the curved blade stirring apparatus. The reaction conditions included a temperature of 373 K, a reaction time of 3 h, a solid acid catalyst loading of 3 g, a cellulose loading of 3 g, a water loading of 2.5 g, a stirring rate of 400 rpm and a reactor size of 90 cm^3.

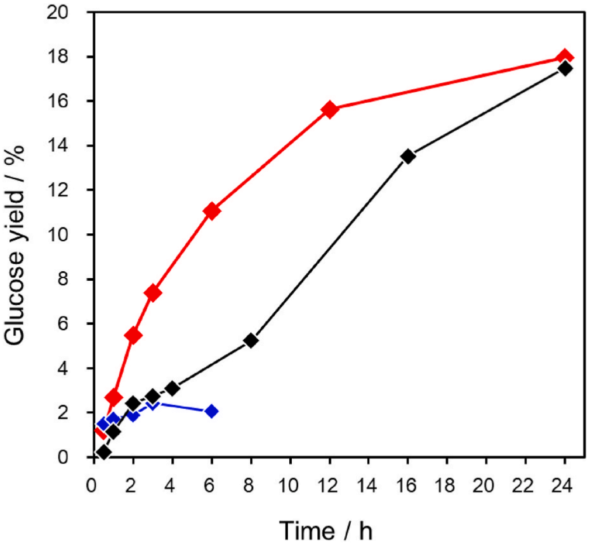

Fig. 3. Glucose yields from hydrolysis as functions of time. The reaction conditions included a reaction temperature of 373 K, a catalyst loading of 3 g, a cellulose loading of 0.9 g, a water loading of 1.6 g (blue), 2.5 g (red) or 3.75 g (black) and a stirring rate of 370 rpm.

2.3. Performance measurements

The efficiency of the hydrolysis reaction in each reactor type was evaluated by monitoring the power required to operate the device (torque transducer: TP-5KCE, Kyowa Electric Instruments Co., Ltd.; rotation detector: MP-962, Ono Sokki Co., Ltd.) and by evaluating catalytic activity. The efficiency, E [mg W^{-1}], was defined as $E = G/P$, where G is the glucose mass obtained from the reaction [mg] and P is the power requirement [W] [47] determined from torque measurements. These trials were all performed under the same conditions, with a solid acid catalyst loading of 6 g, a cellulose loading of 6 g, a water loading of 5 mL, a stirring rate of 400 rpm and a reactor size of 180 cm^3 and a data sampling rate of 500 Hz in the early stages of mixing at room temperature. The torque values were recorded once the system had reached a steady state.

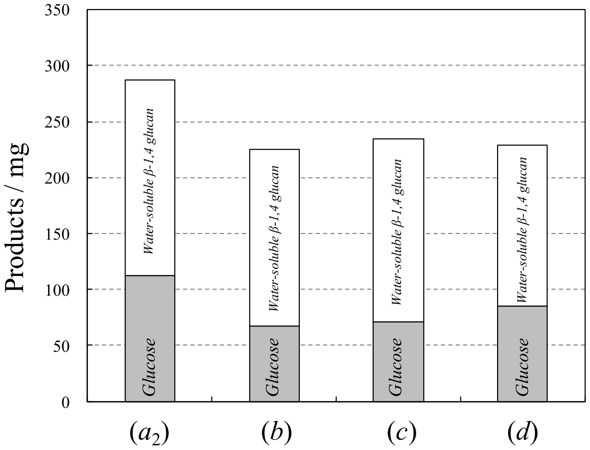

Fig. 4. A comparison of the catalytic activities using various stirring apparatuses. Data are from (a_2) the newly developed rhombic blade stirring apparatus, (b) the screw-type, four-wing stirrer, (c) the two-wing stirrer and (d) the W-type stirring wing device. Data were obtained using a temperature of 373 K, a reaction time of 3 h, a solid acid catalyst loading of 6 g, a cellulose loading of 6 g, a water loading of 5 mL, a stirring rate of 400 rpm and a reactor size of 180 cm^3.

3. Results and discussion

3.1. Catalytic activities

A comparison of the catalytic activities based on the extent of cellulose conversion into glucose for the different mixing modes is presented in Fig. 2. These data confirm that the highest activity was obtained using mode *1* (that is, mixing with the stirring apparatus during the reaction). This mode gave glucose yields of 110.7 ± 4.8 mg (3.69 ± 0.2 %), in agreement with previous reports [37]. The activities associated with modes *2* and *3* (with yields of 49.7 ± 3.0 mg (1.66 ± 0.1 %) and 37.7 ± 3.5 mg (1.25 ± 0.1 %), respectively) were lower than those obtained with mode *1* although not significantly different from each other by Student's *t*-test. These results establish that stirring the mixture at room temperature prior to the reaction was not sufficient to obtain a high glucose yield. Hence, stirring during the reaction was evidently very important. Mode *4*, with no stirring at any point, produced essentially no glucose.

The high performance of the present solid acid catalyst is attributed the capacity of this material to adsorb β-1,4-glucans and cellulose [14]. When this catalyst is brought into close contact with the cellulose, reactions occur that involve the adsorption of both β-1,4-glucans and the cellulose. This solid acid easily adsorbs water-soluble β-1,4-glucans and cellulose on the basis of hydrogen bonding via –OH groups on the catalyst surfaces. In addition, the highly acidic $–SO_3H$ functional groups on the solid acid serve to rupture hydrogen bonds while promoting the hydrolysis of β-1,4 glycosidic bonds in the β-1,4-glucans or cellulose, thus effectively generating glucose from the cellulose. This process is similar to enzymatic hydrolysis, so the present carbon-based catalyst having $–SO_3H$, –COOH and –OH groups can be considered as a highly active inorganic enzyme rather than a solid acid in terms of its mode of action [30,37]. The newly developed reactor demonstrated in this work evidently facilitated the hydrolysis of cellulose when using this solid acid catalyst such that the glucose yield was essentially doubled. This increased performance is ascribed to more intimate contact between the catalyst and the cellulose and to the improved distribution of water throughout the reaction system.

Fig. 3 plots glucose yields as functions of time for trials with varying amounts of water. These data indicate that the optimum water loading was 2.5 g, in agreement with prior results [37]. Using this amount, higher performance was obtained during the first 3 h of hydrolysis, with a glucose yield of 65.92 mg (7.39 %). The plots also exhibit roughly constant hydrolysis rates over this period. After 3 h, all three plots show pronounced decreases in the reaction rate that may be attributed either to a shortage of the water required for the reaction or to blocking of acid sites by the reaction products [17]. In the future, it would be helpful to develop a system capable of continuously providing the required amount of additional water while preventing additional reactions of the product. The deleterious effect of decreasing the water concentration in the reaction mixture is thought to be due to the nature of the present solid acid-catalyzed hydrolysis. In the early stages of the reaction, there is typically a significant excess of water, which promotes the hydrolysis reaction kinetics and provides suitable equilibrium conditions. However, as the reaction progresses, water is consumed. While this markedly increases the acidity of the catalyst, it also decreases the hydrolysis rate. Consequently, the reactor evaluated in this work was assessed using the optimal water loading of 2.5 g [17] by tracking the amount of glucose produced over a 3 h time span.

3.2. Comparison of catalytic activity and its efficiency

Fig. 4 compares the extent of cellulose conversion obtained using the stirring apparatus with the rhombic blades to the results obtained with the more conventional devices. The rhombic blades were found to provide a glucose yield of 112.5 mg while the conventional apparatuses gave similar yields of 67.0, 70.9 and 85.4 mg (see Fig. 4, parts *b*, *c* and *d*, respectively). The extent to which the cellulose was converted into water-soluble β-1,4-glucans was very similar in each case, with values of 174.2, 157.8, 163.5 and

Table 1
Yields of glucose and β-1,4-glucans from hydrolysis trials using 90 and 180 cm^3 reactors.

Stirring apparatus [a]	Catalyst/g	Cellulose/g	Water/g	Glucose yield/mg	Water-soluble β-1,4-glucans yield/mg
Rhombic blades with 90 cm^3 reactor [b]	3.0	3.0	2.5	123.0	38.0
Rhombic blades with 180 cm^3 reactor	6.0	6.0	5.0	112.5	174.2
	3.0	3.0	2.5	53.3	88.5

[a] Reaction conditions: temperature, 373 K; reaction time, 3 h; stirring rate, 400 rpm.

[b] The rhombic blades used in the 90 cm^3 reactor (see Fig. 1 diagrams (ii), (iii) and (iv)).

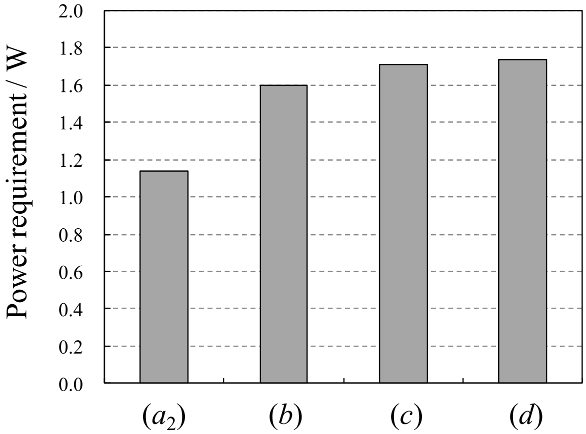

Fig. 5. Comparison of the power requirements of the various stirring apparatuses. Data are from (a_2) the newly developed stirring apparatus with rhombic blades, (*b*) the screw-type, four-wing stirrer, (*c*) the two-wing stirrer and (*d*) the W-type stirring wing device. Results were obtained with a sampling rate of 500 Hz, a solid acid catalyst loading of 6 g, a cellulose loading of 6 g, a water loading of 5 mL, a stirring rate of 400 rpm and a reactor size of 180 cm^3.

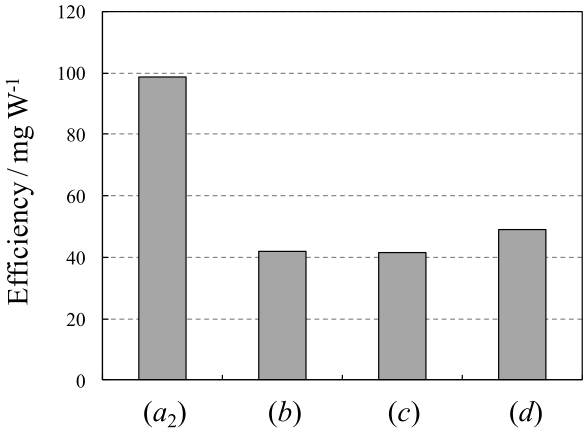

Fig. 6. Comparison of the efficiencies of various stirring apparatuses. Data were obtained from (a_2) the newly developed stirring apparatus with rhombic blades, (*b*) the screw-type, four-wing stirrer, (*c*) the two-wing stirrer and (d) the W-type stirring wing device.

143.8 mg obtained using the rhombic blades, screw-type four-wing stirrer, two-wing stirrer and W-type stirring wing device, respectively. Interestingly, the glucose yield per gram of cellulose was decreased by 50 % when using the larger reactor compared with the use of the smaller reactor (Table 1). Although there was no difference in the β-1,4-glucans yield per gram of cellulose when using in the larger reactor, produced twice when using the larger reactor compared with the use of the smaller reactor (Table 1). There was no difference in performance between the curved and rhombic blades used in the 90 cm^3 reactor (Fig. 2 and Table 1). These results suggest that the catalytic activity was strongly affected by the volume of the reactor. Further investigations are needed to determine viable approaches to scale-up of the reactor so as to retain a uniform processing temperature and a suitable distribution of water throughout the apparatus.

The power required by this newly developed reactor (1.14 W) was 30–35 % lower than those associated with the conventional stirring apparatuses (Fig. 5). In addition, the stirring efficiency as calculated for the new reactor was approximately twice those for the conventional reactors (Fig. 6). The Carr flowability and floodability indices for the present carbon-based catalyst interacting with cellulose at a high adherence of approximately 3 kPa and in the case of a high moisture content (50–100 % of the dry base) indicated extremely poor flowability and that the material was non-floodable [38]. Fig. 6 shows that the new stirring apparatus employing rhombic blades was highly effective during the hydrolysis of cellulose by the solid acid catalyst. This reactor promoted reactions at the solid-solid interfaces by continuously breaking down the agglomerated mixture and preventing arching. The two ends of each blade also removed reactants adhering to the reactor walls and so effectively blended the materials.

4. Conclusions

A high-efficiency reactor incorporating a stirring apparatus for the hydrolysis of pure crystalline cellulose by a carbon-based solid acid catalyst was developed and tested to clarify its performance. This new mixing system improved the contact between the catalyst and cellulose and also enhanced the distribution of water. The power requirement for hydrolysis was reduced by 30–35 % and the efficiency of the new device was twice that of conventional apparatuses. This newly-designed stirring apparatus employed thin, light and tough blades rotating at a power level of 1.14 W. This unit was highly effective at promoting reactions at solid-solid interfaces, based on the continuous breakdown of agglomerates at an adherence pressure of *ca.*3 kPa, and also reduced arching.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Daizo Yamaguchi: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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