


Article

Is Selective Heating of the Sulfonic Acid Catalyst AC-SO₃H by Microwave Radiation Crucial in the Acid Hydrolysis of Cellulose to Glucose in Aqueous Media?

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Abstract: Selective heating of microwave-absorbing solid catalysts in a heterogeneous medium may affect a chemical reaction; such selectivity cannot be achieved by conventional oil-bath or steam heating methods. Moreover, microwave methods are often misunderstood with respect to equipment and temperature measurements, so that additional experimentation is necessary. In this regard, the present study intended to clarify the effect of microwave selective heating on acid hydrolytic processes using a sulfonated activated carbon catalyst (AC-SO₃H). The model reaction chosen was the acid hydrolysis of cellulose carried out in a Pyrex glass microwave reactor, with the process being monitored by examining the quantity of total sugar, reducing sugar, and glucose produced. Heat transfer from the catalyst to the aqueous solution through absorption of microwaves by the catalyst occurred as predicted from a simulation of heat transfer processes. The resulting experimental consequences are compared with those from the more uniform microwave conduction heating method by also performing the reaction in a SiC microwave reactor wherein microwaves are absorbed by SiC. Some inferences of the influence of microwave selective heating of carbon-based catalyst particles are reported. Under selective heating conditions (Pyrex glass reactor), the yield of glucose from the acid hydrolysis of cellulose was 56% upon microwave heating at 200 °C, nearly identical with the yield (55%) when the hydrolytic process was performed under mainly conventional heating conditions in the SiC reactor. Although the beneficial effect of catalyst selective heating was not reflected in the reaction efficiency, there were substantial changes in the state of adsorption of cellulose on the catalyst surface.

Keywords: microwave selective heating; microwave-absorbing heterogeneous catalysts (MAHCs); biomass; cellulose; glucose

1. Introduction

The last two decades have witnessed the emergence of microwave radiation as a new heat source with which to carry out chemical reactions. Microwave energy is not only an efficient heat source, it is also an environmentally-benign energy source that has been widely applied in organic [1], pharmaceutical [2], and peptide syntheses [3], as well as in various aspects of nanotechnology [4]. Combining heterogeneous catalysts and microwave radiation presents several advantages [5] in that some solid catalyst supports (e.g., activated carbon [6]) are strong microwave absorbers and thus can function as an internal heat source within the solution. When microwave non-absorbing solvents (e.g., non-polar solvents) are involved in a catalyzed chemical process, it is possible to selectively heat only the solid catalyst. Most heterogeneous catalyzed reactions occur at the active surface of the catalyst, so that coupling supported metal catalysts with microwave radiation can generate high, albeit undetectable local temperature domains on the surface, with the reaction fully completed under less severe conditions. To the extent that microwave-irradiated catalyst particulates can also serve as an indirect heat source, the use of solvents can, in some cases, be avoided and thus eliminate some of the adverse effects that solvents may have in certain reaction protocols [7].

The use of catalysts in green chemistry is an important practice specified in the *12 Principles of Green Chemistry* [8], particularly with regard to microwave-induced heating of solid catalysts that can increase the green extent and enhance reaction efficiency, not to mention the significant energy savings in chemical processes. Indeed, the effects of microwave-induced selective heating of microwave-absorbing heterogeneous catalysts (MAHCs) on a chemical reaction that originates at the catalyst/solution interface can be substantial. For instance, in the synthesis of 4-methylbiphenyl from the Suzuki–Miyaura coupling reaction, process efficiency was significantly enhanced under microwave selective heating of the solid Pd/AC catalyst as a representative of MAHCs [9]. In addition, selective heating of Pt/AC catalyst particulates by microwaves contributed considerably to enhance reaction efficiency in the dehydrogenation of methylcyclohexane in methylcyclohexane \leftrightarrow toluene cycles, processes of considerable interest in hydrogen energy storage [10]. Microwave selective heating, however, can also lead to the formation of hotspots (micro-plasma) at the heterogeneous catalyst surface [11], a phenomenon that is undesirable and is to be avoided in chemical reactions. Mechanisms of hotspot generation have been elucidated together with the methods to minimize, if not suppress their formation [9,10]; factors to avoid formation of hotspots have also been described [11].

The objectives in our continued systematic studies of microwave-absorbing heterogeneous catalysts (MAHCs) are twofold: (i) other than metal supported catalysts [8,9], examine other types of solid catalysts that might benefit chemical reactions when such catalysts are directly and selectively heated by microwaves in comparison with microwave-originated conduction heating; (ii) assess any beneficial effect(s) that microwave selective heating might impart on hydrothermal catalyzed reactions (high temperatures and pressures). As a result, the current study examined the formation of glucose from the acid hydrolysis of cellulose in the presence of sulfonated activated carbon-based heterogeneous catalyst particulates (AC-SO₃H), a reaction of significant relevance and of important consequence to Green Chemistry.

Cellulose is the most abundant source of biomass (Figure 1). It is a potential alternative to fossil resources for the sustainable production of chemicals and fuels. If the breakdown of cellulose to glucose can be facilitated through microwave selective heating of a catalyst, then the use of biomass in various other fields such as, for example, in bioenergy (e.g., bioethanol, biodiesel) and as a precursor to generate other chemicals might prove highly advantageous [12]. Cellulose processing methods employing homogeneous catalysts or strong acid conditions have been reported [13]. However, these processes are not environment-friendly as the homogeneous catalyst or the strong acids cannot be recycled. Consequently, the acid hydrolysis of cellulose into glucose using solid catalysts that can be recycled (e.g., the MAHCs) would be highly desirable and would fall within the scope of Green Chemistry. If the reaction efficiency of heterogeneous catalysts were enhanced and reaction times shortened via

microwave heating, then significant contributions to green processes for effective renewable energy and production of renewable materials could be achieved.

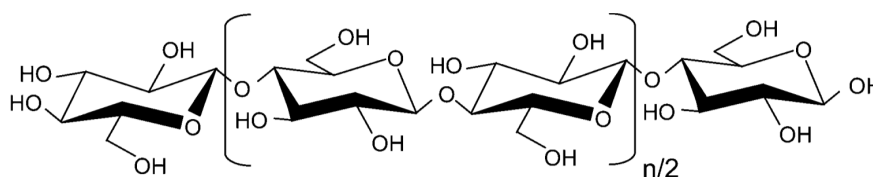


Figure 1. Chemical structure of cellulose.

2. Results and Discussion

2.1. Reactor Consideration for Conventional Heating

One of the characteristics of microwave heating is that heating occurs faster than conventional heating (i.e., heating via thermal conduction) [4]. Although it is possible to heat an aqueous solution over 100 °C in a steel autoclave, it is not possible to treat microwave dielectric heating under the same conditions as the rate of temperature increase under microwave heating is significantly faster. Accordingly, microwave heating and conventional heating in an autoclave (or otherwise) cannot be compared under identical conditions. That is, even if the reaction temperature could be adjusted, the heating rate cannot. Hence, one goal of our study was to clarify some of the features of selective heating of catalysts by microwaves (MAHCs) by a comparison with a more traditional heating method. To achieve the latter, we used an Anton Paar high-pressure SiC cylinder as a reactor known to strongly absorb microwave radiation and thus generate heat; as such, the solution reactants can then be heated by thermal conduction (heat transfer). In addition, since the SiC reactor was heated by microwaves, the sample could then be heated at a heating rate equivalent to the use of microwaves in non-absorbing reactors (e.g., Pyrex glass reactors) [14]. Interestingly, the commercial Anton Paar high-pressure SiC cylinder is widely used as a converted conventional heating method originating from microwave radiation. Germane to the present study, Robinson and coworkers [15] noted that the SiC reactor does not completely preclude the microwaves' electric field from interacting with the reactants. Since their finding was somewhat unexpected, we also investigated the absorption and permeability of microwaves in the SiC cylinder by performing a preliminary experiment in which a LED lamp was ignited with a Schottky barrier diode.

The photograph in Figure 2a shows the ignited LED lamp and confirms the penetration of microwave radiation through the SiC cylinder/reactor positioned in the single-mode applicator. Application of 4-W microwaves was sufficient to ignite immediately the LED lamp located inside the SiC cylinder; this also led to a concomitant increase of temperature of the SiC cylinder. For comparison, a Pyrex glass cylindrical reactor was also used and, as illustrated in Figure 2b, the LED lamp also ignited immediately. Accordingly, both conduction heating and microwave dielectric heating are relevant in experiments performed using a SiC reactor, in accord with the study reported by Robinson and coworkers [15].

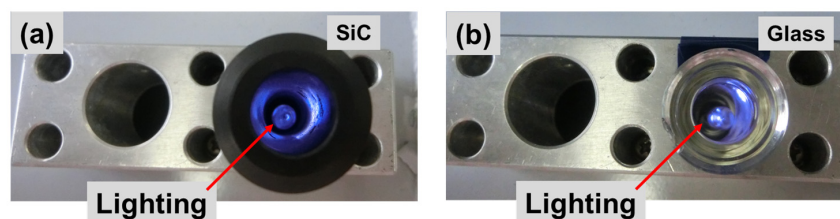


Figure 2. Photographs of LED lamps ignited in (a) a SiC cylinder and (b) a Pyrex glass cylinder both positioned inside a single-mode applicator.

2.2. Temperature Changes in Different Reactors and Selective Heating

Microwave heating efficiencies for the Pyrex glass and SiC reactors were examined using AC-SO₃H catalyst particulates dispersed in aqueous cellulose solutions (10 mL) subjected to continuous irradiation with 70-W microwaves in the Anton Paar Monowave 300 apparatus; samples were stirred continuously at 300 rpm (rotations per minute). The rate of increase of the external temperature was generally lower than at the center of the Pyrex reactor (Figure 3a), with the temperature gradient between the center and the exterior walls being 78 °C after 42 s (Figure 3c). An aqueous cellulose solution exposed to microwave radiation but without the AC-SO₃H catalyst particulates was also examined at an applied microwave power of 70 W in the Pyrex glass reactor (Figure 3a). By comparison, the temperature difference between the center of the sample and the external temperature in the SiC reactor was significantly smaller (see Figure 3b,c).

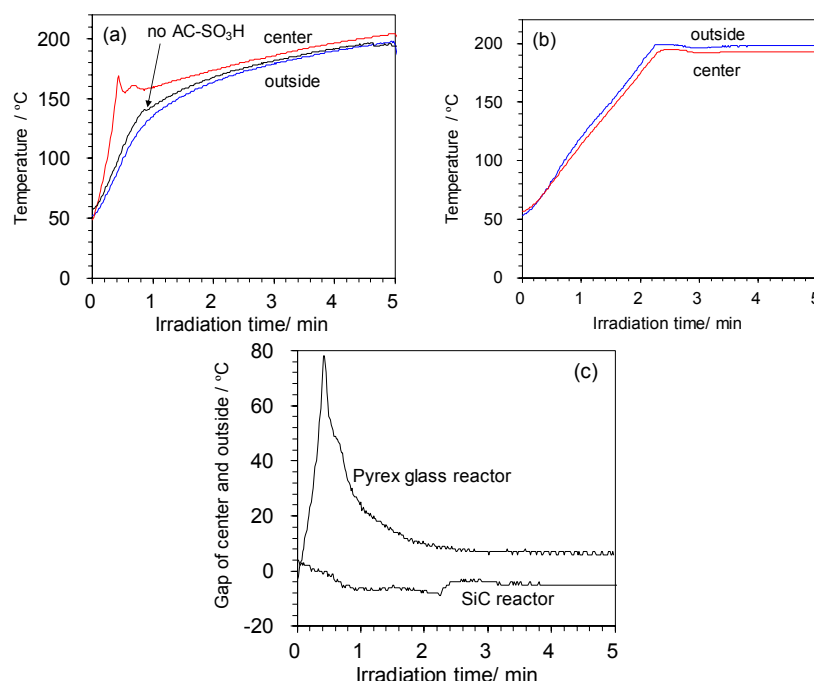


Figure 3. Temperature changes at the center and at the exterior walls of the reactor of the aqueous cellulose solution (10 mL) in the presence of AC-SO₃H catalyst particulates under 70-W microwave heating: (a) Pyrex glass reactor (for comparison, also displayed is the temperature rise without the AC-SO₃H catalyst); (b) SiC reactor; (c) plots illustrating temperature differences between the center and the external walls of the Pyrex glass reactor and the SiC reactor.

In the early heating stage of the AC-SO₃H/cellulose system in the Pyrex reactor, the microwave radiation heated both the aqueous medium and the AC-SO₃H catalyst particles. Thereafter, microwave irradiation caused selective heating of the catalyst as the solution temperature increased (see below). In the SiC reactor case, the external temperature was slightly higher (183 °C) than the water temperature at the center of the reactor (175 °C) after 4 min of microwave irradiation (Figure 3b); temperature remained constant thereafter.

The depth of penetration of the microwaves into the solution was determined using an Agilent Technologies HP-85070B Network Analyzer and an Agilent dielectric high temperature probe capable of measuring up to ~200 °C. The parameters of the microwave heating efficiency typically correlate with the relative dielectric loss factor (ϵ_r''), which is a measure of the quantity of input microwave energy lost to the sample by being dissipated as heat; it is a useful index for the generation of heat because of the interaction of the medium with the microwave radiation field.

Using deionized water alone as an example (Figure 4), the relative loss factor decreased with an increase in temperature. The microwave heating efficiency fell to 35% of its original value on increasing the temperature from 30 °C ($\epsilon_r'' = 8.02$) to 90 °C ($\epsilon_r'' = 2.81$). Hence, any difference in the presence of the AC-SO₃H catalyst is likely due to a decrease in the heating efficiency of water. As well, to the extent that absorption of the microwaves by water falls with increasing temperatures, the microwaves penetrate deeper into the reaction medium, and as the temperature of the activated carbon increases [16] the heating efficiency of microwaves also increases. Consequently, selective heating of the catalyst particulates in the Pyrex reactor is enhanced as the temperature of the medium increases. By comparison, heating of the catalyst by microwaves in the SiC reactor is also expected, albeit not selectively.

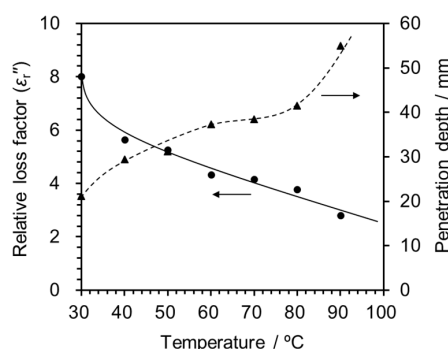


Figure 4. Plots illustrating the relative dielectric loss factor (ϵ_r'') and the penetration depth (mm) of the 2.45-GHz microwaves in deionized water in the temperature range 30–90 °C.

Figure 5 illustrates the temperature distributions in the Pyrex glass and SiC reactors. For the Pyrex reactor, most of the microwaves penetrated through the reactor and heated both the water and the heterogeneous catalyst particulates. At temperatures greater than 90 °C, however, there was a significant drop in the absorption of microwaves by water (see Figure 4), which resulted in the selective heating of the catalyst particles by the incident microwaves. The temperature distribution in the Pyrex reactor decreased in the order: catalyst particles \gg aqueous solution $>$ reactor (Figure 5a). By contrast, most of the applied microwave radiation was absorbed by the SiC reactor and was converted to heat at the inner walls of the reactor. Accordingly, the temperatures at the heterogeneous catalyst and in the aqueous medium were lower than the temperature at the reactor's inner walls (Figure 5b): reactor $>$ water \approx catalyst particles. Although microwaves also penetrated into the medium in the SiC reactor, selective heating of the catalyst particulates was expectedly significantly lower than in the Pyrex reactor.

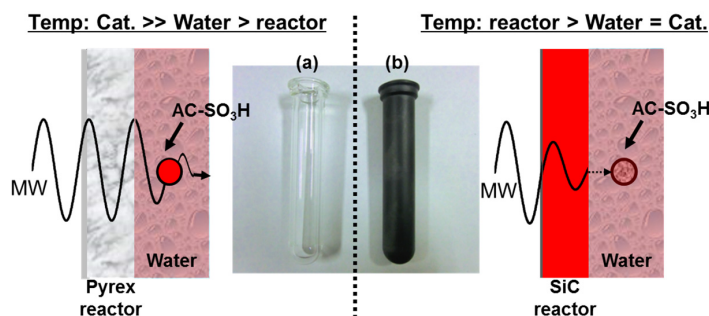


Figure 5. Photographs of (a) the high-pressure Pyrex glass cylinder/reactor and (b) the high-pressure SiC cylinder/reactor. Images of the temperature distribution in the aqueous medium containing the dispersed AC-SO₃H catalyst particulates are also displayed.

2.3. Acid Hydrolysis of Cellulose in the Presence of AC-SO₃H

We now compare the acid hydrolysis of cellulose to produce glucose in the presence of AC-SO₃H catalyst particles under conditions where they were selectively heated directly by the incident microwaves (Pyrex glass reactor; GR) and by heat-transfer from the SiC reactor (SR). The experiments were repeated no less than three times; the error was in all cases less than 5%. The extents of total sugar produced (Figure 6a) and reducing sugar produced (Figure 6b) reflect the efficiency of the acid hydrolysis of cellulose. In this regard, the amount of total sugar generated at 150 °C using the Pyrex glass reactor was nearly 1.7 times greater than what was produced with the SiC reactor. Further heating to 180 °C led to a smaller difference (1.2 times); no significant changes were observed at 200 °C. In the case of reducing sugar, differences in concentrations were rather negligible when comparing the reactions occurring in the two reactors. The amounts of glucose generated with the Pyrex glass reactor and SiC reactor are displayed in Figure 6c. With the Pyrex glass reactor, the extent of acid hydrolysis of cellulose to glucose was 56% upon microwave heating at 200 °C, nearly identical with the yield (55%) in the SiC reactor. Related to this, Fan and coworkers [17] inferred that the enhanced rate of hydrolysis of cellulose is likely due to a notable interaction of microwaves with the biomass, and further demonstrated that the selectivity and yield of glucose depend on the microwave power density and distribution; the latter demonstration was outside the scope of the present study. Their study showed no significant features in biomass conversion even when the catalyst was selectively heated by the microwaves.

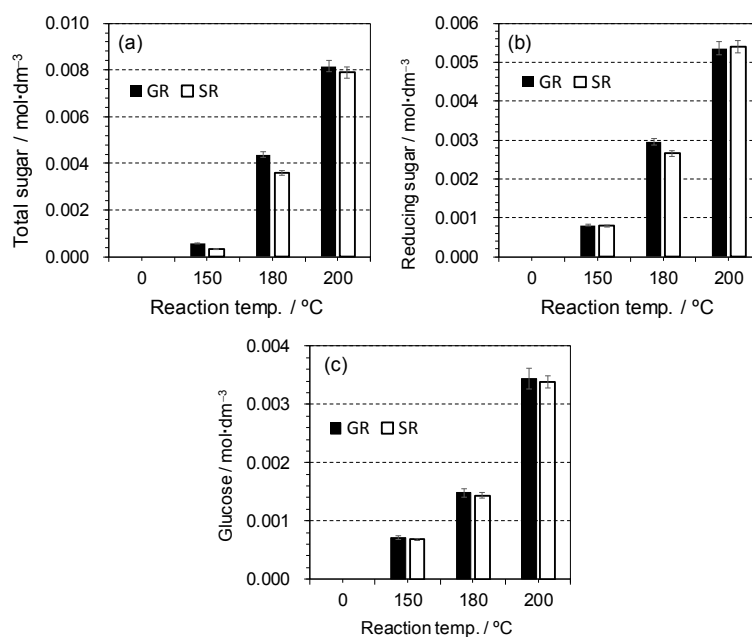


Figure 6. Concentrations of (a) total sugar; (b) reducing sugar; and (c) glucose produced from the AC-SO₃H catalyzed acid hydrolysis of cellulose in aqueous media in the Pyrex glass reactor (GR) and in the SiC reactor (SR) subsequent to heating at 150 °C, 180 °C and 200 °C for 30 min. In all cases the error was less than 5%.

2.4. Changes in the Dispersion of AC-SO₃H Catalyst Particulates in the Cellulose Gel

Selective heating of the AC-SO₃H catalyst by microwaves caused no differences in product yields in the AC-SO₃H catalyzed acid hydrolysis of cellulose in comparison with conduction heating (i.e., Pyrex versus SiC reactors). Nonetheless, closer observations of the samples treated with the 2.45-GHz microwaves revealed that the AC-SO₃H catalyst dispersion in the Pyrex glass reactor was different from the dispersion in the SiC reactor. Photographs of the aqueous cellulose dispersions are displayed in Figure 7 (note: the solutions were transferred from the microwave reactors to the test tubes shown).

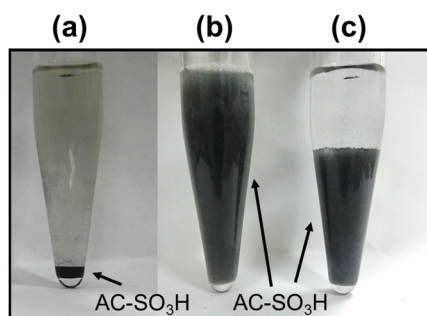


Figure 7. Photographs of AC-SO₃H catalyst particulates in (a) water and (b) in an aqueous cellulose dispersion in the SiC reactor; (c) AC-SO₃H catalyst particulates in the aqueous cellulose dispersion in the Pyrex glass reactor after treatment at, 200 °C for a microwave irradiation time of 30 min.

When the AC-SO₃H catalyst particulates were added to water, they tended to collect at the bottom of the reactor (Figure 7a), while in the presence of cellulose they were dispersed in the aqueous medium. Evidently, when the ultrasonic homogenizer was used to disperse the cellulose, the resulting aqueous medium was transformed into a gel-type dispersion as a result of the breakdown of the cellulose crystallites. There was no clear difference in the dispersion state even when the AC-SO₃H particulates were dispersed in the aqueous cellulose media and heated at 200 °C for 30 min in the SiC reactor by conduction heating from microwave heating the reactor's inner walls (Figure 7b). By comparison, when the particulates were heated at 200 °C for 30 min in the Pyrex glass reactor under microwave dielectric (selective) heating, the degree of dispersion of the AC-SO₃H catalyst particulates decreased (Figure 7c). Under conditions of microwave selective heating the AC-SO₃H catalyst particulates in the Pyrex reactor, the behavior of cellulose was clearly different from the cellulose exposed to conduction heating in the SiC reactor. It would appear, therefore, that the interaction of cellulose with the microwave-selectively-heated AC-SO₃H catalyst surface was somehow affected in the Pyrex reactor.

The hydrolysis of cellulose in the absence of AC-SO₃H catalyst particulates was also examined by subjecting the catalyst-free aqueous cellulose mixture to microwave heating for 30 min at 200 °C; no glucose formed under conditions otherwise identical to those of the catalytic process. This result infers that acid hydrolysis involves an initial interaction of cellulose with the AC-SO₃H catalyst surface followed by proton attack of the cellulose framework from loss of proton by catalyst (−H⁺) to initiate the depolymerization process (see below). Germane to the present study, Suttisawat and coworkers [18] established that the dehydrogenation reaction of decalin to tetralin in the presence of microwave selectively heated Pd/AC catalyst particulates accelerated the adsorption/desorption rates of decalin on the catalyst's surface, a result of differences between the temperature at the catalyst surface and the temperature of the solution. In the present case, the interaction of cellulose with the AC-SO₃H catalyst surface is also impacted by the selective heating conditions.

2.5. Other Characteristics of the Microwave Heating Method Compared to Conventional Heating

Onda and coworkers [19,20] reported that there was little, if any, decrease of catalyst activity in the acid hydrolysis of cellulose carried out by conventional heating in a steel autoclave reactor in the presence of AC-SO₃H catalyst particulates when the latter were recycled no less than three times. Their observation was confirmed in the present study upon recycling the microwave-heated catalyst used in either reactors (Pyrex glass and SiC); no decrease in reaction efficiency occurred when the catalyst particulates were used a second time. Moreover, the microwave-selectively-heated AC-SO₃H catalyst in the Pyrex glass reactor showed no deterioration.

Contrary to the microwave methods employed in the present study that produced glucose in 55% yields on irradiation for 30 min at a temperature of 200 °C, the yield of glucose from the acid hydrolysis of cellulose in the presence of AC-SO₃H catalyst particulates subjected to conventional

heating at 150 °C in the steel autoclave was only 40.5% after 24 h, and 44% when heating for 3 h at 180 °C [19,20]. Clearly, there are obvious advantages in the use of microwave heating methods for which the shortening of reaction time is an effective feature.

Along similar lines, Zhang and Zhao [21] reported the microwave-assisted acid-catalyzed hydrolysis of various celluloses (e.g., α -cellulose, Avicel cellulose, Spruce cellulose, and Sigmacell cellulose) dissolved in the ionic liquid *N*-methylimidazole hydrochloride in the presence of various zeolite catalysts; the maximal yields of glucose ranged from 32.5 to ca. 37% for heating times of 7 to 9.5 min (with HY zeolites present)—the internal temperature was ca. 180 °C, reached using 240-W microwaves. In the absence of the zeolite catalysts, but otherwise under identical conditions, the yield of glucose from the hydrolysis of cellulose was only 7.1% after 8 min of microwave irradiation. By comparison, the yield of glucose was 12.5% upon heating the zeolite (HZSM-5) / cellulose dispersion in an oil bath at 150 °C for 24 h. This led the authors [21] to suggest that, because both the cellulose and the solid acid catalyst were insoluble in the aqueous medium, the reaction occurred essentially on the surface of cellulose as the protons were not freely available to the oxygen atom in the etheral linkage of cellulose; however, when the cellulose was dissolved in the aqueous ionic liquid medium it made the β -glucosidic bonds more accessible to hydrolysis. These authors further deduced that microwave irradiation greatly accelerated the hydrolysis reaction by directly coupling the microwave energy with the molecules present in the reaction mixture, in addition to such other microwave (non-thermal) effects as the lowering of the activation energy and/or increasing the pre-exponential factor (Arrhenius law) as a result of the orientation effect of polar species in the electromagnetic field.

2.6. Brief Mechanistic Considerations

Heat transfer from AC-SO₃H catalyst particulates to the aqueous medium was predicted by carrying out simulation experiments using the COMSOL Multiphysics software (Figure 8). The initial temperature of the catalyst was fixed at 300 °C, while the temperature of the water was assumed to be 200 °C yielding a temperature gradient of 100 °C between the AC-SO₃H catalyst particles and the surrounding aqueous medium. As such, heat transfer should take place from the hotter catalyst particulates to the cooler aqueous medium.

Results of the simulation indicate that the temperature of the surrounding aqueous medium falls to 268 °C at a distance of 5 μ m from the catalyst surface, while at a distance of 10 μ m the temperature drops to 243 °C; no heat transfer from the AC-SO₃H catalyst surface occurs at a distance of 25 μ m (Figure 8b). Therefore, the neighboring domains around the catalyst surface appear to sense microwave selective heating, even though the model used and described in Figure 8a is an approximation owing to the large size of cellulose. Clearly, the temperature of the aqueous medium near the catalyst surface is higher than the temperature of the bulk aqueous medium, yet the effect of selective heating was not reflected experimentally in the product yields.

Conversion of cellulose to glucose did indeed occur by acid hydrolysis in the presence of AC-SO₃H catalyst particulates in aqueous media, which tempts us to infer the more relevant mechanistic steps of its occurrence (Figure 9): **Step 1** involves a concerted protonation of the cellulose from the AC-SO₃H catalyst surface ($-H^+$) and cleavage of the molecular chain of cellulose; **Step 2** shows the hydroxylation event in the hydrolytic process ($-OH$ from the water molecule) ultimately converting the intermediate(s) into glucose in **Step 3** through various consecutive steps that include the restoration of the catalyst surface.

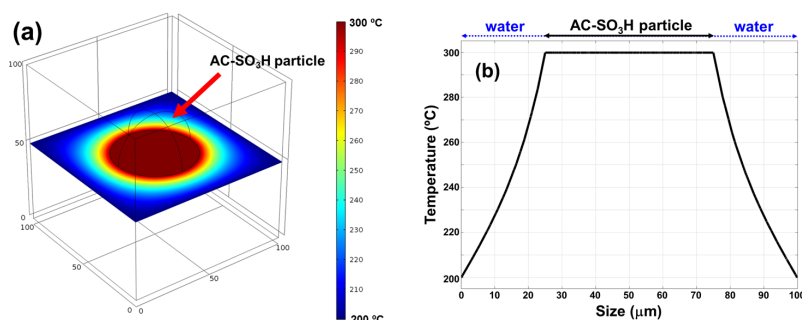


Figure 8. Changes in the temperature of water near the catalyst particulates; initial temperature of the catalyst was set at 300 °C and that of the surrounding water at 200 °C.

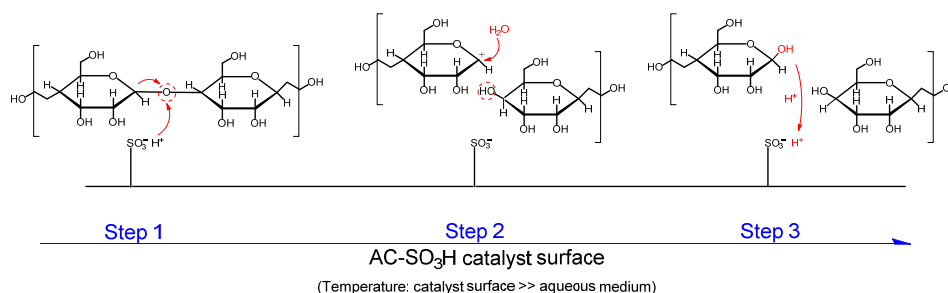


Figure 9. Simplified mechanistic steps in the acid hydrolysis of cellulose under microwave selective heating of the catalyst particulates. **Step 1:** protonation and cleavage of the etheral link. **Step 2:** hydroxylation by a water molecule. **Step 3:** ultimate formation of glucose and restoration of the catalyst surface.

Selective heating of the cellulose/AC-SO₃H catalyst in the Pyrex glass reactor led to an effective catalyzed reaction because of the higher temperature at the catalyst surface compared to the temperature of the aqueous medium in the SiC reactor heated indirectly by conduction heating, albeit the amount of reducing sugar and glucose formed was not actually increased by microwave selective heating. This is likely due to a rate-controlling step of sugar generation originating with the hydrolytic step by the water molecule. The theoretical simulation shows that any temperature benefits from microwave selective heating are only for the surface of the catalyst (Figure 8). The lack of changes in reaction efficiency to produce glucose infers that the modes of heating the reaction components in the Pyrex glass reactor and in the SiC reactor were not a significant factor.

3. Materials and Methods

3.1. Microwave Transparency of SiC Reactor Using a LED Lamp

An experiment was performed to examine the microwave transmission factor of the SiC cylinder using a single-mode applicator, a waveguide, and a LED lamp with a Schottky barrier diode. The cathode and the anode of the LED and the Schottky barrier diode were connected and composed a loop antenna. The microwave radiation is changed by the diode to a direct current causing the LED to ignite. The microwave irradiation setup with the single-mode TE₁₀₃ cavity (transverse electric 103 mode) used to irradiate the reactor contents, and schematically illustrated in Figure 10, included a short plunger, an iris, a three-stub tuner, a power monitor, and an isolator. The continuous microwave radiation was generated from a 2.45-GHz microwave semiconductor generator (GNU-201AA; maximal power, 200 W, Fuji Electronic Industrial Co. Ltd., Saitama, Japan). The resonance of the microwaves was adjusted with the iris and the plunger at 1.5 cycles. The SiC cylinder was setup in the single-mode microwave apparatus at the position of maximal electric field density [22].

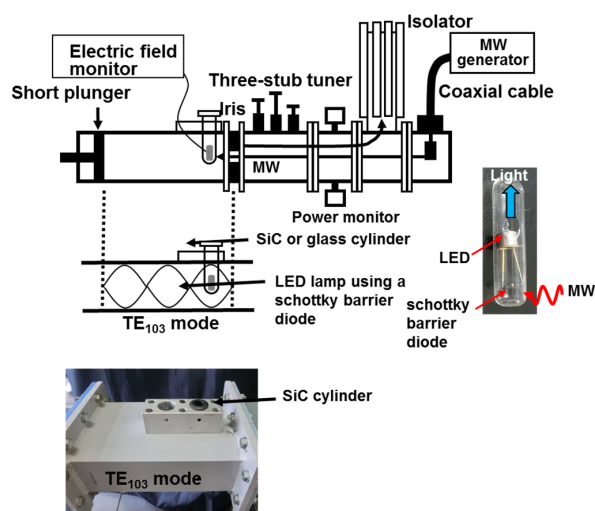


Figure 10. Details of the experimental setup and positioning of the samples in the single-mode microwave resonator.

3.2. Preparation of the AC-SO₃H Heterogeneous Catalyst Particulates

The AC-SO₃H solid catalyst powder was prepared using the method reported by Onda and coworkers [19,20] and by Toda et al. [23]. Typically, activated carbon particles (Wako Pure Chemical Industries Ltd., Osaka, Japan; average diameter, 0.05 cm; 1.0 g) are added to concentrated H₂SO₄ (Wako Pure Chemical Industries Ltd., Osaka, Japan; 20 mL) and subsequently heated under a flow of Ar gas at 150 °C for 16 h. The resulting sulfonated-activated carbon material was washed repeatedly using hot distilled water (3 L; 80 °C), and subsequently treated hydrothermally at 200 °C for 3 h followed by repeated washings with hot distilled water until sulfate ions are no longer detected in the filtrate.

Contact efficiency between cellulose and the catalyst surface is low as cellulose is insoluble in water. The earlier study of the acid hydrolysis of cellulose with AC-SO₃H catalyst treated the cellulose by the ball mill technique followed by heating in a steel autoclave at 150 °C for 24 h with agitation (22 rpm) [19,20]. In the present study, microcrystalline cellulose powders (K.K.; MP Biomedicals, Tokyo, Japan) were dispersed in deionized water (10 mL; time, 30 min) using an ultrasonic homogenizer (UX-300; 51 W; Mitsui Electric Co. Ltd., Noda City, Chiba Prefecture, Japan) yielding a white turbid aqueous solution of dispersed cellulose. No changes in turbidity were noted when the aqueous solution was left standing for 24 h. The sulfonated activated-carbon (AC-SO₃H) powder was then added to the aqueous cellulose solution, followed by microwave heating under hydrothermal conditions for 30 min at 150, 180, and 200 °C. All chemicals used in the experiments were of high grade purity.

3.3. Acid Hydrolysis of Cellulose

A sample solution (10 mL) containing 25 mg of the sulfonated activated-carbon catalysts (AC-SO₃H) was added to the Anton Paar high-pressure Pyrex glass cylinder of the Anton Paar Monowave-300 microwave apparatus (2.45 GHz) and then treated by continuous microwave irradiation (microwave power, 70 W). The temperature distribution at the center of the sample solution was measured with a ruby fiber optic sensor, while a radiation thermometer was used to measure the external temperature of the reactor.

3.4. Analytical Procedures

Total sugar: The molar concentration of total sugar in the solution was determined by the phenol sulfuric acid method. After the reaction, a 0.1-mL sample of the solution was placed in a glass test tube, diluted five-fold, followed by addition of an aqueous phenol (Wako Pure Chem. Ind.) solution

(5 wt %; 0.5 mL) and sulfuric acid (98% acid; 2.5 mL). The 480-nm absorption band was monitored using a JASCO V-650 UV-VIS spectrophotometer.

Reducing sugar: The progress of hydroxylation of the cellulose was assessed by measuring the reducing sugar using the dinitrosalicylic acid (DNS) method, which involved the mixing of 3,5-dinitrosalicylic acid (5 g; Wako Pure Chemical Industries Ltd., Osaka, Japan), phenol (1 g; Wako Pure Chemical Industries Ltd., Osaka, Japan), NaOH (5 g; Wako Pure Chemical Industries Ltd., Osaka, Japan) and Na₂SO₃ (5 g; Wako Pure Chemical Industries Ltd., Osaka, Japan) in deionized water (500 mL). The resulting sample solution (0.2 mL; Wako Pure Chemical Industries Ltd., Osaka, Japan) and the DNS reagent (0.6 mL) were then mixed and subsequently heated in a water bath at 80 °C for 5 min, after which 0.2 mL of Rochelle salt (Wako Pure Chemical Industries Ltd., Osaka, Japan) was added. The resulting mixture was cooled for 30 s in an ice bath and then analyzed by monitoring the absorption band at 505 nm using the JASCO V-650 UV-VIS spectrophotometer.

Glucose: The amount of glucose was determined by the glucose oxidase method using a commercially available test kit (Wako glucose B test; Wako Pure Chemical Industries Ltd., Osaka, Japan).

3.5. Simulation of the Heat Transfer Process

Heat transfer from the microwaved AC-SO₃H catalyst particles to the surrounding aqueous media was simulated using the software COMSOL Multiphysics (Version 4.3a). Physical properties and geometric parameters of the dispersion components used in the simulation are listed in Table 1. A catalyst particle was fixed at the center of the water sample and the temperature distribution was calculated. Although experimentally the sample was stirred, heat distribution in the simulation experiment was left to natural convection.

Table 1. Geometric parameters and physical properties used in the heat transfer simulation with the COMSOL Multiphysics software.

Parameters	Water	AC-SO ₃ H
Radius/μm	100 × 100 × 100	25
Specific heat capacity/kJ·kg ⁻¹ ·K ⁻¹	4.216	1.300
Thermal conductivity/mW·m ⁻¹ ·K ⁻¹	679.1	140

4. Concluding Remarks

This article reports some of the features of the acid hydrolysis of cellulose by microwave dielectric heating of the microwave-absorbing heterogeneous AC-SO₃H catalyst particulates carried out in two different types of reactors that were otherwise identical in shape and size: Pyrex glass reactor versus a SiC reactor. Although the microwaves permeated through the SiC reaction vessel, microwave selective heating of the catalyst particulates occurred only when using the Pyrex glass reactor. The fact that no difference in reaction efficiency was observed in the catalyzed acid hydrolysis of cellulose between microwave selective heating and microwave conductive heating of the catalyst particulates (55% yield of glucose in both cases) suggests that, once protonation of the cellulose's ethereal bond has occurred, the remaining relevant steps occur in solution.

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