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Direct Microwave-Assisted Hydrothermal Depolymerization of Cellulose

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Supporting Information

ABSTRACT: A systematic investigation of the interaction of microwave irradiation with microcrystalline cellulose has been carried out, covering a broad temperature range (150 → 270 °C). A variety of analytical techniques (e.g., HPLC, ^{13}C NMR, FTIR, CHN analysis, hydrogen−deuterium exchange) allowed for the analysis of the obtained liquid and solid products. Based on these results a mechanism of cellulose interaction with microwaves is proposed. Thereby the degree of freedom of the cellulose enclosed CH_2OH groups was found to be crucial. This mechanism allows for the explanation of the different experimental observations such as high efficiency of microwave treatment; the dependence of the selectivity/yield of glucose on the applied microwave density; the observed high glucose to HMF ratio; and the influence of the degree of cellulose crystallinity on the results of the hydrolysis process. The highest selectivity toward glucose was found to be ∼75% while the highest glucose yield obtained was 21%.

The 21st century has generated a demand for new sources of refinery feedstocks due to depleting oil reserves.[1] One such feedstock is sugars from plants which can be converted to chemicals and fuels through fermentation and/or microbial processes.[2] However, sugar is also a food source making its use controversial. Cellulose, the most abundant and readily renewable source of biomass on the planet, has potential to be converted to nonfood-competing sugar, and hence, methodologies that optimize its breakdown to simple sugars are highly sought after.[3] As such, various catalytic, thermal, and enzymatic approaches have been explored.[4] Enzymatic depolymerization tends to need long residence times and high dilution ratios, but is highly selective, while thermal processes are limited by poor energy efficiency and thermal conductivity.[5,6] Furthermore, the high temperatures required for thermal treatment limits glucose selectivity, with the main products being anhydrosugars (e.g., levoglucosan) and secondary breakdown products (e.g., HMF and phenols).[7] Hydrothermal processing offers a route to hydrolyze cellulosic biomass into simple sugars using elevated pressure and temperature.[8] Combining this technique with microwave heating presents a potentially faster, more efficient, and selective method for the thermal treatment of biomass, as water is an effective microwave energy absorber.[6,9] The beneficial effect of microwaves toward cellulose hydrolysis has been reported previously be it only in the presence of strong acid catalysts.[10] Here we report our preliminary investigations on the use of hydrothermal microwave processing, moderating only the temperature and microwave field density to convert cellulose to sugars without additives, making it more industrially favorable.

Initially these experiments were performed in a high energy density laboratory (35 mL) CEM Discover SP (CD) microwave with a maximum pressure of 300 psi (230 °C, accuracy verified previously).[11] Experiments were run in dynamic mode allowing for a system with a controlled variable power input to achieve the desired temperature. During the initial water heating phase, a maximum power input of 300 W was recorded. Each experiment was repeated in triplicate, and the obtained glucose yields were within 7%. The resulting microwave hydrolysis products were analyzed by NMR, HPLC, GC, and electronspray ionization mass spectrometry (ESI). This allowed for both qualitative and quantitative analysis of the formed products (Figures 1 and S1).

HPLC analysis facilitated the identification and quantification of glucose, fructose, xylose, cellobiose, and levoglucosan present in the hydrolysates (Figure 1A). The presence of xylose is attributed to residual hemicellulose in the cellulose samples.[12] As can be seen in Figure 1B/C the total yield of sugar shows a distinct maximum at 220 °C where 14% of the cellulose is converted with a 75% selectivity to glucose (11% yield). ^{13}C NMR and ESI characterization confirmed the presence of 5-hydroxymethylfurfural (HMF) as a major secondary byproduct (see Supporting Information (SI) Figure S1a−h). Note that it is well-known that in subcritical water (100 °C < T < 373.9 °C) HMF is one of the major products from glucose degradation.[13]

The total cellulose depolymerization in the CD microwave experiment was limited to 14% suggesting that only a small fraction of the cellulose is available for hydrolysis under these conditions. Microcrystalline cellulose consists of both amorphous (13%) and crystalline regions (87%) with significantly different structural and thermal properties (Figure S11). Thermal transformations in amorphous cellulose take place between 180 and 230 °C,[14] which is consistent with the

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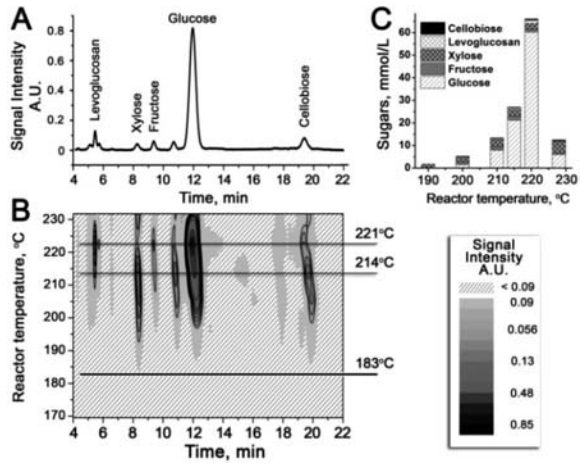

Figure 1. HPLC analysis of the sugars formed during hydrolysis of cellulose in the CD laboratory microwave (1 min holding time): (A) HPLC trace of the hydrolysate obtained at 220 °C; (B) two-dimensional trace of products formed over the temperature range 170−230 °C; (C) sugar mixture composition as a function of temperature.

temperature at which the CD hydrothermal microwave experiment yields the maximal amount of glucose (around 220 °C). Therefore it can be concluded that the crystalline region of cellulose was not involved throughout the process, as major structural changes in this region only occur well above 220 °C.[15]

Hydrogen bonding is a critical factor in polysaccharide structures, and it is well-known that the depolymerization of cellulose depends strongly on the structure of the hydrogen bond network.[16] More specifically the structure of cellulose involves intersheet, interchain, and intrachain hydrogen bonds (Figure 2A). These impart rigidity and stability to the cellulose

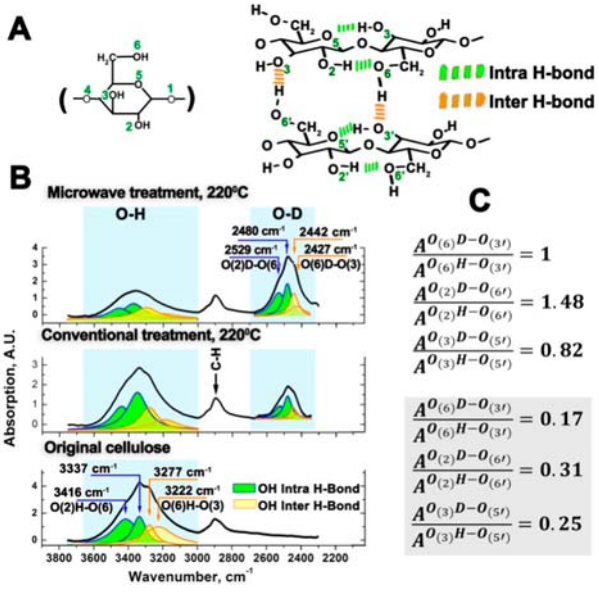

Figure 2. (A) Schematic representation of cellulose and its hydrogen bond network; (B) ATR-FTIR spectrum of original cellulose (bottom), the deuterated cellulose after conventional (middle) and microwave (top) treatment respectively; (C) ratios of either conventional (bottom) or microwave (top) O−D to O−H deconvoluted peak areas.

structure, but can be broken at elevated temperatures.[17] To understand the activation of the amorphous cellulose region on a molecular level, a proton/deuterium exchange experiment was performed at 220 °C under both conventional and microwave conditions. Using ATR-FTIR spectroscopy the accessibility of the different hydrogen bonds could be measured as the ratios between the areas of the OH and OD peaks in the respective 3400 and 2500 cm^{-1} regions (Figure 2B).

It was found that in the remaining cellulose, after conventional hydrothermal treatment, the intrachain O(2)−H···O(6) (3416 and 2529 cm^{-1}) hydrogen bond is the most accessible followed respectively by the O(3)−H···O(5) (3337 and 2480 cm^{-1}) and O(3)···H−O(6) (3222 and 2427 cm^{-1}) hydrogen bonds (see Figure 2C). In contrast, the $CH_2O(6)$ related hydrogen bonds in the remaining cellulose after microwave (CD) treatment, i.e. intrachain O(2)−H···O(6) and interchain O(3)···H−O(6), were found to be more prone to proton/deuterium exchange than the intrachain O(3)−H···O(5) hydrogen bond. It can thus be concluded that after microwave-assisted heating the protons associated with the $CH_2O(6)H$ group are more accessible. The mentioned values and assignments are in agreement with the literature.[18]

At temperatures below 180 °C the CH_2OH groups are hindered from interacting with microwaves while they are strongly involved in hydrogen bonding within both the amorphous and crystalline regions (Figure 3A).[19]

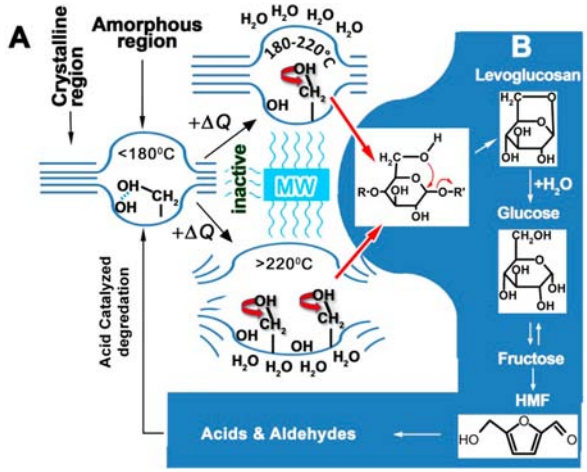

Figure 3. Schematic representation of the cellulose-microwave interaction as a function of temperature: (A) mechanism of CH_2OH group activation; (B) scheme of cellulose degradation toward acids and aldehydes.

Above the softening temperature (180 °C) these CH_2OH groups could be involved in a localized rotation in the presence of microwaves.[20] As such they could act similarly to "molecular radiators" allowing for the transfer of microwave energy to their surrounding environment[21]

In view of the limited presence of water inside the rigid cellulose framework, this is likely to involve collisions between the CH_2OH groups and the anomeric C1 of the same glucose ring thus forming levoglucosan.[22] The latter can easily hydrolyze to glucose (Figure 3B).[23] The data obtained from both conventional and microwave based experiments (see also Figure S2) confirm the molecular explanation of cellulose decomposition and its direct relationship to microwave activation of the CH_2OH pendant groups. Indeed, as shown

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in Figure 4A, from 190 °C onward microwave heating is found to be markedly more efficient toward the hydrolysis of cellulose than conventional heating.

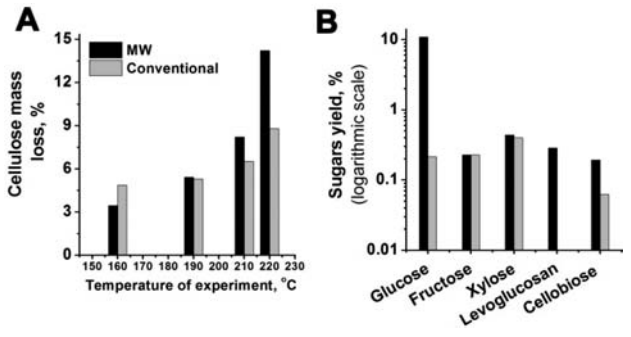

Figure 4. Comparison of CD microwave and conventional hydrolysis: (A) cellulose mass loss; (B) individual sugar yields (220 °C) (logarithmic *Y*-axis).

The maximal glucose yield at 220 °C under microwave treatment was found to be nearly 50 times higher than that under similar conventional hydrolysis conditions. Interestingly, levoglucosan is only obtained under microwave conditions (Figure 4B); its presence suggests that the microwave active center within cellulose is not accessible to the hydrolyzing media.[24]

According to the proposed model, the yield of glucose obtained below 220 °C is only related to the depolymerization of amorphous cellulose and not the crystalline content that becomes active above 220 °C.[15,25] While the CD system is restricted to 230 °C, the efficiency of microwave hydrothermal depolymerization of cellulose at temperatures up to 270 °C was evaluated using a CEM MARS6 (CM6) microwave. With both systems the experiments were performed at the same scale and mass ratio (2 g of cellulose to 20 mL of water). Also, the same heating rate of ∼15 K·min^{-1} and holding time (1 min) at the final temperature were applied. In addition, the reaction temperatures for the CM6 system were verified by measuring its pressure (e.g., 252 °C = 600 psi).[26] As expected the glucose yield at 250 °C is higher than the one obtained at 220 °C, reaching 21% (Figure 5A). This increase of yield is accompanied by a decrease in selectivity from 75% to 36% (Figure 5B). Surprisingly, using the CM6 no activation/depolymerization of amorphous cellulose at 220 °C is observed. This can be explained by the different power densities of the CD and CM6 microwave systems, respectively being 800 and 35 W L^{-1}. As CD involves monomode operation, and CM6 multimode, this difference could be even further accentuated.

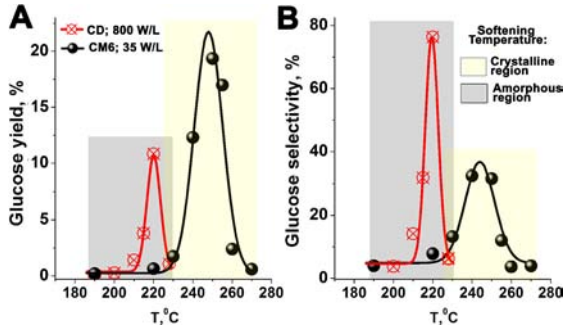

Figure 5. Comparison of CD and CM6 experiments: (A) glucose yield; (B) glucose selectivity for CD microwave. The contributions from the amorphous and crystalline regions are indicated.

The dependence of the glucose yield on the microwave power density suggests that the microwave activation has a strong kinetic dimension. Two competitive processes determine the speed of the CH_2OH group rotation: (i) acceleration by interaction with microwave photons and (ii) deceleration through interaction (e.g., collision, electromagnetic) with neighboring groups. The dominance of either process depends on the degree of freedom of the CH_2OH groups. For depolymerization of cellulose to occur the CH_2OH groups need to acquire the activation energy necessary to provoke the above proposed S_N2 reaction. At high microwave power densities (800 W·L^{-1}) this can already be achieved below 230 °C, while upon the use of lower microwave densities (35 W·L^{-1}) more elevated temperatures (240−260 °C) are required to liberate the CH_2OH groups.

Based on HPLC measurement a glucose yield of 21% was found using the CM6 microwave. This is higher than CD microwave operation at 220 °C (11%) and conventional heating at 250 °C (16%).[27]

From ^{13}C NMR (relaxation time 30 s) the ratio of HMF to glucose in the samples could be accurately determined (Figures 6A and S3a−c), and thus it was possible to calculate an HMF

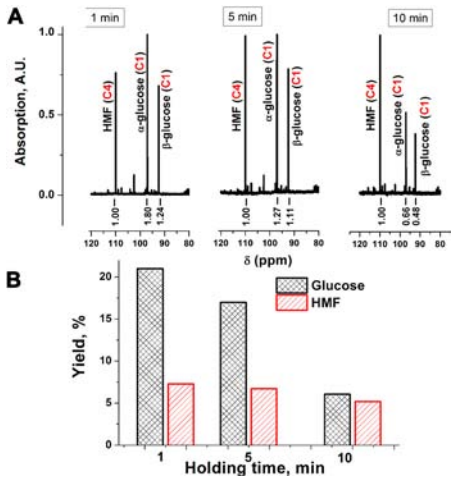

Figure 6. (A) The anomeric carbon regions in the ^{13}C NMR spectra of the freeze-dried cellulose hydrolysis products as a function of the holding time (CM6, 250 °C); (B) the yields of glucose and HMF as a function of the holding time (CM6, 250 °C) determined from both the ^{13}C NMR and HPLC.

yield of 7.5% using the determined glucose value as a standard (Figure 6B). The ratio of glucose to HMF obtained using the CM6 microwave is substantially higher than the one obtained under conventional conditions (2.8 vs 1).[27] The high glucose to HMF ratio at the given hydrolysis temperature of 250 °C further supports the above proposed mechanism. Indeed, while microwaves are able to activate the CH_2OH groups enclosed in cellulose cavities, they are unable to activate these groups in individual glucose monomers as their energy transfers very efficiently to the surrounding water molecules. The remaining 35% (conversion ∼60%) is likely to be composed of water and a range of organic acids and aldehydes, most of which were removed during the freeze-drying process necessary to prepare the NMR samples.[28]

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Over time the concentrations of both glucose and HMF are reduced, therewith showing their intermediate nature in the cellulose hydrolysis process (Figure 6B). It was found that organic acids were produced, due to the degradation of HMF, progressively reducing the pH of the reaction mixture to 3.5, which is in good agreement with the literature.[29] These acids could further accelerate the whole cellulose depolymerization process (see Figure 3B). As to the possible formation of humins, the mass balance combined with the ^{13}C NMR and elemental analysis data rules out this possibility (SI, section X). In conclusion, microwave-mediated cellulose hydrolysis resulted in high glucose yields and selectivities (respectively up to 21% and 75%) compared to conventionally heated noncatalytic processes. Furthermore the amorphous region was activated at significantly lower temperatures than possible under conventional conditions. Moreover, it was demonstrated that the glucose yield and selectivity can be controlled by altering the microwave power density/distribution. Additionally, it was found that the weakening of the hydrogen bond network within the molecular cellulose matrix at temperatures >180 °C allows the polar CH_2OH groups to act similarly to "molecular radiators", initiating the cleavage of the polysaccharide chain and selective formation of glucose. Currently, studies are underway to further improve these yields with the aim of equaling or surpassing the presently highest reported glucose yield (~30%), which is based on the use of a strong acid catalyst.[30] In this respect we are aiming at increasing the yield/selectivity through recycling operations and possible continuous processing. This would make microwave-assisted hydrolysis of cellulose a strong contender for industrial transformation of biomass into sugars.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details of conventional and microwave experiments, setups, *T*-, *P*-, and power profiles; ESI, GC, ^{13}C NMR spectra and CHN analysis of cellulose hydrolysis products after microwave treatment; and FTIR spectra of cellulose at different temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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