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Efficient mechano-catalytic depolymerization of crystalline cellulose by formation of branched glucan chains

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Selective hydrolysis of cellulose into glucose is a critical step for producing value-added chemicals and materials from lignocellulosic biomass. In this study, we found that co-impregnation of crystalline cellulose with sulfuric acid and glucose can greatly reduce the time needed for ball milling compared with adding acid alone. The enhanced reaction time coincides with the rapid formation of branched α(1→6) glycosidic bonds, which have been shown to increase water solubility of β(1→4) glucan oligomers. Co-impregnation of glucose was crucial for the rapid formation of the α(1→6) branches, after which a carbon-based catalyst can rapidly hydrolyze the water-soluble glucan oligomers to 91.2% glucose yield faster than conventional approaches.

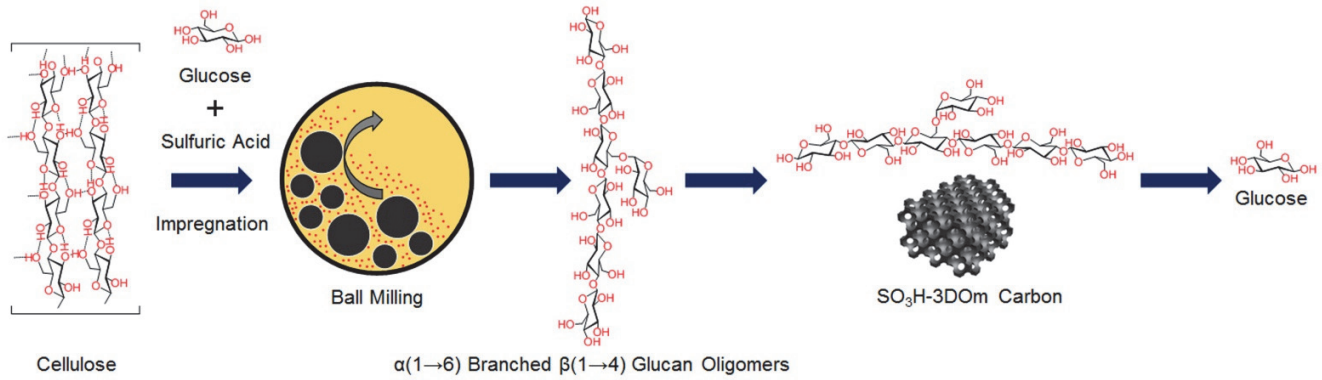
Selective hydrolysis of cellulose into glucose is considered one of the most important chemical reactions for the production of renewable biofuels and platform chemicals from lignocellulosic biomass.[1-6] Compared with the production of biofuels and platform chemicals by upgrading the complex mixture of compounds from bio-oil produced from pyrolysis, hydrolysis of cellulose into glucose can be coupled with several catalytic reactions to produce value added platform chemicals with high selectivity, which is critical for the efficient utilization of the renewable carbon feedstock.[7-9]

Despite the potential of cellulose as a sustainable feedstock, utilization via hydrolysis remains a processing challenge. The biopolymer exhibits low reactivity due to its highly hydrogen-bonded semi-crystalline structure, which not only contributes to its low solubility in conventional solvents, but also limits the interaction between the internal cellulose layers and catalysts. Cellulose is a linear, syndiotactic polymer of β-D-glucose.[7, 10] Anhydroglucose units (AGUs) are bonded by β(1 → 4) glycosidic linkages, and the degree of polymerization (DP) of cellulose and glucan oligomer chains is defined by the number of repeated AGUs. Cellulose has a highly interconnected hydrogen bonding network arising from interactions between hydroxyl groups of neighboring AGUs.[7, 11] Abundant hydrogen bonds lead to the recalcitrant nature of cellulose, requiring an activation energy for acid catalyzed hydrolysis of 125 to 170 kJ mol^{-1}.[7, 12] However, glucose is relatively reactive in the presence of Brønsted acids, having a similar activation energy for dehydration of about 130 kJ mol^{-1}.[13] The similarity in the reactivity of glucose and crystalline cellulose leads to a challenge in the acid catalyzed hydrolysis of cellulose with a high selectivity to glucose. Accordingly, high throughput methods of biomass conversion (*e.g.* pyrolysis) produce products with a high degree of heterogeneity in the resulting chemical compositions with almost no selectivity to glucose.[3, 14] Enzymatic hydrolysis can be performed selectively and requires a lower activation energy (3-50 kJ mol^{-1}).[12] However, the slow reaction rate, high operation cost and catalyst deactivation in the presence of lignin limit the application of the enzymatic process for the large-scale production of glucose from lignocellulosic biomass.[3, 15, 16]

Recently, a two-step strategy has been developed for the selective hydrolysis of crystalline cellulose to increase the efficiency of the acid catalyzed hydrolysis reaction. Namely, crystalline cellulose is first decrystallized into an amorphous phase to reduce the number of hydrogen bonds such that it is more easily hydrolyzed to glucose over acid catalysts. Ionic liquids (ILs) have shown distinct capability for decrystallization of crystalline cellulose; the resulting amorphous cellulose can then be converted into glucose with a high selectivity through enzymatic processes.[16, 17] However, recovery and manufacturing of these expensive ILs limit their practical applications and requires further research efforts.

Mechanical milling of cellulose is an alternative method to reduce cellulose crystallinity.[18, 19] Amorphous cellulose prepared by ball milling contains fewer hydrogen bonds compared with crystalline cellulose, which significantly lowers the hydrolysis reaction temperature.[20] Unfortunately the solubility of amorphous cellulose in water is still low due to a high degree of polymerization, which limits the efficiency of both homogeneous and heterogeneous acid catalysts.

Recently, impregnation of cellulose with catalytic amounts of a strong acid *(e.g.*, H_2SO_4, HCl) has shown effective for decrystallization and depolymerization of crystalline cellulose to produce water-soluble glucan oligomers.[21-23] Surprisingly, the glucan oligomers with DP = 6-9 produced by this method exhibit excellent solubility of up to 34 wt.% in water at room temperature,[22] which is much higher than linear β-glucan oligomers composed of only β(1→4) glycosidic linkages. For example, linear β-glucan oligomers with DP = 5-6 are only 1 wt.% soluble in water.[24, 25] High solubility of oligomers produced from ball milling of acidulated cellulose has been ascribed to the acid-catalyzed formation of new glycosidic linkages during the milling process. Käldström concluded that acid and not free radicals play an important role in the synthesis of these glucan oligomers as the reaction will not proceed under acid-free conditions.[23] Shrotri *et al.* further elucidated the mechanism and found that milling of cellulose with catalytic amount of strong acid forms α(1→6) glycosidically linked branches, which are not present in original cellulose structure.[22] It is believed that the formation of these branches results from the acid-catalyzed repolymerization of glucose monomers produced during the milling process. Although the role of the α(1→6) glycosidic linkages in the depolymerization mechanism is not fully understood, it is likely that branches with α(1→6) glycosidic linkages on large cellulose chains can inhibit the relamination of exfoliated cellulose chains by increasing the steric hindrance between adjacent layers, thus preventing the stacking and reformation of interchain hydrogen bonds. Once the branches begin to form, the sub-layers in the cellulose structure may be more accessible, and the



Scheme 1 Proposed two-step process to produce glucose from crystalline cellulose. Cellulose is first co-impregnated with glucose (or other low molecular weight saccharides) and sulfuric acid. The resulting acidulated cellulose is ball-milled to produce branched glucan oligomers, which are subsequently reacted over a sulfonated carbon catalyst to selectively produce glucose.

delamination and subsequent depolymerization of the entire cellulose particle could proceed. The rate of depolymerization during milling could therefore be limited by the rate of α(1→6) linkage formation and amount of available glucose.

Given that formation of branches with α(1→6) linkages is critical for the production of water-soluble glucan oligomers, we hypothesize that the addition of low molecular weight saccharides (LMSs) in the acidulated ball milling process can increase the rate of α(1→6) glycosidic linkage formation through acid catalyzed condensation between the C1-OH group of the LMSs and a C6-OH group on an AGU of the oligomer chain. Following this hypothesis, crystalline cellulose was co-impregnated with both LMSs and acid, and then ball-milled to study the effects of co-impregnation on the solubility of the produced glucan oligomers. The results indicate that the co-impregnation of glucose can largely improve the performance of the depolymerization process. In addition, we observed that using carbon-based acid catalysts can break down the water-soluble glucan oligomers more efficiently compared with homogenous acid due to an adsorption-enhanced reaction rate.

Acidulated ball-milled cellulose (ABMC) was formed by co-impregnation of microcrystalline cellulose (MCC) with an aqueous solution of LMSs and sulfuric acid followed by evaporation of water as shown in Scheme 1. Impregnation was performed for four different LMSs including glucose, maltose (glucose dimer with α(1→4) linkage) and the oligomers made by milling the acid-only impregnated cellulose for 4.0 h. The achieved samples were named *i*h-*j*-ABMC where *i*h represents the milling time (in hours), and *j* represents the LMS species that are co-impregnated. The samples prepared without LMS species were named *i*h-N-ABMC. MCC was impregnated with glucose to form *i*h-G-ABMC, maltose to form *i*h-M-ABMC, and oligomers from 4h-N-ABMC to form *i*h-O-ABMC. A control sample was also prepared by physically mixing glucose with microcrystalline cellulose impregnated only with acid named 0h-PM-ABMC. The impregnation procedure is further described in the supplementary information.

Typical HPLC chromatograms of 2h-G-ABMC is shown in Fig. S1. To identify the components in the solution, standards of linear β(1→4) glucan oligomers including cellohexaose, cellopentaose, cellotetraose, cellotriose and cellobiose as well as isomaltose (glucose dimer with α(1→6) linkage), were analyzed on the same column and also shown in Fig S1. The data suggests the β(1→4) glucan oligomers of different chain lengths can be distinctly separated using an Agilent Hi-Plex-Na HPLC column. However, the difference in retention time between oligomers with the same degree of polymerization such as for isomaltose (α(1→6) dimer) and cellobiose (β(1→6) dimer). Furthermore, it was found that the response factors from the refractive index (RI) detector on HPLC for all five linear β(1→4) glucan oligomers as well as for isomaltose are similar, varying less than 3%. The amount of glucan oligomers with DP ≤ 6 was thus calculated based on these measured response factors. Because oligomers with β(1→4) and α(1→6) linkages with the same length were difficult to separate, the product distribution was denoted as G2, G3, G4, *etc.*. The largest peak in the chromatogram of milled samples has a shorter retention time compared to the standard linear glucan oligomers with DP ≤ 6. The peak was assigned to all glucan oligomers with DP > 6. Given the similarity in response factor for all five of the glucan oligomers and isomaltose, an average response factor was used to calculate the amount of glucan oligomers with DP > 6. The total glucan oligomers determined by the HPLC measurement was used to calculate the soluble portion of the ball-milled samples. To further confirm this calculation, 2h-G-ABMC was dispersed in deionized water, and the insoluble and large particles were removed by filtration with a 0.20 μm membrane filter. The amount of total soluble glucan oligomers measured by this method after evaporation was found to be 92.3 ± 4.3 wt.%, compared to 92.7 wt.% as measured by HPLC.

The total amount of soluble glucan oligomers in each *i*h-*j*-ABMC sample prepared by milling for 1.0 and 2.0 h are shown in Fig. 1. The percentage of individual glucan oligomers with the chain lengths DP ≤ 6 as well as total soluble glucan oligomers detected by HPLC are shown in Table 1. It was found that co-impregnation with glucose greatly decreases the time needed for milling. 71.2 wt% of the 1h-G-ABMC sample was soluble in water, which was similar to the soluble portion of 4h-N-ABMC (64.5 wt.%). Increasing the milling time to 2.0 h yielded 2h-G-ABMC with an even higher soluble portion of 92.7 wt.%. Interestingly, the distribution of glucan oligomers achieved from the co-impregnation of glucose was different from those made without adding glucose. Namely, for the samples with similar soluble portions, 1h-G-ABMC contains 47.5 wt.% of glucan oligomers with DP > 6 while 4h-N-ABMC only contains 29.8 wt.% of glucan oligomers with DP > 6. Levoglucosan (LGA) was also detected in amounts ranging from 0.0 to 6.5 wt.%. Detailed information about LGA determination (characterization section and Fig. S1-S3) is included in supplementary information. In addition to glucan oligomers and LGA, 5-hydroxymethylfurfural (HMF), formic acid and levulinic acid were also observed in the soluble portion. Trace amounts of HMF (0.13-0.20 wt.%),

Table 1 Yields of glucose and glucan oligomers in the soluble component of different acidulated ball-milled cellulose measured by HPLC

j-ABMC	Time (h)	LGA (wt.%)	G1 (wt.%)	G2 (wt.%)	G3 (wt.%)	G4 (wt.%)	G5 (wt.%)	G6 (wt.%)	G(DP > 6) (wt.%)	Total (wt.%)
N-ABMC[1]	0	0.2	0.3	0.1	0.1	0.1	0.1	0.1	3.6	4.7
	1	0.5	1.6	1.2	1.3	1.5	1.4	1.1	9.5	18.1
	2	0.8	2.7	2.2	2.4	2.6	2.4	2.0	16.0	31.3
	3	1.4	4.3	3.5	3.4	3.5	3.3	2.8	23.1	45.3
	4	3.6	6.4	5.9	5.4	5.2	4.4	3.8	29.8	64.5
	5	4.7	9.4	7.5	6.2	5.4	5.2	4.5	41.0	84.0
	6	6.5	12.1	9.4	7.6	6.3	4.8	4.9	40.4	92.0
G-ABMC[2]	0	0.1	1.0	1.4	2.0	0.7	3.0	0.3	8.4	10.7
	1	1.5	3.9	4.0	3.8	3.7	3.5	3.3	47.5	71.2
	2	2.9	6.3	5.7	5.2	4.9	4.7	4.5	58.5	92.7
	3	3.3	3.9	7.1	6.2	5.5	4.9	4.8	55.7	91.5
M-ABMC[3]	0	0.1	1.3	2.3	1.1	1.0	0.7	0.5	5.3	12.4
	1	1.1	3.3	3.8	3.1	3.0	2.8	2.5	28.8	48.4
	2	2.3	5.7	5.5	4.8	4.6	4.3	3.9	46.6	77.7
O-ABMC[4]	0	0.1	1.4	0.9	0.6	0.6	0.5	0.5	5.5	10.0
	1	0.3	1.9	1.3	1.3	1.3	1.2	1.0	8.3	16.5
	2	0.6	1.7	2.0	1.9	1.9	1.9	1.5	11.9	23.2
PM-ABMC[5]	3	1.4	9.2	3.0	2.2	2.3	2.3	2.0	15.6	37.9
	4	2.5	9.6	4.5	3.4	3.3	3.2	2.7	22.3	51.4
	5	3.6	10.0	6.0	4.7	4.3	4.0	3.7	32.0	68.1
	6	4.3	10.7	7.2	5.3	5.0	4.5	4.1	38.8	79.8

[1]Only acid was impregnated.
[2]Glucose and acid were co-impregnated.
[3]Maltsoe and acid were co-impregnated.
[4]4h-N-ABMC and acid were co-impregnated.
[5]Acid only impregnated cellulose and physically mixed with glucose.

levulinic acid (0.15-0.31 wt.%) and formic acid (0.06 to 0.12 wt.%) were found in most samples milled for longer than 2.0 h. These trace furans and organic acids are not believed to the significantly contribute catalytically in neither the milling nor the aqueous phase reactions.

To understand the structure of water-soluble glucan oligomers formed by the milling process, ^{1}H-NMR spectra were collected for the *i*h-*j*-ABMC samples and the relative abundance of each anomeric hydrogen is shown in Table 2. Representative ^{1}H-NMR spectra normalized using an internal standard are shown in Fig. 2 for 2h-G-ABMC and 2h-N-ABMC. Peaks from anomeric hydrogens appear in the 5.2 to 4.3 ppm δ range.[22] The peak position of the hydrogens on the α and β reducing ends (α-RE and β-RE, respectively), α(1→6), and β(1→4) anomeric hydrogens have been reported in literature[22] as indicated in Fig. 2. Abundance was calculated by a comparison of the integrated individual peak areas (A_{Hi}) in the ^{1}H-NMR spectra:

$$Abundance = \frac{A_{Hi}}{\sum A_{Hi}} \times 100\%$$

As shown in Table 2, both α and β reducing end as well as α(1→6) hydrogen peaks increase with increasing milling time, indicating a decrease in chain length and an increase in branching, both of which likely contributed to a higher solubility. It is clear that *i*h-G-ABMC samples have many more α(1→6) bonds than *i*h-N-ABMC. Namely, 9.7 % of AGUs contain α(1→6) bonds for 1h-G-ABMC, while only 2.2 % and 7.3 % of AGUs contain α(1→6) bonds for 2h-N-ABMC and 4h-N-ABMC, respectively. The increased breakdown rate has significant implications for the economic feasibility for mechanical pretreatment of cellulose as demonstrated by the economic analysis of Hick *et al.*.[26]

Several control experiments were performed to understand the effects of co-impregnation. Instead of impregnation with glucose and acid together, microcrystalline cellulose was first impregnated with H_2SO_4 and water, and dried at 50 °C to form 0h-N-ABMC. Thereafter, 1.75 g of 0h-N-ABMC was physically mixed with 0.25 g of glucose to form 0h-PM-ABMC. After 3.0 h of milling, 37.9 wt.% of the 3h-PM-ABMC sample was soluble compared with 91.5 wt.% for 3h-G-ABMC, indicating that co-impregnation with both glucose and acid is crucial for enhancing the efficiency of the milling process. One explanation for the improvement may be that co-impregnation enhances the transport of glucose and provides feasible interaction for branching to rapidly occur. In addition, it was found that impregnated glucose started reacting with cellulose during the impregnation process. The amount of water-soluble glucan oligomers in the glucose co-impregnated cellulose sample (0h-G-ABMC) detected after 15 minutes of sonication and 3.0 min of vortexing was 10.7 wt.% (Table 1). However, only 1.0 wt.% of free glucose were detected in the soluble portion, which is much less than the amount of glucose (12.5 wt.%) added in the beginning of the impregnation process. The ^{1}H-NMR spectra of the soluble portion revealed that 7.0% of AGUs contain α(1→6) bonds, while the soluble portion of the 0h-N-ABMC sample does not show any amount of α(1→6) linkages as shown in Table 2. These results clearly indicate that glucose can react with cellulose under acidic and static condition even without the milling.

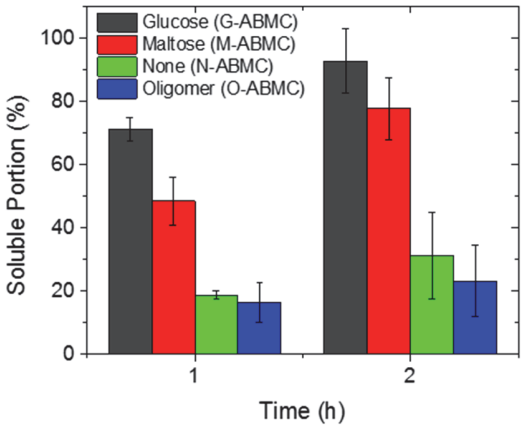


Fig. 1 Soluble portion percentage from acidulated ball-milled cellulose samples after 1.0 and 2.0 h of milling determined by HPLC. Error bars present a 95% confidence interval of the average soluble portion.

We further investigated the potential of co-impregnation of cellulose with glucan oligomers to enhance the efficiency of the milling process. Co-impregnation with maltose forms 0h-M-ABMC. Co-impregnation of cellulose with 4h-N-ABMC containing both α(1→6) linkage and β(1→4) linkage formed 0h-O-ABMC. The total amount of water-soluble glucan oligomers measured after milling the two samples for 1.0 and 2.0 h are shown in Fig. 1. The soluble portion of 1h-M-ABMC and 2h-M-ABMC was 44 wt.% and 77 wt.%, respectively. The solubility at identical milling times for maltose impregnated samples was less than that of the samples made by co-impregnating with glucose, but was higher than that of the samples prepared with acid only. The slower increase in soluble portion from co-impregnation with maltose may result from the requirement that maltose first hydrolyze into glucose. This hypothesis is supported by the slower rate of increase in α(1→6) linkage as shown in Table 2, which is likely directly related to available glucose in the samples. The depolymerization rate was even lower when larger oligomers were impregnated (Fig .1).

In order to selectively hydrolyze the produced water-soluble glucan oligomers into glucose, three dimensionally ordered mesoporous imprinted carbon (3DOm carbon) with SO_3H catalyst groups on the surface were used (SO_3H-3DOm carbon). Nitrogen physisorption and small angle X-ray scattering (SAXS) patterns for both parent 3DOm carbon and SO_3H-3DOm carbon are shown in Fig. S4 and S5, and the textural properties of the two samples are shown in Table S1. The BET surface areas for the parent and SO_3H-3DOm carbons are 1445 and 1191 $m^2\ g^{-1}$, respectively. The number of acid sites on the SO_3H-3DOm carbon was found to be 0.57 mmol g^{-1}. Adsorption of glucose and the water-soluble glucan oligomers from 2h-G-ABMC was performed on SO_3H-3DOm carbon. Adsorption isotherms plotted against the Langmuir fitting are shown in Fig. 3 with the adsorption capacity (Q_m), Langmuir Constant (K_L) and R^2 of the fitting shown in Table 3. Adsorption of water-soluble glucan oligomers was much stronger than glucose on the SO_3H-3DOm carbon; the adsorption capacity for the water-soluble glucan oligomers was 546 mg g^{-1}, while the capacity for glucose was only 118 mg g^{-1}. The Langmuir constant, K_L, was 3.41 L g^{-1} for the water soluble glucan oligomers, which was over 40 fold higher than the Langmuir constant for glucose of 0.082 L g^{-1}. This result was consistent with previous results which show that the adsorption affinity of glucan oligomers on the carbon surface increases with increasing the chain length[27, 28]. It is possible that adsorption of glucan oligomers onto the carbon surface is driven by van der Waals type interactions between the glucan oligomers and carbon surface, which may include

Table 2 Anomeric AGU abundance in different acidulated ball-milled cellulose samples calculated from ^{1}H-NMR

i-ABMC (Impregnation)	Time (h)	α-RE[1] (%)	α(1→6)[1] (%)	β-RE[1] (%)	β(1→4)[1] (%)	Soluble Portion[2] (wt.%)
N-ABMC[3]	0	8.1	0.0	15.2	76.7	4.7
	1	8.1	0.4	19.4	72.0	18.1
	2	8.9	2.2	17.0	72.0	31.3
	3	8.5	6.5	17.1	67.9	45.3
	4	8.0	7.3	17.4	67.3	64.5
	5	10.2	6.8	23.3	59.6	84.0
	6	12.7	6.5	25.2	55.5	92.0
G-ABMC[4]	0	19.7	7.0	40.3	33.1	10.7
	1	7.0	9.7	13.6	69.7	71.2
	2	8.5	9.0	19.5	63.0	92.7
	3	10.0	9.6	20.7	59.7	91.5
M-ABMC[5]	1	9.2	6.6	20.8	63.4	48.4
	2	8.7	7.6	20.0	63.7	77.7
PM-ABMC[6]	3	15.2	3.4	34.7	46.7	37.9
	4	12.5	5.6	28.8	53.1	51.4
	5	11.1	5.7	22.6	60.5	68.1
	6	10.4	6.6	23.7	59.2	79.8

[1]Abundance of AGU anomers in the soluble portion of ball-milled cellulose samples, measured by ^{1}H-NMR.
[2]Percentage of total material, measured by HPLC.
[3]Only acid was impregnated.
[4]Glucose and acid were co-impregnated.
[5]Maltsoe and acid were co-impregnated.
[6]Acid only impregnated cellulose and physically mixed with glucose.

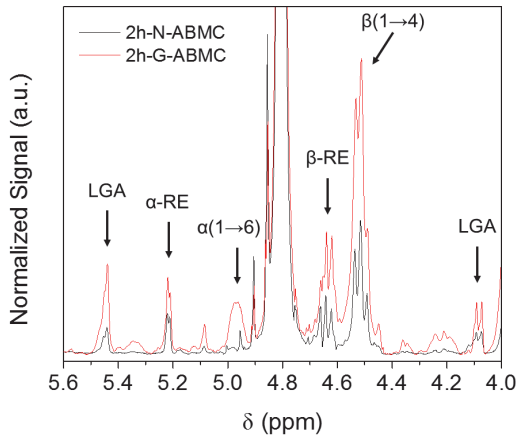


Fig. 2 ^{1}H-NMR spectra of 2.0 h ball-milled cellulose co-impregnated with glucose (2h-G-ABMC) and 2.0 h ball-milled cellulose impregnated only with acid (2h-N-ABMC).

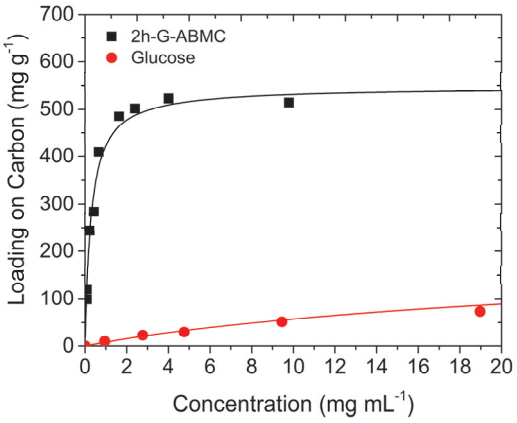


Fig. 3 Adsorption isotherms for glucose and water-soluble glucan oligomers from 2.0 h ball-milled cellulose co-impregnated with glucose (2h-G-ABMC) on SO_3H-3DOm carbon at room temperature. Data points are from experiments. Line is a fitted Langmuir model.

Table 3 Langmuir isotherm constants of saccharides adsorption on SO_3H-3DOm-carbon at room temperature

Component	Q_m mg g^{-1}	K_L L g^{-1}	R^2
Glucose	118	0.082	0.9242
2h-G-ABMC	546	3.42	0.9423

previously demonstrated CH-π interactions between carbohydrates and aromatic functional groups[29]. It has also been explained by entropy favored adsorption due to the release of water molecules by adsorption of glucan oligomers on the carbon surface through a hydrophobic interaction[27]. Such interactions may benefit from an increasing number of repeat units within the glucan oligomers, which can increase the number of CH-π interactions.

Glucose yield and acid site turn over frequency (TOF) for the hydrolysis of 2h-G-ABMC over SO_3H-3DOm carbon sample are shown in Fig. 4A. The TOF of SO_3H-3DOm carbon, measured at 120 °C after 2.0 h with less than 20% conversion, was nearly 6 fold higher than the one of HCl (1.48 and 0.25 (mol glucose)(mol H$^+$)$^{-1}$ h^{-1}, respectively), which we propose is due to the synergy between strong adsorption of glucan oligomers and the sulfonic acid sites on the carbon catalyst. 2h-G-ABMC, non-milled acidulated cellulose (0h-N-AMCC) and non-milled microcrystalline cellulose (0h-MCC) were hydrolyzed using SO_3H-3DOm carbon at 165 °C. A glucose yield of 91.2% was achieved in 1.0 h when 2h-G-ABMC was used over SO_3H-3DOm carbon, while only 7.0 and 1.7% glucose yield for the 0h-N-ABMC and 0h-MCC were achieved, respectively (Fig. 4B). The results indicate that combining the co-impregnation approach with carbon-based acid catalyst is a highly efficient process to selectively depolymerize crystalline cellulose to glucose. The glucose yield after one, two and three runs using the same carbon catalyst was found to be 91.2, 87.2 and 84.5%, demonstrating good hydrothermal stability and reusability of the carbon catalyst (Fig. S6). The average carbon balance was 92.8%, which is likely due to the adsorption of unreacted glucan oligomers on the 3DOm carbon surface.

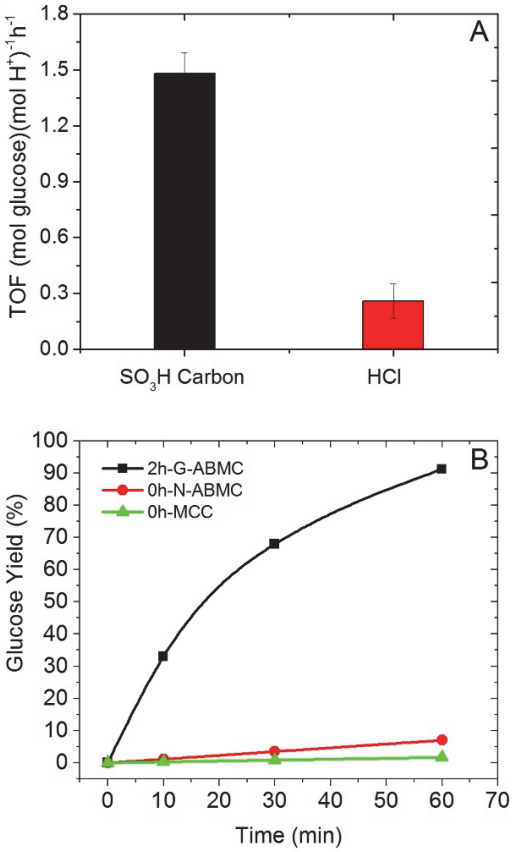


Fig. 4 A) Turnover frequency (TOF) of SO_3H-3DOm carbon and HCl for 2.0 h ball-milled cellulose co-impregnated with glucose (2h-G-ABMC) at 120 °C in water (reaction time: 2.0 h, conversion: < 20%), and B) Glucose yield from 2h-G-ABMC, non-milled acidulated cellulose (0h-N-ABMC) and microcrystalline cellulose (0h-MCC) over SO_3H-3DOm carbon at 165 °C.

Conclusion

We found that co-impregnation of crystalline cellulose with sulfuric acid and glucose greatly improves the efficiency of ball milling to selectively produce glucose. By co-impregnating with glucose, cellulose fibers that were exfoliated by the sheer force of ball milling can react with glucose to form α(1→6) branches, which prevent re-lamination of the glucan chains, thus allowing for a rapid production of water-soluble glucan oligomers. Co-impregnation with maltose shows improvement as well, but the decrease in milling time was not as substantial as when glucose was used. In addition, carbon-based acid catalysts can rapidly hydrolyze the water-soluble glucan oligomers to glucose with high selectivity (91.2% yield) due to enhanced adsorption of glucan oligomers on the carbon surface.

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Notes and references

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† Electronic supplementary Information (ESI) available. See DOI:

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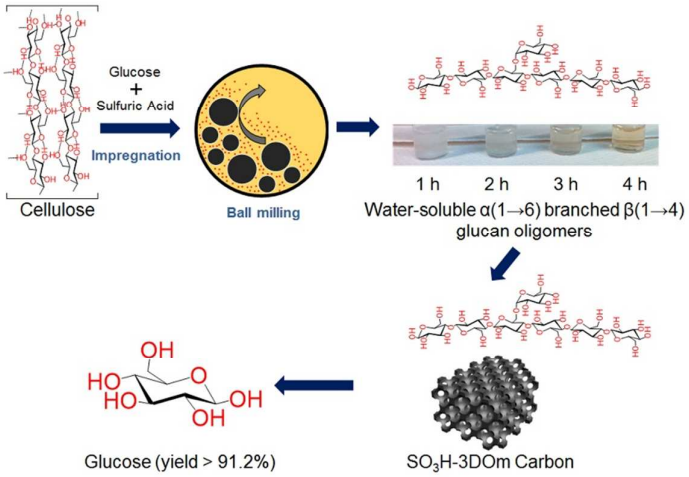

Formation of branched glucan chains by co-impregnation with glucose can greatly improve efficiency of mechano-catalytic depolymerization of crystalline cellulose