# Supplementary Material: Mechanochemistry-Assisted Hydrolysis of Softwood over Stable Sulfonated Carbon Catalysts in a Semi-Batch Process

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## 1. Physicochemical characterization of catalyst

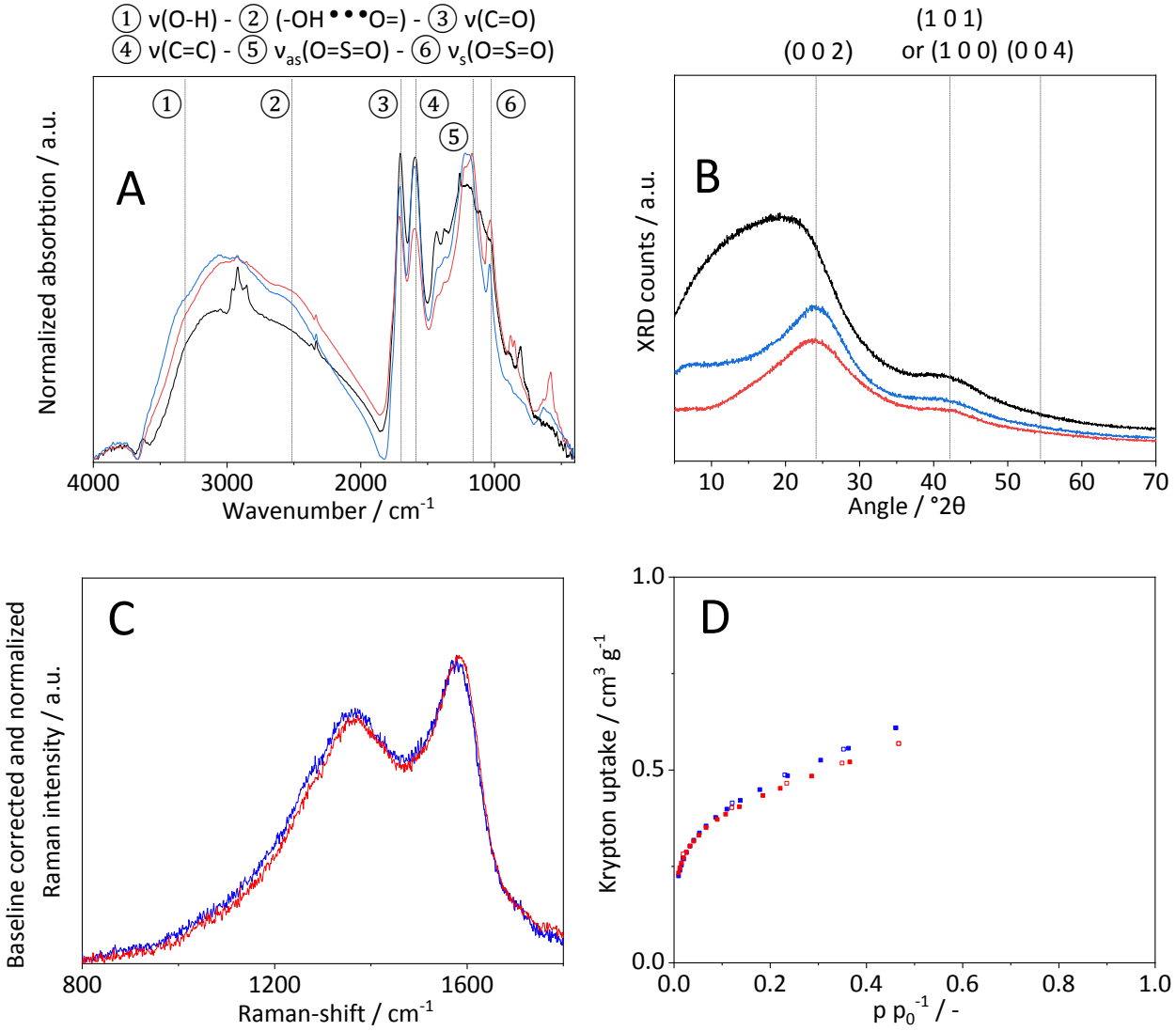


**Figure 1. (A)** FTIR spectra of carbonized (–), sulfonated (–) and hydrothermally treated (–) catalyst samples. **(B)** XRD patterns of carbonized (–), sulfonated (–) and hydrothermally treated (–) catalyst samples. **(C)** Raman spectra of sulfonated (–) and hydrothermally treated (–) catalyst samples. **(D)** Krypton adsorption/desorption isotherms of sulfonated (■/□) and hydrothermally treated (■/□) catalyst samples.

## 2. Physicochemical properties of catalyst

**Table 1.** Physicochemical properties of catalyst samples. [a] Determined using elemental analysis. [b] Calculated from the sulphur content. [c] Determined using Krypton physisorption. [d] Determined using laser diffraction. BM denotes ball-milled.

| Sample | C [%] [a] | H [%] [a] | O [%] [a] | -$SO_3H$ [µmol $g^{-1}$] [b] | BET Area [$m^2$ $g^{-1}$] [c] | Particle size [µm][d] |
|---|---|---|---|---|---|---|
| C-350 | 74.9±0.2 | 3.9±0.1 | 21.1±0.1 | 0 | n.A. | 56.4 |
| C-350-$SO_3H$ | 54.5±1.1 | 3.5±0.2 | 36.5±0.2 | 2068±57 | 2.1 | 52.8 |
| C-350-$SO_3H$-HT | 63.2±1.1 | 3.4±0.1 | 31.8±1.0 | 869±29 | 2.2 | 27.6 |
| C-350-$SO_3H$-HT-BM | 57.0 | 2.9 | 37.5 | 788 | n.A. | 12.5 |

## 3. Yields, temperature profile and flow-rate during hydrolysis of cellulose over C-350-$SO_3H$-HT

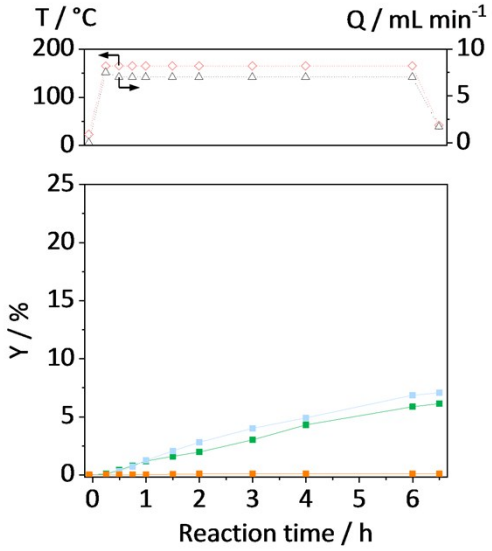


**Figure 2:** Yields of oligosaccharides (■), monosaccharides (■) and dehydration products (■) achieved with pristine cellulose in presence of C-350-$SO_3H$-HT. Reaction conditions: 165 °C, 6.5 h, 3 wt% cellulose, S/C = 7/2, 1 mM EDTA & 15-C-5, $\tau$ = 35 min., impeller speed = 600 rpm.

## 4. Influence of the impeller speed on the conversion of cellulose in presence of C-350-$SO_3$H-HT

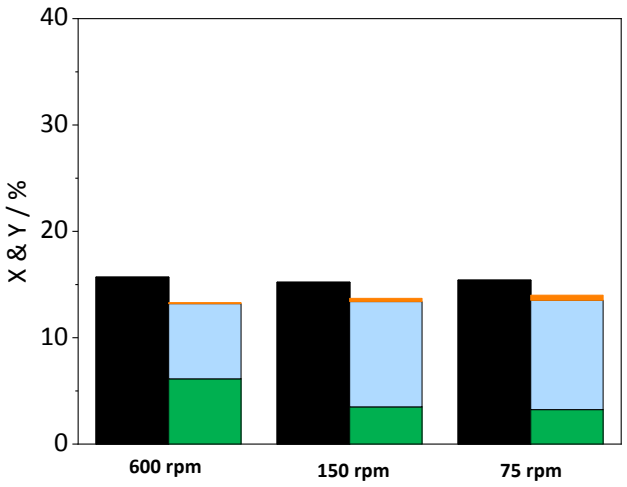


**Figure 3:** Conversion (■) and yields of oligosaccharides (■), monosaccharides (■) and dehydration products (■) achieved during the hydrolysis of cellulose in presence of EDTA and 350-$SO_3$H-HT at different impeller speeds. Reaction conditions: 165°C, 6.5 h, 3 wt% cellulose, S/C = 7/2, 1 mM EDTA & 15-C-5, $\tau$ = 35 minutes.

## 5. Full width at half maximum (FWHM) of deconvoluted diffraction peaks

**Table 2.** FWHM of the deconvoluted diffraction peaks determined for the crystal planes in cellulose.

| Sample | FWHM (1 0 1) / ° | FWHM (1 0 $\bar{1}$) / ° | FWHM (0 2 1) / ° | FWHM (0 0 2) / ° | FWHM (0 0 4) / ° |
|---|---|---|---|---|---|
| Cellulose | 2.43 | 2.04 | 1.42 | 1.46 | 1.88 |
| BM-1 h | 2.28 | 2.04 | 2.74 | 1.47 | 1.73 |
| BM-4 h | 2.68 | 3.42 | 3.14 | 1.41 | 1.70 |
| BM-8 h | 2.87 | 4.36 | 4.40 | 1.39 | 1.72 |
| BM-18 h | 3.54 | 4.98 | 4.20 | 1.27 | 1.74 |
| BM-54 h | 3.52 | 6.59 | 4.85 | 1.23 | 2.46 |

## 6. Properties of pre-treated cellulose samples

**Table 3.** Properties, conversion and reaction yields achieved with pre-treated cellulose in presence of C-350-$SO_3H$-HT. Reaction conditions: 165 °C, 6.5 h, 3 wt% pre-treated cellulose, S/C = 7/2, 1 mM EDTA & 15-C-5, $\tau$ = 35 min., impeller speed = 600 rpm. * O: Oligosaccharides, M: Monosaccharides and D: Dehydration products. BM denotes ball-milled.

| Sample | Conversion / % | Yield: O-M-D*/ % | Particle size ($d_{50,V}$) / µm | Crystallite size /nm | CI / % | Solubility – yield / % |
|---|---|---|---|---|---|---|
| Cellulose | 15.2 | 6.1/7.1/0.1 | 50.8 | 4.8 | 65.3 | 0.05 ± 0.01 |
| BM-1 h | 16.6 | 2.5/9.7/0.4 | 22.4 | 4.3 | 64.7 | 0.19 ± 0.01 |
| BM-4 h | 17.3 | 4.8/11.3/0.4 | 20.5 | 3.9 | 59.2 | 0.27 ± 0.01 |
| BM-8 h | 22.5 | 6.1/13.6/0.7 | 21.8 | 3.6 | 59.1 | 0.32 ± 0.02 |
| BM-18 h | 27.2 | 7.8/15.9/0.8 | 24.6 | 3.5 | 57.4 | 0.41 ± 0.01 |
| BM-54 h | 32.9 | 9.2/19.5/0.9 | 22.4 | 3.5 | 56.5 | 0.79 ± 0.02 |
| BM-18 h + 5% $H_2O$ | 34.0 | 12.0/19.4/0.9 | 43.4 | 3.4 | 52.0 | 0.53 ± 0.01 |
| Amorphous cellulose | 27.1 | 14.8/10.4/0.6 | 93.3 | 2.2 | 20.1 | 0.95 ± 0.36 |

## 7. Crystallinity index, particle size and SEM images of ball-milled cellulose

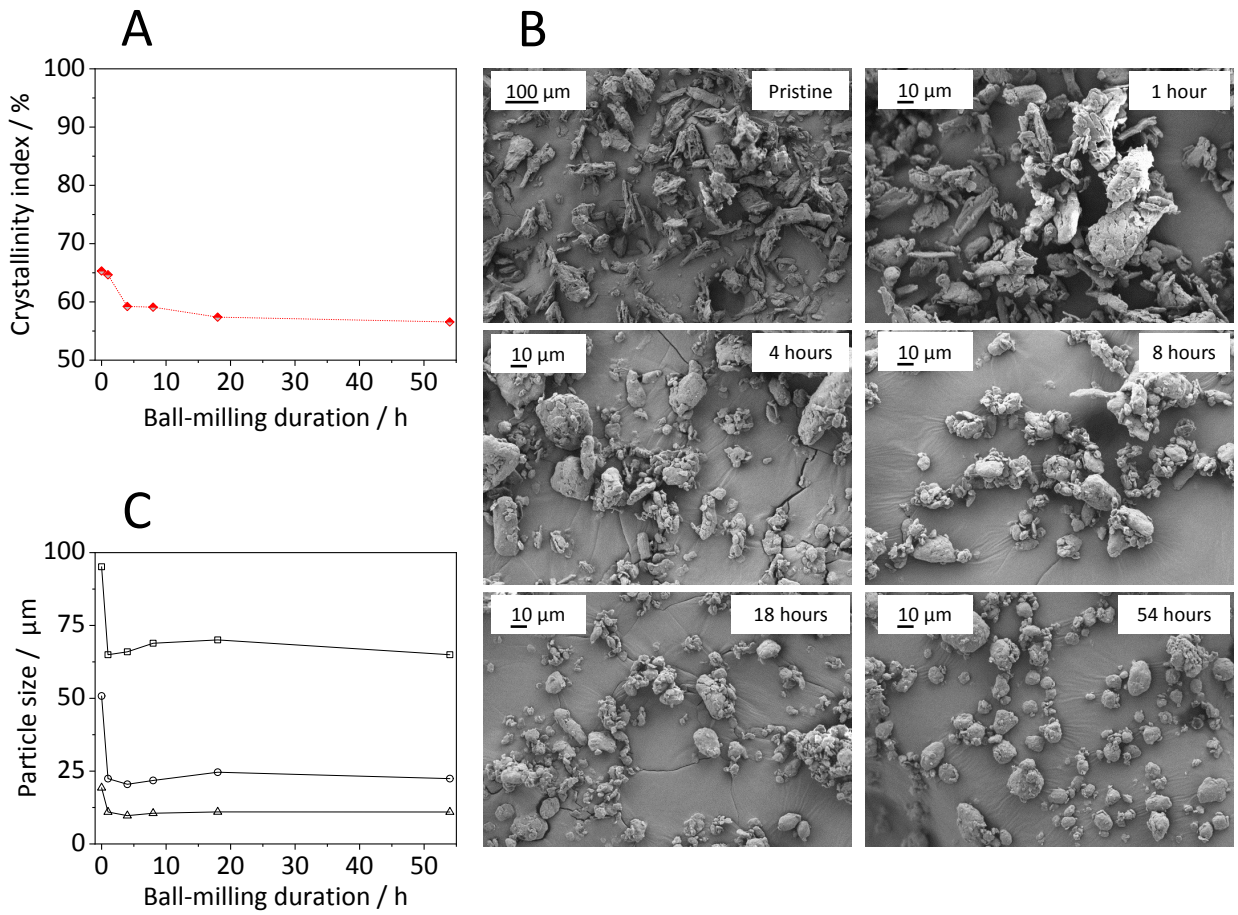


**Figure 4. (A)** Crystallinity index (◆), **(B)** SEM images and **(C)** particle size distribution ($d_{10,V}$: △ – $d_{50,V}$: ○– $d_{90,V}$: □) of ball-milled cellulose.

## 8. Crystallinity index, particle size and SEM images of wet ball-milled cellulose

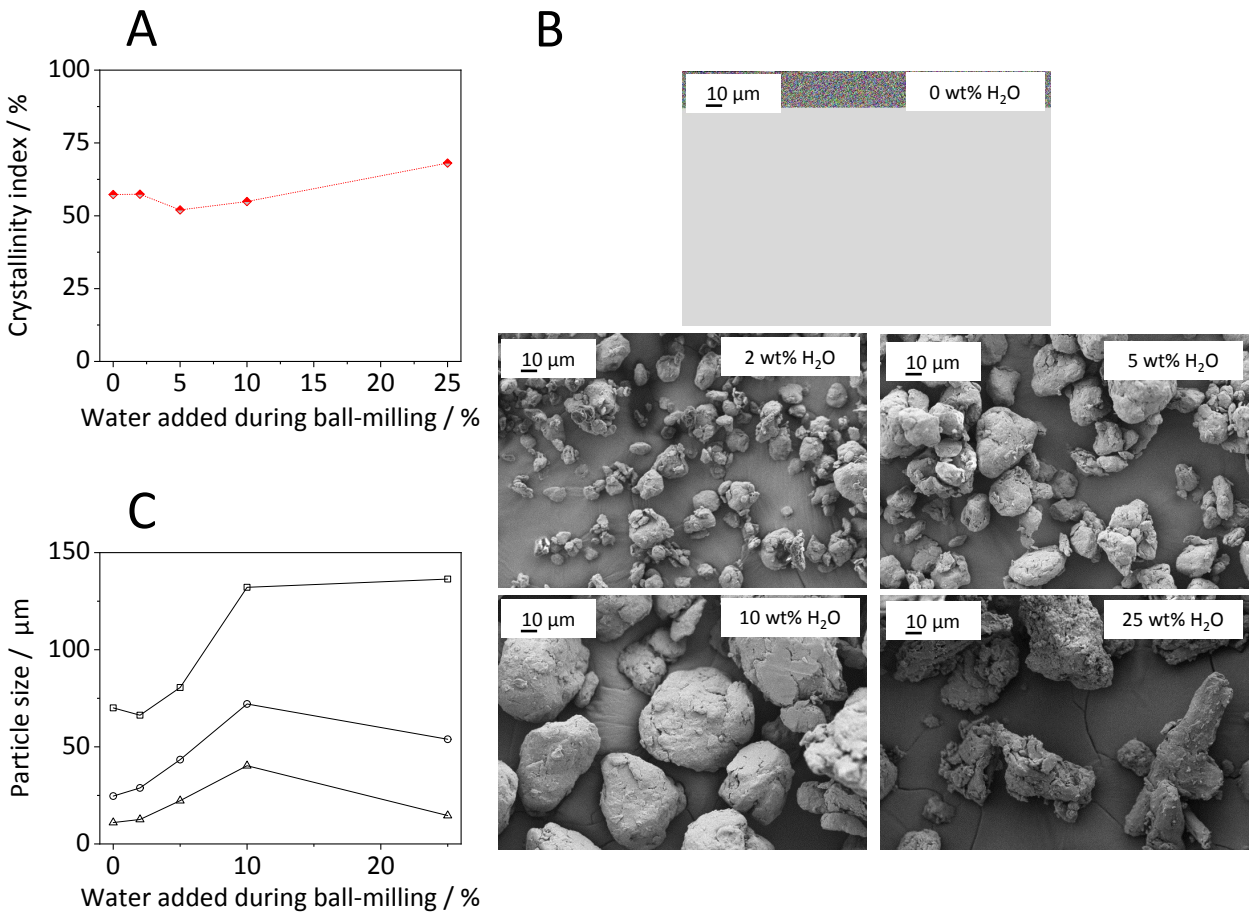


**Figure 5. (A)** Crystallinity index (◆), **(B)** SEM images and **(C)** particle size distribution ($d_{10,v}$: △ – $d_{50,v}$: ○– $d_{90,v}$: □) of cellulose ball-milled in presence of $H_2O$.

## 9. Yields during hydrolysis of wet ball-milled cellulose in presence of C-350-$SO_3$H-HT

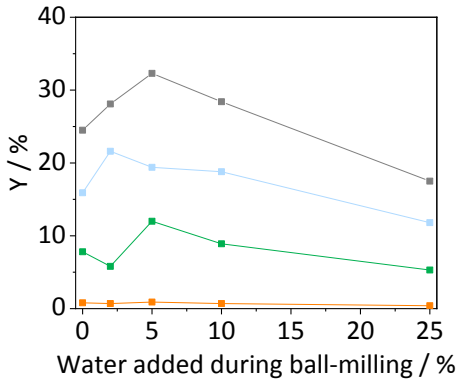


**Figure 6.** Yields of oligosaccharides (■), monosaccharides (■), dehydration products (■) and total yield (■) achieved with wet ball-milled cellulose in presence of C-350-$SO_3$H-HT. Reaction conditions: 165 °C, 6.5 h, 3 wt% wet ball-milled cellulose, S/C = 7/2, 1 mM EDTA & 15-C-5, $\tau$ = 35 min., impeller speed = 600 rpm.

## 10. FTIR Spectra of pre-treated cellulose samples

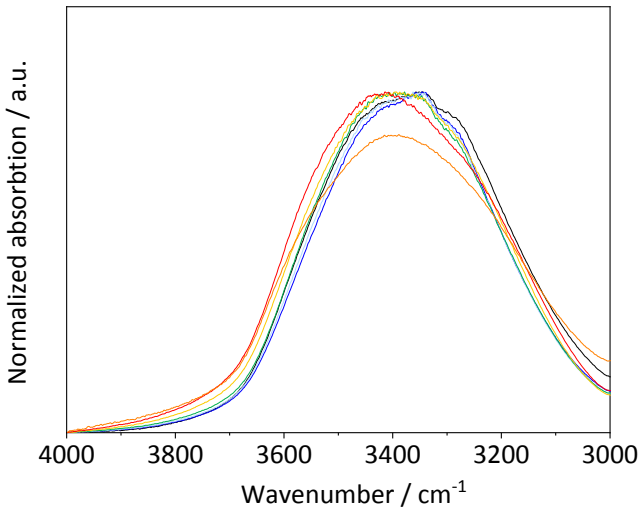


**Figure 7.** FTIR spectra of pristine (–), BM-1 h (–), BM-4 h (–), BM-8 h (–), BM-18 h (–), BM-54 h (–), BM-18 h + 5% $H_2O$ (–) and amorphous cellulose (–) in the 4000-3000 $cm^{-1}$ wavenumber region.

## 11. Ion-chromatograms of soluble species in pristine and pre-treated cellulose

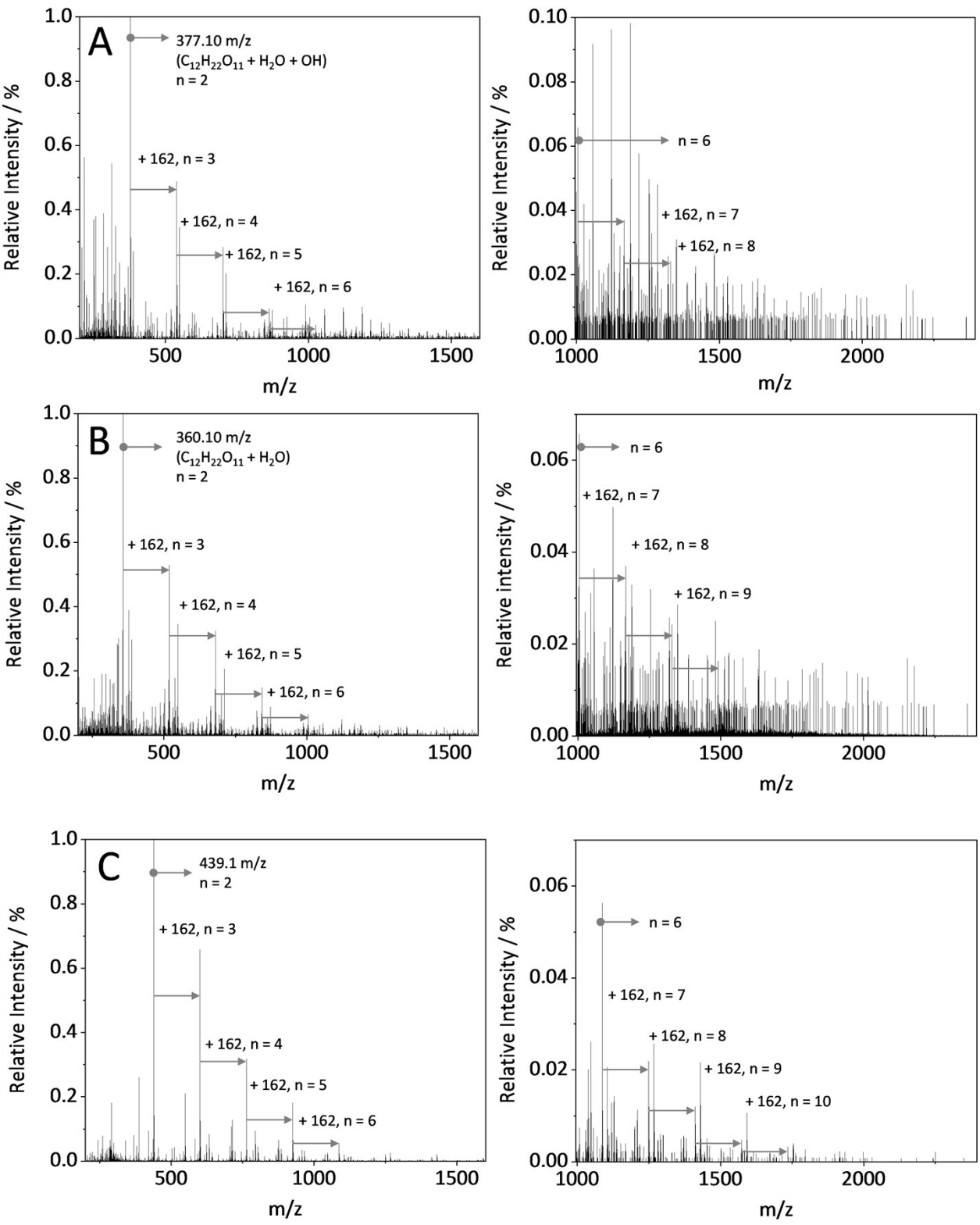


**Figure 8.** ESI-MS total ion-chromatograms of soluble species in **(A)** Cellulose, **(B)** BM-54 h and **(C)** CBM-10/1.

## 12. XRD patterns of cellulose residues recovered after pathway experiments

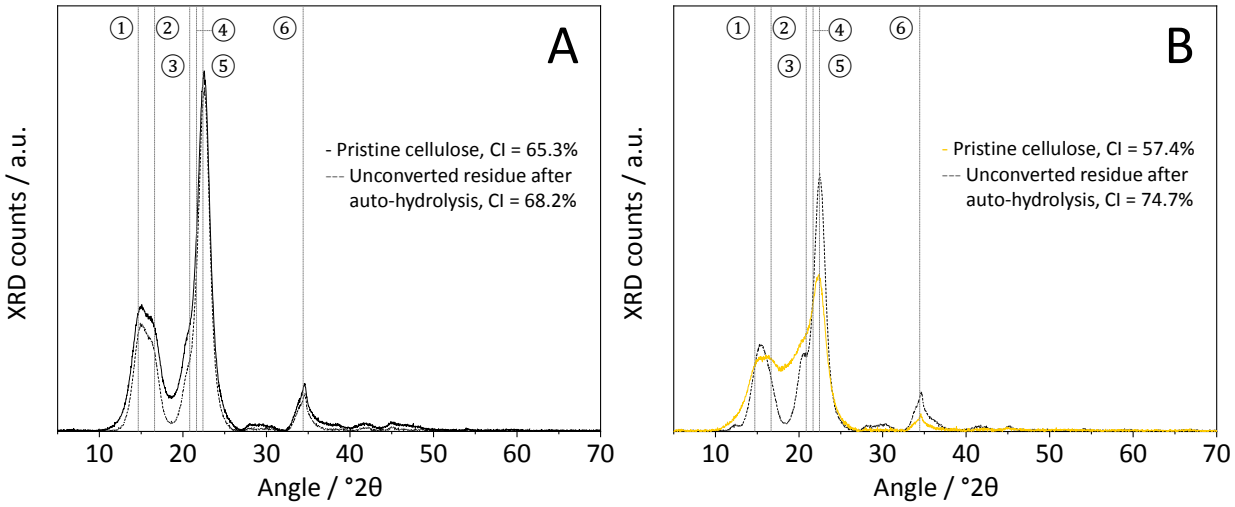


**Figure 9. (A)** Powder X-ray diffraction patterns of pristine cellulose (–) and the residue recovered after the auto-hydrolysis experiment (---). **(B)** Powder X-ray diffraction patterns of cellulose ball-milled for 18 hours (–) and the residue recovered after the auto-hydrolysis experiment (---).① - (1 0 1), ② - (1 0 $\bar{1}$), ③ - (0 2 1), ④ - para-crystalline, ⑤ - (0 0 2), and ⑥ - (0 0 4).

## 13. Measured and calculated XRD pattern of a physical mixture of ball-milled cellulose and ball-milled C-350-$SO_3$H-HT

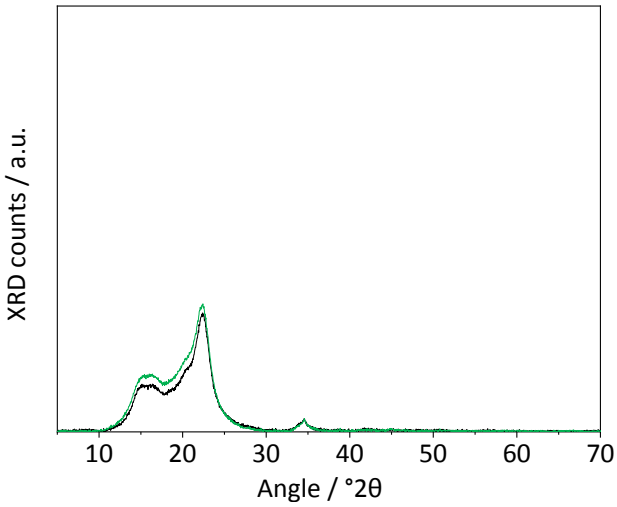


**Figure 10.** XRD diffraction patterns of a physical mixture (S/C = 7/2) of individually ball-milled cellulose and ball-milled C-350-$SO_3$H-HT (–) and the calculated diffraction pattern of a mixture (S/C = 7/2) of ball-milled cellulose and ball-milled C-350-$SO_3$H-HT determined by linear combination (–).

## 14. Liquid phase adsorption of cellobiose onto C-350-$SO_3H$-HT

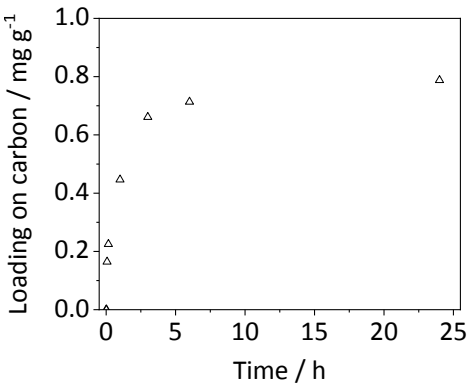


**Figure 11.** Cellobiose adsorption onto C-350-$SO_3H$-HT. Conditions: 25 °C, 100 mg C-350-$SO_3H$-HT per 1 mL of 20 mM cellobiose solution.

## 15. Particle size distribution of the sample CBM -7/2

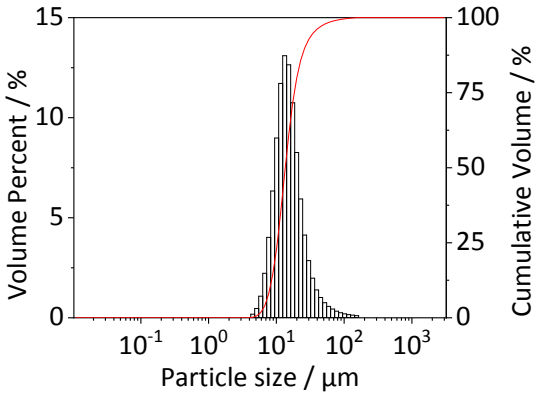


**Figure 12.** Particle size distribution of the sample CBM-7/2 measured with laser diffraction.

## 16. Properties of CBM treated cellulose

**Table 4.** Properties, conversion and reaction yields achieved with CBM treated cellulose. Reaction conditions: 165 °C, 6.5 h, 3 wt% CBM cellulose, 1 mM EDTA & 15-C-5, $\tau$ = 35 min., impeller speed = 600 rpm. *O: Oligosaccharides, M: Monosaccharides and D: Dehydration products. CBM denotes concerted ball-milling.

| Sample | Conversion / % | Product yield: O-M-D*/ % | Particle size ($d_{50,V}$) / µm | CI / % | Solubility – yield / % |
|---|---|---|---|---|---|
| CBM-10/1 | 21.3 | 9.4/9/0.6 | 19.1 | 36.2 | 3.9 |
| CBM-7/2 | 55.3 | 17.4/35.3/1.2 | 13.5 | 31.6 | 32.4 |
| CBM-2/1 | 77.8 | 22.8/44.8/1.5 | 14.9 | 28.9 | 49.2 |
| CBM-1/1 | 78.2 | 17.4/50.0/1.4 | 15.0 | 24.8 | 64.1 |
| CBM-7/2 - No sulf. | 26.9 | 12.8/12.3/0.3 | 7.6 | 35.9 | 0.7 ± 0.1 |
| CBM-7/2 - Deac. | 35.3 | 15.4/18.5/0.2 | 9.9 | 34.7 | 1.9 ± 0.4 |

## 17. SEM Images and FTIR spectra of fresh and recycled catalyst

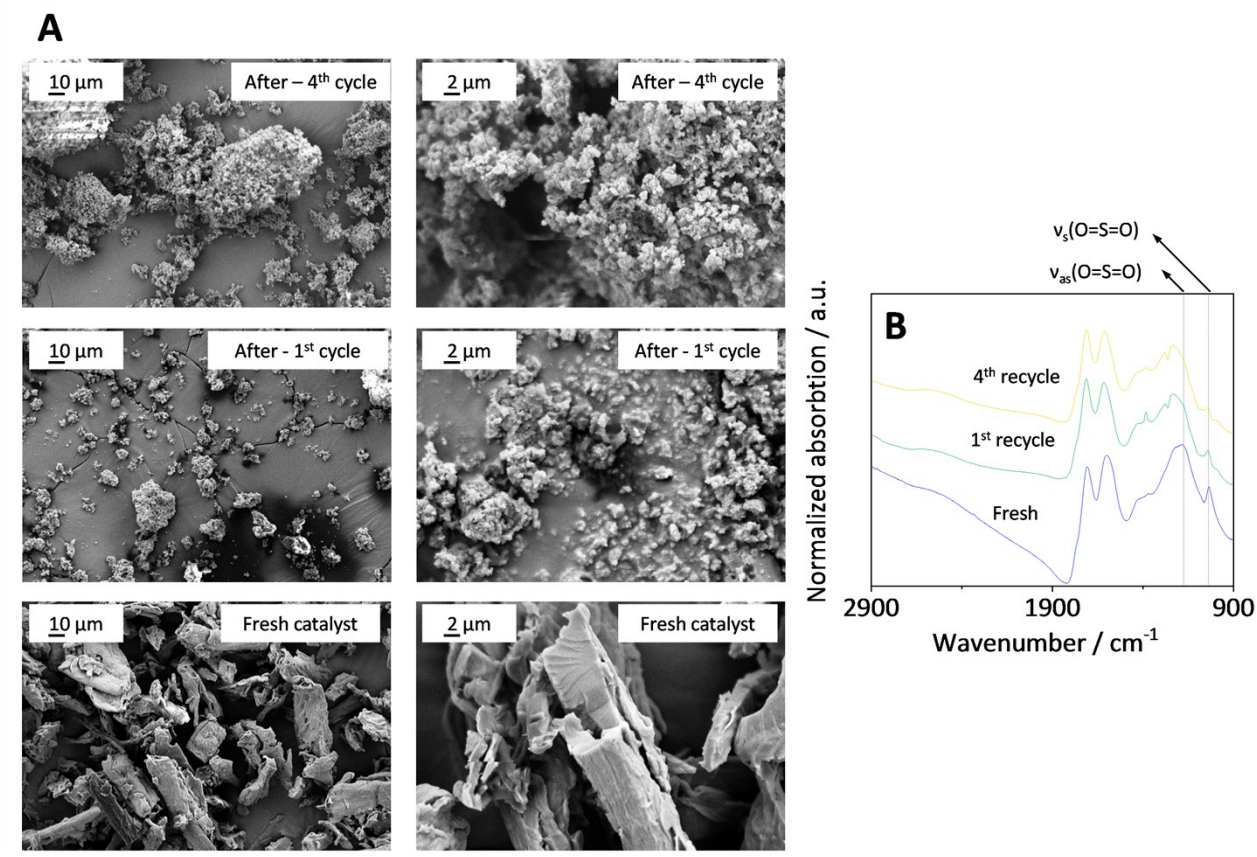


**Figure 13. (A)** SEM images and (**B)** FTIR spectra of fresh and recycled catalyst.

## 18. XRD diffraction patterns of CBM treated cellulose prepared at different substrate-to-catalyst ratios

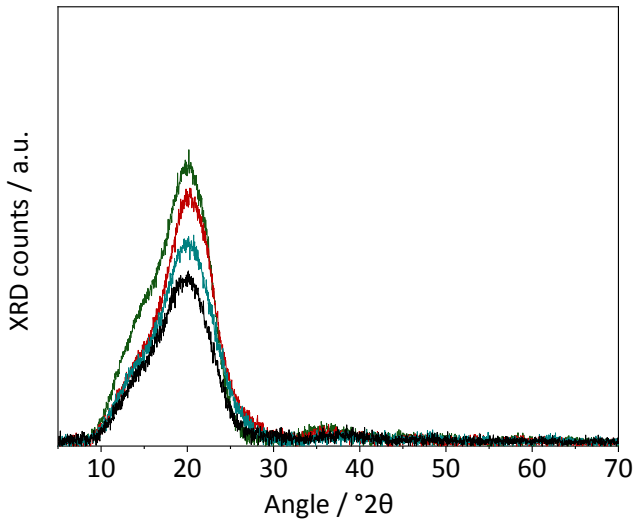


**Figure 14. (A)** Powder X-ray diffraction patterns of cellulose subjected to CBM treatment at different substrate-to-catalyst ratios, CBM-10/1 (–), CBM-7/2 (–), CBM-2/1 (–) and CBM-1/1 (–).