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1 **Hydrothermal decomposition of various crystalline celluloses as treated by**
2 **semi-flow hot-compressed water**

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34 **Abstract**

35 Various types of crystalline celluloses I, II, III_I, III_{II}, IV_I and IV_{II} that have been adjusted for
36 their degree of polymerization (*DP*) were treated by semi-flow hot-compressed water (HCW)
37 at 230-270°C/10 MPa/15 min in order to study their chemical decomposition. The treatments
38 resulted in either partial or complete decomposition of the celluloses and the decomposed
39 products were primarily recovered as hydrolyzed, dehydrated and fragmented ones as well as
40 organic acids in the water-soluble (WS) portions. Their results of chemical decomposition
41 and its kinetics revealed that the celluloses decomposition is dependent on the types of
42 crystalline celluloses as well as temperature of the HCW treatment. The outcome from the
43 WS portions at 270°C/10 MPa/15 min showed that the degree of difficulty for decomposition
44 is lower in group II (cell II, cell III_{II}, cell IV_{II}) than group I (cell I, cell III_I, cell IV_I),
45 indicating that group II is less resistant to decomposition by HCW treatment. Therefore, the
46 decomposition behaviors of the cellulose are due to the inherent differences in the crystalline
47 structures.

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49 **Keywords** Cellulose, Cotton linter, Crystalline structure, Hydrolysis, Semi-flow hot-
50 compressed water

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68 **Introduction**

69 Currently, almost all ethanol from renewable carbon is obtained from food-based
70 sources such as starch and molasses. The shortage of capacity and competition from food
71 requirement drives the need for lignocellulose, such as grasses and woods, to serve carbon
72 resources for promising biofuels [1]. Cellulose as one of the main components in
73 lignocellulose with approximate production of 1.5×10^{12} tons each year globally has high
74 potential to be exploited for this purpose [2, 3]. It can be chemically converted into
75 fermentable saccharides, however, this is usually hindered by its great resistance to
76 hydrolysis [4].

77 Cellulose is a linear crystalline homopolymer consisting of β -1,4-linked D-
78 glucopyranose units. It exists in six known polymorphs of celluloses (I, II, III_I, III_{II}, IV_I, IV_{II})
79 identified by their characteristic X-ray diffraction (XRD) patterns as well as ¹³C nuclear
80 magnetic resonance (NMR) spectra. In nature, cellulose has high degree of polymerization
81 (*DP*), in a range of about 6000 to 15000 glucopyranose units [5] which makes it highly
82 crystalline and not easy to be separated or dissolved in almost any solvents [6,7]. Thus,
83 numerous biological, chemical, and/or physical treatments such as enzymatic saccharification,
84 acid/alkali treatments, steam explosion, supercritical and subcritical treatments have been
85 applied and developed for cellulose hydrolysis [8-14].

86 Hydrothermal treatment in hot-compressed water (HCW) has been proposed as a
87 promising method to hydrolyze cellulose mostly due to its non-toxic, non-catalytic and
88 environmentally benign properties [15-18]. Furthermore, over conventional method, it has
89 advantages such as limited corrosion problem, no sludge generation, low capital and
90 operational cost, as well as no significant degradation of cellulose at normal operating
91 conditions [19]. The conventional methods such as acid/alkali treatment and acid/alkali
92 pretreatment followed by enzymatic hydrolysis are associated with serious economic and
93 environmental constraints due to the heavy use of chemicals.

94 Hot-compressed water is highly pressurized, high temperature liquid water at
95 subcritical condition, below the critical point of water at 374°C/22.1 MPa [20]. It is
96 characterized by a higher ionic product and thus higher concentration of H⁺ and OH⁻ ions,
97 compared to ambient water, offering a highly interesting reaction medium for hydrolysis
98 processes. In addition, acid neutralization is not required because the concentration of H⁺ ion
99 is a function of temperature, and decreases when the temperature is lowered. Many studies
100 have confirmed that cellulose can be largely hydrolyzed in subcritical water without addition
101 of a catalyst [21-26].

102 The experimental results using a flow-type HCW treatment showed that glucose yield
103 increases with increasing temperature [27]. It has less significant degradation reactions as
104 compared with batch-type treatment that makes it preferable for hydrolysis process of
105 lignocellulose [28-30]. It has been reported that 4-22 % of cellulose could be hydrolyzed by
106 flow-type HCW treatment (200-230°C/34.5 MPa/15 min) [31].

107 To the best of authors' knowledge, studies have been done on analysis of cellulose
108 hydrolysis by using HCW treatment; however, the comprehensive investigation has been
109 rarely conducted on various crystalline celluloses as feedstocks. The physical characteristics
110 such as crystallinity and *DP* of various crystalline cellulose residues as treated by semi-flow
111 HCW were thoroughly explored in previous study together with a brief evaluation on the
112 water-soluble (WS) portions [32]. Therefore, as a further approach, the primary objective of
113 this work is to study quantitatively the chemical decomposition from various crystalline
114 celluloses as treated by semi-flow HCW through the yields of WS portions.

115

116 **Materials and Methods**

117 Preparation of various types of crystalline cellulose samples

118 Cotton linter (Buckeye 1AY-500), in the form of cellulose I (cell I), was used to
119 prepare various types of crystalline celluloses. Cellulose II (cell II) was prepared from cell I
120 through mercerization by soaking it into 20.0 % of aqueous NaOH solution for 24 h at
121 ambient condition of temperature (20°C) and pressure (0.1 MPa), followed by washing
122 thoroughly with water and freeze-drying [33]. As for celluloses III_I (cell III_I) and III_{II} (cell
123 III_{II}), they were prepared from cell I and cell II, respectively. Cell I and cell II were soaked in
124 100 % ethylenediamine for 24 h at ambient condition, washed with dried methanol and kept
125 under vacuum.

126 The prepared cell III_I and cell III_{II} were further used for the preparation of celluloses
127 IV_I (cell IV_I) and IV_{II} (cell IV_{II}), by firstly soaking them in glycerol for 3 d at ambient
128 condition. They were then heated in a reaction vessel at 260°C/0.6 MPa for 30 min and
129 cooled down to ambient condition [34]. The product was, then, washed with water and
130 acetone successively, and dried in vacuum. Basically, the converted celluloses consisted of
131 group I (cell I, cell III_I, cell IV_I) and group II (cell II, cell III_{II}, cell IV_{II}). Their chemical
132 compositions were also analyzed and all these celluloses were found to contain similar
133 monosaccharide components of about 99.9 wt% glucose and 0.1 wt% xylose [35].

134 To compare the decomposition products from the water-soluble (WS) portions on
135 various types of crystalline celluloses by semi-flow HCW treatment, cellulose with similar

136 *DP* are necessary for their evaluation. Consequently, these celluloses were adjusted by trial
137 and error for their *DP*s by changing the treatment condition mentioned above for converting
138 cell I to various forms of celluloses.

139

140 The determination of *DP* and crystallinity of the celluloses

141 The celluloses were dissolved in 0.5 M cupriethylenediamine (Cuen) by viscometry as
142 per TAPPI method [36]. The *DP* of the celluloses was then calculated from the intrinsic
143 viscosity $[\eta]$ according to the equation $DP^{0.905} = 0.75[\eta]$ [37]. For the crystallinity
144 determination, Gaussian functions were used to deconvolute the XRD patterns of various
145 crystalline celluloses [38]. These XRD patterns were recorded by X-ray diffractometer
146 Rigaku RINT 2200 [32].

147

148 Treatment of various crystalline cellulose samples by semi-flow HCW treatment

149 The prepared celluloses as starting materials were then treated individually in a semi-
150 flow HCW system. The conversion system and its operational procedures as explained
151 elsewhere were adapted for this study [24-26]. Briefly, about 0.4 g of cellulose was treated
152 individually within a 5 mL reaction vessel. The ambient distilled water from a water tank was
153 flown through the reaction vessel by a pump in order to pressurize the system at 10 MPa
154 controlled by a back-pressure regulator. To raise the temperature, the preheating unit
155 monitored by thermocouples was used to reach at the designated temperatures of 230, 250
156 and 270°C for about 20 min under 10 MPa and remain constant for additional 15 min, totally
157 35 min. In addition, another heating unit was installed at the reaction vessel to maintain the
158 designated temperature in the reaction vessel, into which the HCW was passed through at the
159 flow-rate of 10 mL/min.

160 These treatments yielded insoluble residues [32] and WS portions. After the HCW
161 passing through the reaction vessel, the WS portions were cooled down immediately by the
162 cooling system to terminate all reactions and collected every 5 min. They were allowed to
163 settle in ambient temperature and pressure for a minimum of 12 h. Though no precipitation
164 was observed after at least 12 h, it was filtered by 0.45 μm membrane prior to the subsequent
165 analyses.

166

167 Analytical methods

168 The WS portions collected were analyzed and characterized by using high-
169 performance anion exchange chromatography (HPAEC), high-performance liquid

170 chromatography (HPLC) and capillary electrophoresis (CE). The HPAEC system (Dionex
171 ICS-1000 system) equipped with the CarboPac PA-1 column (4 mm x 250 mm) and
172 electrochemical detector for pulsed amperometric detection was employed and operated at
173 35°C and flow-rate of 1.0 mL/min under the helium atmosphere for monosaccharides and
174 cello-oligosaccharides in the WS portions. The mobile phase was a gradient-programmed
175 mixture of deionized water, 0.2 M NaOH and 2.0 M CH₃COONa, as eluents. All eluents
176 contained in 3 separate reservoirs were degassed by an aspirator and subsequently purged
177 with helium to prevent the absorption of CO₂.

178 The HPLC system (Shidmadzu, LC-10A) equipped with a Shodex Sugar KS-
179 801/Ultron PS-80P columns and refractive index/UV-Vis detector was applied. The eluent
180 used was deionized water at a flow-rate of 1.0 mL/min and oven temperature was set to be
181 80°C for the columns. The CE (Agilent; Germany) was used to assay the low molecular
182 weight organic acids. A fused-silica capillary (Agilent; 75 µm diameter, 104 cm total length,
183 95.5 cm effective length) was used at 15°C.

184 Concentrations of the products in the WS portions were calculated based on the peak
185 areas on chromatograms obtained from HPAEC, HPLC and CE. A set of standards with
186 known concentrations, containing the compounds that were to be identified both
187 quantitatively and qualitatively, was prepared and analyzed together with the samples by
188 using the relevant analytical equipment as mentioned above [18, 24, 25].

189

190 **Results and Discussion**

191 To investigate the decomposition behaviors on various types of crystalline celluloses
192 by semi-flow HCW treatment, the celluloses must have the same *D*P_s as the starting
193 materials. Thus, a direct comparison between the celluloses is feasible, as listed in Table 1.
194 Treatments by semi-flow HCW were then carried out for these celluloses at temperatures of
195 230, 250 and 270°C under 10 MPa for 15 min (230-270°C/10 MPa/15 min).

196

197 **Decomposition kinetics**

198 The semi-flow HCW treatment decomposed various crystalline celluloses either
199 partially or completely to the WS portions. The yield on WS portions from various crystalline
200 celluloses as shown in Fig. 1, is a function of treatment temperatures. At constant treatment
201 time, the yield on WS portions increased as the temperature increased. They were measurable
202 even at lower temperature, 230°C/10 MPa, with approximately 10-30 wt% and increased to
203 more than 70 wt% at higher temperature, 270°C/10 MPa. At 270°C/10 MPa/15 min, cell II

204 was shown to be totally decomposed to WS portions as compared with other celluloses. The
205 overall results from Fig.1 illustrated that higher yields were obtainable for group II celluloses
206 than group I.

207 Figure 2 shows the Arrhenius plot of the present results according to the pseudo-first-
208 order reaction kinetics. The relationship between natural logarithms of reaction constants, $\ln k$,
209 and T^{-1} shows good linear fits with the results indicating that the decomposition follows the
210 pseudo-first-order reaction kinetics. Every parameter used such as time, pressure and DP on
211 the celluloses were kept constant, satisfying the assumption that the Arrhenius-plot is
212 temperature dependent. Though, the data points obtained in this study are only based on three
213 different temperatures profile, the degree of decomposition could be determined reliably and
214 the comparison of kinetics on various crystalline celluloses can be done directly.

215 The apparent activation energies, E_a , for the celluloses can be calculated from Fig. 2.
216 Activation energy of any reaction mainly explains its degree of temperature-sensitiveness;
217 reactions with higher E_a are high in temperature-sensitiveness, while the reactions with lower
218 E_a are low temperature-sensitive [39]. It can also be said that E_a is defined as the minimum
219 energy required for decomposition to occur. The smaller E_a for decomposition of cellulose
220 signifies the requirement of less energy for its decomposition and *vice versa*. In Fig.2, it was
221 shown that different slopes obtained for each of the celluloses suggested different E_a for
222 cellulose decomposition in the studied temperature range.

223 Table 2 shows the obtained E_a for all celluloses within the treatment temperatures.
224 The E_a for group I and group II celluloses are, respectively, greater than 70 kJ/mol and in
225 between 50-60 kJ/mol. It is apparent that the celluloses in group I have higher E_a than those in
226 group II, which implies an easier decomposition process for group II celluloses by semi-flow
227 HCW treatment. However, due to the aforementioned limitations such as limited numbers of
228 experiments carried out in a relatively narrow temperature range, the obtained E_a must be
229 judged critically. The acquired E_a was based on the best fit curves. As a result, a higher E_a
230 was obtained for cell IV_I as compared with cell I and cell III_I. Since comparison of E_a was
231 done between group I and group II, the above observation of group I having higher E_a than
232 group II is valid.

233 These E_a are lower than previously reported, 164 kJ/mol [7] and 145 kJ/mol [40]
234 without catalysts, whereas, 144 kJ/mol and 100 kJ/mol [41] in dilute sulfuric acid catalyst.
235 The differences in E_a could be due to various definitions of decomposition processes and
236 treatment conditions used. For instance, Sasaki et al. [40] studied just the kinetics of cellulose

237 hydrolysis only at elevated temperatures (above 290°C/25 MPa), whereby in this work the
238 kinetics of various cellulose decomposition was measured at 230-270°C/10 MPa.

239 Here, the observed decomposition of cellulose in subcritical water appears to be as
240 good as that occurring in dilute sulphuric acid hydrolysis [41]. Cellulose firstly undergoes a
241 rapid weight loss and followed by a slow hydrolysis step of the remaining cellulose. The high
242 reactivity is associated with accessible amorphous regions in cellulose that are more
243 vulnerable to chemical attacks than the crystalline regions [42]. The reaction temperature has
244 influence on the solvent properties of water [15, 43]. It has been suggested that the shift in
245 solvent properties affects the kinetics of cellulose decomposition [44, 45]. However, in this
246 present work, the constant E_a implies that the reaction mechanism of the hydrothermal
247 decomposition is not distinctly affected. The lower E_a obtained indirectly showed that the
248 decomposition of various celluloses in this system is a catalytic process, in agreement with
249 the literature [41].

250

251 Quantification of water-soluble (WS) portions

252 Figure 3 shows the reaction scheme of cellulose I decomposition into hydrolyzed and
253 degraded products as treated by semi-flow HCW treatment, adapted from [32]. In the present
254 work, the WS portions for various crystalline celluloses obtained from each treatment were
255 found to follow a similar decomposition pathway as in Fig. 3. It is important to know the
256 decomposition pathway of cellulose as the degraded products inhibit the fermentation process
257 for ethanol production [46].

258 Under the HCW conditions, the ionization constant of water increases with
259 temperature and the amount of dissociation also increases, compared with normal
260 temperature and pressure. The glucosidic linkages of cellulose are cleaved and cellulose
261 starts to hydrolyze into cello-oligosaccharides, and subsequently, hydrolyzed to
262 monosaccharide of glucose [20, 25, 47, 48]. Isomerization of glucose occurred producing
263 fructose and mannose. These monosaccharides are unstable at high temperature and thus
264 some parts of them are further converted into their degraded products such as furfural,
265 5-hydroxymethyl furfural (5HMF), levoglucosan through dehydration, and erythrose,
266 glycolaldehyde, methylglyoxal through fragmentation [49]. Prolonged treatment, however,
267 allows further degradation to take place, generating other products such as organic acids.

268 The resulted WS portion percentages based on the dried weight of cellulose samples
269 clearly indicated that the celluloses have been converted to the hydrolyzed and degraded
270 products. The hydrolyzed products are comprised of cello-oligosaccharides, glucose, fructose

271 and mannose, whereas the degraded products consist of dehydrated and fragmented products,
272 as well as organic acids. Their productions were recorded higher in hydrolyzed products as
273 compared with degraded products, and more yields were obtained as treatment temperatures
274 increased.

275 These WS portions were calculated similarly as in the previous studies [24, 25]. The
276 cello-oligosaccharides were consisted of cellobiose, cellotriose, cellotetraose, cellopentaose,
277 cellohexaose and other cello-oligosaccharides with the higher *DP*. The more existence of the
278 cello-oligosaccharides with the higher *DP* shows that the cellulose has more resistance
279 against hydrolysis by semi-flow HCW treatment. In addition to cello-oligosaccharides and
280 glucose, a smaller amount of fructose was also detected and only traces of mannose were
281 identified.

282 A much lower yield of the WS portions obtained at 230°C/10 MPa/15 min (data not
283 shown) was due to the difficulty of the crystalline structures of celluloses to be hydrolyzed at
284 such lower temperature [26]. The cello-oligosaccharides observed could be obtained from the
285 paracrystalline cellulose. The observed fructose is not a sugar component in cotton linter, but
286 it may be isomerized from glucose after hydrolysis from cellulose [50, 51].

287 To evaluate the decomposition behavior of various crystalline celluloses in details, the
288 results from 270°C/10 MPa/15 min would be more appropriate, as at this condition,
289 crystalline cellulose is known to decompose [20, 25, 26]. Table 3 shows the comparison
290 between hydrolyzed and degraded products for the two groups of cellulose samples at
291 270°C/10 MPa/15 min. It can be seen that for both group I and group II celluloses, more than
292 50 wt% of hydrolyzed products were obtained as compared with degraded products. It was
293 reported that about 31.2, 28.1 and 20.5 wt% of hydrolyzed products obtained from the
294 cellulose of Japanese cedar, Japanese beech and Nipa frond, respectively [52]. However,
295 there were no results for *DP* of the cellulose from this study that it can be compared with.
296 The higher yield in WS portions observed in this present work could probably due to the
297 shorter *DP* celluloses used for the starting materials.

298 According to Fig. 3, the hydrolyzed products were produced at the early stage of
299 cellulose decomposition pathway. This could signify that these celluloses have resistance
300 against decomposition. The total hydrolyzed products for cell I and cell III_I is similar but
301 much lesser than cell IV_I, whereas the highest hydrolyzed products obtained in group II is
302 from cell III_{II}, followed by cell IV_{II} and cell II. Overall, celluloses in group II have resulted
303 more hydrolyzed products than those in group I. The observation is similar for the degraded
304 products.

305 Figures 4 and 5, respectively, illustrated how the hydrolyzed and degraded products
306 were obtained at every 5 min intervals at 270°C/10 MPa/15 min. In Fig. 4, only the yields of
307 cello-oligosaccharides, glucose and fructose were shown. These yields are comparable with
308 the results in the literatures [20, 24-26]. Based on these results, the cellulose has been cleaved
309 into cello-oligosaccharides at the early stage of the treatment time and the production of
310 glucose and fructose was seen to occur simultaneously. Celluloses in both group I and group
311 II have similar behaviors; however, more products were seen from group II celluloses. The
312 cello-oligosaccharides and glucose were recovered from the treatment time of 35 min. The
313 crystalline structure of cellulose remained unchanged at temperatures around 230°C [53], thus,
314 the WS portions emerged from the time-up (0-20 min treatment time) could be from
315 paracrystalline cellulose, and the time-at (20-35 min treatment time) was from cellulose.

316 Generally, these monosaccharides are further degraded by dehydration or
317 fragmentation process [15, 24, 54, 55]. Figure 5 illustrated more dehydrated products were
318 obtained than fragmented products and organic acids. During the treatments, it can be seen
319 that the degraded products were generated at almost similar time as the hydrolyzed products
320 (Fig.4). Moreover, the productions of dehydrated and fragmented products as well as organic
321 acids were generated concurrently. Both group I and group II celluloses in Fig.5 have the
322 same trends as in Fig. 4, i.e., more products resulted from group II celluloses. The generation
323 of hydrolyzed products started to be noticeable from around 3 min (Fig. 4) and followed by
324 degraded products (Fig. 5) about 10 min later. This sequence is parallel with that shown in
325 Fig. 3 at which the hydrolyzed products were produced earlier in the decomposition pathway,
326 and later on followed by the production of degraded products.

327 Figure 6 shows the yield in wt% for the individual degraded products in the WS
328 portions for both group I and group II celluloses as treated by semi-flow HCW at
329 270°C/10 MPa/15 min. The dehydrated products detected were consisted of furfural, 5HMF
330 and levoglucosan, whereas fragmented products such as erythrose, glycolaldehyde and
331 methylglyoxal. While for organic acids, acetic, formic, lactic and glycolic acids were
332 identified. The furfural in Fig. 6 can not only be produced from pentose but also from hexose
333 such as glucose. This means that the formation of furfural is possible without pentose via
334 five-carbon ketoses pathway as proposed in the literature [56].

335 Glycolaldehyde and erythrose were formed via retro-aldol condensation in
336 glycolaldehyde/erythrose pathway [44, 51], while methylglyoxal was produced via
337 glyceraldehyde/dihydroxyacetone pathway in hexose fragmentation. Nevertheless, the
338 production of methylglyoxal in this case was too minute that it was excluded from Fig.6. The

339 production of furfural and 5HMF was significant as compared with other degraded products.
340 The organic acids produced are the results of further degradation of dehydrated and
341 fragmented products [51, 57]. Lactic acid production was only a trace to be included in Fig. 6.
342 All the sequences of degradation reactions and productions are agreeable with Fig. 3.

343 Based on those results above, it can be seen that group II celluloses dominated both
344 the hydrolyzed and degraded products as compared with group I celluloses. The result on the
345 WS portions at 270°C/10 MPa/15 min revealed that the degree of difficulty for
346 decomposition is greater for celluloses in group I than those in group II.

347

348 **Conclusion**

349 This study reveals the essential effects of various crystalline celluloses on their
350 chemical decomposition and its kinetic behaviors as treated by semi-flow HCW. Both
351 decomposition rate and E_a are helpful in defining the degree of difficulty for decomposition
352 of various crystalline celluloses, however, the E_a obtained were merely based on empirical
353 relationships of Arrhenius equation. Consequently, the direct method is more preferable than
354 the latter. Nevertheless, this study showed the new kinetic data as there was no previous data
355 on these specific reaction systems.

356 These treatments can be used as viable decomposition media for celluloses at which
357 under the given treatment conditions, cellulose is more readily hydrolyzed with less degraded
358 products. Group I celluloses (cell I, cell III_I, cell IV_I) have shown to have more resistance to
359 decompose than group II celluloses (cell II, cell III_{II}, cell IV_{II}). Based on this evidence, it was
360 clear that the decomposition behaviors are due to the different crystalline forms of celluloses.
361 Therefore, it is recommended to transform cellulose I to the other for a better hydrolysis
362 reaction. These presented data are useful for understanding how various types of crystalline
363 celluloses are chemically decomposed, providing useful insights to efficient utilization of
364 lignocellulose for biofuels and biochemicals.

365

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373 **References**

- 374 1. Bommarius AS, Katona A, Cheben SE, Patel AS, Ragauskas AJ, Knudson K, Pu Y
375 (2008) Cellulase kinetics as a function of cellulose pretreatment. *Metab Eng* 10:370-381
- 376 2. O'Sullivan AC (1997) Cellulose: the structure slowly unravels. *Cellulose* 4:173-207
- 377 3. Klemm D, Heublein B, Fink HP, Bohn A (2005) Cellulose: fascinating biopolymer and
378 sustainable raw material. *Angew Chem Int Ed* 44:3358-3393
- 379 4. Galbe M, Zacchi G (2002) A review of the production of ethanol from softwood. *Appl*
380 *Microbiol Biotechnol* 59:618-628
- 381 5. Zugenmaier P (2008) Crystalline cellulose and cellulose derivatives: characterization and
382 structures. Heidelberg, Germany, pp3-4
- 383 6. Mes-Hartree M, Dale BE, Craig WK (1988) Comparison of steam and ammonia
384 pretreatment for enzymatic hydrolysis of cellulose. *Appl Microbiol Biotechnol*
385 29:462-468
- 386 7. Schacht C, Zetzl C, Brunner G (2008) From plant materials to ethanol by means of
387 supercritical fluid technology. *J Supercrit Fluids* 46:299-321
- 388 8. Grous WR, Converse AO, Grethlein HE (1986) Effect of steam explosion pretreatment
389 on pore size and enzymatic hydrolysis of poplar. *Enzyme Microb Technol* 8:274-280
- 390 9. Inoue H, Yano S, Endo T, Sasaki T, Sawayama S (2008) Combining hot-compressed
391 water and ball milling pretreatments to improve the efficiency of the enzymatic
392 hydrolysis of eucalyptus. *Biotechnol Biofuels* 1:1-9
- 393 10. Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, Ladisch M (2005)
394 Features of promising technologies for pretreatment of lignocellulosic biomass.
395 *Bioresour Technol* 96:673-686
- 396 11. Camacho F, González-Tello P, Jurado E, Robles A (1996) Microcrystalline cellulose
397 hydrolysis with concentrated sulphuric acid. *J Chem Tech Biotechnol* 67:350-356
- 398 12. Karr WE, Holzapple MT (2000) Using lime pretreatment to facilitate the enzymatic
399 hydrolysis of corn stover. *Biomass Bioenergy* 18:189-199
- 400 13. Targoński Z (1985) Alkali process for enhancing susceptibility of autohydrolysed beech
401 sawdust to enzymatic hydrolysis. *Enzyme Microb Technol* 7:126-128
- 402 14. Saka S, Konishi R (2001) Chemical conversion of biomass resources to useful chemicals
403 and fuels by supercritical water treatment. In: Bridgwater AV (ed) *Progress in*
404 *thermochemical biomass conversion*. Blackwell, Oxford, pp1338-1348

- 405 15. Kruse A, Dinjus E (2007) Hot-compressed water as reaction medium and reactant.
406 Properties and synthesis reactions. *J Supercrit Fluids* 39:362-380
- 407 16. Bobleter O, Niesner R, Rohr M (1976) The hydrothermal degradation of cellulosic
408 matter to sugars and their fermentative conversion to protein. *J Appl Polym Sci*
409 20:2083-2093
- 410 17. Bobleter O, Bonn G, Concin R (1983) Hydrothermalysis of biomass-production of raw
411 material for alcohol fermentation and other motor fuels. *Alternative En Sourc* 3:323-332
- 412 18. Yu Y, Wu HW (2010) Understanding the primary liquid products of cellulose hydrolysis
413 in hot-compressed water at various reaction temperatures. *Energy Fuels* 24:1963-1971
- 414 19. Hsu T-A (1996) Pretreatment of biomass. In: Wyman CE (ed) *Handbook on bioethanol:*
415 *production and utilization*. Taylor and Francis, Bristol, pp179-195
- 416 20. Phaiboonsilpa N, Yamauchi K, Lu X, Saka S (2010) Chemical conversion of
417 lignocellulosics as treated by two-step hot-compressed water. In Yao T (ed) *Zero-Carbon*
418 *Energy Kyoto 2009. Green Energy and Technology*, Springer, Tokyo, pp166-170
- 419 21. Sasaki M, Kabyemela B, Malaluan R, Hirose S, Takeda N, Adschiri T, Arai K (1998)
420 Cellulose hydrolysis in subcritical and supercritical water. *J Supercrit Fluids* 13:261-268
- 421 22. Saka S, Ueno T (1999) Chemical conversion of various celluloses to glucose and its
422 derivatives in supercritical water. *Cellulose* 6:177-191
- 423 23. Kumar S, Gupta RB (2008) Hydrolysis of microcrystalline cellulose in subcritical and
424 supercritical water in a continuous flow reactor. *Ind Eng Chem Res* 47:9321-9329
- 425 24. Lu X, Yamauchi K, Phaiboonsilpa N, Saka S (2009) Two-step hydrolysis of Japanese
426 beech as treated by semi-flow hot-compressed water. *J Wood Sci* 55:367-375
- 427 25. Phaiboonsilpa N, Yamauchi K, Lu X, Saka S (2010) Two-step hydrolysis of Japanese
428 cedar as treated by semi-flow hot-compressed water. *J Wood Sci* 56:331-338
- 429 26. Phaiboonsilpa N, Tamunaidu P, Saka S (2011) Two-step hydrolysis of nipa (*Nypa*
430 *fruticans*) frond as treated by semi-flow hot-compressed water. *Holzforschung*
431 65:659-666
- 432 27. Adschiri T, Hirose S, Malaluan RM, Arai K (1993) Non-catalytic conversion of cellulose
433 in supercritical and subcritical water. *J Chem Eng Jpn* 26:676-680
- 434 28. Ehara K, Saka S (2002) A comparative study on chemical conversion of cellulose
435 between the batch-type and flow-type systems in supercritical water. *Cellulose*
436 9:301-311
- 437 29. Sakaki T, Shibata M, Sumi T, Yasuda S (2002) Saccharification of cellulose using a hot-
438 compressed water-flow reactor. *Ind Eng Chem Res* 41:661-665

- 439 30. Liu C, Wyman CE (2003) The effect of flow rate of compressed-hot water on xylan,
440 lignin, and total mass removal from corn stover. *Ind Eng Chem Res* 42:5409-5416
- 441 31. Mok WS, Antal MJ Jr (1992) Uncatalyzed solvolysis of whole biomass hemicelluloses
442 by hot-compressed liquid water. *Ind Eng Chem Res* 31:1157-1161
- 443 32. Abdullah R, Ueda K, Saka S (2013) Decomposition behaviors of various crystalline
444 celluloses as treated by semi-flow hot-compressed water. *Cellulose* 20:2321-2333
- 445 33. Isogai A, Atalla RH (1998) Dissolution of cellulose in aqueous NaOH solutions.
446 *Cellulose* 5:309-319
- 447 34. Isogai A, Usuda M, Kato T, Uryu T, Atalla RH (1989) Solid-state CP/MAS ¹³CNMR
448 study of cellulose polymorphs. *Macromolecules* 22:3168-3172
- 449 35. TAPPI Standard Methods T222 om-88 1988
- 450 36. TAPPI Standard Methods T230 om-82 1982
- 451 37. Sihtola H, Kyrklund B, Laamanen L, Palenius I (1963) Comparison and conversion of
452 viscosity and DP-values determined by different methods. *Paperi ja Puu* 45:225-232
- 453 38. Park S, Baker JO, Himmel ME, Parilla PA, Johnson DK (2010) Cellulose crystallinity
454 index: measurement techniques and their impact on interpreting cellulase performance.
455 *Biotechnol Biofuels* 3:1-10
- 456 39. Xin J, Imahara H, Saka S (2009) Kinetics on the oxidation of biodiesel stabilized with
457 antioxidant. *Fuel* 88:282-286
- 458 40. Sasaki M, Adschiri T, Arai K (2004) Kinetics of cellulose conversion at 25 MPa in sub-
459 and supercritical water. *J Amer Inst Chem Engrs*, 50:192-202
- 460 41. Mok WSL, Antal MJ, Varhegyi G (1992) Productive and parasitic pathways in dilute
461 acid-catalyzed hydrolysis of cellulose. *Ind Eng Chem Res*. 31:94-100
- 462 42. Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K (2000) Dissolution and hydrolysis
463 of cellulose in subcritical and supercritical water. *Ind Eng Chem Res* 39:2883-2890
- 464 43. Marshall WL, Franck EU (1981) Ion product of water substance, 0-1000°C,
465 1-10000 bars new international formulation and its background. *J Phys Chem Ref Data*
466 10:295-304
- 467 44. Sasaki M, Furukawa M, Minami M, Adschiri T, Arai K (2002) Kinetics and mechanism
468 of cellobiose hydrolysis and retro-aldol condensation in subcritical and supercritical
469 water. *Ind Eng Chem Res* 41:6642-6649
- 470 45. Deguchi S, Tsujii K, Horikoshi K (2008) Crystalline-to-amorphous transformation of
471 cellulose in hot and compressed water and its implications for hydrothermal conversion.
472 *Green Chem* 10:191-196

- 473 46. Palmqvist E, Hahn-Hägerdal B (2000) Fermentation of lignocellulosic hydrolysates.
474 II: Inhibitors and mechanisms of inhibition. *Biores Technol* 74:25-33
- 475 47. Antal MJ, Mok WSL (1990) Four-carbon model compounds for the reactions of sugars
476 in water at high temperature. *Carbohydr Res* 199:111-115
- 477 48. Kruse A, Gawlik A (2003) Biomass conversion in water at 330-410°C and 30-50 MPa.
478 Identification of key compounds for indicating different chemical reaction pathways.
479 *Ind Eng Chem Res* 42:267-279
- 480 49. Antal Jr MJ, Mok WSL (1990) Mechanism of formation of 5-(hydroxymethyl)-2-
481 furfuraldehyde from D-fructose and sucrose. *Carbohydr Res* 199:91-110
- 482 50. Srokol Z, Bouche AG, Estrik AV, Strik RCJ, Maschmeyer T, Peters JA (2004)
483 Hydrothermal upgrading of biomass to fuel; studies on some monosaccharide model
484 compounds. *Carbohydr Res* 339:1717-1726
- 485 51. Kabyemela BM, Adschiri T, Malaluan RM, Arai K (1999) Glucose and fructose
486 decomposition in subcritical and supercritical water: detailed reaction pathway,
487 mechanisms and kinetics. *Ind Eng Chem Res* 8:2888-2895
- 488 52. Phaiboonsilpa N, Saka S (2012) Hydrolysis behaviors of lignocellulosics as treated by
489 two-step semi-flow hot-compressed water. Proceedings of the 10th International
490 Symposium on Supercritical Fluids (ISSF 2012), May 13-16, 2012, San Fransisco,
491 California, USA: http://issf2012.com/handouts/documents/144_004.pdf Accessed 10
492 April 2014
- 493 53. Phaiboonsilpa N, Lu X, Yamauchi K, Saka S (2009) Chemical conversion of
494 lignocellulosics as treated by two-step semi-flow hot-compressed water. In: Proceedings
495 of the World Renewable Energy Congress 2009 - Asia, May 19-21, 2009, Bangkok,
496 Thailand, pp 235-240
- 497 54. Kumar S, Gupta R, Lee YY, Gupta RB (2010) Cellulose pretreatment in subcritical water:
498 Effect of temperature on molecular structure and enzymatic reactivity. *Bioresour*
499 *Technol* 101:1337-1347
- 500 55. Xiao LP, Sun ZJ, Shi ZJ, Xu F, Sun RC (2011) Impact of hot-compressed water
501 pretreatment on the structural changes of woody biomass for bioethanol production.
502 *BioResource* 6:1576-1598
- 503 56. Kallury RKMR, Ambidge C, Tidwell TT, Boocock DGB, Anglevor FA, Steward DJ
504 (1986) Rapid hydrothermolysis of cellulose and related carbohydrate. *Carbohydr Res*
505 158:253-261

506 57. Yoshida K, Kusaki J, Ehara K, Saka S (2005) Characterization of low molecular weight
507 organic acids from beech wood treated in supercritical water. *Appl Biochem Biotechnol*
508 121-124:795-806

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540 **List of figure captions**

541

542 **Fig. 1** The yield on WS portions from various types of crystalline celluloses as treated at
543 different temperatures under 10 MPa for 15 min (230-270°C/10 MPa/15 min) by semi-flow
544 HCW

545

546 **Fig. 2** The Arrhenius plot for various crystalline celluloses using pseudo-first order reaction
547 kinetics as treated by semi-flow HCW at 230-270°C/10 MPa/15 min

548

549 **Fig. 3** Decomposition pathway of crystalline cellulose I as treated by semi-flow HCW

550

551 **Fig. 4** The hydrolyzed products of cello-oligosaccharides, glucose and fructose in the WS
552 portions from various types of crystalline celluloses as treated by semi-flow HCW at
553 270°C/10 MPa/15 min. Top figure corresponds to treatment temperature (*open squares*)

554

555 **Fig. 5** The degraded products of dehydrated, fragmented and organic acids products in the
556 WS portions from various types of crystalline celluloses as treated by semi-flow HCW at
557 270°C/10 MPa/15 min. Top figure corresponds to treatment temperature (*open squares*)

558

559 **Fig. 6** The degraded products in WS portions from various types of crystalline celluloses as
560 treated by semi-flow HCW at 270°C/10 MPa/15 min

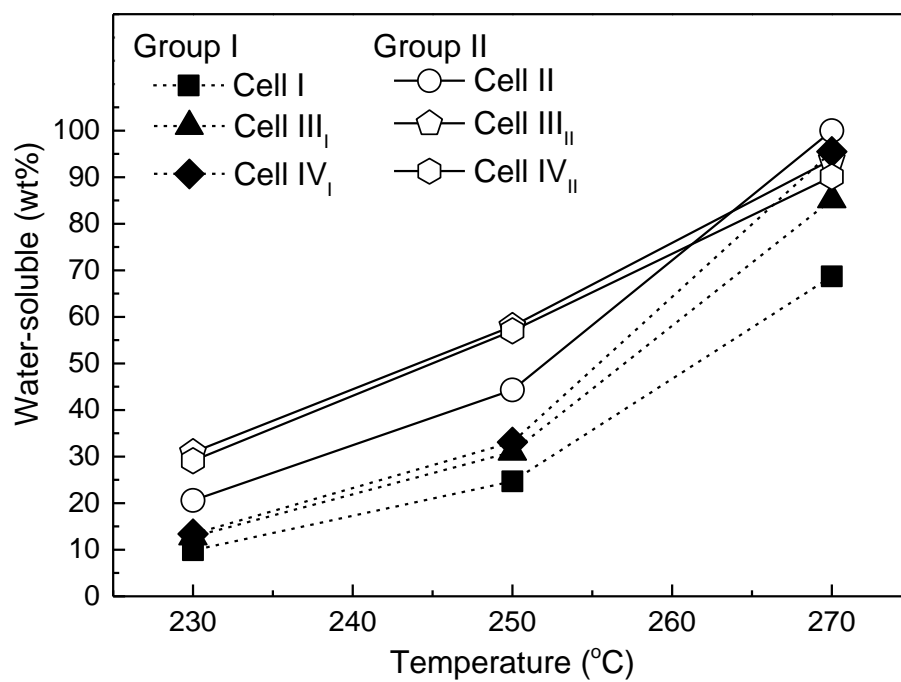


Fig. 1 The yield on WS portions from various types of crystalline celluloses as treated at different temperatures under 10 MPa for 15 min (230-270°C/10 MPa/15 min) by semi-flow HCW

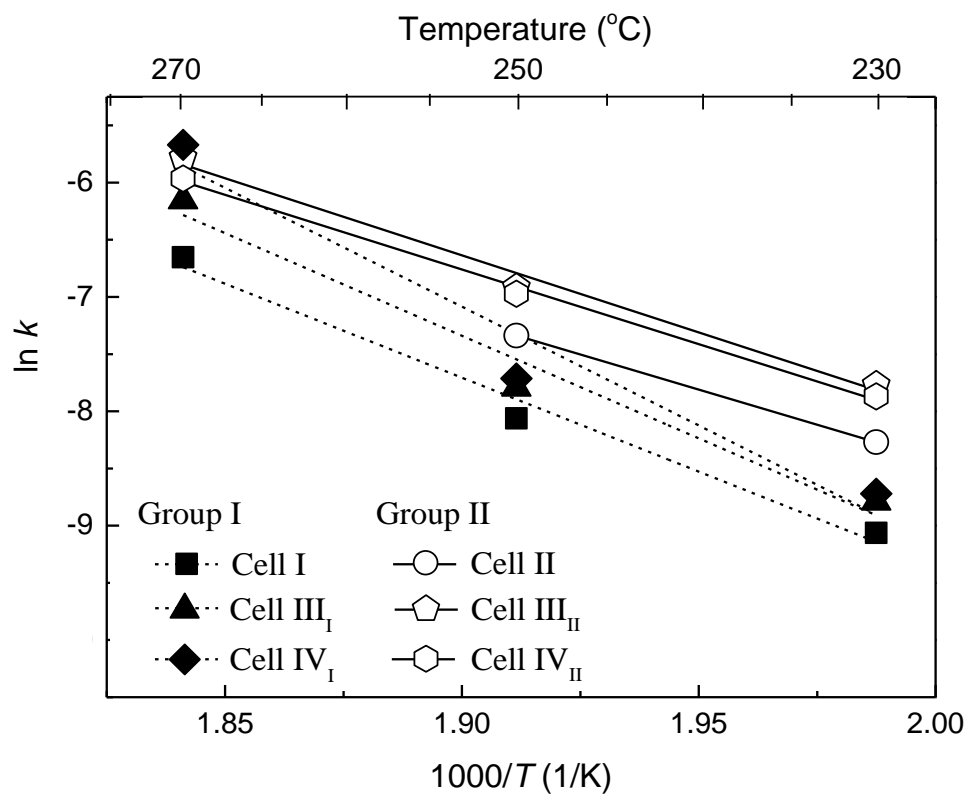


Fig. 2 The Arrhenius plot for various crystalline celluloses using pseudo-first order reaction kinetics as treated by semi-flow HCW at 230-270 $^{\circ}\text{C}$ /10 MPa/15 min

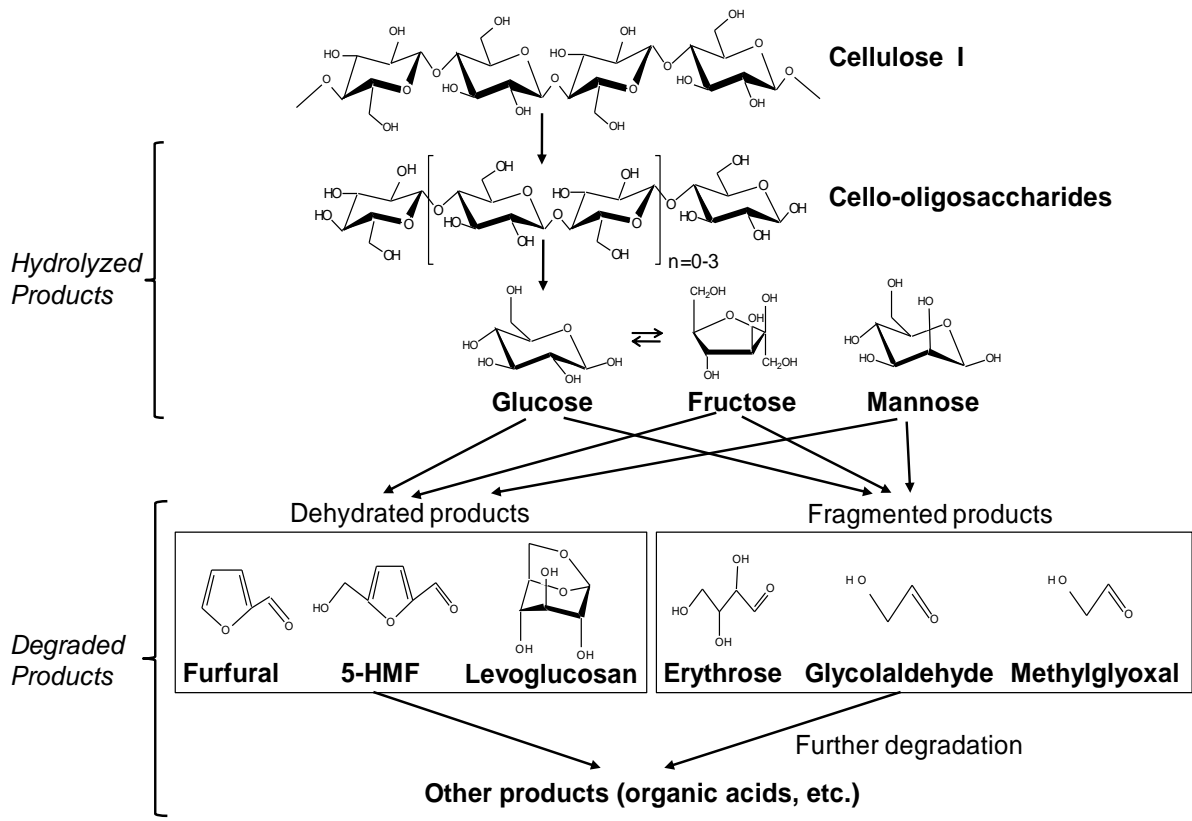


Fig. 3 Decomposition pathway of crystalline cellulose I as treated by semi-flow HCW

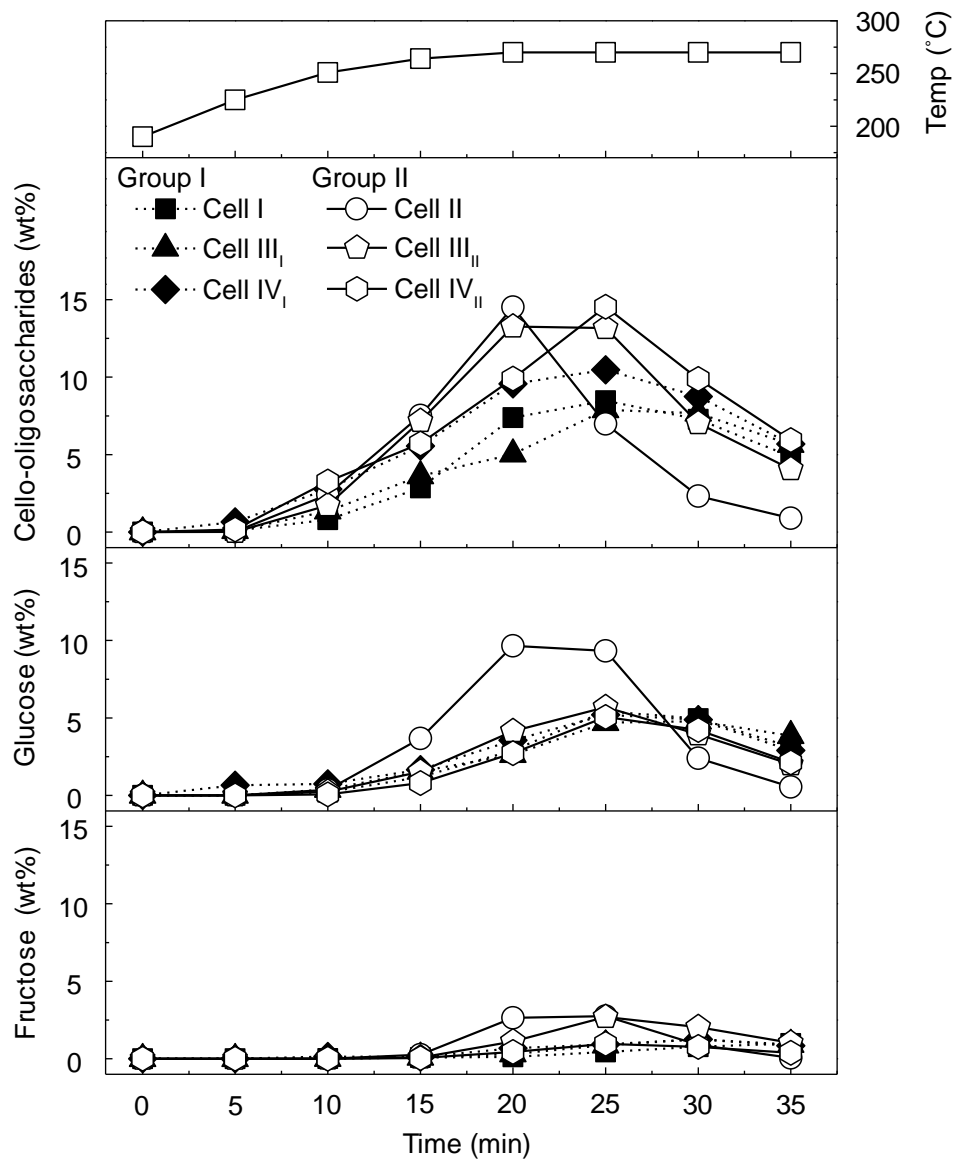


Fig. 4 The hydrolyzed products of cello-oligosaccharides, glucose and fructose in the WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min. Top figure corresponds to treatment temperature (*open squares*)

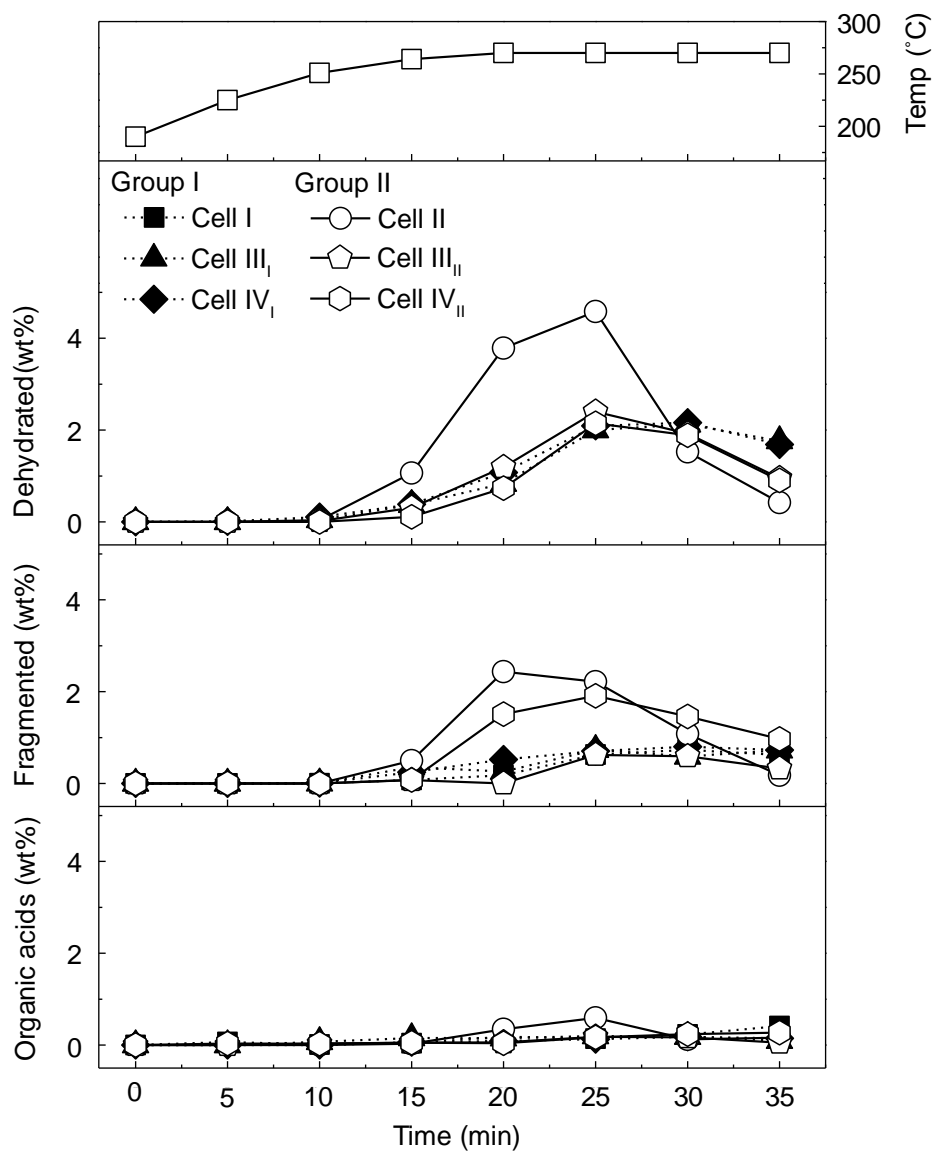


Fig. 5 The degraded products of dehydrated, fragmented and organic acids products in the WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min. Top figure corresponds to treatment temperature (*open squares*)

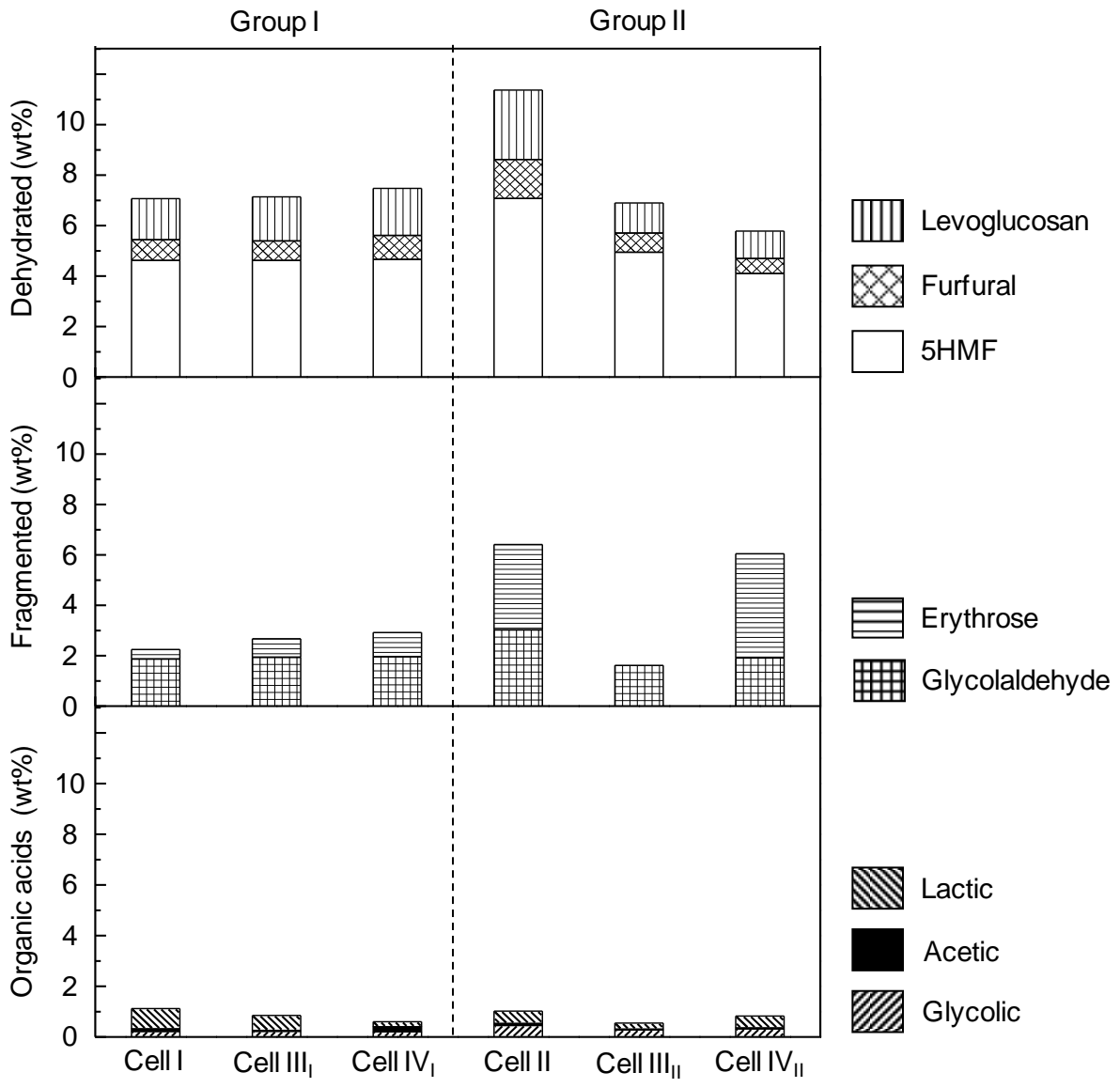


Fig. 6 The degraded products in WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min

Table 1 The crystallinity and *DP* for various types of crystalline celluloses prepared in this study

	Cellulose	Crystallinity (%)	<i>DP</i>
Group I	Cell I	92	176
	Cell III _I	86	164
	Cell IV _I	90	167
Group II	Cell II	85	173
	Cell III _{II}	87	176
	Cell IV _{II}	85	164

Table 2 The apparent activation energies of various types of crystalline celluloses as treated by semi-flow HCW at 230-270°C/10 MPa/15 min

	Cellulose	Activation energy, E_a (kJ/mol)
Group I	Cell I	71.4
	Cell III _I	78.0
	Cell IV _I	90.2
Group II	Cell II	53.3
	Cell III _{II}	59.0
	Cell IV _{II}	56.6

Table 3 The total hydrolyzed and degraded products of WS portions from various types of crystalline celluloses as treated by semi-flow HCW at 270°C/10 MPa/15 min

	Cellulose	Hydrolyzed product (wt%)	Degraded product (wt%)
Group I	Cell I	52.0	10.5
	Cell III _I	52.7	10.6
	Cell IV _I	67.0	11.1
Group II	Cell II	67.3	18.8
	Cell III _{II}	71.0	8.9
	Cell IV _{II}	67.0	12.6