Optimization of the process of chemical hydrolysis of cellulose to glucose

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Abstract

We studied the acid hydrolysis of cellulose in an aqueous medium with the aim of maximizing glucose yield and minimizing the formation of by-products. The influence of reaction parameters such as temperature, acid concentration, acid strength and type of cellulose precursor on glucose yield was investigated. We observed that moderate reaction temperature and low acid concentration resulted in the highest glucose yield with little formation of levulinic acid. Strong acid (p*Ka* < 0) is required to achieve high glucose yield. The crystallite size of the cellulose also affects its reactivity; cellulose with higher crystallite size is more resistant to hydrolysis catalyzed by acid. The highest selectivity for glucose over levulinic acid was recorded at a reaction temperature of 413 K and a sulfuric acid concentration in the range of 0.2-0.5 mol/L. Under these reaction conditions, no levulinic acid was detected, but the glucose yield reached 20% in only 2 h.

***Keywords*:** cellulose, hydrolysis, sulfuric acid, glucose, levulinic acid.

1. Introduction

Lignocellulosic biomass, which comes from the woody parts of plants, can be hydrolyzed to yield chemical components that can be used as renewable carbon sources to produce biofuels. Lignocellulose comprises three main C-based polymers (cellulose, hemicellulose and lignin) which, when taken apart, yield chemical components that can be used to produce biofuels.

The conceptual approach to deconstruct cellulose into sugar monomers is similar to the one followed for decades in conventional oil refineries to produce fuels and chemicals. Thus, it is believed that, in the future, different biorefinery platforms (thermal, oily, chemical and biochemical) can supply marketable biofuels and biochemical products to replace, at least in part, those obtained from fossil precursors. The development of second and third generation biofuels has made it possible to use lignocellulosic biomass and algae for large-scale biofuel production that does not compete with food production as did first-generation biofuels made from corn, sugar cane, canola and soy (Morales-delaRosa & Campos-Martin 2014).

Lignocellulosic biomass can be used to produce bio-ethanol, a promising alternative to crude oil as an energy source. There are two main processes involved in the conversion: (i) hydrolysis of the cellulose present in the lignocellulosic biomass into sugar monomers, and (ii) fermentation of the sugars to produce ethanol (Limayem & Ricke 2012; Sun & Cheng 2002).

Cellulose is a glucose polymer that can be easily deconstructed via hydrolysis into monomers, which can be used at a sugar biorefinery to produce high energy-density fuels and chemicals (Alonso et al. 2010; Brandt et al. 2013; Geboers et al. 2011; Huang et al. 2008). A simple way to hydrolyze the cellulose to glucose is to use an

49 acid catalyst. The glucopyranosyl monomers are linked by β-(1,4) glycosidic bonds,
50 and these bonds can be hydrolyzed in the presence of an acid catalyst (El-Zawawy
51 et al. 2011; Tian et al. 2010). Chemocatalytic hydrolysis of cellulose has seen several
52 periods of revival and has occasionally been combined with biocatalytic fermentation
53 steps to convert sugars to secondary chemicals (Maki-Arvela et al. 2011). The most
54 industrially important process is hydrolysis by concentrated or dilute mineral acids,
55 predominantly sulfuric acid (Van de Vyver et al. 2011). An advantage of this process
56 over enzymatic hydrolysis is its high hydrolysis rate. However, depending on the
57 reaction conditions, glucose can be further degraded into other smaller molecules,
58 thus decreasing the yield (Geboers et al. 2011). Moreover, some of the degradation
59 products of glucose act as inhibitors in subsequent fermentation steps. In the
60 degradation reactions, glucose is dehydrated to yield 5-hydroxymethylfurfural (5-
61 HMF), which in turn undergoes further decomposition to levulinic acid and formic acid
62 in aqueous media (Alonso et al. 2013; Brandt et al. 2013).

63 To the best of our knowledge, there is no report describing a way to optimize glucose
64 yield in the chemoselective hydrolysis of cellulose into glucose. Accordingly, this
65 work was undertaken with the aims of optimizing the process variables of the
66 chemical hydrolysis of cellulose to glucose and defining the operational conditions of
67 temperature, acid concentration, catalyst strength and type of cellulose that maximize
68 the glucose yield.

69

70 **2. Experimental Section**

71 Acids, fibrous cellulose (C6288) and microgranular cellulose (C6413) both from
72 cotton linters were purchased from Sigma-Aldrich and used without any further

purification or treatment. Hydrolysis reactions were carried out batch-wise in a magnetically stirred 100 mL thermostated Teflon-lined steel Berghof reactor equipped with a pressure addition funnel. In a typical run, 0.5 g of cellulose and 40 mL of water were mixed in the reactor, and the suspension was heated to the reaction temperature (393 to 453 K). Then, 10 mL of acid solution was added dropwise to the reactor, and “reaction time” was measure from this moment. The total volume of liquid in the reactor was 50 mL. The acid concentration in the reactor ranged from 0.2 to 2.5 mol/L. Aliquots were periodically taken from the reactor. In all cases, the reaction was stopped after 2 h, and the mixture was quickly cooled. The solution was filtered off, centrifuged and thoroughly washed with distilled water, and finally the solid was dried at 353 K overnight. The amount of solid isolated was determined by weighing.

The liquid was analyzed by HPLC (Agilent Technologies HPLC 1200 series). The chromatographic separations were carried out in an AMINEX HPX-87H column at 338 K, using 0.6 mL/min of sulfuric acid aqueous solution (0.01 mol/L) as the mobile phase. The sugars (glucose, xylose, etc.) and dehydration products (5-hydroxy-methylfurfural and levulinic acid) were analyzed by using a refractive index detector. The components were identified by comparing their retention times with those of reference samples. The products were quantified by using internal calibration curves. The glucose and levulinic acid yields were calculated with the following equations:

$$\% \text{ Glucose Yield} = G_{con} * 100 / G_{Mx} \quad (1)$$

$$\% \text{ Levulinic Avid Yield} = L_{con} * 100 / L_{Mx} \quad (2)$$

G_{con} is the glucose concentration measured, G_{Mx} is the maximum concentration of glucose that can be obtained based on the amount of cellulose fed to the reactor, L_{con}

97 is the levulinic acid concentration and L_{Mx} is the maximum concentration of levulinic
98 acid that can be formed from the cellulose added.

99 X-ray diffraction profiles of samples were recorded with a X'Pert Pro PANalytical
100 diffractometer equipped with a CuKα radiation source (λ = 0.15418 nm) and
101 X'Celerator detector based on RTMS (Real Time Multiple Strip). The samples were
102 ground and placed on a stainless steel plate. The diffraction patterns were recorded
103 in steps over a range of Bragg angles (2θ) between 4 and 90°, at a scanning rate of
104 0.02° per step and an accumulation time of 50 sec. Diffractograms were analyzed
105 with the X'Pert HighScore Plus software.

106

107 **3. RESULTS**

108 We studied the hydrolysis of cellulose to sugar with the objective of maximizing
109 glucose yield. For this purpose, we investigated several reaction variables, such as
110 reaction temperature, catalyst concentration, acid catalyst strength and cellulose
111 precursor type (fibrous or microgranular). No attention was paid to the behavior of 5-
112 hydroxymethyl furfural (5-HMF) because its concentration was very low. The 5-HMF
113 concentration was low because the hydrolysis reaction was carried out in an aqueous
114 medium and because secondary reactions occurred simultaneously (Figure 1), which
115 has been observed by other authors under similar reaction conditions (Girisuta et al.
116 2013). Indeed, 5-HMF decomposes by hydration into levulinic acid and formic acid.
117 Therefore, this work focuses only on the conversion of cellulose into glucose and
118 levulinic acid.

119

120 ***3.1. Effect of acid concentration***

First, we investigated the effect of catalyst (sulfuric acid) concentration on the glucose yield. At low reaction temperature, using a higher concentration of sulfuric acid, results in a higher glucose yield (Figure 2). The concentration of glucose increases linearly with acid concentration, except at the highest concentration (2.5 mol/L). The glucose concentration was found to drop slightly when long reaction times are used. In general, the extent of levulinic acid formation is low, and it increases with the sulfuric acid concentration (Figure 2). This increase is abrupt, however, for a sulfuric acid concentration of 2.5 mol/L. Moreover, the concentration of levulinic acid increases sharply with long reaction times. Such changes in levulinic acid formation occur in parallel with a drop in glucose concentration (Figure 2). A similar trend was observed when reaction temperature was increased to 413 K (Figure 3). The rate of glucose formation increases linearly versus time when acid concentration is increased as in the previous case but it deviates from linearity at long reaction times when 2.5 mol/L acid is used. A different behavior is observed in the profile of glucose formation: the concentration increases sharply at short reaction times (up to 30 min), then reaches a maximum and finally decreases sharply (Figure 3). It is also observed in Figure 3 that the levulinic acid concentration is very low if sulfuric acid concentration is low (0.5 and 0.2 mol/L). A low concentration of levulinic acid is obtained at short reaction times when 1.1 mol/L acid is used, although it increases at long reaction times. In contrast, the formation of levulinic acid is fast for an acid concentration of 2.5 mol/L, and it reaches a concentration that corresponds to a yield of 60% with respect to the cellulose fed.

The kinetic profiles of glucose formation at 433 K are somewhat different. With the exception of a sulfuric acid concentration of 0.2 mol/L, the glucose concentration

145 increased at low reaction times, then reached a maximum and finally decreased
146 (Figure 4). The consecutive reactions of cellulose hydrolysis to glucose and glucose
147 conversion to levulinic acid have been observed by other authors (Girisuta et al.
148 2013; Gurgel et al. 2011). Significantly, both the reaction time and concentration that
149 provide maximum yield depend on the acid concentration. Higher concentration of
150 acid corresponded to an earlier maximum and a lower concentration of glucose
151 (Figure 4). The concentration profiles indicate that, at a reaction temperature of 433
152 K, levulinic acid is formed at all concentrations of the acid (Figure 4). However, the
153 shape profiles are somewhat different for different concentrations. For an acid
154 concentration of 2.5 mol/L, the levulinic acid profile shows a quick increase at short
155 reaction times (15 min), and then the increase slows at longer reaction times. At 1 h
156 reaction time, the concentration of levulinic acid corresponds to a yield of 60% with
157 respect to the cellulose fed. As the concentration of acid decreases, the formation
158 rate of levulinic acid drops. However, the increase in the concentration of levulinic
159 acid is not linear: an increase in the formation rate was found once the glucose
160 concentration reached its maximum (Figure 4). The observed behavior is related to
161 the reaction scheme (Figure 1). Strong acids catalyze the hydrolysis of cellulose to
162 glucose, but these acids also catalyze the subsequent dehydration reaction to 5-
163 hydroxy-methylfurfural (HMF) and the formation of levulinic acid (Girisuta et al. 2013;
164 Gurgel et al. 2011; Pilath et al. 2010). The observed behavior is clearly an example
165 of consecutive reactions; the higher concentration of acid and higher temperature
166 clearly favors secondary reactions that yield levulinic acid. Because the cellulose
167 hydrolysis was conducted in aqueous media, HMF was not detected. When it forms,
168 the HMF quickly reacts to form levulinic acid.

169

170 ***Effect of temperature***

171 The yield to levulinic acid was very low for sulfuric acid concentrations in the range of
172 0.5 - 0.2 mol/L and temperatures of 393 and 413 K, as the main objective of this work
173 was the optimization of glucose yield from cellulose hydrolysis, so we decided to
174 focus on studying the effect of temperature in the lowest region of acid concentration.

175 When a concentration of 0.5 mol/L was used, a linear increase in the concentration of
176 glucose was observed at the lowest temperature even though a reduction in the
177 increase of glucose concentration at long reaction times was recorded at a reaction
178 temperature of 433 K (Figure 2a, Figure 3a, Figure 4a). In general, levulinic acid
179 formation is rather low but increases with reaction temperature (Figure 2b, Figure 3b,
180 Figure 4b). However, at a reaction temperature of 413 K, the levulinic acid
181 concentration is moderate at short reaction times, but increases quickly at longer
182 reaction times. This change in levulinic acid formation happens at the same time as
183 the slowing of the increase in glucose concentration (Figure 2, Figure 3, Figure 4),
184 this decrease in sugars formation was observed previously (Amarasekara & Wiredu
185 2012).

186 A similar trend is observed with a concentration of 0.2 mol/L (Figure 2a, Figure 3a,
187 Figure 4a), an increase in the reaction temperature causes an increase in the rate of
188 formation of glucose, and an increase in the glucose concentration is linear for the
189 lower temperatures tested (393 and 413 K). This linearity is lost at long reaction
190 times with a reaction temperature of 433 K (Figure 4a). In general, the levulinic acid
191 formation is low and increases with sulfuric acid concentration (Figure 2b, Figure 3b,
192 Figure 4b). However, when the reaction temperature is 433 K, the levulinic acid

concentration is not very high at short reaction times, but increases at longer times. It is clear that the change in levulinic acid formation occurs when the glucose formation is higher because is a secondary product from glucose (Figure 4b).

The catalytic behavior is in agreement with previous studies of the degradation of cellulose, which reported that secondary products are formed from glucose at temperatures higher than 413 K (Girisuta et al. 2013; Gurgel et al. 2011; Pilath et al. 2010). These data indicate unambiguously that conditions of low sulfuric acid concentration (0.5 mol/L and 0.2 mol/L) and moderate temperature (413 K) yield the highest concentration of glucose and produce a very low concentration of levulinic acid.

3.2. Effect of the acid strength of the catalyst

We determined the effect of acid strength on cellulose hydrolysis. For this purpose, several acids with p*Ka* values ranging from 4.8 to -6.6 were used (Table 1). The concentration of every acid catalyst was kept constant at 0.2 mol/L. We note that the reaction temperature used depends on the acid strength of the catalyst (Figure 5); the less acidic catalyst requires a higher reaction temperature to produce measurable amounts of glucose product. There is a correlation between the cellulose conversion and acid strength: the higher the p*Ka*, the less active the catalyst (Figure 5, Table 1). Consequently, a higher reaction temperature is needed. For all samples, glucose yield increases at higher temperatures. However, as all catalysts were tested at 433 K, their performances can be compared. Figure 2a, Figure 3a, Figure 4a and Figure 5 show the hydrolysis yields, which indicate that the strength of the acid has a strong effect on glucose yield: higher glucose yields are obtained with stronger acids (lower

p*Ka*). This trend is similar to what was reported for the hydrolysis of cellulose dissolved in ionic liquids (Morales-delaRosa et al. 2012; Rinaldi & Schüth 2009). However, the two acids with negative p*Ka* values produced similar glucose yields. This is due to the fact that a strong acid is needed to hydrolyze the β-glycosidic bonds (Shimizu et al. 2009). The most promising results have been obtained with acids like sulfuric acid and p-TSA, which have negative p*Ka* values. For these two acids, the yield of levulinic acid was also quantified (Figure 6). These two catalysts produced a very low concentration of levulinic acid at lower temperatures (393 K and 413 K), but the yield increased slightly at 433 K. We also observed that the levulinic acid concentration increases at long reaction times, as the linearity of glucose yield decreases.

3.3. Effect of cellulose type

The crystalline structures of the two types of commercial cellulose were revealed by X-ray diffraction (Figure 7). The XRD profiles show a prominent cellulose peak at 23º, due to the (200) reflection, and other less intense peaks at about 15º, 17º and, which are characteristic of $(1\bar{1}0)$, (110), reflections respectively and a composite signal due to the diffraction of several peaks that includes (004) at 34º, (Nishiyama et al. 2012; Park et al. 2010). The intensity of the peaks is rather high, indicating good crystallinity. The crystalline index (CI) was calculated according to the following equation:

$$CI = (I_{23} - I_{18})/I_{23} \quad (3)$$

Here, I_{23} and I_{18} are the net intensities of the peak at 23º and the signal at 18º respectively, (Park et al. 2010), this index is also known as Segal CI (French & Santiago Cintrón 2013). Using this procedure, we found that the CI was about 85% for the microgranular sample and 92% for the fibrous sample (Table 2). However, recent studies showed showed a very good agreement between crystallite size and CI which do not imples presence of amorphous material (French & Santiago Cintrón 2013), because CI can over-estimates the amount of "amorphous" material due to the overlap of the neighboring diffraction peaks in the area of 18º. We have calculated the peak width at half of the maximum peak intensity (PWHM) values of the most intense peak for both samples (Table 2) and the crystalline size using the Scherrer equation with shape factor of 1.0 (French & Santiago Cintrón 2013). PWHM (Peak Width Half Maximum) of microgranular sample is larger than fibrous counterpart that implies a smaller crystallite size for migrogramular cellulose (6.6 nm) than 7.6 nm for fribrous one (Table 2). Based on these data and previous works we can indicate that the the amount of "amorphous" material are overestimate using the CI method.

These two types of cellulose (microgranular and fibrous) were hydrolyzed with sulfuric acid and p-TSA (0.2 mol/L) at a reaction temperature of 413 K. For the microgranular sample, the glucose concentration was found to increase almost linearly with reaction time (Figure 8). For the fibrous sample, some deviation from linearity was observed in the glucose yield, and for a given reaction time the glucose yield of the fibrous sample was lower than that of the microgranular sample.

The yield of glucose was similar for the two acids employed, although a slightly higher glucose yield was obtained when sulfuric acid was used as a catalyst. This

263 improvement is more evident when using fibrous cellulose. Apparently, higher acidity
264 is required for the hydrolysis of cellulose with high crystallite size (fibrous samples).

265

266 **4. DISCUSSION**

267 The hydrolysis of cellulose implies breaking of the β-1,4-glycosidic bonds of the
268 polymeric structure which is an essential step for the conversion of cellulose into
269 oligosaccharides. Direct hydrolysis of lignocellulose with acids has long been studied
270 and many processes were reported to be effective. In most of these studies mineral
271 acids (HCl, H_2SO_4) and organic acids (oxalic, maleic, fumaric) were found particularly
272 suited for the production of glucose, that can degrade first to hydroxymethyl furfural
273 (HMF) and finally to levulinic acid and formic acid (FA) (Scheme 1). Acid hydrolysis of
274 cellulose is a kinetic process which is mostly controlled by: (i) the nature of cellulose
275 precursor, (ii) the pKa of the acid, (iii), the acid concentration, and (iv) the reaction
276 temperature.

277 As most cellulose is crystalline, harsh conditions (high temperatures, high acid
278 concentrations) are required in order to liberate glucose from these tightly associated
279 chains. If hydrolysis temperature is high, occurrence of pyrolysis and other side
280 reactions become important, and the amount of tars and other difficult to handle by-
281 products increases as the temperature is raised above a given temperature levels. In
282 addition, controlling reaction times for maximum glucose yields at very short
283 hydrolysis times presents severe commercial challenges.

284 The data obtained by comparing the concentration of acid hydrolysis clearly indicate
285 the possibility to control the hydrolysis to desired products. Under conditions of
286 hydrolysis with high concentrations of strong acid, a high yield to glucose is obtained

in the first minutes of reaction time but the glucose breaks down at longer reaction times (Amarasekara & Wiredu 2012; Lenihan et al. 2010), under high acid concentration high yield to secondary products (levulinic acid) is obtained. These secondary reactions have been minimized when low acid concentration is employed, especially for 0.2 mol/L concentration.

Another important parameter to tune the products to be obtained is the hydrolysis temperature. At higher temperature, the hydrolysis of cellulose to glucose was very fast but simultaneously the glucose decomposes rapidly to secondary products. So, to obtain high glucose selectivity is necessary to operate at moderate temperatures (393K), at this temperature the hydrolysis rate is moderate but the formation of levulinic acid is very small. However, high selectivity to levulinic acid can be obtained when high hydrolysis temperature is employed.

Despite the low glucose yields afforded in this study, there is a potential to intensify cellulose hydrolysis in dilute H_2SO_4. As reported in Figure 8, the glucose yield was found to be substantially higher with microgranular cellulose using either H_2SO_4 or p-TSA. This reactivity patterns is similar to that reported by Kupiainen et al. (Kupiainen et al. 2010) who found two-fold higher glucose yield from organosolv pulp than from microcrystalline cellulose. In other words, more deconstructed polymeric precursor becomes more reactive to acid attack, and there is no need to increase so much reaction temperature, with subsequent inhibition of the consecutive reactions leading to levulinic acid.

With regards to the effect of the nature of the acid used (Figures 3, 4 and 5a-d) on the product distribution it is clear that H_2SO_4 and p-TSA acids produce higher amounts of hydrolysis products, although at higher reaction temperatures they are

311 able to drive the transformation of cellulose quite further, providing higher amounts of
312 dehydration products HMF and then levulinic acid. This behaviour is due to the
313 higher acid strength of both acids in comparison with AA, OA and H_3PO_3 acids. The
314 superior strength of H_2SO_4 (pKa = -6.6) probably boost the depolymerization of
315 cellulose into glucose, but also the transformation of the evolving monosaccharide
316 into the corresponding dehydration products, leading to an overall higher yield
317 towards solubilized products than that recorded with the other acids.

318 We have detected that for a given reaction time the glucose yield of the fibrous
319 sample was lower than that of the microgranular sample. This finding is consistent
320 with what would be expected when taking into account the higher crystallite size of
321 the fibrous sample. The hydrolysis of cellulose is slower when the cellulose crystallite
322 size is higher, because a sample with low crystallite size has more surface area per
323 gram of sample (Park et al. 2010) and lower length chain (Nishiyama et al. 2012),
324 these properties increase the reaction rate of the hydrolysis of cellulose chains
325 (Girisuta et al. 2007; Sharples 1957; Sharples 1958).
326

327 **5. Conclusions**

328 In the present work, we investigated the acid hydrolysis of cellulose in an aqueous
329 medium to maximize the glucose yield and minimize the formation of by-products. At
330 low concentrations of sulfuric acid, the selectivity for glucose was high, but it
331 decreased with increasing acid concentration. This effect is more evident at long
332 reaction times. High reaction temperatures increase the reaction rate, but the glucose
333 yield increases at short reaction times and then decreases at longer reaction times.
334 This effect was found to be even more evident with increasing acid concentration. It

was also revealed that the yield of levulinic acid followed an opposing trend. This is due to the occurrence of secondary reactions that form levulinic acid at the expense of glucose (Figure 1). A high yield of levulinic acid (60%) was recorded at 433 K for a reaction time of 1 h and an acid concentration of 2.5 mol/L. In addition, the acid strength of the catalyst is also a key factor in cellulose hydrolysis. A higher glucose yield can be obtained if an acid of low pKa (stronger acid) is employed. A strong acid (pKa < 0) is essential for high glucose yield. The crystallite size of the cellulose influences its reactivity, because samples with larger crystallite size are more resistant to chemical hydrolysis. The highest selectivity for glucose over levulinic acid is obtained at 413 K and a sulfuric acid concentration of 0.2 to 0.5 mol/L. Under these conditions, a glucose yield of 20%, with no levulinic acid, was recorded with a reaction time of only 2 h.

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REFERENCES

Alonso DM, Bond JQ, Dumesic JA (2010) Catalytic conversion of biomass to biofuels. Green Chem. 12(9): 1493

Alonso DM, Gallo JMR, Mellmer MA, Wettstein SG, Dumesic JA (2013) Direct conversion of cellulose to levulinic acid and gamma-valerolactone using solid acid catalysts. Catal. Sci. Tech. 3(4): 927

Amarasekara AS, Wiredu B (2012) Aryl sulfonic acid catalyzed hydrolysis of cellulose in water. Appl. Catal., A 417-418: 259-262

360 Brandt A, Gräsvik J, Hallett JP, Welton T (2013) Deconstruction of lignocellulosic
361 biomass with ionic liquids. Green Chem. 15(3): 550
362 El-Zawawy WK, Ibrahim MM, Abdel-Fattah YR, Soliman NA, Mahmoud MM (2011)
363 Acid and enzyme hydrolysis to convert pretreated lignocellulosic materials into
364 glucose for ethanol production. Carbohydr. Polym. 84(3): 865-871
365 French A, Santiago Cintrón M (2013) Cellulose polymorphy, crystallite size, and the
366 Segal Crystallinity Index. Cellulose 20(1): 583-588
367 Geboers JA, Van de Vyver S, Ooms R, Op de Beeck B, Jacobs PA, Sels BF (2011)
368 Chemocatalytic conversion of cellulose: opportunities, advances and pitfalls.
369 Catal. Sci. Tech. 1(5): 714
370 Girisuta B, Dussan K, Haverty D, Leahy JJ, Hayes MHB (2013) A kinetic study of
371 acid catalysed hydrolysis of sugar cane bagasse to levulinic acid. Chem. Eng.
372 J. 217: 61-70
373 Girisuta B, Janssen LPBM, Heeres HJ (2007) Kinetic Study on the Acid-Catalyzed
374 Hydrolysis of Cellulose to Levulinic Acid. Industrial & Engineering Chemistry
375 Research 46(6): 1696-1708
376 Gurgel LVA, Marabezi K, Zanbom MD, Curvelo AAdS (2011) Dilute Acid Hydrolysis
377 of Sugar Cane Bagasse at High Temperatures: A Kinetic Study of Cellulose
378 Saccharification and Glucose Decomposition. Part I: Sulfuric Acid as the
379 Catalyst. Industrial & Engineering Chemistry Research 51(3): 1173-1185
380 Huang HJ, Ramaswamy S, Tschirner UW, Ramarao BV (2008) A review of
381 separation technologies in current and future biorefineries. Sep. Purif.
382 Technol. 62(1): 1-21

383 Kupiainen L, Ahola J, Tanskanen J (2010) Comparison of Formic and Sulfuric Acids
384 as a Glucose Decomposition Catalyst. Industrial & Engineering Chemistry
385 Research 49(18): 8444-8449
386 Lenihan P, Orozco A, O'Neill E, Ahmad MNM, Rooney DW, Walker GM (2010) Dilute
387 acid hydrolysis of lignocellulosic biomass. Chem. Eng. J. 156(2): 395-403
388 Limayem A, Ricke SC (2012) Lignocellulosic biomass for bioethanol production:
389 Current perspectives, potential issues and future prospects. Prog. Energy
390 Combust. Sci. 38(4): 449-467
391 Maki-Arvela P, Salmi T, Holmbom B, Willfor S, Murzin DY (2011) Synthesis of sugars
392 by hydrolysis of hemicelluloses--a review. Chem. Rev. 111(9): 5638-5666
393 Morales-delaRosa S, Campos-Martin JM (2014) Catalytic processes and catalyst
394 development in biorefining In: Waldron KW (ed) Advances in biorefineries. vol
395 Woodhead Publishing Series in Energy. Woodhead Publishing, Oxford, UK. p
396 152-198
397 Morales-delaRosa S, Campos-Martin JM, Fierro JLG (2012) High glucose yields from
398 the hydrolysis of cellulose dissolved in ionic liquids. Chem. Eng. J. 181-182:
399 538-541
400 Nishiyama Y, Johnson G, French A (2012) Diffraction from nonperiodic models of
401 cellulose crystals. Cellulose 19(2): 319-336
402 Park S, Baker JO, Himmel ME, Parilla PA, Johnson DK (2010) Cellulose crystallinity
403 index: measurement techniques and their impact on interpreting cellulase
404 performance. Biotechnology for biofuels 3: 10
405 Pilath HM, Nimlos MR, Mittal A, Himmel ME, Johnson DK (2010) Glucose Reversion
406 Reaction Kinetics. J. Agric. Food. Chem. 58(10): 6131-6140

Rinaldi R, Schüth F (2009) Acid Hydrolysis of Cellulose as the Entry Point into Biorefinery Schemes. ChemSusChem 2(12): 1096-1107

Sharples A (1957) The hydrolysis of cellulose and its relation to structure. Transactions of the Faraday Society 53(0): 1003-1013

Sharples A (1958) The hydrolysis of cellulose and its relation to structure. Part 2. Transactions of the Faraday Society 54(0): 913-917

Shimizu K-i, Furukawa H, Kobayashi N, Itaya Y, Satsuma A (2009) Effects of Brønsted and Lewis acidities on activity and selectivity of heteropolyacid-based catalysts for hydrolysis of cellobiose and cellulose. Green Chem. 11(10): 1627

Sun Y, Cheng J (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour. Technol. 83(1): 1-11

Tian J, Wang J, Zhao S, Jiang C, Zhang X, Wang X (2010) Hydrolysis of cellulose by the heteropoly acid H3PW12O40. Cellulose 17(3): 587-594

Van de Vyver S, Geboers J, Jacobs PA, Sels BF (2011) Recent Advances in the Catalytic Conversion of Cellulose. ChemCatChem 3(1): 82-94

Table 1 Acid catalysts used for the hydrolysis of cellulose.

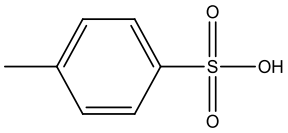
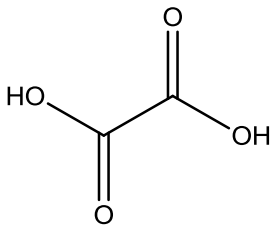
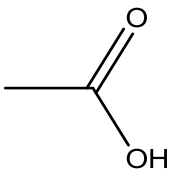
Formula	Abbreviation	pKa
H_2SO_4	H_2SO_4	-6.6
	*p*-TSA	-2.5
	OA	1.19
H_3PO_4	H_3PO_4	2.1
	AA	4.8

Table 2 Peak width half maximum (PWHM), crystallite size, intensity at 18º and 23º and Segal CI of studied samples.

Sample	PWHM (º)	Crystallite size (nm)	Intensity at 18º (c.p.s.)	Intensity at 23º peak (c.p.s.)	CI
Microgranular	1.37	6.6	1739	11755	85 %
Fibrose	1.16	7.8	1657	20507	92 %

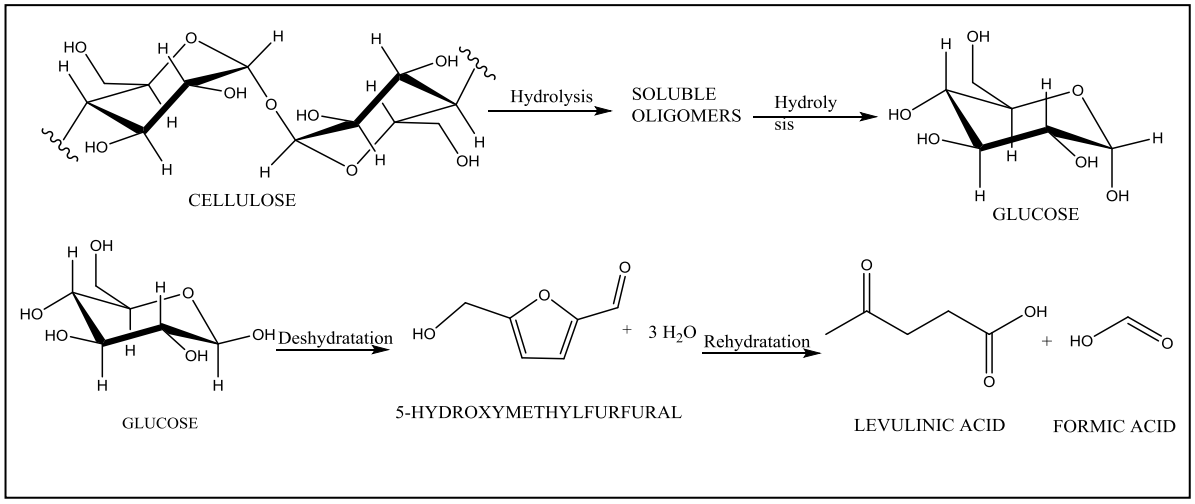


Figure 1 Successive reactions that can occur during cellulose hydrolysis.

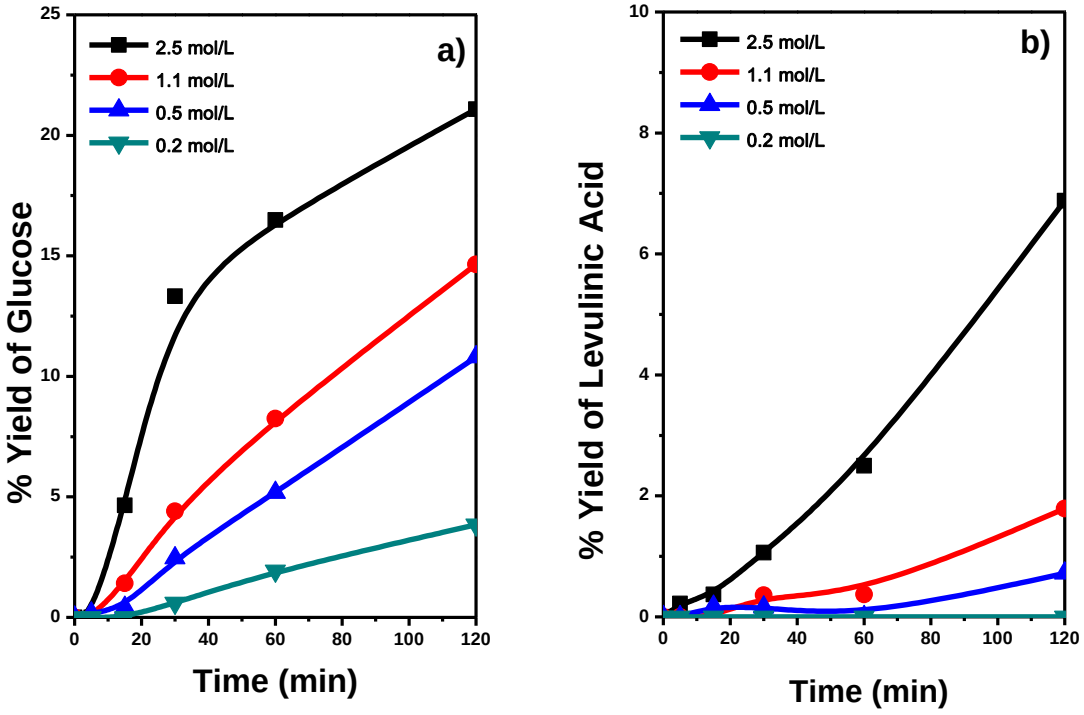


Figure 2 Hydrolysis of cellulose in different concentrations of H_2SO_4 at 393 K.

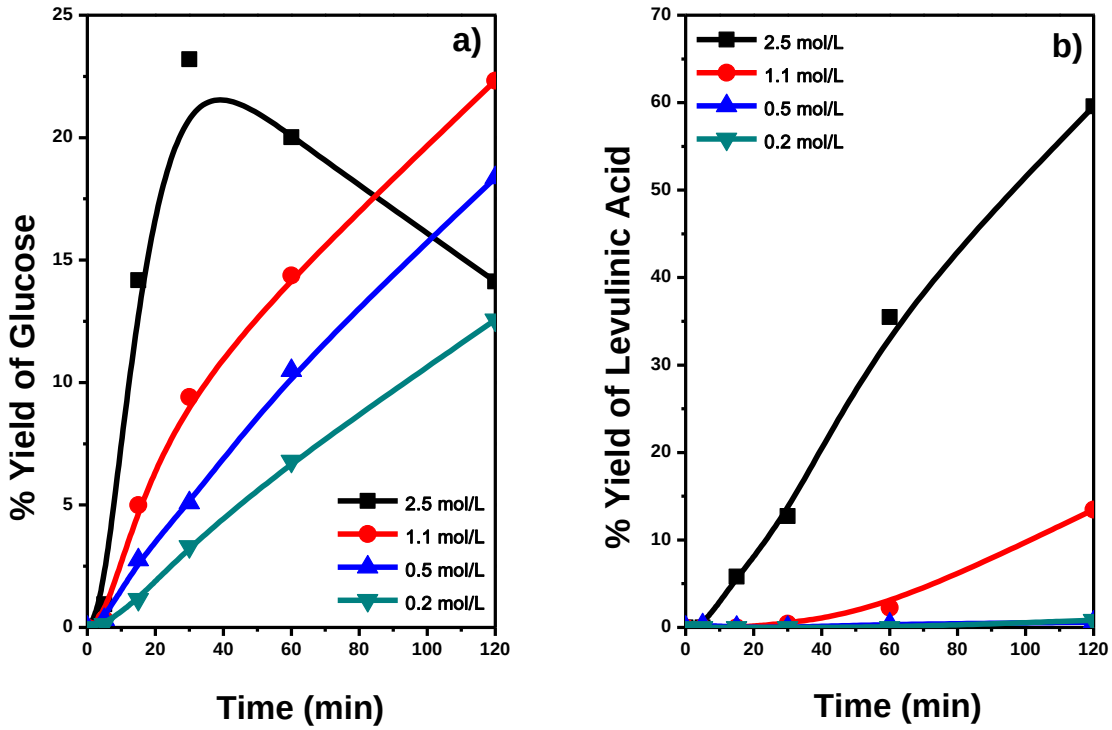


Figure 3 Hydrolysis of cellulose in different concentrations of H_2SO_4 at 413 K.

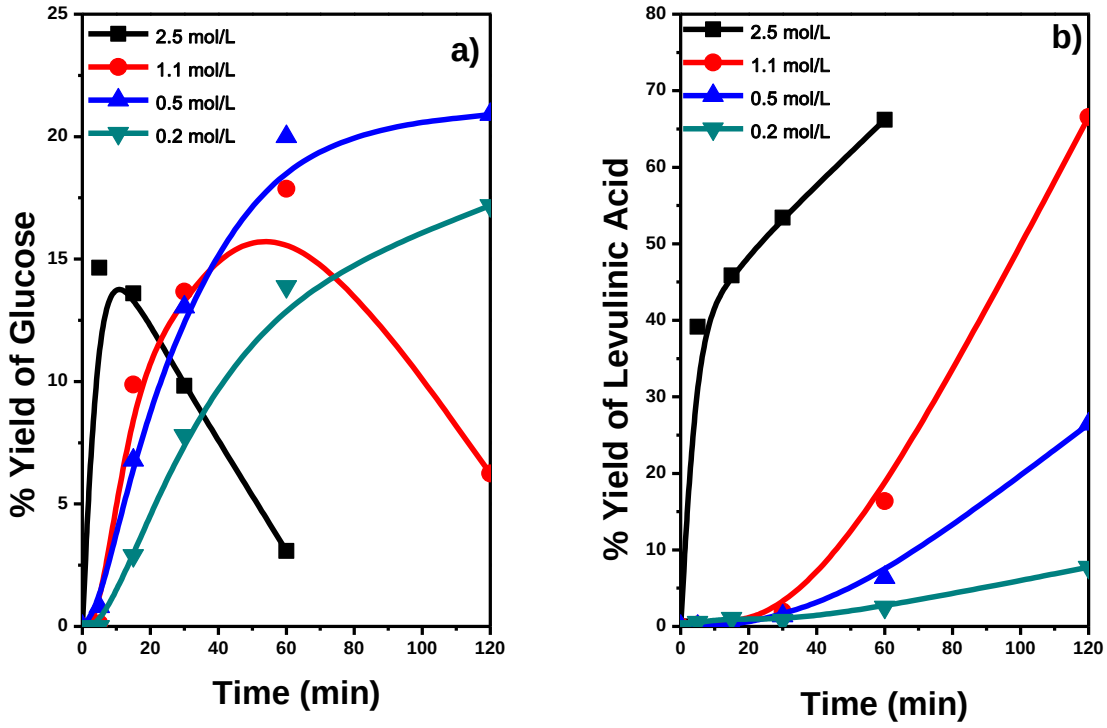


Figure 4 Hydrolysis of cellulose in different concentrations of H_2SO_4 at 433 K.

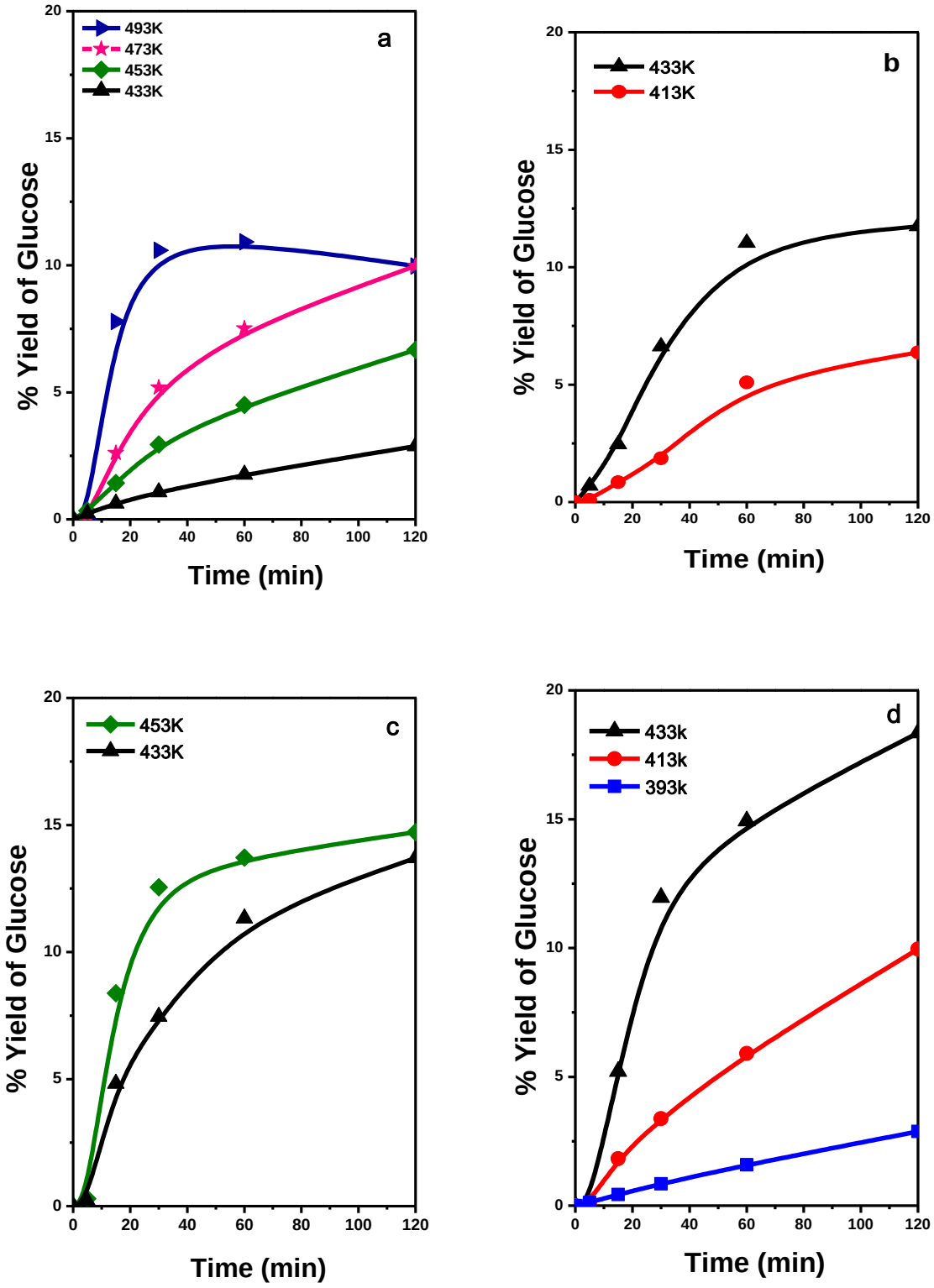


Figure 5 Yield of glucose in the hydrolysis of cellulose catalyzed by different acids (0.2 mol/L in water) a) AA, b) H_3PO_4, c) OA and d) p-TSA, using different reaction temperatures.

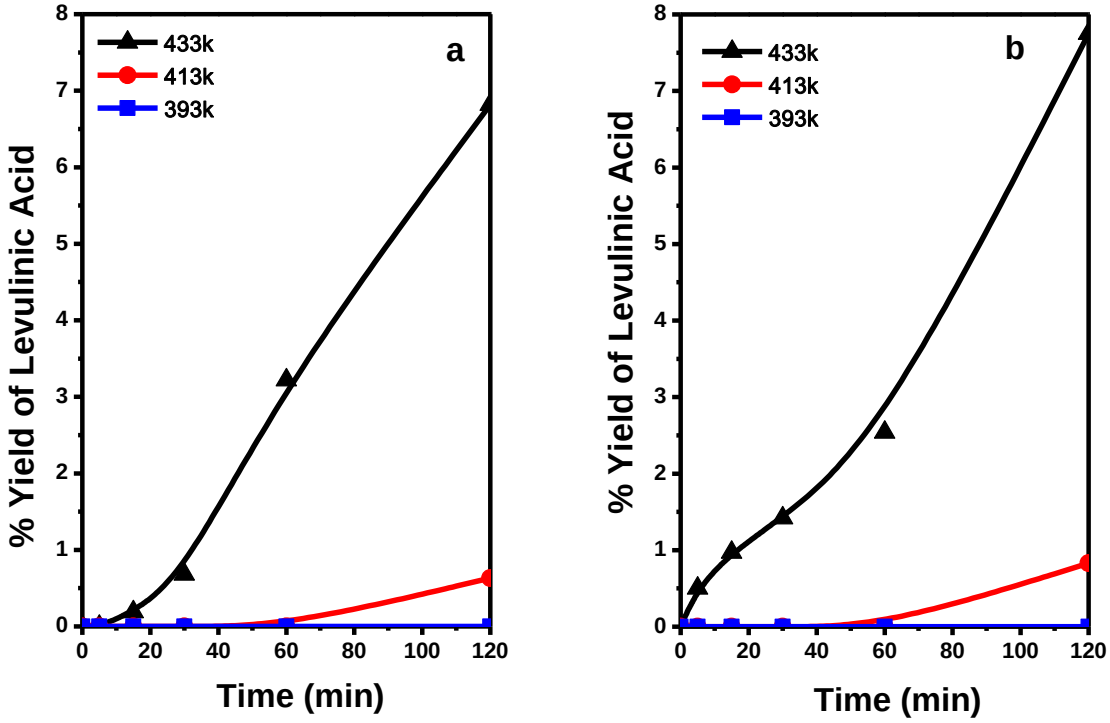


Figure 6 Yield of levulinic acid in the hydrolysis of cellulose using 0.2 mol/L p-TSA (a) or H_2SO_4 (b) in water at different temperatures.

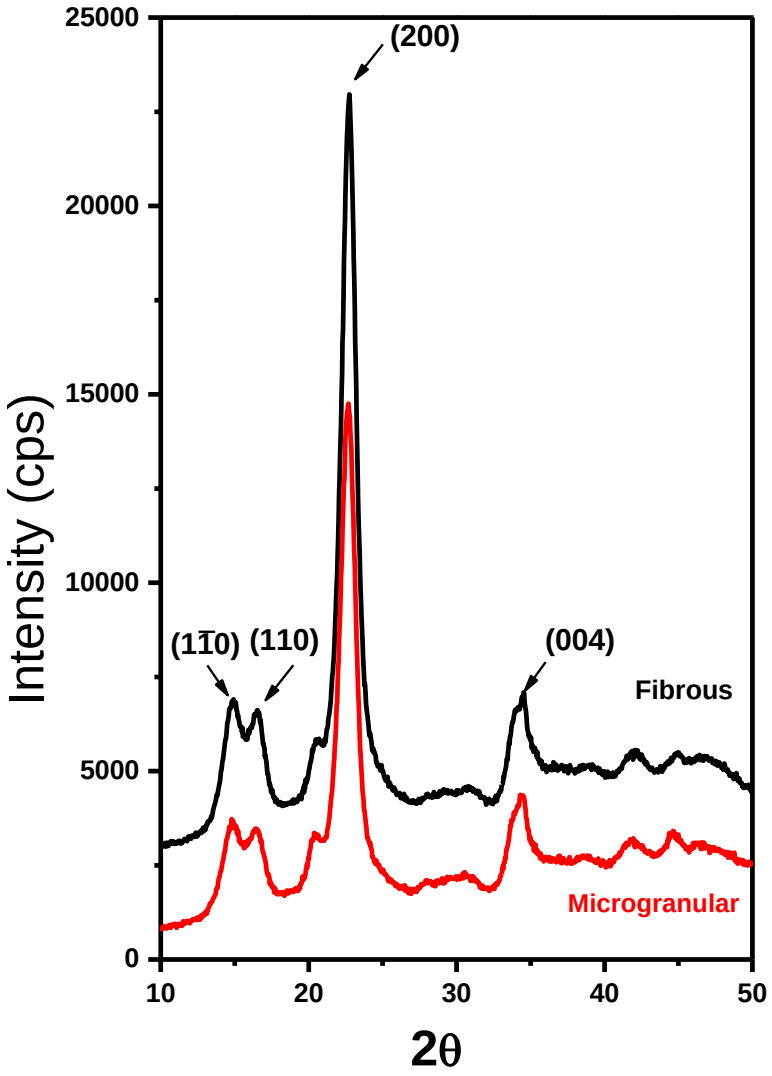


Figure 7 XRD patterns of both cellulose samples.

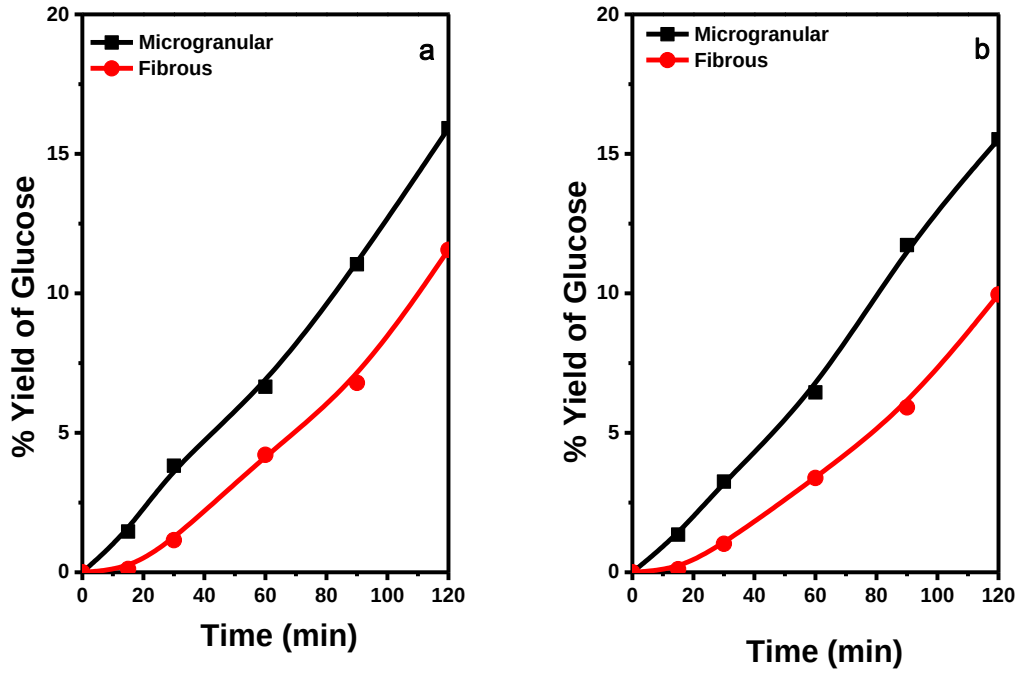


Figure 8 Yield of glucose in the hydrolysis of two different kinds of cellulose using 0.2 mol/L sulfuric acid (a) or p-TSA (b) in water at a reaction temperature of 413 K.