Supplementary Information for

Green biorefinery---The ultra-high hydrolysis rate and behavior of *populus tomentosa* hemicellulose autohydrolysis under moderate subcritical water conditions

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1 Effect of hydrolysis degree on crystallinity

Hemicellulose has a great influence on the degree of crystallinity. As can be seen from Fig. 1(a), with the removal of hemicellulose, the crystallinity on the whole shows a rising trend. During the process when the removal rate of hemicellulose is greater than 60%, the crystallinity decreases in different stages, and these falling points correspond to the crystallinity of 170 °C and 180°C for 0 min, 90 min and 120 min. After removing these falling points, the relationship between hemicellulose removal rate and crystallinity is shown in Fig. 1(b), from which it can be found that the hemicellulose removal rate between 20% and 80% shows a linear upward trend, and the crystallinity increases before and after the hemicellulose removal rate between 20% and 80%. The improvement of crystallinity is not only due to the degradation of hemicellulose. When the reaction temperature is higher and the reaction time is longer, the amorphous region of cellulose will be destroyed a lot, and the crystallinity will also rise.
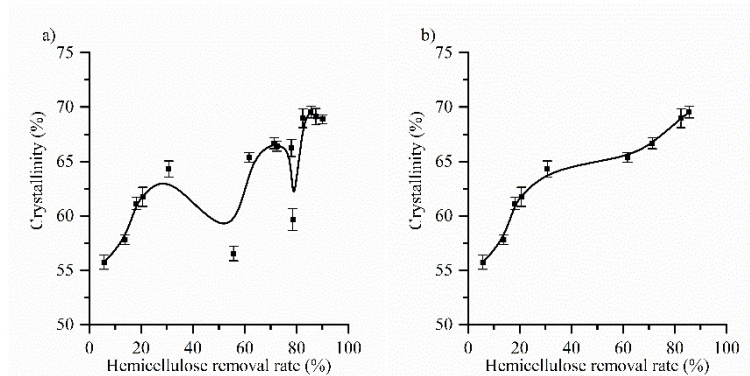
Note: hemicellulose removal is calculated according to xylose, rhamnose, arabinose, mannose and galactose.

Fig. 1 The influence of hydrolysis degree and hemicellulose removal rate on crystallinity of autohydrolysis residues

2 Effect of hydrolysis degree on the reducing sugar content of the hydrolysate

The reducing sugar content of the hydrolyzate was determined by the DNS method. The reduction end concentration of sugars not only reflects that of mono- and oligosaccharides in the hydrolyzate, but is also related to the degradation and further transformation of polysaccharides therein.

Fig.2 shows the effect of time on the reducing sugar concentration of the aqueous solution for reaction temperatures of 160°C, 170°C, and 180 °C. At a holding time of 0 min, the reducing sugar concentrations for the above temperatures were not significantly different (1.2 g/L, 1.4 g/L, and 1.7 g/L, respectively), in the process of heating up, the ion accumulation of water increases, the hydrogen bond between water molecules weakens, the relative dielectric constant decreases, the viscosity and surface tension of water decreases.[1-3] At the beginning of the reaction, the H$^+$ concentration in the hydrolysate is low, and the degradation of cellulose and hemicellulose is less. With the extension of the reaction time, the H$^+$ concentration increases continuously, and the degradation degree of hemicellulose and cellulose increases.[4] The difference of reducing sugar concentration was increasing at different temperatures. At 160 °C, the reducing sugar concentration of the hydrolyzate uniformly increased from 1.2 g/L to 5.4 g/L. When the temperature was 170 ° C, the pH value of the hydrolysate continued to decrease at 0-60 min, resulting in the breaking of the glycoside bond in hemicellulose, so hemicellulose continued to degrade rapidly into oligosaccharides, increasing the reducing sugar concentration to 6.0 g / L at a constant rate. At times of 60–90 min, oligosaccharides were continuously produced and concomitantly cleaved under acidic conditions to afford monosaccharides and other oligosaccharides.[5] Therefore, the reduction

end is increased, which resulting in a rapid rise of reducing sugar concentration to 12.2 g/L. At times of 90–120 min, oligosaccharide decomposition continued. As pentoses are vulnerable to attack by hydronium ions at high temperature, some of them were converted into furfural and other substances, which resulted in the saturation of reducing sugar concentration at 12.4 g/L.[6] At 180 °C, the reducing sugar concentration rapidly increased to 11.8 g/L after 40 min. At longer times, the rate of monosaccharide degradation exceeded that of oligosaccharide degradation, and the apparent reducing sugar concentration thus decreased to 7.0 g/L. After 90 min, monosaccharide degradation and transformation reached a state of equilibrium, and the reducing sugar concentration saturated at 7.1 g/L, about 60% of the maximum concentration (11.8 g/L), which indicated that 40% monosaccharides was degraded to furfural and other low molecular substances, in agreement with the amount of produced furfural (manuscript Fig. 4).
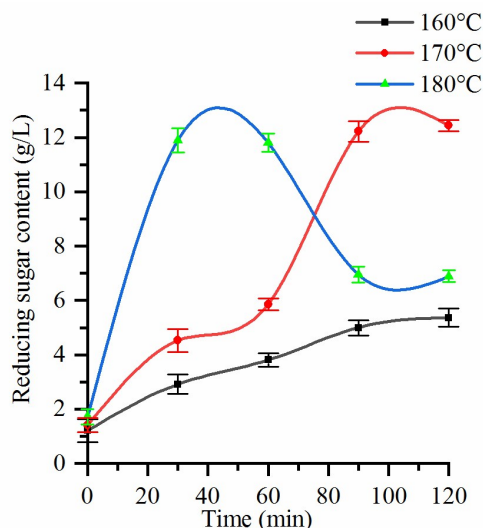

Fig.2 The influence of temperature and time on the concentration of reducing sugar in hydrolysate

3 Effect of hydrolysis temperature and time on holocellulose removal

Holocellulose is the general term for cellulose and hemicellulose cellulose and hemicellulose, which is the most used component of wood fiber biomass. The change of cellulose and hemicellulose content during chemical treatment affects the properties of fiber products and, to a certain extent, reflects fiber quality. Therefore, it is very important to study the change of holocellulose content under autohydrolysis conditions. Hemicellulose is easily removed during autohydrolysis, with some of its components converted into furfural and other substances. Cellulose and hemicellulose have fundamentally different properties due to (i) the close connection of glucose chains in cellulose coupled with the absence of other branched chains and (ii) the fact that cellulose

has macro- and supramolecular structures. During hydrolytic pretreatment, high-temperature steam induces partial degradation of cellulose. Fast and complete degradation can only be achieved at 300 °C, whereas ordinary hot water pretreatment can only induce the thermal degradation of amorphous cellulose to mainly afford low molecular weight glucan.[7] As mentioned above, high-temperature autohydrolysis increases solution acidity (manuscript Fig. 1), thus leading to the degradation of the amorphous cellulose zone and the partial degradation of the crystalline zone. Under acidic conditions, glucose produced by cellulose degradation is further converted into products such as 5-hydroxymethylfurfural, erythrose, acetone aldehyde, glyceraldehyde, 1,6-gluconic anhydride, furfural, and low molecular weight acids.[8]

Fig. 3 a,b show the change process of holocellulose content in raw materials (a) and holocellulose removal rate (b) with time under 160 ° C, 170 ° C and 180 ° C, respectively. According to the curve trend, the change of holocellulose removal rate in autohydrolysis can be divided into two stages: at 160 °C, holocellulose removal rate rapidly increased from 13% to 37% in the first stage (0-60 min), subsequently slowly increasing to 46% in the second stage (>60 min). At 170 °C, holocellulose removal rate rapidly increased from 15% to 40% in the first stage (0-60 min), subsequently slowly increasing to 48% in the second stage (>60 min). Therefore, the change of holocellulose removal rate followed the same trend as pH and xylose content changes, i.e., at 170 °C, mainly hemicellulose was hydrolyzed. At 180 °C, the removal rate increased rapidly from 19 to 48% in the first stage (0-30 min) and subsequently slowly rose to 53% in the second stage (>30 min).

According to Fig. 3b, for the reaction time is 0 min, removal rates of 13.08%, 15.84%, and 18.95% were obtained at 160°C, 170°C, and 180 °C, respectively.Therefore, the maximum removal rate was about one time of the minimum value, indicating that temperature had a great influence on holocellulose removal during heating. At 160°C and 170 °C, The pH of the hydrolysate decreased gradually, and the removal rate of holocellulose increased steadily. Holocellulose removal rate stably increased with time, subsequently saturating at a certain value positively correlated with temperature, what's more the higher the temperature, the higher the removal rate. At the temperature of 180 ° C, when the reaction time is 120 min, the concentration of H^+ in the solution is the highest and the acidity is the strongest, leading to the partial removal of glucose from cellulose, so the removal rate of holocellulose reaches equilibrium and then rises again. In conclusion, temperature

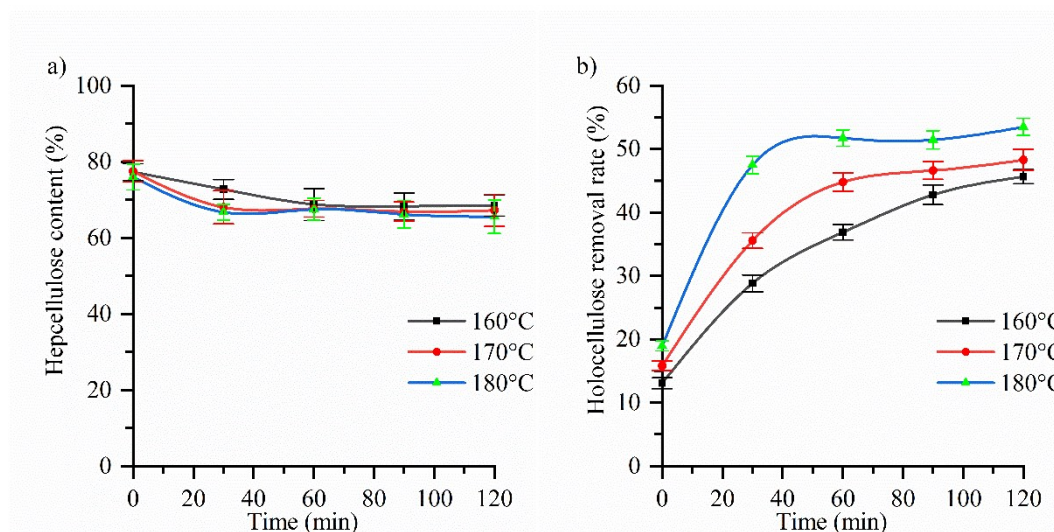plays an important role in the removal of hemicellulose in autohydrolysis.

Fig.3 The influence of temperature and time on (a) holocellulose content, (b) holocellulose removal rate

4 Effect of hydrolysis intensity on hydrolysis extent and solid content

The hydrolysis rate is related to the dissolution of cellulose, hemicellulose, lignin and other chemical components. The solid formed by the dissolved substances determines the solid content of the autohydrolysate, and some of them will continue to degrade into volatile substances. Both hydrolysis rate and solid content reflect the changing behavior of chemical components in self hydrolysis, which has a great influence on bio refining. The extent of autohydrolysis increased with time because of the continuous removal of raw material components. Fig. 4a shows the change of hydrolysis rate with reaction time at 160 ° C, 170 ° C and 180 ° C. From the curve trend, when the reaction temperature was 160 ° C, the hydrolysis rate increased from 17% to 41%; when the reaction temperature is 170 ° C and 180 ° C, it can be divided into two stages: fast hydrolysis stage was observed at 0–60 min, while slow hydrolysis stage was observed after 60 min, In the rapid hydrolysis stage, the hydrolysis rate increases rapidly from 20% to 40% when the reaction temperature equaled 170 °C, while increases from 21% to 44% was observed at 180°C. In the slow hydrolysis stage, hydrolysis rate rises slowly to 43%, 48% at 170°C, and 180 °C, respectively. At a holding time of 0 min, hydrolysis extents of 17%, 19%, and 21% were obtained for temperatures of 160°C, 170°C, and 180 °C, respectively, i.e., the difference between these values was smaller than that between the corresponding pH values (manuscript Fig. 1), which indicated that hemicellulose side chains were easier to degrade than the main chain. In the rapid hydrolysis stage, with the increase of reaction

time, hemicellulose is degraded due to the increase of acidity of autohydrolysate, which indicated that reaction time played an important role in the rapid hydrolysis stage. In the slow hydrolysis stage, the difference between hydrolysis extents (and hence, the role of time) became less significant with increasing time. However, at 180 °C, hydrolysis extent eventually increased to 43%, which was significantly higher than that obtained at 170 °C, indicating that temperature played a key role in the change of hydrolysis extent at the later stage of the reaction. With the extension of the reaction, the chemical composition of the hydrolyzate reached equilibrium, which was manifested in the slow increase of raw material hydrolysis extent, and the removed part of lignin was easily adsorbed on the raw material surface at a later stage to hinder the further increase of hydrolysis extent.[9]

The solid content of the hydrolyzate reflects the dissolution and degradation of chemical components of poplar wood powder. Fig. 4b shows the change of solid content with reaction time at 160 ° C, 170 ° C and 180 ° C. From the curve trend, the change of solid content can be divided into two stages at different temperatures. At 160 °C, the solid content increased from 7.2 g/L to 17.7 g/L in the first stage (0-60 min), subsequently slowly increasing to 20.8 g/L in the second stage (>60 min). At 170 °C, the solid content rapidly rose from 7.8 g/L to 21.3 g/L in the first stage (0-30 min) and subsequently saturated at 23.2 g/L in the second stage (>30 min). At 180 °C, the solid content rapidly rose from 9.2 g/L to 26.9 g/L in the first stage (0-30 min) and decreased to 17.0 g/L in the second stage (>30 min). This behavior was ascribed to the fact that after 30 min at 180 °C, the removed pentoses were largely converted into small molecules such as furfural (manuscript Fig. 4) and organic acids. The evaporation of volatiles such as furfural during solid content determination at 105 °C resulted in underestimated solid content.

As shown in Fig. 4b, when the reaction time is 0 min, the increase of solid content with increasing temperature was consistent with the trend observed for hydrolysis rate. What's more the time of autohydrolysis in the first stage decreased from 60 to 30 min, indicating that an increase of temperature could significantly increase the rate of autohydrolysis. In the second stage of the insulation process, temperature continued to play a key role. At different temperatures, some hydrolysis products were converted into volatiles, which led to a slow rise of solid content in the second stage and even a solid content decrease at 180 °C. Notably, the solid content at 180 °C was lower than that obtained at 160 °C. All the analysis shows that temperature was the main factor affecting solid content and hydrolysis extent.
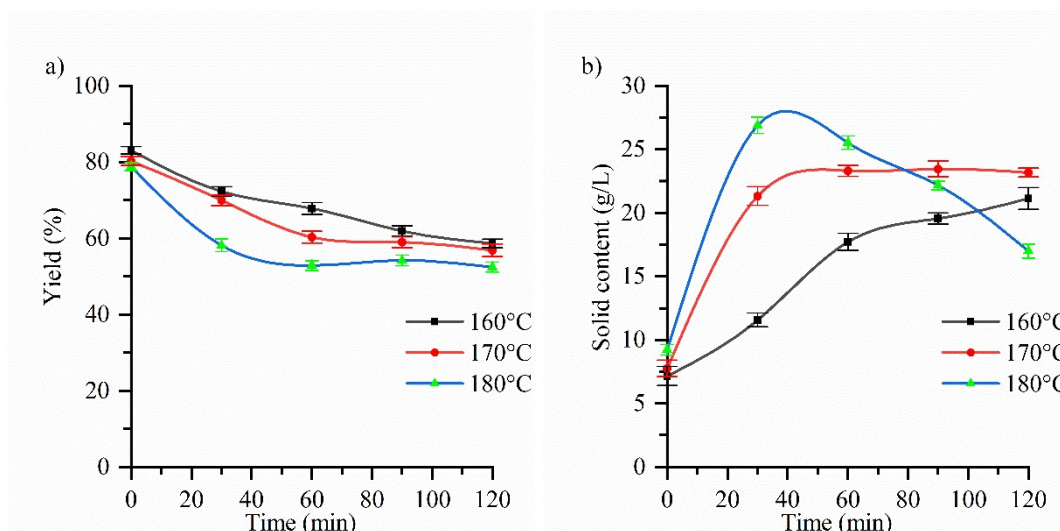
Fig.4 The influence of temperature and time on (a) yield and (b) solid content of hydrolysate

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