

One-Step Acid Bleachable Pretreatment with a Recyclable Acid Hydrotrope and Chlorate for Biomass Valorization

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Abstract

Pretreatment is a necessary step to converting lignocellulosic biomass from its native form into a more accessible form for the value-added utilization of its main components. Herein, we developed a one-step acid bleachable pretreatment method using a recyclable acid hydrotrope (*p*-toluenesulfonic acid, *p*-TsOH) and chlorate to achieve the fibers bleaching and lignin extraction simultaneously. Under a mild condition (C80T80t45), 84.33% of hemicellulose and 76.79% of lignin were dissolved out. The obtained dispersed fibers with a high whiteness of 60.13% ISO can be used for papermaking or ethanol production. The results from quasi-simultaneous enzymatic saccharification and combined fermentation (Q-SSF) of the pretreated substrate indicated that the ethanol concentration and yield reached to 39.30 ± 0.57 g/L and $82.36 \pm 1.15\%$, respectively. What's more, according to the results of lignin characterization, the aromatic rings in extracted lignin were opened forming dicarboxylic acids as well as derivatives due to the oxidation of chlorate, which is beneficial for its catalytic upgrading and composites preparation. Therefore, this study is important to valorization of lignocellulosic biomass.

Introduction

As the most abundant renewable resource on the earth, lignocellulosic biomass is a promising candidate to replace petroleum feedstock. It contains three major components, namely cellulose, hemicellulose, and lignin (Shao et al., 2022). According to the species, the content of cellulose is about 30 ~ 50% (Pattnaik et al., 2022). Cellulose, a natural linear polymer (polysaccharide) with a molecular repeat unit comprised of a pair of d-anhydroglucose ring units joined by β -1,4-glycosidic bonds (Boonmahitthisud et al., 2022), can be used for traditional papermaking or converted to reducing sugars after enzymatic hydrolysis for fuels and chemical products preparation (Weerasai et al., 2018). Nevertheless, due to the inherent complex polymer structure of lignocellulose, highly-ordered hydrogen bonds, and the indigestibility of lignin restrict the utilization of cellulose (Hongdan et al., 2013). Therefore, an effective pretreatment is necessary to remove the natural barrier for components separation and comprehensive utilization (Cardona et al., 2018).

Lignin, the most abundant natural bioresources of aromatic compounds, has shown great potential in bio-jet fuels and compound material preparation (Jin et al., 2022). The changes in structural features during extraction directly affect its application and upgrade conversion. In papermaking industry, lignin was usually dissolved out by alkali and sulfite (Wang & Zhao, 2021). The pulp can be obtained via bleaching, pulping, and sieving process (Mannai et al., 2018). However, a high temperature of $150^{\circ}\text{C} \sim 170^{\circ}\text{C}$ was used during cooking (Chio et al., 2019). What's more, the serious condensation of lignin molecules led to the reduction of its utilization value. In order to prevent lignin structure from being damaged during pretreatment, many lignin extraction methods have been developed such as using organic solvents (ethanol, acetic acid, and gamma-valerolactone), ionic liquids, and deep eutectic solvents (DES) (Zhuang et al., 2016). However, there are some challenges for biomass pretreatment using organic solvents concluding high cost, high energy consumption, and flammability (Yang et al., 2022). The industrial application of ionic liquids and DES in biomass pretreatment is also limited due to the high

cost and high treat temperature (120 ° C ~ 150 ° C) (Weerachanchai & Lee, 2017) (Wang & Lee, 2021). Therefore, it is essential to explore a pretreatment approach that can extract lignin under mild conditions.

In the previous studies, we used a recyclable acid hydrotrope (*p*-toluenesulfonic acid, *p*-TsOH) to selectively extract lignin and hemicellulose under a temperature range from 80 ° C to 90 ° C (Ji & Lv, 2020). For example, the removal of lignin in hybrid poplar wood reached 90% under a mild condition (80 ° C, 20 min). The obtained lignin exhibited a high content of β -O-4 bonds. The acid hydrotrope was recycled with a commercial recrystallization technique (Ji et al., 2017). The pretreated substrate containing abundant cellulose was treated via short time (10 s) ultrasonic pretreatment to form dispersed pulp directly. The obtained fibers can be used for traditional papermaking and also producing ethanol by enzymatic fermentation (Ji et al., 2020). Besides, in the process of industrial paper bleaching, NaClO is one of effective reagents for pulp bleaching. NaClO₂ is used to separate lignin to obtain fiber materials under acid conditions (Han et al., 2022). What's more, NaClO can facilitate the ClO₂ release from NaClO₂ to further improve bleaching ability.

In this study, we combined the function of removing lignin by acid hydrotrope and the ability of pulp bleaching by chlorate to develop a one-step acid bleachable pretreatment method. The physical properties and enzymatic digestibility of obtained fibers under different pretreatment conditions were explored. Subsequently, the produced pulp was converted into ethanol by a Q-SSF process. At the same time, the structure of the extracted lignin was characterized by FTIR, TGA, 2D-HSQC NMR, and GPC.

Materials And Methods

Materials

Poplar wood chips were kindly provided by Shandong Sun Paper Industry Joint Stock Co., Ltd (Jining, China); Sodium citrate, Sodium hypochlorite, Sodium Chlorite, and *p*-TsOH were purchased from Macklin Biochemical Co., Ltd (Shanghai, China); H₂SO₄ (95% ~ 98%, wt. %) was bought from Yantai Far Eastern Fine Chemical Co., Ltd (Yantai, China); Cellulase (Cellic®Tec2) was obtained from Novozymes (Beijing, China). All chemical reagents used were of analytical grade.

Pretreatment

2 g of poplar wood powder with sizes of 40 ~ 60 mesh, 0.5 g NaClO₂, and 10 ml of NaClO solution were added to the *p*-TsOH solution (80 wt. %) in a round bottom flask, and the mixture was heated in an oil bath. At the end of the reaction, the solids and freely drainable spent liquor were separated by a Büchner funnel using filter paper (Hangzhou Specialty Paper Co., Ltd.). After washing with deionized water and freeze drying, the solid was used for component analysis and enzymatic hydrolysis. The lignin in spent liquor was precipitated by dilution with a certain amount of water, then dialyzed, freeze-dried for next characterization. A milled wood lignin (MWL) was used for a comparison.

Component analysis of the pretreated substrate was conducted according to the method from the National Renewable Energy Laboratory. In short, dry fiber materials (0.3 g) and 3 ml H₂SO₄ (72%) were added in the pressure battle to soak for 2 h. After adding 84 ml of ultrapure water, the hydrolysis reaction was carried out at 121 ° C for 1 h. The concentrations of monosaccharides in the liquor were measured on a high-performance liquid chromatography (HPLC, Ultimate 3000, Thermo Scientific) system equipped with a separating column (Aminex HPX- 87H, Bio-Rad, CA, United States) and a refractive index detector (RID-20A, Shimadzu, Japan).

Fibers quality analysis

Fibers quality analysis was performed on a Fiber Quality Analyzer (LDA96, Canada OPTEST Company). Handsheet with a basis weight of 60 g/m² was prepared according to the SCAN-C 26:76 standard. The whiteness of pulp was obtained by measuring the whiteness of handsheet with a whiteness tester (YQ-Z-48B, Hangzhou Qingtong Boke Automation Technology Co., Ltd. Hangzhou, China).

Enzymatic hydrolysis and Q-SSF

Enzyme hydrolysis was carried out on a shaking bed incubator at 200 rpm and 50 ° C. The pretreated substrate and cellulase loading were 2 g /100 ml sodium citrate buffer (pH = 4.8) and 15 FPU CTec 2/g glucan, respectively. During the saccharification procedure, 400 µl of the supernatant was taken out to measure the concentration of glucose. The ethanol fermentation was preceded through a Q-SSF with a high pretreated substrate loading (15%, wt. / volume). After enzymatical pre-hydrolysis for 6 h to release a certain amount of monosaccharide, the activated yeast seeds (Angel Yeast Co., Ltd. Hubei, China) at loading of 0.6 g dry cell/g substrate were inoculated into the partially hydrolyzed slurry to initial the Q-SSF for high titer ethanol production. The concentration of ethanol was detected using a HPLC system equipped with a refractive index detector (RID-20A, Shimadzu, Japan).

Lignin characterization

For the FTIR analysis, the lignin was scanned on an infrared spectrometer (ALPHA, BRUKER, Germany) with a wavenumber range from 500 to 4000 cm⁻¹, a scanning resolution of 4 cm⁻¹, and a frequency of 60 times per second.

The TGA measurement was performed on a thermogravimetric analyzer (STA449-F3, NETZSCH Scientific Instruments Trading CO., Ltd., Germany) in nitrogen atmosphere. The temperature range and heating rate were 35 ° C ~ 800 ° C and 10 ° C /min, respectively (Li et al., 2020).

For 2D-HSQC NMR detection, 40 mg of lignin sample was dissolved in 0.5 ml DMSO-*d*₆. The measurement was performed on Bruker 600 MHz spectrometer (AVANCE III, BRUKER, Germany) at 25 ° C (Ji et al., 2017).

The weight-average (M_w) and number-average (M_n) molecular weight of lignin were measured on a gel-permeation chromatography (GPC, OMNISEC, Waters CO, USA). The acetylated lignin (4 mg) was

dissolved in 2 mg/mL tetrahydrofuran (THF). The solution-state samples were analyzed by a chromatography column (Styragel® HR 4 THF, 7.80×300 mm, Ireland) with an injection volume of 20 µl and a column temperature of 35 ° C. THF was used as the mobile phase and the flow rate was 0.60 ml/min. Polystyrene was used for calibration(Ji et al., 2020).

Results And Discussion

Pretreatment

Figure 1 shows the effects of different pretreatment conditions on the changes in the contents of three components of biomass. Increasing pretreatment temperatures and times significantly promoted the removal of lignin and hemicellulose. For example, the dissolution of hemicellulose increased from 70.86–81.14% at pretreatment temperature of 70 ° C when the pretreatment time was prolonged from 15 min to 45 min. Similarly, the removal of lignin also increased from 57.98–66.30% under same condition. With same pretreatment time of 45 min, increasing temperature from 70 ° C to 80 ° C, the removal of lignin and hemicellulose increased with 3.19% and 10.49%, respectively. Under a mild condition (C80T80t45), 84.33% of hemicellulose and 76.79% of lignin were dissolved out. In addition, 87.44% ~ 95.10% of original cellulose retained in the pretreated substrates suggesting that the one-step acid bleachable pretreatment method could be used to perform biomass pretreatment. The obtained pretreated substrate was subsequent treated via 10 s ultrasonication to form a dispersed fibers pulp for papermaking or ethanol production. The collected lignin was characterized to evaluate its structural properties.

Fibers quality analysis

After 10 s ultrasonication, the biomass matrix was dissociated as shown in Fig. 2 (a). Increasing pretreatment severity improved lignin dissolution resulting in complete disperse of fibers. Under the pretreatment condition of T80 t45, the fibers were completely dispersed in water forming pulp. The obtained fibers showed a light color with a whiteness of 60.13% ISO by the oxidative bleaching of NaClO and NaClO₂. Meanwhile, the color of the collected lignin was lighter than that of black liquor from traditional papermaking.

The fibers quality of the fibers was analyzed in Table 1. The content of number-average fine fibers increased from 66.30–73.28% when the pretreatment severity increased from T60 t30 to T70 t30, which may be attributed to long fibers dissociation from biomass matrix. However, a high pretreatment severity (T80 t45) inevitably caused the hydrolysis of fibers by cleaving the β-1, 4-glycosidic bonds resulting in a low content of fine fibers of 62.24%. Similarly, the widths of the fibers decreased from 35.68 nm to 24.29 nm as the pretreatment severity was enhanced from T70 t15 to T80 t45. Through the traditional paper fabrication, the handsheets were prepared with the obtained fibers and their whiteness was also measured as shown in Fig. 3. The fibers obtained from the pretreatment of T80 t45 exhibited a good paper forming performance. The whiteness of handsheet reached to as high as 60.1% ISO. The results indicated that a high level of fibers dispersion facilitated the paper formation by the increasing the

intramolecular hydrogen bonds between the hydroxyl groups of cellulose molecular chains. Therefore, the one-step acid bleachable pretreatment was very effective approach to obtain pulp from biomass under mild conditions. Although a low ratio of length to width of the fibers (< 45) maybe face the challenges of mechanical properties reduction of papers when compared with other commercial pulp, blending the fibers with commercial pulp could significantly reduce the consumption of commercial pulp for industrial papermaking. What's more, due to containing less lignin and hemicellulose contents, the fibers with a high whiteness may be suitable for the preparation of dissolved pulp.

Table 1
Analysis of fibers quality obtained from different pretreatment conditions

Sample	Fines A%	Fines B%	Lc (w) mm	Lc (n) mm	Width μm
T60t30	66.30	4.07	0.48	0.32	35.68
T70t15	71.09	0.68	0.40	0.29	36.45
T70t30	73.28	1.90	0.46	0.30	34.17
T70t45	58.19	1.06	0.43	0.31	31.06
T80t45	62.24	1.03	0.41	0.31	24.29

Fines A: Number-average fine fiber content; Fines B: Weight-average fine fiber content; Lc (n): Number-average fiber length; Lc (w): Weight-average fiber length; Width: Fiber width

Enzymatic hydrolysis and ethanol fermentation

The pretreated substrates from different pretreatment conditions were enzymatically hydrolyzed to evaluate their cellulase digestibility. A certain amount of hydrolyzed sample was taken out at intervals to detect the concentration of glucose during enzymatic hydrolysis for the calculation of the saccharification yield of glucan. The results of enzymatic saccharification of pretreated samples are presented in Fig. 4. Obviously, increasing the pretreatment severity improved the enzymatical hydrolysis of the pretreated substrate. Because a high pretreatment severity caused the dissolution of most of lignin and hemicellulose, the cell walls thus became more porous under this pretreatment condition. The removal of barrier from natural matrix resulted in high cellulase digestibility. The enzymatic hydrolysis efficiency achieved at $89.6 \pm 1.9\%$ for the pretreated substrate from the pretreatment condition of C80 t45 after 72 h. Therefore, an optimal pretreatment condition of C80 t45 was determined to pretreat raw biomass. The obtained pretreated substrates were employed to produce ethanol via a Q-SSF process.

According to the results in Fig. 4, an optimal pretreatment condition (C80 T45) for enzymatic hydrolysis was determined. The pretreated substrate obtained from C80 T45 was pre-hydrolyzed enzymatically to release a certain amount of monosaccharide. After inoculating activated yeast seeds into the partially hydrolyzed slurry, a Q-SSF was initiated to produce high titer ethanol. Figure 5 displays the changes in ethanol yield and concentrations of glucose and ethanol during fermentation. After 6 h of

saccharification of the pretreated substrate, the glucose concentration reached as high as 60.50 ± 0.77 g/L ensuring an adequate carbon source for subsequent fermentation. At this time, yeast seeds were inoculated in liquefied sample for fermentation. As shown in Fig. 8, the concentration of glucose decreased rapidly and the concentration of ethanol increased within 24 h of fermentation, indicating that part of glucose has been rapidly converted into ethanol under aerobic conditions. The highest ethanol concentration (39.30 ± 0.57 g/L) was detected after 60 h fermentation. The ethanol yield achieved at $82.36 \pm 1.15\%$ based on the theoretical yield. However, the terminal ethanol concentration decreased slightly with the extension of fermentation time to 72 h. This may be that ethanol was involved in the metabolism of yeast with the depletion of monosaccharides. In a word, *p*-toluenesulfonic acid/chlorate pretreatment can effectively extract lignin in lignocellulose biomass under mild conditions and improve the enzymatic hydrolysis of glucan. Therefore, it is important to the valorization of lignocellulosic biomass.

Lignin characterization

The structural changes in the extracted lignin samples obtained under pretreatment conditions were analyzed by FTIR spectroscopy as shown in Fig. 6. The signals were assigned based on a previous literature (Ji et al., 2017). The characteristic peak at 3450 cm^{-1} was assigned to the hydroxyl (-OH) of aromatic or aliphatic species. The absorption peak at 2937 cm^{-1} was attributed to the C-H asymmetric vibrations of methyl ($-\text{CH}_3$). The absorption peak at 2840 cm^{-1} was C-H symmetric vibrations of methylene ($-\text{CH}_2-$). The absorption peaks from 1000 cm^{-1} to 1700 cm^{-1} were weakened and even disappeared in the FTIR spectroscopy of obtained lignin via *p*-TsOH/chlorate pretreatment. Figure 5 shows the characteristic absorption peaks of MWL at 1605 cm^{-1} (the stretching vibration of aromatic ring and carbonyl groups), 1510 cm^{-1} (the stretching vibration of aromatic ring skeletal), 1420 cm^{-1} (the aromatic ring C-H deformation stretching vibrations), 1120 cm^{-1} (the stretching vibration of C=O ratios of syringyl (S) units C-O groups), and 1030 cm^{-1} (the C-H plane deformation stretching vibration of aromatic ring). However, the characteristic peaks of aromatic ring above were not found in their corresponding positions for the extracted lignin during *p*-TsOH/chlorate pretreatment. Therefore, the aromatic ring structure of lignin was broken due to oxidation reaction. It may be that some ester compounds with carbonyl C=O or substances containing quinone groups were generated owing to oxidative ring opening of aromatic functional groups, which was confirmed with the enhanced absorption intensity at 1720 cm^{-1} . What's more, the characteristic peak at $1640 \sim 1650\text{ cm}^{-1}$ was assigned to *o*-quinone structure according to a previous publication (Ouyang et al., 2019). A study about the structural changes in treated Chinese fir lignin by using acidic NaClO_2 demonstrated that ClO_2 reacted with aromatic hydroxyl of lignin to form the monomethyl muconate or the *o*-quinone structure (Ouyang et al., 2019). The results suggested that the obtained lignin with partial oxidation was very helpful for its subsequent chemical modification and utilization (Ji et al., 2018).

Figure 7 displays the TG and DTG curves of lignin samples with a temperature range from $50^\circ\text{C} \sim 800^\circ\text{C}$. The weight losing process is divided into four stages from the TG and DTG curves. During the initial

thermal decomposition stage (35 ° C ~ 150 ° C), the weight losing was not obvious mainly due to release of moisture or lose of small molecule impurities. During the second stage (150 ° C ~ 280 ° C), the weight lose rate increased gradually due to initiated lignin depolymerization. Then aromatic ether bonds in lignin were opened to produce various phenolic substances. During the main weight losing range (280 ° C ~ 550 ° C), the appearance of the maximum peak on the DTG curve indicated that the major structures of lignin were decomposed. For instance, the benzene ring and C-C bond began to be cleaved to generate H₂O and small molecule volatiles. During the final stage (550 ° C ~ 800 ° C), both TG and DTG curves were smooth, indicating that the benzene rings of lignin were decomposed or aromatized under the high temperature to form a stable coke residue finally. The results indicated that the temperature at maximum decomposition rate of the extracted lignin was lower than that of MWL. This may be attributed to the degradation of lignin aromatic ring during pretreatment as the analysis from FTIR results.

The chemical structural properties of the lignin samples obtained from different pretreatment conditions (T70 t15, T70 t45, and T80 t45) were analyzed by 2D HSQC NMR. Meanwhile, a MWL was used for a comparison. Figure 8 (a) and (b) show the structural signals of the side chain region (δ_C/δ_H 50.0–90.0/2.50-6.00 ppm) and benzene ring region (δ_C/δ_H 100.0-150.0/5.50–8.50 ppm) of lignin, respectively. For MWL, the typical interunit linkages, such as methoxy groups (OMe, δ_C/δ_H 55.6/3.71 ppm), β -aryl-ether bonds (β -O-4', A), resinol (β - β' , B), and phenylcoumaran (β -5', C), were detected in the side chain region. For the extracted lignin, the differences in cross signal intensities of these chemical bonds indicated that their contents in lignin molecules have changed. Specifically, the signals response of C _{α} -H _{α} , C _{β} -H _{β} , and C _{γ} -H _{γ} correlation in β -O-4' substructure (A) at δ_C/δ_H 71.9/4.85 ppm, 84.4/4.4 ppm together with 85.6/4.2 ppm and 59.4/3.7 ppm were weakened with the increased pretreatment severity. This may be due to the cleavage of β -O-4 bonds in lignin molecules caused by the *p*-TsOH hydrolysis and the effective chlorine (ClO₂) oxidation. Moreover, the C _{α} -H _{α} and C _{γ} -H _{γ} correlations in resinol (β - β') substructures at δ_C/δ_H 87.7/5.5 ppm and δ_C/δ_H 63.4/3.6 ppm also showed similar phenomenon. The oxidation of ClO₂ may have caused the cleavage of C-C bonds between benzene rings resulting in the depolymerization of lignin.

In the aromatic region, the cross-signals from syringyl (S) and guaiacyl (G) units were easily detected for MWL. For example, the cross-signal at δ_C/δ_H 103.8/6.69 ppm correlated the C_{2,6} - H_{2,6} in S units. The G units showed their correlations of C₂-H₂ at δ_C/δ_H 110.9/7.00 ppm. Besides, *p*-coumaric acid (PCA) was also found with its correlations of C_{2,6} - H_{2,6} and C_{3,5} - H_{3,5} at δ_C/δ_H 130.0/7.46 ppm and 115.4/6.84 ppm, respectively. However, the cross signals at 104.00/6.70 ppm (C_{2,6}-H_{2,6}, S unit), 111.10/6.98 ppm (C₂-H₂, G unit), 114.70/6.71 ppm (C₅-H₅, G unit), and 118.90/6.80 ppm (C₆-H₆, G unit) were not detected in the aromatic region for the extracted lignin, which further confirmed that the benzene rings in lignin molecule were broken during lignin extraction. The possible reactions scheme of the lignin during extraction was shown in Fig. (c), the aromatic rings of monomers in lignin molecules were opened to form dicarboxylic acids as well as derivatives. The C-H deformation vibrations of alkyl chain were clearly observed at 1460 cm⁻¹. Therefore, the obtained lignin containing more carboxyl groups has a huge potential in catalytic upgrading and composites preparation (Upton & Kasko, 2016).

The molecular weight properties of extracted lignin concluding M_w , M_n , and PDI were measured to evaluate its degradation and condensation. The results were shown in Table 2. As the pretreatment severities increased from T60 t30 to T80 t45, the M_w s of extracted lignin decreased from 4077 ± 95 g/mol to 3328 ± 53 g/mol. Meanwhile, M_n s showed a similar trend with M_w s, indicating a significant degradation of lignin during pretreatment. The changes in molecular weight of lignin are usually related to its depolymerization at low pretreatment severities and the recondensation at high pretreatment severities. A high pretreatment severity facilitated the cleavage of β -O-4 bonds in lignin molecules by *p*-toluenesulfonic acid/chlorate. The fragmentation of lignin molecules resulted in the decrease of its molecular weight. Meanwhile, it was clear that no clear increase of molecular weight appeared, demonstrating that a slight recondensation occurred in this pretreatment process. In other words, the depolymerization reaction played a more important role than recondensation reaction during the whole pretreatment. However, PDI of the extracted lignin exhibited an opposite trend with M_w and M_n when increasing pretreatment severities. The potential reason for this could be attributed to the comprehensive depolymerization/ fragmentation of lignins under harsh conditions. These extracted lignin samples with a low molecular weight (M_w , 4077 ± 95 – 3328 ± 53 g/mol) and narrow polydispersity (PDI, 1.22–1.62) may have a huge potential in industrial applications.

Table 2
The M_w , M_n , and M_w/M_n of MWL and lignin samples obtained from different pretreatment conditions.

Samples	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)
T60t30	4077 ± 95	3332 ± 85	1.22
T70t15	3794 ± 121	2943 ± 53	1.27
T70t30	3587 ± 109	2343 ± 43	1.53
T70t45	3472 ± 156	2159 ± 76	1.61
T80T45	3328 ± 53	2051 ± 55	1.62

Conclusion

In this study, a one-step acid bleachable pretreatment method was developed with a recyclable acid hydrotrope and chlorate. Under mild conditions, about 85% of lignin was dissolved out. The pretreated substrate was subsequent treated via 10 s ultrasonication to form a dispersed fibers pulp for papermaking or ethanol production. What's more, according to the results of lignin characterization, the aromatic rings in extracted lignin were opened forming dicarboxylic acids as well as derivatives under the oxidation of chlorate, which is beneficial for its catalytic upgrading and composites preparation. Therefore, this study is important to the valorization of lignocellulosic biomass.

Declarations

Acknowledgements

Not applicable.

Author contributions

Zhen Zhang and Xuehui Shi conducted the experiments; Hairui Ji and Xingxiang Ji designed the experiments; Hairui Ji and Zhen Zhang analyzed the results and wrote the paper. Furong Tao, Xuehui Shi, Zhongjian Tian, and Jiachuan Chen provided guidance for experiment design.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Figures

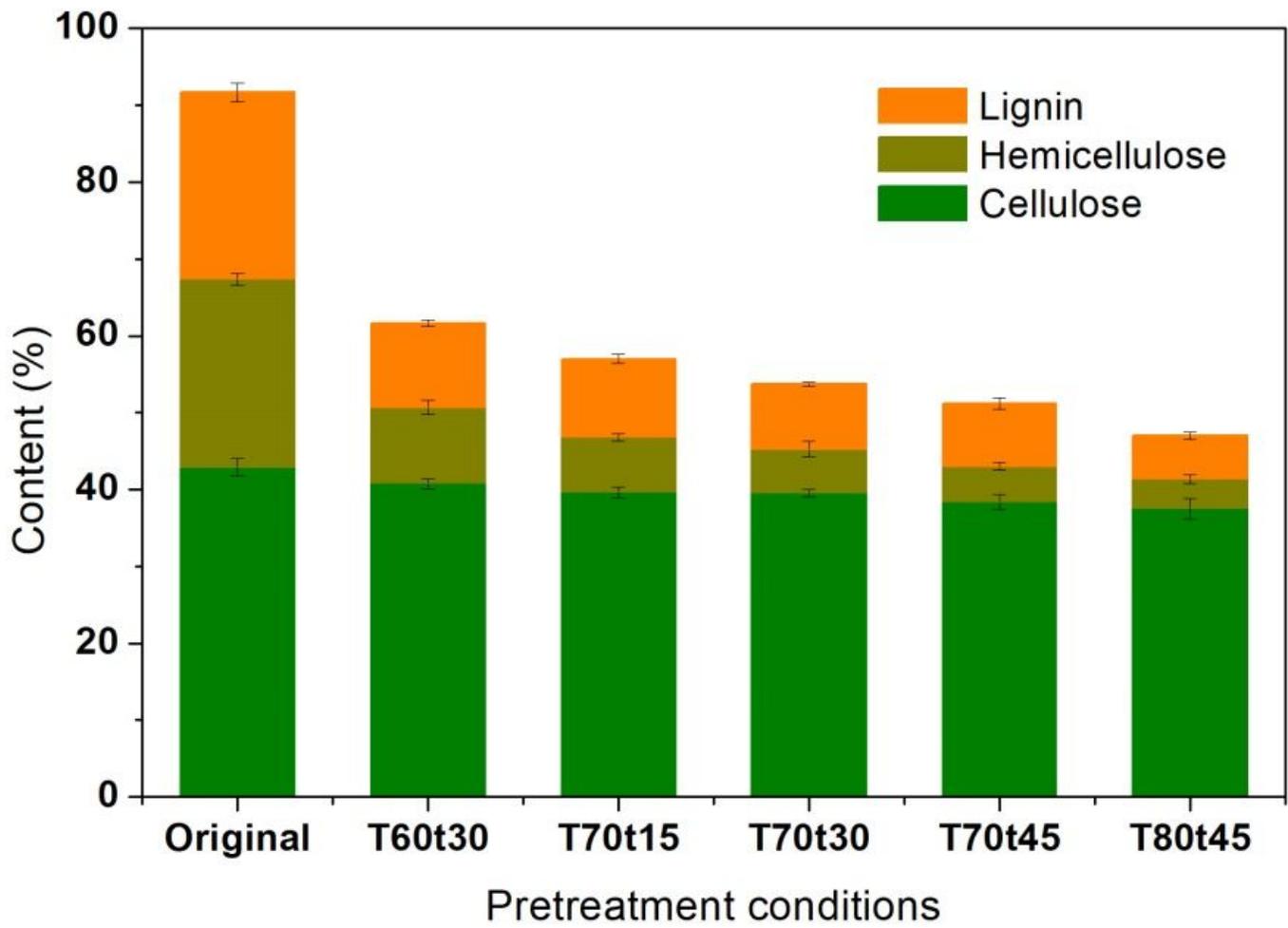


Figure 1

The contents of three components in pretreated substrates (Cx stands for the acid concentration; Tx stands for the pretreatment temperature; tx stands for the pretreatment time).

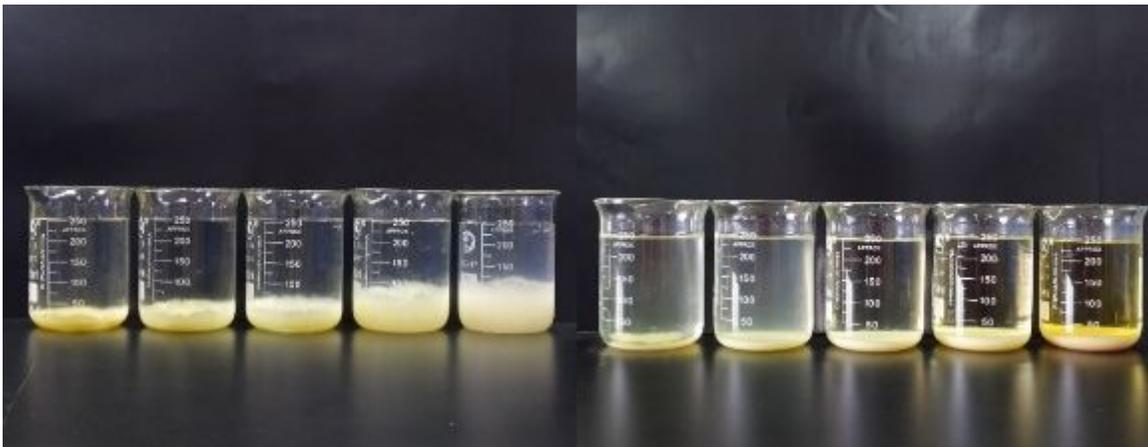


Figure 2

The appearances of the fibers obtained under each condition after 10 s ultrasonication treatment (a) and the collected lignin (b).

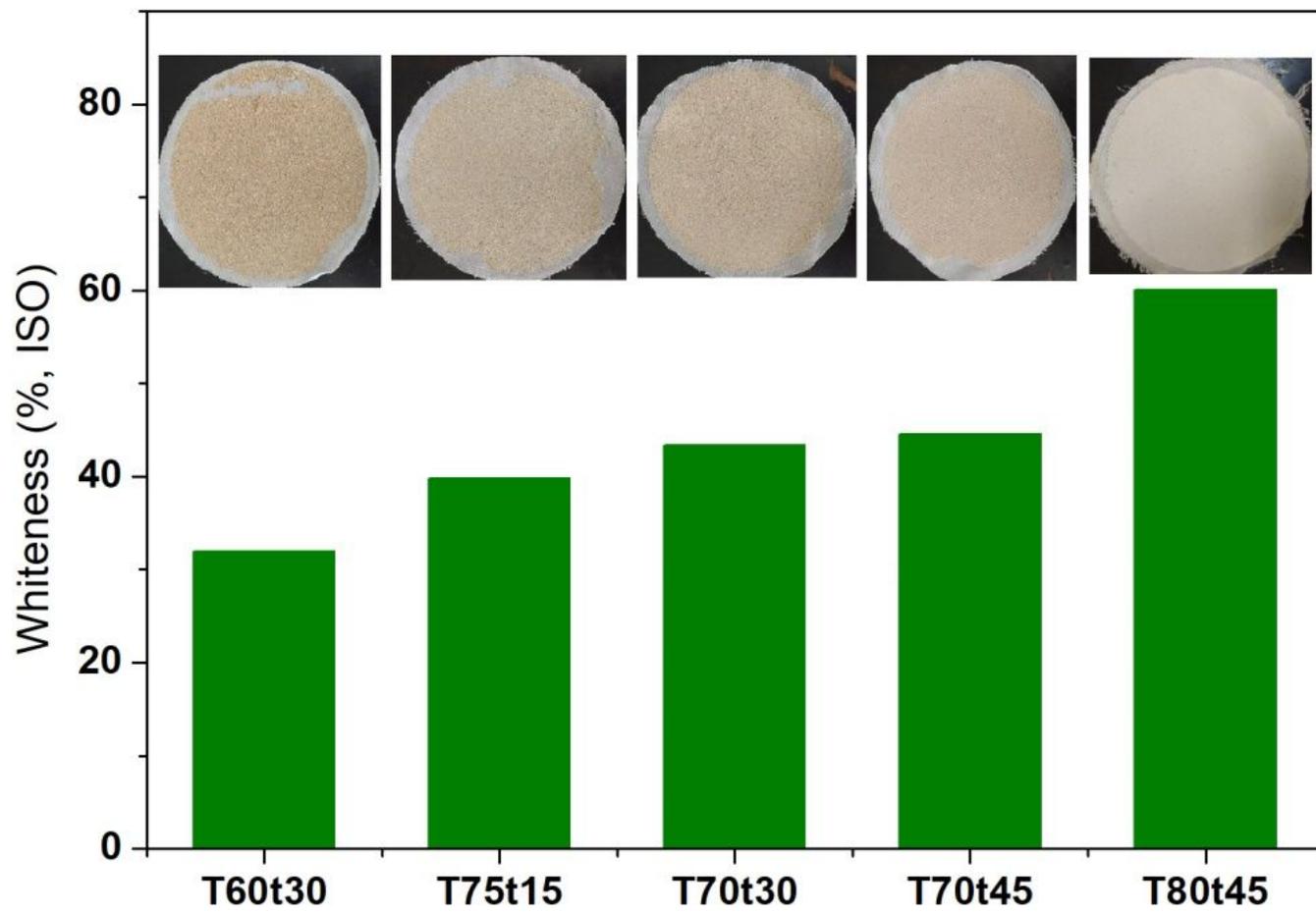


Figure 3

The whiteness of the handsheet under each pretreatment condition

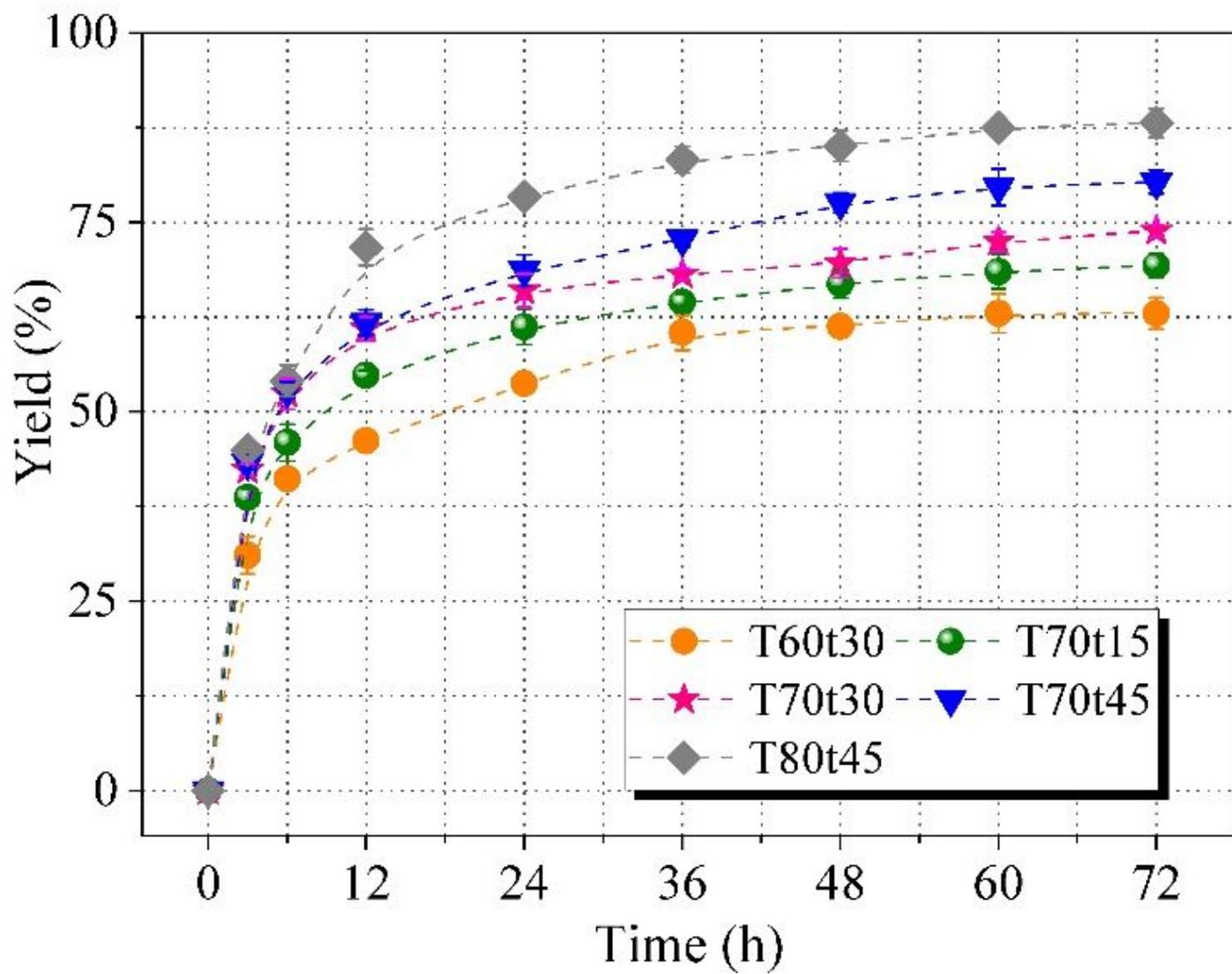


Figure 4

Enzymatic hydrolysis of pretreated substrates obtained from different pretreatment conditions

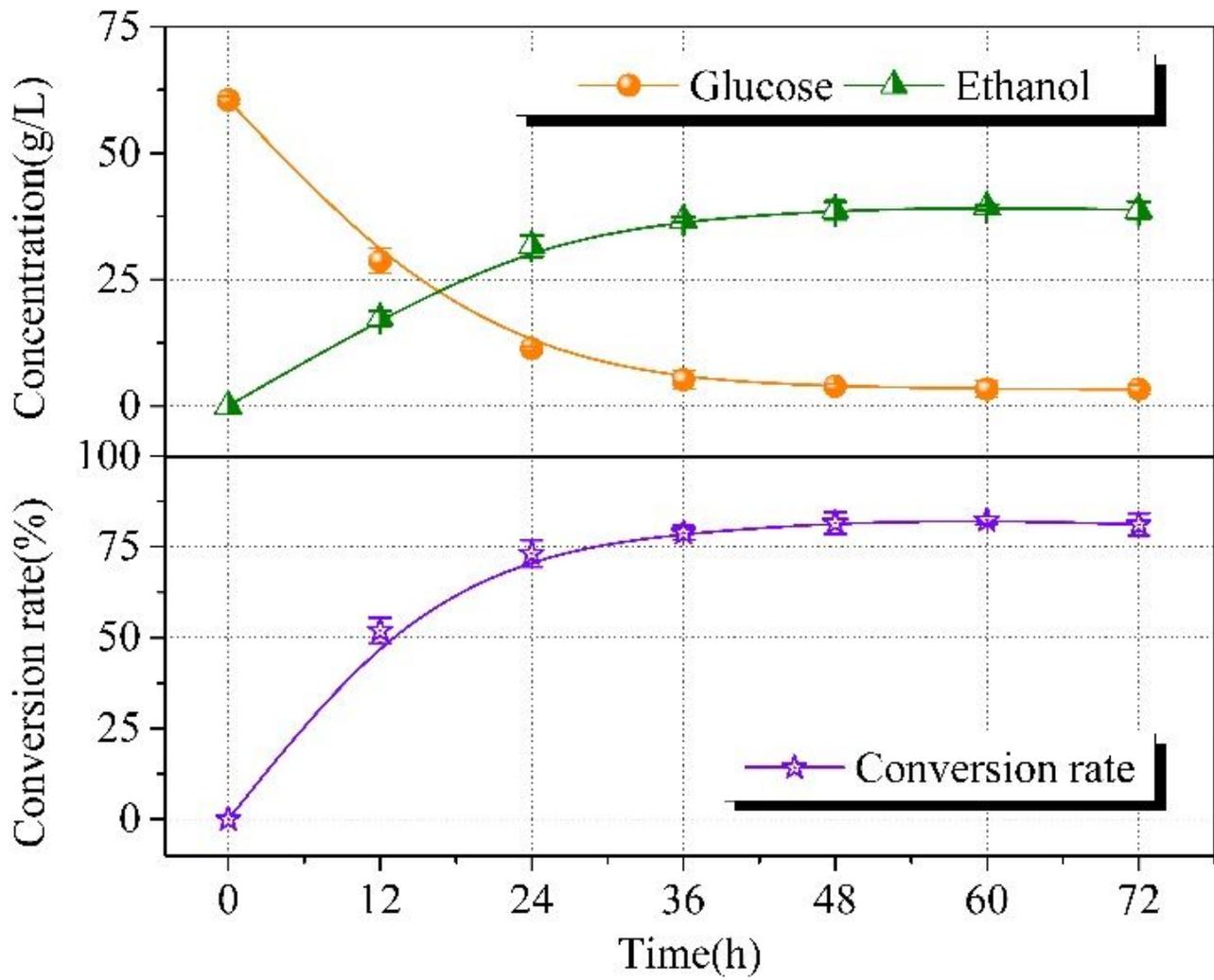


Figure 5

The concentrations of glucose and ethanol and the ethanol yield in the Q-SSF process

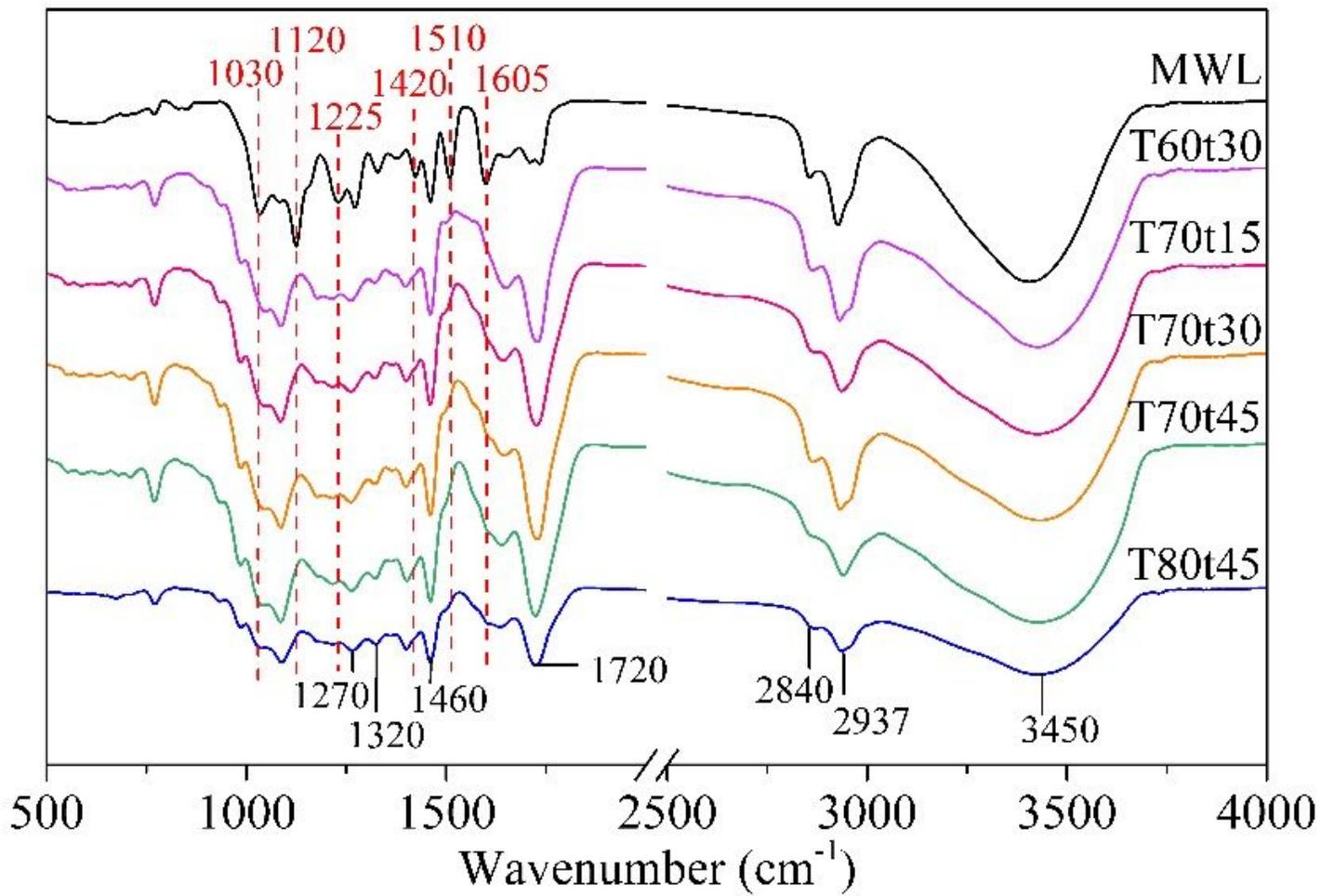


Figure 6

The FTIR spectra of lignin samples.

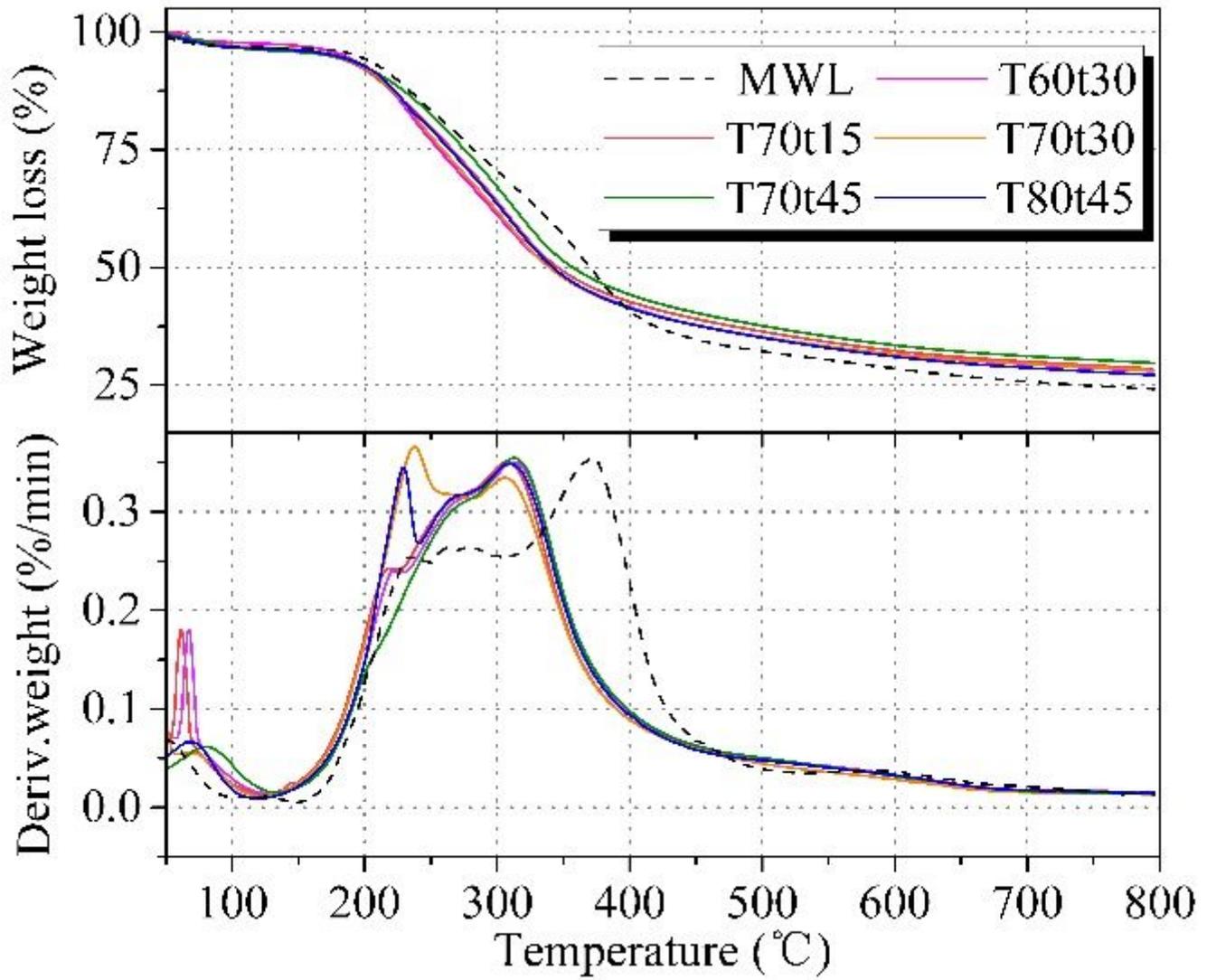


Figure 7

The TGA curves of lignin samples.

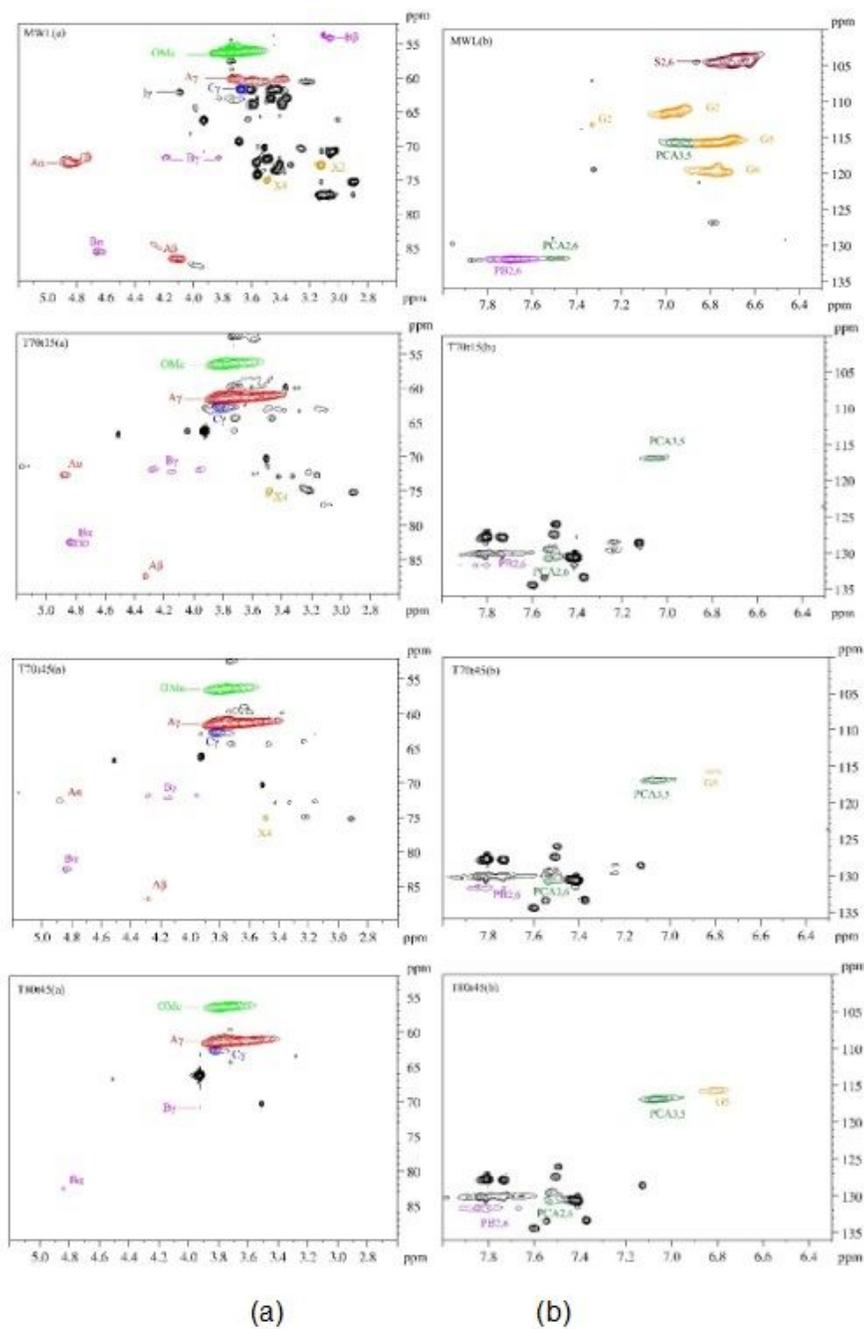


Figure 8

The side chain region (a) and benzene ring region (b) of 2D HSQC NMR spectrum of lignin samples and its possible reactions scheme (c) during extraction.

Supplementary Files

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