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# Integration of hemicellulose pre-extraction and solid alkali-oxygen cooking processes for lignocellulose fractionation with emphasis on xylan valorization

**Yetao Jiang*, Xiaoyu Wang*, Zhen Wu*, Jiaxing Xu*, Lei Hu*,†, and Lu Lin**,†**

*Jiangsu Key Laboratory for Biomass-based Energy and Enzyme Technology, School of Chemistry and Chemical Engineering,
Huaiyin Normal University, Huaian 223300, Jiangsu, China
**College of Energy, Xiamen University, Xiamen 361102, Fujian, China

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**Abstract**−Cooking with active oxygen and solid alkali (CAOSA) is a mild and environmentally friendly method for separation of lignin components. The degradation mechanism of hemicellulose associated with this method has been investigated. It was found that the hemicellulose-derived polysaccharides were directly oxidized rather than hydrolyzed to monosaccharides for degradation. To avoid the undesirable degradation of hemicellulose components by CAOSA, the idea of separating hemicellulose first in the form of xylan to produce xylooligosaccharide was presented by this study. Although hydrothermal autocatalysis has been commonly used in hemicellulose separation, the effects of acid-enhanced hydrothermal method and alkali-suppressed hydrothermal method on hydrothermal autocatalysis were systematically compared for the first time, and it was found that the acid-enhanced method was beneficial for highly selective extraction of xylan. Then, the hemicellulose-removed bamboo was treated with CAOSA process to separate lignin from cellulose. It was found that solid alkali dosage of CAOSA could be evidently decreased for hemicellulose-removed bamboo, which was helpful to reduce the cost of CAOSA. Coupling hemicellulose pre-extraction and CAOSA lignin fractionation strategy, a comprehensive biorefinery case for bamboo biomass could be anticipated.

Keywords: Hemicellulose, Xylooligosaccharide, CAOSA, Hydrothermal Autocatalysis

## INTRODUCTION

Xylooligosaccharide (XOS) is a functional polymeric sugar composed of 2-7 xylose molecules bound together with the $\beta$-1, 4-glucosidic bond [1]. Compared with soybean oligosaccharide, fructose oligosaccharide and isomaltose oligosaccharide commonly used, xylooligosaccharide has its unique advantages [2]. It can selectively promote the proliferation activity of intestinal bifidobacterium, which enhances the efficiency of bifidobacterium and is 10-20 times as much as other oligosaccharides, leading to a very high added value [3]. At present, XOS mainly comes from biomass raw material of corn cob and the related technology is relatively mature, but there are also bottlenecks restricting the industrial development [4]. For example, due to the obvious regional restriction of corn planting, the production of XOS is mostly in the northern corn producing areas, which easily leads to the problem of uneven production distribution and excessive local competition pressure. In addition, corn cob is obviously seasonal, easy to mildew and not easy to store, which brings inconvenience to the stable supply of raw materials for production. Furthermore, the loose structure of corn cob makes it easy to introduce impurities such as lignin derivatives during xylan extraction process, which inevitably increases the subsequent cost of purification.

Bamboo has a relatively high content of xylan, less impurities and low ash content, so it has the potential to be an ideal raw material for preparing XOS. Known as the "kingdom of bamboo", China is rich in bamboo resources, with more than 400 species [5]. The growth period of bamboo is usually 3-5 years, giving a short growth cycle. Bamboo can be felled all the year round, which will not be subject to seasonal restrictions [6]. What is more, bamboo is mainly distributed in the south of the Yangtze River and grows more densely. The area of bamboo forests in Fujian, Jiangxi and Zhejiang provinces alone is nearly half of the whole country, which can achieve good regional complementarity with the corn cob raw materials in the north. Therefore, bamboo as raw material for XOS production has many advantages over corn cob.

Cooking with active oxygen and solid alkali (CAOSA), developed by our group, is a promising alternative approach for both lignocellulose fractionation and biomass pretreatment [7]. In the CAOSA approach, non-toxic and harmless aqueous cooking with oxygen and Mg-based solid alkali is applied instead of undesirable chemicals, such as strong alkalis and sulfides. The pollution control of the CAOSA process is fairly simple, as there is no source to generate sulfurous or odorous compounds. Notably, chemical recovery promises to be relatively simple and does not require causticizing or sintering, which are expensive but unavoidable in the recycling of traditional sodium alkali [8]. Because CAOSA is an environmentally friendly delignification pretreatment involving neither toxic chemicals nor fermentable inhibitors, it is found that the pulp obtained after CAOSA treatment presents particularly advantageous properties for enzymolysis [9] and catalytic valorization [10]. Although CAOSA technique could remove lignin efficiently and protect cellulose well, poor selectivity of hemicellulose component is also obviously based on the results of previous

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†To whom correspondence should be addressed.
E-mail: hulei@hytc.edu.cn, lulin@xmu.edu.cn

studies. After CAOSA treatment, part of the hemicellulose is degraded and dissolved in the cooking liquid, while part remains in the pulp, which significantly reduces the comprehensive utilization efficiency of the three components [11]. The reported pretreatment methods only focus on the promoting effect of cellulosic ethanol, but pay little attention to the separation and conversion efficiency of hemicellulose as well [12,13]. Previous studies have transformed CAOSA wastewater composed of lignin and hemicellulose derivatives to formic and acetic acids [14]. For specific bamboo biomass, integration of hemicellulose pre-extraction and CAOSA processes with emphasis on hemicellulose to produce XOS is proposed in this study. First, hemicellulose degradation pathway during CAOSA process was explored. And then, three extraction methods of hydrothermal autocatalysis, acid-enhanced hydrothermal treatment and alkali-suppressed hydrothermal treatment were compared in detail to obtain the best extraction conditions of xylan from bamboo. Eventually, hemicellulose-removed bamboo was suffered from CAOSA process to separate cellulose and lignin. It was found that solid alkali dosage of CAOSA could be evidently decreased for hemicellulose-removed bamboo, which helped to reduce the cost of CAOSA method. Coupling hemicellulose pre-extraction and CAOSA lignin fractionation strategy, a comprehensive biorefinery case for bamboo biomass was anticipated.

## EXPERIMENTAL

### 1. Materials

Bamboo chips were supplied by Mujiangweihua Perfumery Plant (Jiangmen, China). Glycolic acid and 3-hydroxyl propionic acid were purchased from Aladdin Industrial Inc. (Shanghai, China). All other chemicals were analytical reagents and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Pilot hemicellulose pre-extraction reactions were operated in high-pressure tanks. Kilo-experiments, including hemicellulose pre-extraction and the following CAOSA treatment, were performed in our own-developed ball-shaped digester with an effective volume of 22 L. Details on high-pressure tanks [15] and ball-shaped digester [8] have been described previously.

### 2. Pilot Hemicellulose Pre-extraction Experiments

Typically, bamboo chips (5 g, dry weight, 10-20 mesh) and deionized water (50 mL) at a solid-liquid ratio of 1 : 10 were put into high-pressure tanks and were kept at 180 °C and 20 rpm for 50 min, 60 min, 70 min, 80 min, 90 min, 100 min, 110 min, 120 min and 130 min, respectively. After the reaction, the reaction tank was taken out and cooled rapidly. Then the content of xylose, glucose, acetic acid, furfural, 5-HMF and xylan in the extract was measured. Analogously to the above steps, extra acetic acid equal to 1% of the substrate mass was added in the acid-enhanced hydrothermal method experimental group, and magnesium oxide equal to 0.5% of the substrate mass was added in the alkali-suppressed hydrothermal method experimental group. The heat procedure was conducted in high-pressure tanks until the set time. The subsequent operation was the same.

### 3. Kilo-scale Experiments of Extraction and Cooking

Bamboo chips (1 kg) and water (10 kg) were added to a ball-shaped digester to pre-extract hemicellulose under the optimum conditions. After the reaction, solid/liquid separation was carried out. The pretreated bamboo, MgO (120 g), and water (4 kg, taking the amount of pretreated bamboo moisture into account) were added to a ball-shaped digester as well, and the apparatus was pressurized with 2 MPa $O_2$. The CAOSA process was performed at 165 °C for 3 h. After the reaction, the cooking liquor was separated from the solid bamboo pulp for further analysis. The bamboo pulp was washed repeatedly and filtered by using a filter-bag of 100 mesh to give a clean pulp for further analysis.

### 4. Qualitative and Quantitative Analysis

Qualitative analysis of degradation products was identified as their trimethylsilylated derivatives using GC-MS. First, the cooking liquor was adjusted to pH 11 by ammonia. Then the supernatant was evaporated followed by dissolving with 0.1 M HCl. The solution was evaporated as well, followed by freeze-drying. The residual was silylated with pyridine-hexamethyldisilazane-chlorotrimethylsilane (10 : 2 : 1) at room temperature for 3 hours. Quantitative analysis of the main degradation products was carried out by adopting an external standard method of high performance liquid chromatography (HPLC). Because the components in cooking liquor were very complicated, only glucose, xylose, glycolic acid, hydracrylic acid, formic acid and acetic acid concentrations of the cooking liquor were quantified. To determine the content of glucan and xylan, the obtained supernatant was hydrolyzed by 4 wt% $H_2SO_4$ according the Analytical Procedure of National Renewable Energy Laboratory (NREL) of the United States. Content of cellulose, hemicellulose and lignin was tested referring to the method given by the NREL as well.

HPLC analysis was performed on an Waters 2695 Separation Module equipped with a refractive index detector and a Bio-Rad Aminex HPX-87H ion exclusion column (300 mm×7.8 mm). The column oven temperature was 65 °C, and the mobile phase was 5 mM $H_2SO_4$ at a flow rate of 0.6 mL/min. External standard method by peak height was applied to quantify here. GC-MS analysis was performed with Thermofisher Trace 1300 & ISQ LT GC-MS instrument with a TR-5MS column (15.0 m×250 μm×0.25 μm). The following programmed temperature was used in the analysis: 313 K (2 min)-10 K/min-553 K (2 min). The carrier gas was He with a flow rate of 1.2 mL/min and the split ratio was 1 : 100. The mass spectra were obtained by electron impact ionization (EI), at an electron energy of 70 eV and with a 25 μA emission current.

## RESULTS AND DISCUSSION

### 1. Hemicellulose Degradation Pathway During CAOSA

The content of the three major components in the bamboo raw materials used in this study was cellulose 43.4 wt%, hemicellulose 22.3 wt%, and lignin 27.6 wt%. The pulp yield after cooking of CAOSA was 51.3 wt%, and the content of the three major components in the pulp was cellulose 71.5 wt%, hemicellulose 20.3 wt%, and lignin 4.6 wt%. Accordingly, the lignin removal rate reached 91.5%, while the loss rate of cellulose and hemicellulose was 15.5% and 53.3%, respectively. Considering the pulp loss caused by washing pulp, the actual loss rate of cellulose and hemicellulose might be lower. However, more than half of hemicellulose components were degraded in the process of CAOSA for bamboo biomass, so

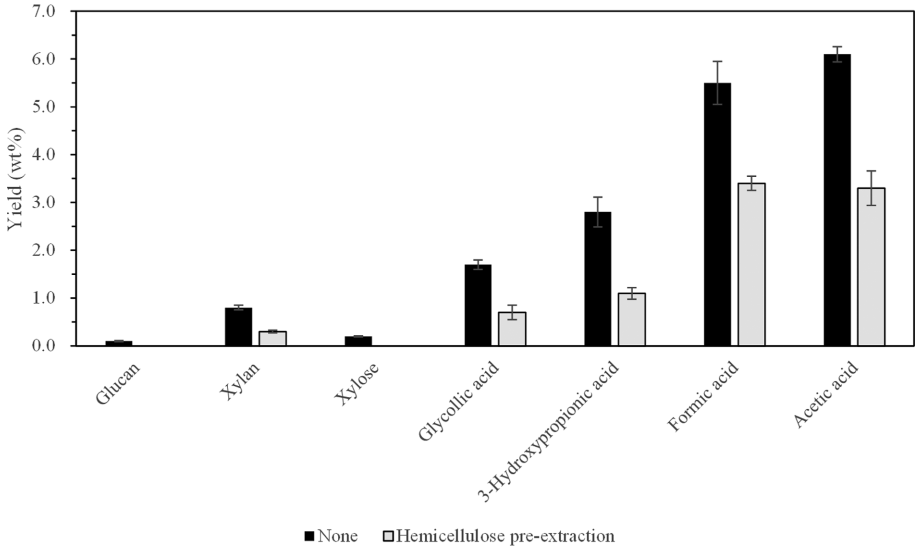


**Fig. 1. Effect of hemicellulose pre-extraction on the yield of sugars and acidic degradation products in the cooking liquor of CAOSA.**

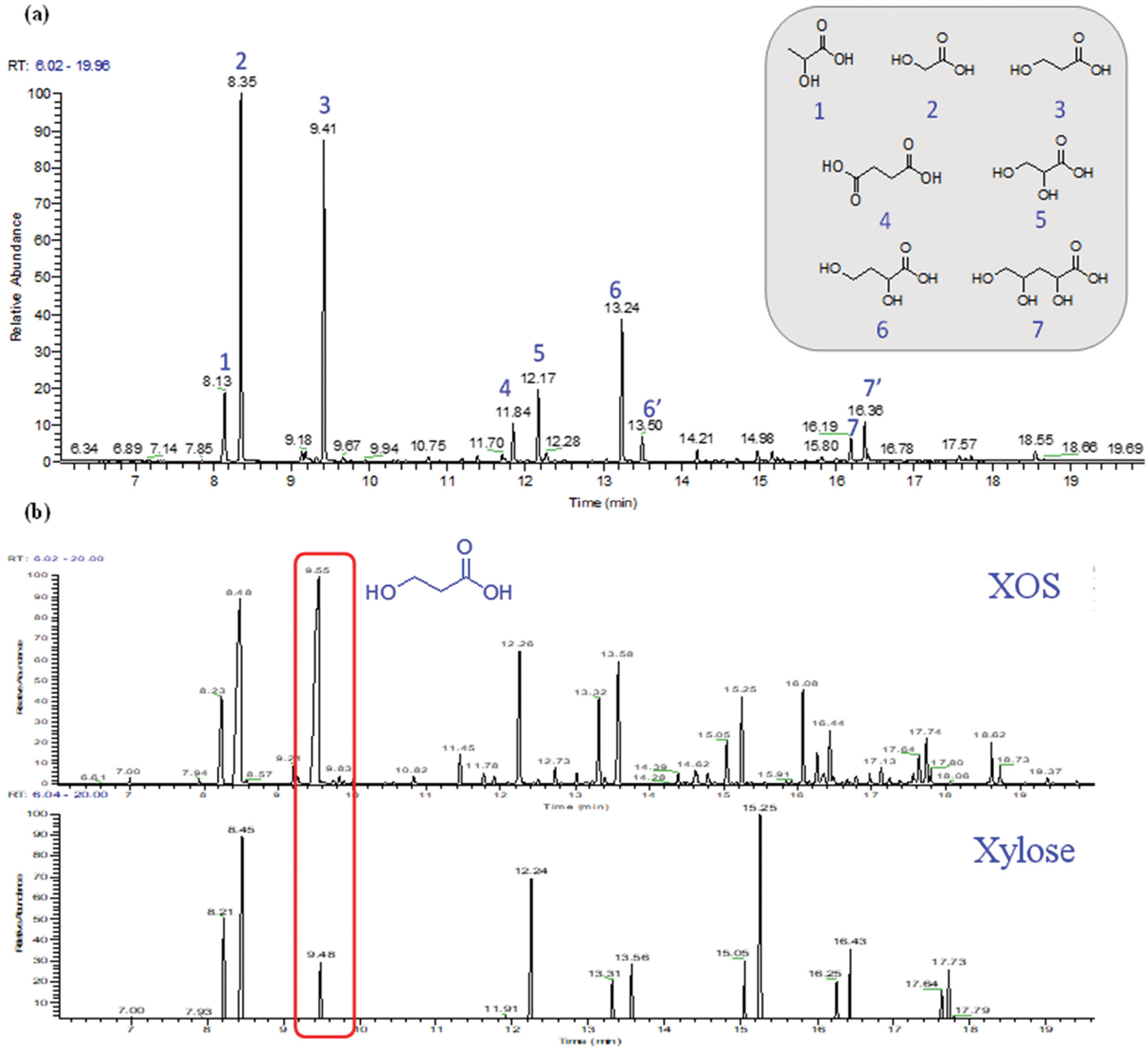


**Fig. 2. (a) Identification of degradation products in the cooking liquor as their trimethylsilylated derivatives by GC-MS; (b) detection of degradation products as their trimethylsilylated derivatives by GC-MS using xylose and XOS as the model compounds.**

it was necessary to explain the hemicellulose degradation mechanism in the cooking process.

In previous study, degradation products of typical CAOSA cooking liquor were analyzed [16]. One of the possible sources of these degradation products was hemicellulose components lost during cooking. To investigate the effect of hemicellulose on the cooking process, bamboo chips were treated with hydro-thermal treatment at 180 °C for 1 h before CAOSA processing, which could eliminate about 67% of hemicellulose in bamboo. Comparing the major degradation products of the cooking liquor from raw bamboo and hemicellulose pre-extracted bamboo as shown in Fig. 1, it can be seen that hemicelluloses extracted before cooking significantly decreased the yield of four major organic acid products, which confirmed that degradation products from hemicellulose made a non-negligible contribution to the cooking liquor ingredient apart from lignin.

Fig. 2(a) indicates the result of GC-MS analysis of the derivatization of the degradation products of CAOSA. It can be found from Fig. 2(a) that the small-molecule products were mainly hydroxyl acid compounds, among which glycolic acid and 3-hydroxyl propionic acid had relatively high proportions. Both lignin and hemicellulose could decompose to formic and acetic acids, whereas hydroxyl acid compounds might all come from carbohydrates [17]. To estimate whether the hemicellulose degradation process was involved in a monosaccharide intermediate, xylose and XOS were used as model substrates, respectively, under the same condition of CAOSA reaction. As shown in Fig. 2(b), the degradation products were kinds of hydroxy acids for both xylose and XOS, but the relative selectivity of 3-hydroxyl propionic acid to glycolic acid was different. XOS could give 3-hydroxyl propionic acid with a higher selectivity, which was more similar to the cooking liquor analysis results. Although small amounts of xylose were detected, it was reasonable to speculate that hydrolytic depolymerization by xylose intermediate might not be the only reaction pathway. Combined with peeling reaction mechanism [18], it was considered that the degradation of hemicellulose in the process of CAOSA was accompanied by peeling reaction. As shown in Fig. 3, the endosaccharides of the main chain of xylan were the first to undergo aldosterone isomerism. Then 4-C occurred $\beta$-alkoxy elimination, forming methylene structure, further oxidizing 2-C and 3-C diketone structure, causing carbon-carbon bond to break and producing glycolic acid and 3-hydroxypropionic acid. If 2, 3-diketone could be isomerized to 1, 2-diketone and further oxidized to break bonds, the formation pathway of 2, 4-dihydroxybutyric acid (Fig. 2(a), compound 6) was well explained, which was second only to 3-hydroxypropionic acid and glycolic acid. The oxidative bond breaking of xylose occurred mainly between 1-C and 2-C, and tri-carbon products were seldom formed. In conclusion, apart from hydrolytic depolymerization of hemicellulose to xylose in the CAOSA process, the peeling reaction and the oxidative C-C cleavage of the bamboo substrate were also considered as possible reaction pathways.

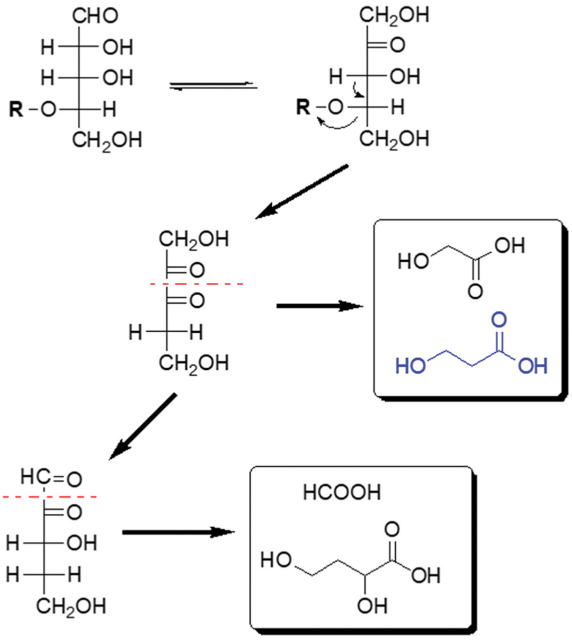


**Fig. 3. Possible reactions of the end xylose in hemicellulose during CAOSA process.**

## 2. Effect of Acid/Base on Hydrothermal Autocatalytic Extraction of Xylan

Based on the experimental results, in the process of CAOSA treating bamboo biomass, more than half of the hemicellulose component was converted to small molecule organic acids by peeling reaction and oxidation degradation, which not only reduced the utilization value of hemicellulose component but also increased the dosage of solid alkali. In view of the advantages of XOS obtained from bamboo, the purpose of this study was to isolate hemicellulose in the form of high-value xylan to prepare XOS. The traditional preparation methods of XOS include hydrothermal autocatalysis, alkali extraction combined enzymatic hydrolysis, and hydrothermal extraction combined enzymatic hydrolysis [19,20]. Since the biomass itself contains a certain amount of acetyl group, it can release acetic acid under hydrothermal action, and realize the autocatalytic hydrolysis of hemicellulose components. Hydrothermal extraction combined enzymatic hydrolysis was considered as an efficient and selective method. However, the dissolution process of hemicellulose is accompanied by series reactions from hyperxylcan to xylooligosaccharide to monosaccharide to furfural to repolymer. The difficulty of this method is to improve the extraction efficiency while ensuring the selectivity of xylan during the first step of hydrothermal extraction.

Yu-huanyan et al. [21] found that in the process of hydrothermal extraction of corn cob hemicellulose, adding a small amount of NaOH could effectively avoid the formation of by-products, mainly because NaOH could partially neutralize the acetyl groups that fall off, making the extraction process at the appropriate acid concentration, which also plays an important role in the extraction of hemicellulose xylan. In view of the different content of acetyl groups in different biomass, and the degree of hydrolysis and peeling of acetyl groups in different structures is not the same, some autocatalytic conditions are just right, some need to add acid to promote, some need to add alkali to inhibit. The following study systematically investigated for the first time the effect of the optimal acetyl group content on hydrothermal xylan removal for bam-

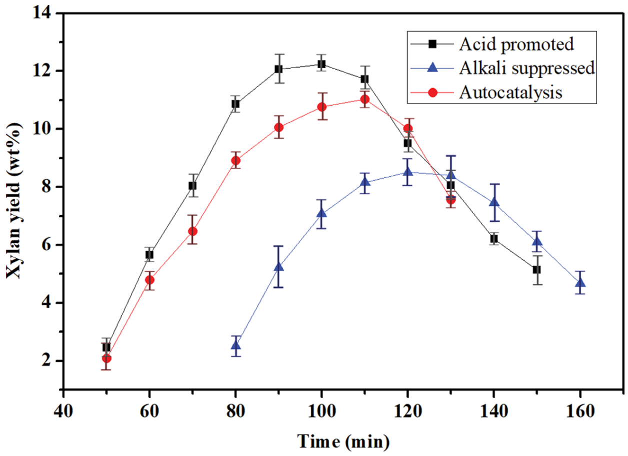


**Fig. 4. Effect of reaction time on the yield of xylan.**

boo biomass.

As shown in Fig. 4, the extraction rates of xylan at different reaction times by acid-enhanced hydrothermal method, alkali-suppressed hydrothermal method and hydrothermal autocatalytic method were studied. With the reaction time, the extraction rate of acid-enhanced xylan would have a relatively high growth period between 50 and 90 min, a plateau period between 90 and 110 min, and a peak value at 100 min. At this point, the extraction rate could reach 12.2 wt%, while after 110 min, it showed a slow decline trend. Because hemicellulose was closely bound to other components and could not be completely stripped in a short reaction time, so the extraction rate of xylan in the early stage was low. As the reaction progressed, the hemicellulose gradually hydrolyzed so that the xylan content in the extract gradually increased, thus reaching the maximum value. However, xylan was also completely hydrolyzed at a certain temperature. Therefore, with the extension of reaction time, the xylan in the extract was hydrolyzed into xylose and even converted into downstream products, resulting in the decrease of xylan selectivity. Since this is very unfavorable for the preparation of XOS, it was necessary to control the reaction time to ensure that the content of xylan in the extract was at a high level.

According to acid-enhanced hydrothermal method, hydrothermal autocatalytic method and alkali-suppressed hydrothermal method, the maximum xylan extraction rate corresponding to the three extraction methods was successively reduced and the optimal reac-

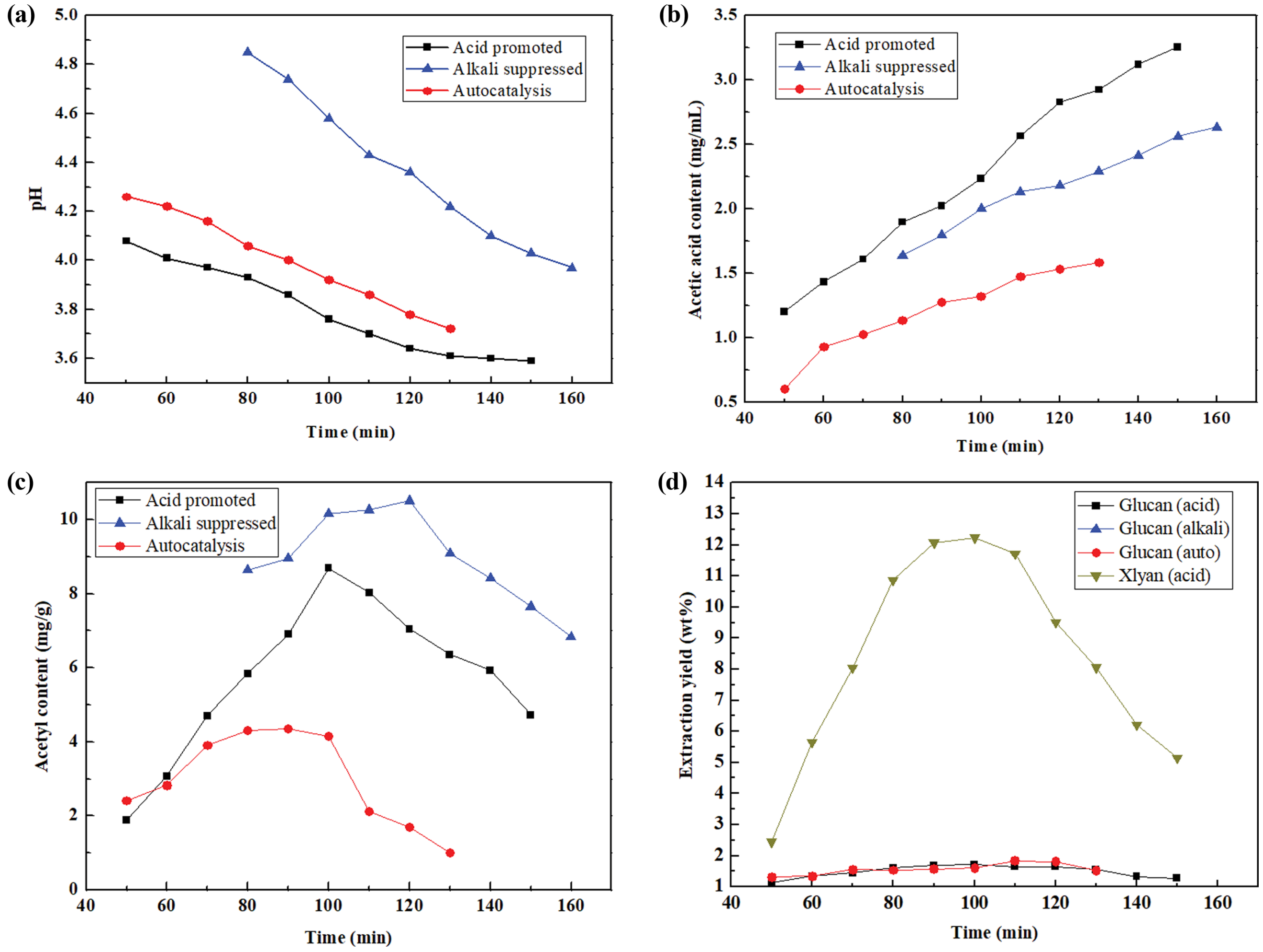


**Fig. 5. Effect of reaction time on (a) pH of extracting solution; (b) acetic acid content in extracting solution; (c) acetyl content in xylan; (d) the yield of glucan.**

tion time was successively delayed. This indicated that although the content of acetyl group of bamboo biomass was relatively high, it was difficult to hydrolyze off and difficult to realize effective autocatalysis. Therefore, the acid-enhanced method was beneficial for the highly selective dissolution of xylan. In addition, the hydrothermal method has a short plateau period and the extraction rate of xylan might vary greatly in a short period, which is not conducive to controlling the reaction time in actual operation. The platform period of alkali-suppressed method was long but the peak value was low. Based on the above analysis, the extraction of bamboo biomass xylan by acid-enhanced hydrothermal method was optimized.

As can be seen from Fig. 5(a), a comparative analysis was made of the pH changes of the extracts with the temperature of the three extraction methods. The pH values of the three groups as a whole showed a gradually decreasing trend. Among them, the pH values of the alkali-suppressed method were generally higher than those of the acid-enhanced method and the autocatalytic method, while the pH values of the latter two were relatively close. From the perspective of trend, the decline rate of alkali-suppressed method was faster, while that of autocatalysis method was slow; that of acid-enhanced method showed a trend of slow decline first and then gradual decline. The overall downward trend might be due to the gradual hydrolysis of cellulose and hemicellulose and the gradual shedding of acetyl groups with the progress of the reaction. As a result, the content of acidic substances in the extract increased, which enhanced the acidity of the solution and led to the gradual decrease of the pH value of the solution. At the same time, because such acidic substances could react with the base, the pH value corresponding to the alkali-suppressed method decreased more rapidly.

Therefore, the changes of acetic acid content in the extract corresponding to the three methods were compared and analyzed in Fig. 5(b). It can be seen that the acetic acid content of the three methods increased gradually at a similar rate but with slight differences in the content. This was because the structure of xylan contains acetyl groups, which would fall off and form free acids during the reaction, playing an autocatalytic role in the reaction and speeding up the reaction process. At the same time, because the three methods added different substances in the early stage of the reaction, it would promote or inhibit the generation of acetic acid, leading to the difference in acetic acid content.

Because the structure of xylan contains acetyl group, the acetyl content in xylan determines the amount of free acetic acid, which is formed after shedding, thus affecting the reaction process. The differences in the content of acetyl group in xylan extracted by the three methods were compared and analyzed. As can be seen from Fig. 5(c), the change trends of the three methods first increased and then decreased with a peak in the middle. This could be ascribed to the gradual hydrolysis of hemicellulose in the early stage of the reaction, which increased the content of xylan in the extract. At this time, the acetyl group in the structure of xylan had not yet fallen off or the degree of falling off was low, so the content of acetyl group in the extract gradually increased. With the reaction, although hemicellulose was further hydrolyzed and the content of xylan increased, the acetyl group in xylan began to fall off gradually, so that the rate of shedding was higher than the rate of formation. Therefore, the content of acetyl group in xylan in the extract decreased gradually. Finally, at the later stage of the reaction, the xylan in the extract began to hydrolyze and the acetyl group in the xylan further fell off, resulting in a rapid decrease in the acetyl group content in the xylan in the extract.

In addition, the comparison of the three methods shows that the content of acetyl group in xylan in the alkali-suppressed method, acid-enhanced method and autocatalytic method decreased successively under the same reaction time. Because at the early stage of the reaction, alkali-suppressed method adding magnesium oxide might have inhibited the shedding of acetyl groups, which kept the acetyl group content in xylan at a high level. However, this inhibition was not conducive to the formation of autocatalysis. The whole process of alkali-suppressed method was delayed compared with acid-enhanced method and autocatalytic method. As a result, the extraction rate of xylan by alkali-suppressed method was lower. However, for the acid-enhanced method, acetic acid added in the early stage of the reaction promoted the removal of acetyl groups, and the generated acetic acid had a self-catalytic effect, which not only accelerated the reaction rate but also made the reaction more complete, so that the extraction efficiency of xylan was higher. Through comparative analysis, it could be seen that autocatalysis had a large influence on bamboo biomass raw material. Adding an appropriate amount of acetic acid in the early stage of the reaction could speed up the overall process of the reaction and improve the yield of the target product. Therefore, acid-enhanced extraction was a more reasonable treatment method for bamboo.

The effects of the three methods on the extraction rate of glucan were compared and analyzed. As can be seen from Fig. 5(d), the extraction rate of glucan for the three methods did not change significantly with the reaction and remained at a low level, within the range of 1% to 2%. As a contrast, the extraction rate of xylan by acid-enhanced method was much higher than that of glucan. The acid-enhanced method could extract as much xylan as possible while keeping more glucan in bamboo raw material residues or keeping the degree of hydrolysis of cellulose at a low level. Since the extraction rate of glucan did not change too much in the reaction, it could be considered to take a specific method to remove this part at the early stage of the experiment, so as to simplify the subsequent product impurity removal process.

Furfural could be obtained by acid catalyzed reaction of hemicellulose, so the changes of furfural content with time of the three extraction methods were compared and analyzed. Fig. 6(a) indicates that the furfural content of all three elements increased gradually. The increase trend of auto-catalysis method and alkali-suppressed method was similar and slow, while the content of furfural of acid-enhanced method increased more rapidly, which might have been caused by the strong acidity of the whole extraction process of acid-enhanced method. From the perspective of content, in the case of acid-enhanced method, when the extraction rate of xylan was the highest, that is, when the reaction time was 100 min, the concentration of xylan was 10.75 mg/g and the concentration of furfural was 0.95 mg/g, which meant that the xylan extracted by this method had been partially degraded.

The 5-hydroxymethylfurfural (HMF) could be obtained by acid catalyzed reaction of cellulose. In the experiment, the HMF con-

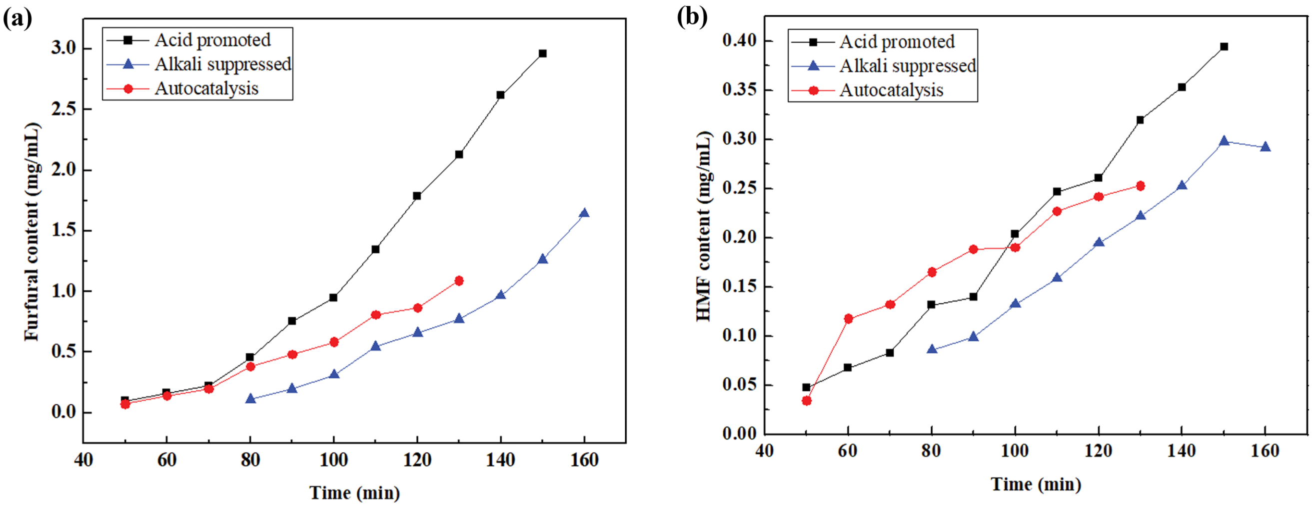


**Fig. 6. Effect of reaction time on (a) furfural content in extracting solution; (b) HMF content in extracting solution.**

**Table 1. Comparison of untreated, conventional CAOSA-treated and hemicellulose pre-extracted CAOSA-treated bamboo compositions**

| Sample | Cellulose (wt%) | Xylan (wt%) | Lignin (wt%) | % Mass loss |
|---|---|---|---|---|
| Bamboo raw materials | 43.4±0.1 | 22.3±0.3 | 27.6±0.4 | N |
| Conventional CAOSA | 71.5±0.5 | 20.3±0.2 | 4.6±0.2 | 48.7±0.3 |
| Hemicellulose pre-extracted CAOSA | 79.9±0.4 | 9.8±0.1 | 7.5±0.2 | 61.1±0.5 |

tent of the three extraction methods was compared and analyzed over time. As shown in Fig. 6(b), the HMF content of the three methods was relatively close and showed a trend of gradual increase, and the content of HMF was all at a low level. For example, in the acid method, when the extraction rate of xylan was the highest, that is, when the reaction time was 100 min, the concentration of xylan was 10.75 mg/g, while the concentration of HMF was only 0.21 mg/g, which was almost negligible as an impurity. Interestingly, the HMF content in a case of the autocatalytic reaction was higher than that of the acid-promoted reaction after 100 min.

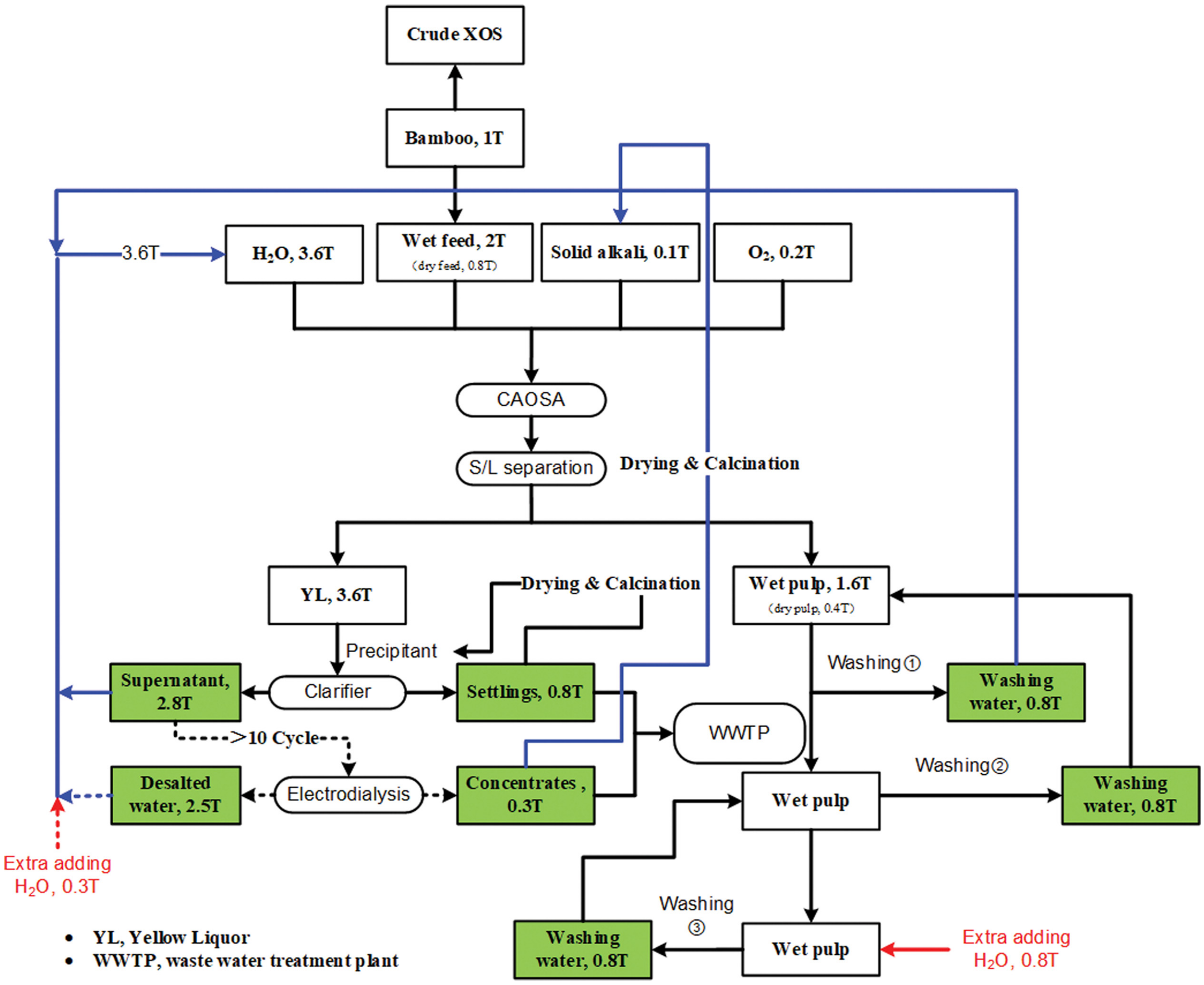
### 3. Hemicellulose Pre-extraction Combined with CAOSA Technology

Designed based on CAOSA, a comprehensive biorefinery case with hemicellulose pre-extraction was presented. 1 kg of bamboo chips was added to a ball-shaped digester, the xylan was extracted according to the optimized extraction conditions of section 3.2, and then the solid alkali-oxygen cooking was carried out. When alkali dosage was reduced from 15 wt% to 12 wt%, the process of removing lignin by cooking could still proceed normally. This helped to indicate that part of the alkali consumed by hemicellulose degradation had been saved. The composition analysis of bamboo raw material, pulp obtained by conventional CAOSA and pulp obtained by that of pre-extracting hemicellulose was carried out. As shown in Table 1, since the pretreatment step dissolved the hemicellulose xylan, the hemicellulose content in the pulp obtained after extraction and cooking was reduced from 20.3 wt% of conventional cooking to 9.8 wt%. It might be that the pretreatment process had changed the lignin structure, such as the formation of a more stable condensation structure, resulting in an increase in the residual lignin content from 4.6 wt% of conventional cooking to 7.5 wt%. The pulp color obtained by pretreatment and cooking was darker than that obtained by direct cooking. The integration of pretreatment and CAOSA led to the cellulose content in the pulp being increased from 71.5 wt% to 79.9 wt%. In conclusion, the feasibility of hemicellulose pre-extraction combined with CAOSA technology was preliminarily confirmed.

A biorefining case could be presented here. First, the hemicellulose components were separated by hydrothermal autocatalysis assisted by the organic acid of recycled yellow liquor. Further selective oxidation of CAOSA yellow liquor could produce formic and acetic acids [14]. And then CAOSA was conducted to separate the cellulose and lignin components. High purity xylo-oligosaccharide products could be prepared by enzymatic hydrolysis, decolorization, proteinization, desalination and monosaccharide from the xylan-extracted solution obtained by pretreatment [7]. CAOSA cellulose could be catalyzed into a series of platform compounds, such as 5-formyl oxymethylfurfural [15], and could also be used to prepare cellulosic materials [22]. Adding strong alkali (such as NaOH and CaO) to the cooking yellow liquor could simultaneously recover alkali and lignin, which could be recycled in the cooking process [8]. Lignin could be catalytically degraded to produce aromatic compounds [23]. Besides, a flow chart of water consumption based on hemicellulose-first separation and CAOSA processes was drawn as shown in Scheme 1. Only 1.1 ton of water was needed for the whole process of each ton of raw material, which was comparable to existing processes [24].

## CONCLUSIONS

XOS are mainly prepared from lignocellulosic biomass which is



**Scheme 1. Calculation of unit water consumption based on hemicellulose-first separation and CAOSA processes.**

rich in xylan. Bamboo is a kind of raw material with unique advantages. In this study, the influence of acid and base on hydrothermal autocatalytic extraction of xylan was investigated for the first time. It was found that acid-enhanced method was beneficial to highly selective dissolution of xylan. Although the acetyl group content of bamboo is relatively high, it was difficult to hydrolyze and peel off. Bamboo raw material was reacted at 180 °C in 0.1% acetic acid solution for 100 min, and the extraction rate of xylan was up to 12.2%. CAOSA is a new method for the separation of biomass components, but it also inevitably leads to the degradation of hemicellulose. This paper first explained the direct degradation mechanism of hemicellulose mainly through polysaccharides. Then an experimental procedure coupling hemicellulose pre-extraction and CAOSA lignin fractionation was performed. When the amount of alkali was reduced from 15 wt% to 12 wt%, the cooking process of removing lignin could still proceeded normally. This could be ascribed to the avoidance of alkali consumption caused by the degradation of hemicellulose components. Higher purity cellulose pulp could provide a good basis for downstream applications. The integration of hemicellulose pre-extraction and CAOSA treatment increased cellulose content in pulp from 71.5 wt% to 79.9 wt%. Finally, the water consumption of the whole process was calculated, and only 1.1 ton of water was needed for each ton of raw materials to realize slurry washing and alkali recovery. This study provides some theoretical basis and technical support for the utilization of lignocellulosic biomass in the future.

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