

Low-Temperature Alkali-Anthraquinone Pretreatment of Wheat Straw: Gradual Dissolution of Lignin and Carbohydrate Retention in Pretreated Solids

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This paper presents a comprehensive study of wheat straw that was alkali-pretreated with NaOH loadings from 60 to 220 mg NaOH/g dry straw and a 0.5% anthraquinone (AQ) loading at 90 °C for 1, 2, and 3 h. Images of the residual solids were taken with a scanning electron microscope. A full compositional analysis of the raw material and residual solids, yield of compounds dissolved in the black liquor (BL), and molecular weight (M_w) after the different pretreatments were presented to track the dissolution process of lignin and carbohydrates. The ratio of the lignin fraction to carbohydrates dissolved in the BL was used for an analysis of the reaction selectivity. The cellulose retained 90% of the carbohydrates in the pretreated straw, while 75% of the lignin was dissolved in the BL gradually with an intermediate value of M_w . Low-molecular weight lignin ($M_w \sim 1800$ and degree of polymerization ~ 1.05) was dissolved out with the 60 mg NaOH/g dry straw loading. When the NaOH loading was increased to 220 mg NaOH/g dry straw, the M_w of the lignin was 4300 to 4700.

Keywords: Alkali pretreatment; Low temperature; Wheat straw; Lignin; Selective pretreatment

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INTRODUCTION

Wheat straw is one of the most abundant and low-cost sources of biomass that is widely distributed around the world. The Food and Agriculture Organization of the United Nations (FAO) has reported that 100 million tons of wheat straw is produced annually in more than 100 countries (FAO 2013). Wheat straw can be used in many areas, such as feeding, composting, and fermentation (Hassanein and Koumanova 2010; Zhan 2010; Baig *et al.* 2015). Thus, this superior biomass source should be considered a potential future energy and chemical resource. However, this sustainable biomass source is currently being wasted, and the majority of it is burned on the spot in China (Zhang 2008; Zhan 2010). The inefficiency and low economic benefit block the development of new applications and promotion, which is possibly because of its inherent composition and structure.

Lignocellulose is found primarily in plant cell walls. Plant cell walls are complicated natural composites with three major constituents, cellulose, hemicellulose, and lignin. The cellulose in plants is comprised of crystalline β -1,4-glucans, which accounts for 28% to 45% of the dry matter in plants. The crystallinity of cellulose is a key factor that negatively affects biomass digestibility (Duan *et al.* 2013). The crystalline structure is surrounded by hemicellulose and lignin, which makes it difficult for wheat straw to be hydrolyzed and broken down by chemicals (Mittal *et al.* 2011). Hemicellulose, which is mostly composed of xylose, arabinose, mannose, and glucuronic acid units, is a diverse group of natural and heterogeneous branched biopolymers (degree of

polymerization, DP = 80 to 200) found in plant cell walls. Several applications for the carbohydrate fractions obtained by the fractionation process have been investigated (Gao *et al.* 2016).

Lignin, as a complex aromatic compound, can be dissolved or removed from lignocellulose with difficulty, which presents a challenge for pulping and dissolution in chemicals (Sewalt *et al.* 1997). Meanwhile, as the second-most common biopolymer on earth, lignin plays an important role in the production of bio-fuel, bio-materials, and chemicals (Li *et al.* 2015; Lyckeskog *et al.* 2016; Zhao *et al.* 2016; Zhang and Chen 2017). Lignin can be transformed into high value-added chemicals in two ways: degradation into low-molecular weight (LMW) compounds (Sun *et al.* 2015) or polymerization into high-molecular weight (HMW) compounds (Rios *et al.* 2014). The degradation of lignin into LMW compounds has yielded practical chemicals such as bio-fuel, phenols, and aromatics (Singh *et al.* 2014). Applications for HMW lignin include the production of adhesives, carbon fiber, and thermally-stable copolyesters by increasing the DP (Meek *et al.* 2016). However, because of the complex structure and wide molecular weight distribution, lignin that is isolated from biomass cannot be applied in the previously mentioned applications directly. Therefore, pretreatment is a necessary step to obtain a narrower molecular weight distribution and high-activity lignin, which results in lignin that is better suited for bio-conversion applications.

Thus, it is necessary to develop a pretreatment for making full use of this biomass. Pretreatment can break down the crystal structure of lignocellulose for easier dissolution in chemicals. Also, lignin-enriched products dissolved from lignocellulose could be used for suitable conversion.

Alkali pretreatment is considered to be a promising chemical treatment method because of its low operation cost and reduction of holocellulose degradation (Zhang *et al.* 2011). Alkali pretreatment mainly effects the degradation of ester bonds and cleavage of glycosidic linkages when the pretreatment is performed above 100 °C (Srinorakutraral *et al.* 2013). These effects lead to an increase in the solubility and dissolution of lignin, which causes swelling of the cellulose structure and partial decrystallization of cellulose. However, the drawback of traditional alkali pretreatment is that when collecting lignin from lignocellulosic biomass, polysaccharides, especially hemicellulose and cellulose, are dissolved at high-temperature pretreatment conditions (> 100 °C) (Agbor *et al.* 2011). The addition of anthraquinone (AQ) can oxidize the carbohydrate end groups and mitigate hemicellulose loss *via* peeling reactions because the carbohydrate acid end groups are more stable in an alkali media. Therefore, AQ is widely used in traditional pulping processes to increase the retention of hemicellulose, which can increase pulp yields and improve the tensile strength (Heitner *et al.* 2010). However, very few studies on alkali-AQ pretreatment have been done. Karp *et al.* (2015) studied the alkali-AQ pretreatment of switchgrass with high pretreatment temperatures (> 100 °C). It was found that the optimal pretreatment conditions were 154 mg NaOH/g dry switchgrass, 130 °C, and 30 min. Li *et al.* (2012) researched different alkali-based pretreatments of corn stover, including NaOH-AQ, and found that an NaOH-sulfite pretreatment at 140 °C led to a high lignin removal and carbohydrate recovery with better enzymatic digestibility. However, a study focused on the alkali-AQ pretreatment of wheat straw at low temperatures was unfamiliar to the authors.

Theoretically, alkali pretreatment of wheat straw with AQ at low temperatures could avoid the traditional alkali pretreatment disadvantages. First, alkali pretreatment is generally more effective on agricultural residues and herbaceous crops. The rate of delignification during soda pulping of wheat straw can reach approximately 60% at 100 °C

(Epelde *et al.* 1998). Second, a low temperature of approximately 90 °C and the addition of AQ could protect cellulose from degradation. Finally, because lignin removal is markedly increased as the temperature increases above 100 °C to 130 °C (Karp *et al.* 2015), the low temperature could dissolve lignin into the black liquor (BL) at a steady rate.

To investigate the low temperature alkali-AQ pretreatment of wheat straw, the effect of different alkali loadings and pretreatment times on the dissolution of lignin and carbohydrates was studied. This paper presents a comprehensive study of the alkali pretreatment of wheat straw with NaOH loadings of 60 to 220 mg NaOH/g dry straw, 1:5 solid-to-liquor ratio, and a 0.5% AQ loading at 90 °C for 1, 2, and 3 h. The compositions of the pretreated straw and fraction of the BL were determined to analyze the dissolution process of wheat straw.

EXPERIMENTAL

Materials

Wheat straw was harvested from Jining, Shandong province of China in the summer of 2014. It was cut to 3- to 5-cm lengths and air-dried for 2 d or more.

Alkali Pretreatment

The soda-AQ pretreatment of the dry wheat straw pieces (100 g) was conducted in a 1-L glass beaker, which was heated in a water bath at 90 °C with a 30-min heat ramp. The NaOH loadings were varied from 60 to 220 mg NaOH/g dry straw, and the AQ loading was held constant at 0.5% (w/w) by dry wheat straw with a 1:5 solid-to-liquor ratio. To ensure full contact with the NaOH solution, the wheat straw was mixed well before it was poured into the glass beaker and the beaker was shaken every half hour. At the end of each pretreatment, the beakers were removed from the water bath and rapidly cooled in cold tap water. The BL was separated by squeezing the soaked straw, and then the residue was thoroughly washed with 90 °C distilled water until the wash water was clean.

Scanning Electron Microscopy (SEM)

Imaging with scanning electron microscopy (VEGA3-SBH, TESCAN) was performed. Samples were air-dried prior to imaging and mounted on aluminum stubs using conductive carbon tape. The stubs were then sputter-coated with approximately 10 nm of gold-sputter coater (SBC-12, KYKY Technology Co., Ltd, Beijing, China). The imaging was performed with a beam accelerating voltage of 10 kV.

Crystallinity Measurements

To examine and compare the crystalline structure of both the untreated and alkaline-treated samples, X-ray diffraction (XRD) was performed on an Empyrean diffractometer (PANalytical B.V, Almelo, Holland) with CuK α radiation that had a wavelength (λ) (K α 1) of 0.15406 nm generated at 40 kV and 40 mA. The samples were dried in a vacuum oven with P₂O₅ at 35 °C for 48 h. The scans were obtained from 2 θ values of 10° to 90° at a scanning speed of 1° per min. The crystallinity (CI) of the cellulose samples was calculated according to the peak deconvolution method with the ratio between the area of the crystalline contribution and total area, as described by Goikhman *et al.* (1992) and shown below as Eq. 1,

$$CI = 1 - \frac{A_{am}}{A_{sample}} = 1 - \frac{\int_{2\theta_1}^{2\theta_2} I_{am} d2\theta}{\int_{2\theta_1}^{2\theta_2} I_{sample} d2\theta} \quad (1)$$

where A_{am} is the area under the amorphous curve ($^{\circ}$), A_{sample} is the area under the sample intensity curve ($^{\circ}$), $2\theta_1 = 13.5^{\circ}$, and $2\theta_2 = 49.5^{\circ}$.

Fractionation of Lignin and Hemicellulose from the Black Liquor (BL)

The scheme for the fractionation of BL is illustrated in Fig. 1. The BL was first acidified with 12% (w/w) sulfuric acid until a pH of 8.5 was achieved for the removal of SiO_2 through centrifugation, and then the pH was adjusted to 2.0 for the precipitation of the crude lignin, which was named C1. The water phase was treated with the following steps: (1) precipitated with $Ba(OH)_2$ to get rid of SO_4^{2-} ; (2) centrifuged at 8000 rpm for 20 min, and then the supernatant was dialyzed with a dialysis bag (MD of 55 to 2.0) to remove molecules and ions less than 2000 in molecular weight. The residue was freeze-dried as the water was solubilized and concentrated to approximately 100 mL at a reduced pressure; (3) the carbohydrate fractions were obtained from the freeze-dried concentrated liquor, which was named C2.

$$Y_{lignin} (\%) = \frac{W_{C1}}{W_{BL}} \times 100(\%) \quad Y_{carbohydrate} (\%) = \frac{W_{C2}}{W_{BL}} \times 100(\%) \quad f = \frac{Y_{lignin}}{Y_{carbohydrate}} \times 100 \quad (2)$$

In Eq. 2, W_{C1} is the oven-dry weight of freeze-dried C1 (g), W_{C2} is the oven-dry weight of freeze-dried C2 (g), and W_{BL} is the oven-dry weight of the BL (g)

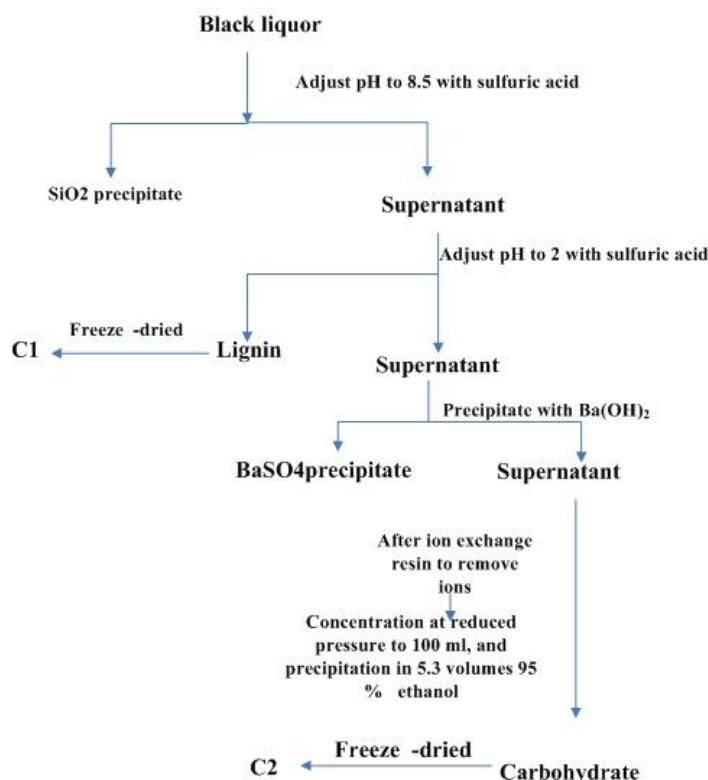


Fig. 1. Scheme for the fractionation of lignin and hemicellulose from the BL

Molecular Weight Analysis

Gel permeation chromatography (GPC) was used to determine the molecular weights of the obtained hemicellulose and lignin. GPC was performed on a Waters 1525 binary HPLC pump with a Waters 717 plus auto-sampler, Waters 2414 refractive index detector, and a Breeze (V3.3) GPC work station (Waters, Milford, USA). Prior to the analysis, the lignin and other organic samples included in C1 were dissolved in tetrahydrofuran (THF), while the hemicellulose in C2 was dissolved in water. The eluent flow was 1 mL/min, and the system was maintained at 35 °C during the analysis. Glucan and polystyrene were used as reference substances for hemicellulose and lignin, respectively.

Component Analysis of the Pretreated Straw

The analysis of the typical composition, including cellulose (Kurschner-Hoffner method), lignin (TAPPI T 222 om-11), and pentosan (TAPPI T 223 cm-10), was carried out with referenced standard methods. The analyses were conducted with three repetitions, and the relative standard deviation was below 5%.

The sugar concentrations (cellulose, D-xylose, D-glucose, arabinose) in the pretreated wheat straw were analyzed by a high performance liquid chromatograph (HPLC) (Waters 2695e systems, Waters) equipped with a refractive index detector (Waters 410, Waters) and Aminex HPX-87H anion-exchange column (300 x 7.8 mm, Bio-Rad Corp., Hercules, USA) using 5 mM sulfuric acid as the mobile phase at a flow rate of 0.5 mL/min. The column temperature was maintained at 50 °C.

After pretreatment with different alkali loadings and reaction times, the composition of the residual straw was measured with at least three repetitions. The dissolved proportions of wheat straw were calculated according to the equations below,

$$\text{Percent yields (\%)} = \frac{M_r}{M_s} \times 100(\%) \quad \text{Composition of the pretreated straw (\%)} = \frac{P_{M_r}}{\sum P_{M_r}} \times 100(\%) \quad (3)$$

where M_s is the oven-dry weight of the pretreated straw (g), M_r is the weight of the components (ash, lignin, cellulose, *etc.*) of the pretreated straw (g), and P_{M_r} is the percent yield of the components in the pretreated solid (%)

$$\text{Monosaccharide composition of residual (\%)} = \frac{\text{Monosaccharides g/L}}{\sum \text{Monosaccharide compositions g/L}} \times \text{Pretreated solid} \times 100(\%) \quad (4)$$

RESULTS AND DISCUSSION

Composition of the Pretreated Straw

The percent yields of the components retained in the pretreated straw are displayed in Fig. 2a as a function of the NaOH loading for the three different pretreatment times (1, 2, and 3 h).

As can be seen in Fig. 2a, the results displayed the expected trend of a decreased retention of solids as the pretreatment time and NaOH loading increased. When the NaOH loading was 140 mg NaOH/g dry straw or higher, the loss of raw material was around 3% to 5%, while it was approximately 10% to 15% for the 60 mg NaOH/g dry straw loading. The alkali pretreatment is a process whereby the alkaline lignin, carbohydrates, ash, and a small amount of extracts are dissolved out. Before the NaOH loading reached 140 mg

NaOH/g dry straw, the content of cellulose in the pretreated straw was basically stable. The percent yield of cellulose in the pretreated straw only slightly decreased when the NaOH loading was 180 mg NaOH/g dry straw or higher. At the same pretreatment condition, 75% Klason lignin, 90% acid soluble lignin, and 50% pentosan were dissolved out of the raw material.

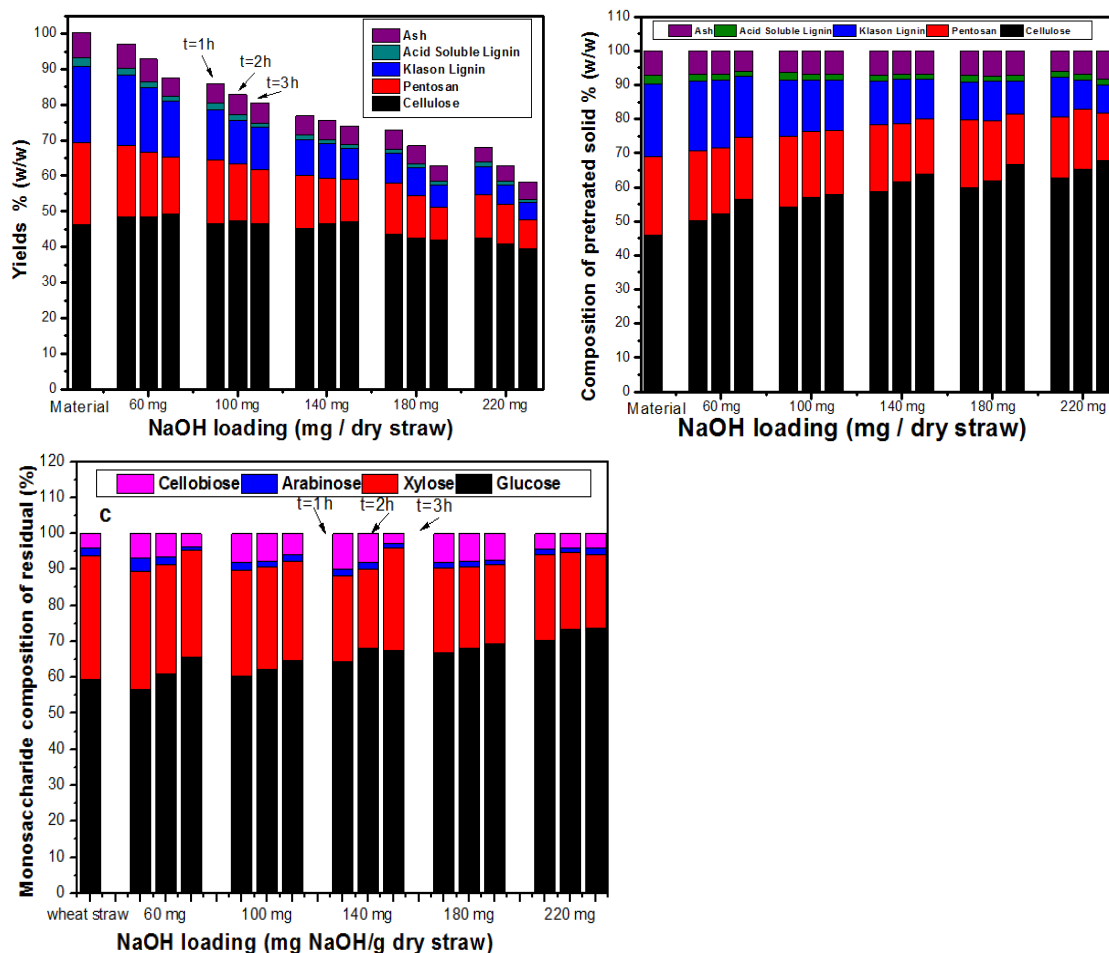


Fig. 2. a) Percent yield of the components in the pretreated straw; b) Composition of the proportions in the pretreated straw; c) Monosaccharide composition of the pretreated straw

As shown in Fig. 2b, the content of alkali-soluble components, such as lignin and pentosans, tended to decrease as the NaOH loading was increased. Cellulose has relatively stable properties under moderate alkali pretreatment conditions. However, as more lignin and hemicellulose were dissolved in the BL, the proportion of cellulose in the total solution tended to increase as both the NaOH loading and pretreatment time increased. The total proportions, as can be seen in Fig. 2b, showed the trend of cellulose enrichment present in the pretreated straw. The cellulose content in the pretreated straw increased from 45.3% to 67.5%. At the same time, the Klason lignin content only accounted for 8.3% of the pretreated straw, and approximately half of the pentosan was dissolved out of the raw material. The proportion of ash and acid lignin in the pretreated straw showed relatively small changes, with a loss of only 2% to 3%.

These results indicated that the severity of the pretreatment conditions, especially the alkali loading, had a degradation effect on the cellulose. This effect may have been

related to a peeling reaction, although the alkali pretreatment at such a low temperature (90 °C) was not enough to cause serious change to the crystal region.

The percentages of monosaccharides shown in Fig. 2c were derived from the sugar compositional analysis of the residual pretreated straw. From the original sugar compositional analysis of the wheat straw, cellulose accounted for 63%. The alkali pretreatment increased the percentage of cellulose in the pretreated straw, while the percentage of hemicellulose decreased with an increase in the NaOH loading and pretreatment time. An exceptional result was that the treatment with the lowest alkaline loading (60 mg NaOH/g dry straw) and shortest pretreatment time (1 h) essentially did not affect the proportion of cellulose and hemicellulose. This meant that a mild alkali pretreatment has little effect on the dissolution of carbohydrates. Figure 2c reflected this, as only less than 10% of the components dissolved out of the material.

With a longer pretreatment time, more arabinoxylan was dissolved. Simultaneously, the percentage of arabinose present decreased in the rest of the hemicellulose; the decrease was from 5% at the start to 3% after 2 h and 2% after 3 h. Because arabinose is a branched chain link sugar unit of the arabinoxylan macromolecular chain, it combines with the hydroxy of the main chain to form 1-3 glycosidic bonds, which is a relatively stable connection. The alkali pretreatment at such a low temperature (90 °C) and low NaOH loading was not enough to break these bonds. Moreover, when the NaOH loading was 140 mg NaOH/g dry straw or higher, the percent of arabinose in the pretreated straw fluctuated in response to the pretreatment time, and its proportion in the pretreated straw stayed at 2% to 3%. Therefore, the effect of alkali on the selective decomposition of glycosidic bonds in the arabinoxylan and arabinose units was negligible. An increase in the severity of the pretreatment only caused more of the arabinoxylan to dissolve out of the cell walls.

X-Ray Diffraction (XRD) Analysis of the Pretreated Straw

The wheat straw samples pretreated with 60 to 220 mg NaOH/g dry straw for 1, 2, and 3 h were compared with XRD analysis. The XRD patterns shown in Fig. 3a, 3b, and 3c were a reflection of the crystalline cellulose structure in the straw. The patterns were essentially the same, except that the height of the peaks at the 2θ values 18° and 22.8° varied for each pretreatment condition. It was easy to see that as the alkali loading and pretreatment time increased, the intensities of the two peaks increased. The only exception was the XRD curve of the straw with a 60 mg NaOH/g dry straw loading pretreated for 1 h, which was almost unchanged from that of the untreated straw. The crystallinity was calculated with the area proportion of the total crystalline region, and the relationship between the crystallinity of the samples and alkali dosage is displayed in Fig. 3d. The crystallinity of the samples increased as the alkali amount and pretreatment time increased, which was considered the result of the amorphous matter, such as alkaline-soluble lignin and hemicellulose, being progressively removed from the straw. As a result, the increase in crystallinity corresponded with the elevated level of cellulose in the pretreated straw. As for the effect of the alkali loading on the cellulose in the straw, the possibility of destructive effects from the cellulosic crystal structure was not taken into account because the alkali pretreatment at such a low temperature (90 °C) was not enough to cause severe change to the crystal region, as was already discussed.

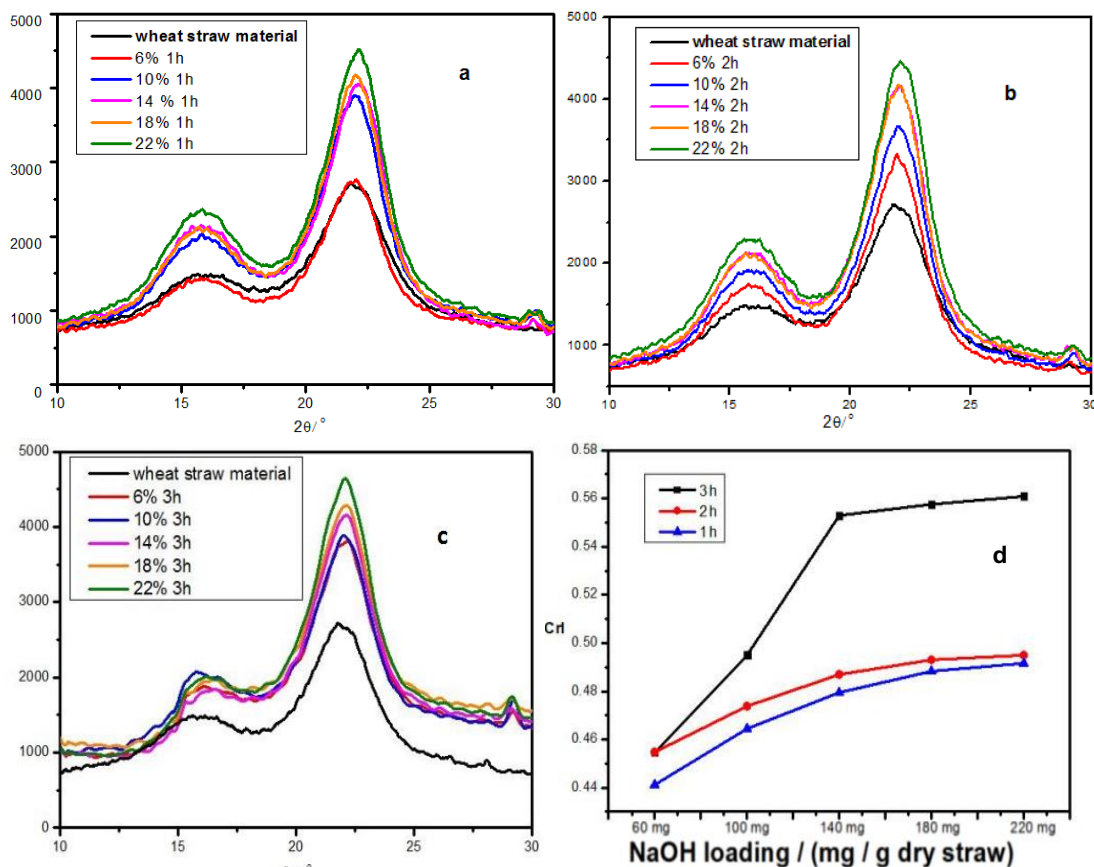


Fig. 3. XRD peaks of the wheat straw pretreated for (a) 1, (b) 2, and (c) 3 h; d) Crystallinity of the pretreated straw as a function of the NaOH loading and pretreatment time

SEM of the Pretreated Straw

A great deal of the alkaline-soluble components that exist in wheat straw are well known. Because alkali pretreatment can extract a lot of the soluble matter from the straw, the micro-structure and morphology of the tissue is inevitably influenced. Figure 4 visually displays the photographs of the macro-structure (top row) and micro-structure (bottom two rows) of the original wheat straw and wheat straw pretreated with 60 to 220 mg NaOH/g dry straw (from left to right).

It was evident from Fig. 4 that the macro morphological structures became looser as the alkali loading increased. When the NaOH loading amount was 140 mg NaOH/g dry straw, part of the wheat tissue was found to have separated into streaks and fibrous bundles. Subsequently, the higher loadings of alkali increased the amount of separation and the wheat straw became light in color.

It was observed that the tissue that collapsed and became pulp was mainly from the straw leaves. Compared with the leaves, the stem tissue of the straw did not disintegrate easily, even when the alkali loading was 220 mg NaOH/g dry straw, and there did not appear to be a distinct color difference between the tissues treated with 60 and 220 mg NaOH/g dry straw. This meant that the removal of lignin from the stem was not as easy as removal from the leaves.

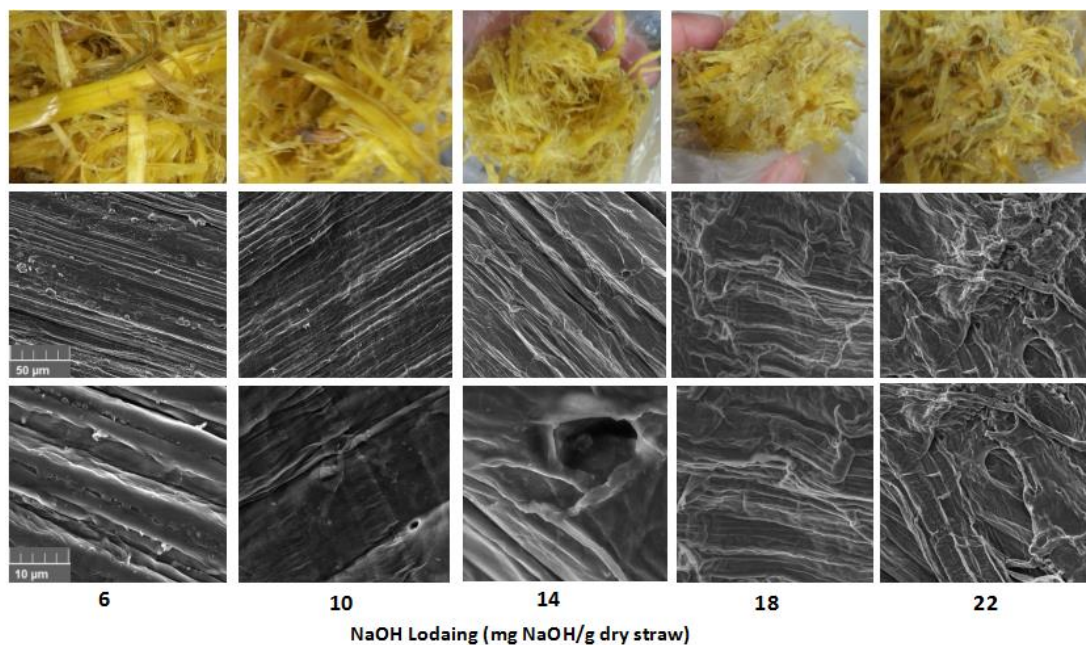


Fig. 4. Stereoscopic micrographs (top row) and SEM images (bottom two rows) of the soda-AQ pretreated wheat straw

For the micro-structure of the straw, the original straw and straw pretreated with five different alkali dosages were observed by SEM. Compared with the somewhat obscured surface of the original straw, the venation of the stem vascular bundles became distinctly undulated after pretreatment and were similar to that of the original straw, until the alkali loading was 100 mg NaOH/g dry straw. Thereafter, pretreatment with a 140 mg NaOH/g dry straw loading caused the compact fibrous bands to become sparse and coarse. This was largely the result of the removal of a considerable amount of soluble components from the straw, and the resulting loosened tissue collapsed, shrank, and adjacent fibrous bands closed-up because of the hydrogen bonding interaction that occurred when the treated straw was air-dried. Furthermore, the original linear fibrous bands appeared deformed, bent, and even curled when the alkali loading was 180 mg NaOH/g dry straw or higher. In other words, the pretreatment, even at the low temperature of 90 °C, was able to change the straw structure if the alkali loading was 180 mg NaOH/g dry straw or higher, although the straw tissue did not reach the level of fibrous band disaggregation.

The above discussion was concerned with the percentage of solids that were retained after the pretreatment and the physical changes in the carbohydrate portions of the remaining biomass, which demonstrated the dramatic modification of the biomass cell wall structure that took place after lignin removal and rather unremarkable changes in the cellulose crystallinity. It was seen that the alkaline pretreatment at relatively mild conditions was able to remove substantial amounts of lignin from the wheat straw, which could make the plant cell wall polysaccharides much more amenable to digestion by pulping and biomass refining. At the same time, because of the structural changes shown in Fig. 4, the bulk density increased by 20% to 30%, which is good news for industrial biomass conversion applications.

Composition of the BL

The BL derived from the pretreated straw had a complex composition. It contained residual alkali, lignin groups, carbohydrates, and more. The dissolved lignin and

carbohydrates in the BL were extracted by the process given in Fig. 1, and the percentage of these components was calculated with Eq. 2. The residual NaOH reflected the amount of alkali that reacted with the material, and the lignin and carbohydrates obtained from the BL at different reaction times represented the process of dissolution.

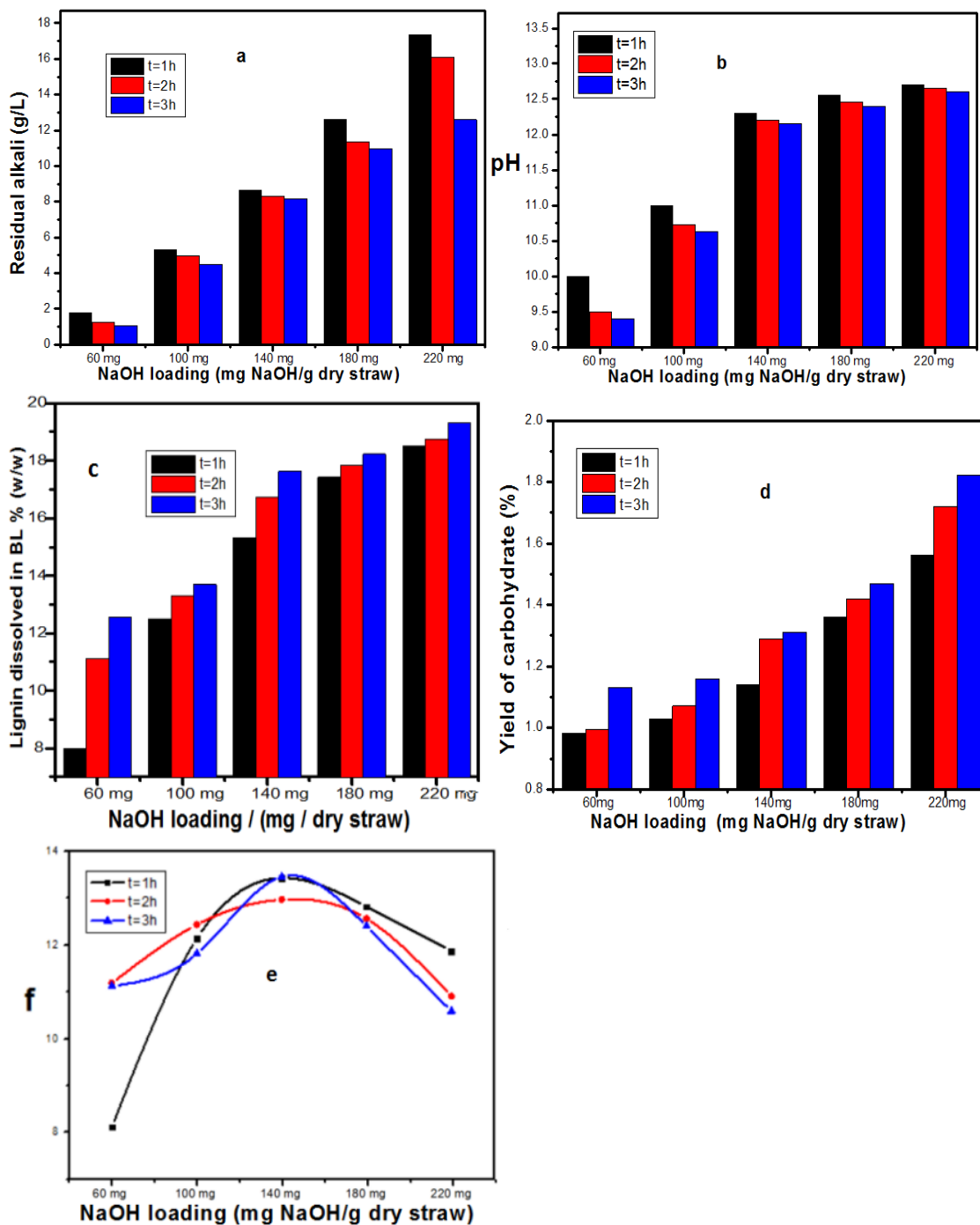


Fig. 5. Composition of the BL: (a) residual alkali, (b) pH, (c) carbohydrates, and (d) lignin; (e) values of the fraction optimization function (f)

As shown in Figs. 5c and 5d, more lignin and carbohydrates were dissolved in the BL as the NaOH loading and pretreatment time increased, which was similar to the trend observed for the proportions of the total components in the pretreated straw (seen in Fig. 2a). However, two different components had different dissolution behaviors.

At the lowest NaOH loading of 60 mg NaOH/g dry straw, only approximately 1% of carbohydrates were dissolved out during the 2-h pretreatment. This may have been a consequence of the fast consumption of alkali in the initial pretreatment stage, such that there was not enough residual alkali to continue the reaction. The dissolution of carbohydrates only occurred on the surface layer, and the pretreated straw retained the structural integrity under this mild condition. However, increasing the pretreatment time to 3 h, the alkali pretreatment was able to soften the internal structure of the straw, as can be seen in Fig. 4, which improved the dissolution of carbohydrates. It was seen that if the pretreatment time was 3 h and the NaOH loading was 60 mg NaOH/g dry straw, there was a noticeable improvement to the dissolution of carbohydrates.

These results cannot be separated from the serious structural modification of the pretreated straw. When the NaOH loading was 220 mg NaOH/g dry straw and the pretreatment time was 3 h, 50% of the hemicellulose was dissolved in the BL. Compared with the carbohydrates, the dissolution of lignin appeared to be highest at the lowest NaOH loading (60 mg NaOH/g dry straw). It was inferred from this that lignin can be easily dissolved out with a mild alkali pretreatment, while carbohydrates require more severe pretreatment conditions. As the pretreatment severity increased, the carbohydrate dissolution rate increased exponentially. At the same time, the lignin dissolution reached an equilibrium when the NaOH loading was 180 mg NaOH/g dry straw. It is worth mentioning that the 140 mg NaOH/g dry straw loading was the turning point for the equilibrium, as can be seen in Fig. 5e, and the lignin content at this point was the highest. If the goal is to get more dissolution of compounds from the raw material, especially carbohydrates, more NaOH should be loaded and the pretreatment time should be prolonged. However, a higher addition of alkali and longer pretreatment time is not good for industrial applications because of the low economic efficiency. Therefore, choosing the appropriate alkaline pretreatment depends on the production goal.

Gel Permeation Chromatography (GPC) Analysis

With analysis of the GPC, the M_w and M_n of carbohydrate and lignin, which were dissolved into the BL, are shown in Fig. 6. As it can be observed, the M_w of the carbohydrate was all above 6000 (about 45 monosaccharide units) and up to 7000 (about 56 monosaccharide units), on a g/mole basis, which is three times that of lignin. It is worth pointing out, the M_w and M_n of carbohydrates reach the lowest point at the 140 mg NaOH / g dry straw NaOH loading for 2 h and the DP of this point is lowest too ($n=1.06$). Before that point, each NaOH loading has a lowest peak, when the pretreatment time reaches 2 h. When the alkali loading reached 18% or greater, and with a prolonged the pretreatment time, the M_w continuously increased. The M_w of the carbohydrate rose to its highest level of 8488 at 220 mg NaOH / g dry straw NaOH loading for 3 h. It can be inferred from this that before the NaOH loading has reached 140 mg NaOH / g dry straw, the group of low molar weight carbohydrates will first dissolve into the BL. The alkali pretreatment at such low temperatures (90 °C) was not enough to cause any conspicuous change of the crystal structure. So, the alkaline effect on the hemicellulose can be ruled out as the basic reason for this. With NaOH loading reaching 180 mg NaOH / g dry straw or more, the larger molar mass can be dissolved into BL because the gaps between the cellulose enlarge and

more alkaline-soluble groups/material can be removed from the cell wall, and the M_w becomes more dispersed.

The M_w of lignin rose from 1200 at 60 mg NaOH / g dry straw NaOH loading to a maximum of 4500 at 220 mg NaOH / g dry straw NaOH loading. The average molar weight never stopped increasing, while the average molar number reached a gentle peak. This is not hard to see from Fig. 6 (b), before 140 mg NaOH / g dry straw NaOH loading, when pretreated time was 1 h, the M_w of lignin was all below 1500 (about 6 to 8 lignin units). When the pretreatment time was prolonged to 2 h, the M_w of lignin could reach about 2000 (about 10 to 12 lignin units) under 140 mg NaOH / g dry straw NaOH loading. It can be inferred that a weak pretreatment condition (60 mg NaOH / g dry straw) cannot make any alkali-soluble compositions in the straw dissolved into the BL. As shown in Fig. 4, the structure of straw after 60 mg NaOH / g dry straw pretreatment remained intact compared with untreated straw. This structure is not good for the dissolution of the lignin and carbohydrates. Under prolonged pretreatment, the DP of the 60 mg NaOH / g dry straw increased from 1.03 to 1.05. This light increase reflects that under weak alkali pretreatment conditions, the low molecule weight (LMW) lignin was dissolved out from raw straw in an intermediate mass distribution form. However, when NaOH loading increased to 10%, the pH environment of the solution could reach 10.5. Although this condition is moderate for pretreatment, prolonging pretreatment time can also bring about greater dissolution of the lignin groups and thereby effectively soften the wheat straw structure. Special attention should be paid to the fact that polydispersity is increased with M_w . When NaOH loading increased to 180 mg / g dry straw or higher, the M_w of the dissolved lignin in the BL reached 4300 to 4800. Due to strong severity pretreatment conditions will make high molecular weight lignin groups be dissolved into the BL with a wider distribution. Molecular weight distribution (MWD) could reach 1.8.

From the view of effective utilization of lignin, lignin can be preferably dissolved out of the straw gradually. Two kinds of intermediate M_w lignin could be obtained from two pretreatment conditions. Low molecular weight (LMW), M_w ranged from 1700 to 2000 and could be obtained at 60 mg / g dry straw, and HMW M_w ranged from 4300 to 4800 and could be obtained from 220 mg / g dry straw NaOH loading, respectively.

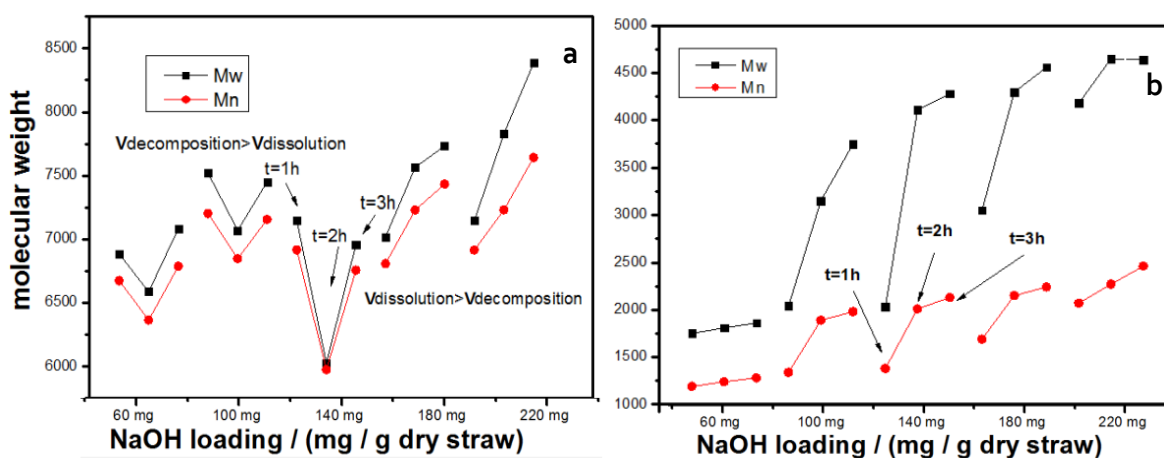


Fig. 6. (a) Weight-average (M_w) and number-average (M_n) molecular weights of the carbohydrate fraction; (b) M_w and M_n of the lignin dissolved in the BL

CONCLUSIONS

Low temperature and the addition of anthraquinone (AQ) could protect cellulose from dissolution by alkali, with only a 3% glucose loss, and 35% xylan and 75% lignin dissolution in the black liquor (BL). The BL obtained from the pretreated wheat straw at different pretreatment conditions contained a large fraction of intermediate M_w lignin that could provide a valuable stream for upgrading if technologies can be developed to utilize these species. These results can serve as a guide for the biorefinery industry to optimize lignin removal, while minimizing the loss of carbohydrates during an alkaline pretreatment.

ACKNOWLEDGEMENTS

This research was supported by the National Natural Science Foundation of China (21276119).

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Article submitted: July 2, 2017; Peer review completed: September 17, 2017; Revised version received and accepted: September 25, 2017; Published: September 28, 2017.
DOI: 10.15376/biores.12.4.8550-8564