

**ALKALINE SOLVENT COOKING TREATMENT OF CORK  
AND COMPONENT ANALYSIS OF FILTRATES**

SHANGGUAN WEIWEI, WANG QINGGUO, YUAN YIDAN, SONG XIAOZHOU  
NORTHWEST A&F UNIVERSITY, COLLEGE OF FORESTRY  
SHAANXI, CHINA

ZHU MINGQIANG  
NORTHWEST A&F UNIVERSITY, COLLEGE OF MECHANICAL  
AND ELECTRONIC ENGINEERING  
SHAANXI, CHINA

(RECEIVED JUNE 2018)

**ABSTRACT**

This study aimed to determine the effects of alkaline solvent treatment on the physical properties of cork, and to analysis the filtrate components of cork after cooking treatment. Potassium hydroxide (KOH), alkaline hydrogen peroxide (AHP), and ammonium hydroxide (AOH) were used as solvents. The properties of treated cork including color, volume, hardness, compression resilience ratio, and filtrate components of different solvent treatments were investigated. The results showed an increase in the cork's volume, changes in color, and decrease in lightness after three solvent treatments. Hardness and compression resilience decreased after three solvents cooking, and the difference in the compression resilience ratio between 15 min and 24 h was at a minimum when cork was cooked in KOH solvent. The analyses of filtrate components after KOH and AHP cooking treatments indicated that the hemicelluloses content was generally higher than lignin content. Moreover, water-soluble lignin, obtained from the three solvent filtrates, consisted of a small amount of monosaccharides, such as arabinan, galactan, glucan, and xylan. Nuclear magnetism (NMR) spectra analysis demonstrated that the lignin in KOH and AOH filtrates consisted of G units and H units, while S units only appeared in KOH-immersed lignin. This study shows that solvent treatment changes cork's physical and chemical properties based on the solvent type and concentration.

**KEYWORDS:** *Quercus variabilis* cork, solvent cooking, physical properties, filtrate components.

## INTRODUCTION

Cork is the outer bark of the cork oak. It can be first obtained after the 20–25 years growth of cork oak, which it is known as virgin cork. Thereafter, the cork produced every 9–15 years is called reproduction cork. The chemical composition of cork is different from that of other lignocellulosic materials. Suberin is the main component, accounting for 30–50% of cork's cell walls (Pereira 2007, 2013), it is mainly deposited on the secondary walls of cork. The lignin content of cork has been found to range from 20–25%, and the polysaccharide content is relatively small (Ferreira et al. 2016, Pereira 2007, Song et al. 2018). Due to chemical component differences in cork and lignocellulosic materials, cork's performance is unique compared with other biomass materials. It is light, compressible, and impermeable and has characteristics of low thermal conductivity, energy-absorbing capacity, and high friction resistance (Pereira 2007). It is widely used for bottle stoppers, decorative materials, buoyancy, insulation, etc. (Fortes 1993, Silva et al. 2005).

The main source of cork is *Q. suber* and *Q. variabilis*. *Q. suber* is mainly cultivated in Europe, and *Q. variabilis* is widespread in the northwest of China, north and south China, central China and southwest of China (Song 2017). The structure and composition of *Q. variabilis* is similar to that of *Q. suber*. Compared with *Q. suber*, *Q. variabilis* cork has a higher density and a lower elasticity (Miranda et al. 2013). Because of its renewable characteristics and excellent performance, extensive research has been conducted on *Q. suber* cork's properties and applications (Pereira 2007, 2015), however, research on *Q. variabilis* cork is scarce. Therefore, *Q. variabilis* was focused in this study.

Solvent cooking treatment is widely used in wood modification, especially alkaline delignification (Balberčák et al. 2018) or mildly alkaline delignification (Balberčák et al. 2017) and pre-treatment (Gigac et al. 2017) by modifying chemical compositions. It is known for being effective and saving time and energy (Zhu 2015a). Alkaline hydrogen peroxide (AHP) treatment has shown effective delignification on several lignocellulosic substrates (Alvira et al. 2010). Solvent treatment also causes cleavage of inner-molecular  $\alpha$  and  $\beta$ -aryl ether linkages on lignin molecules (Gierer 1982). Research has found that the presence of oxygen molecules in alkali treatment leads to degradation of the cellulose chain. After AHP treatment, the content of oxygenated carbons in wood samples is higher than that of untreated samples due to oxidation in treated samples during alkaline hydrogen peroxide processing (Zhu et al. 2015b).

Cooking treatment is an important process for pretreatment in the cork industry. Previous studies have shown that water cooking has a great impact on cork's properties. Cork volume increases and impurities decrease after cooking, facilitating subsequent processing of cork (Zhao et al. 2009). After boiling, cell wall corrugations reduce, and volume increases with boiling time. Research has also demonstrated a 10–15% and 5–7% expansion in radial and tangential directions, respectively (Rosa et al. 1990). After a short immersion time, the increase of volume ceases because the cell walls are saturated with water (Rosa and Fortes 1993). The porosity of untreated cork in previous studies has been found to be 8.2%, decreasing to 4.0% after boiling treatment (Cumbre et al. 2000).

During cork processing, modification treatment was conducted using chemical solvents. For the final product of cork, solvents were used to bleach the product for aesthetic reasons. Song et al. (2018) used sodium hydroxide to cook the cork samples. It was found that the color change of alkali-treated cork (cooking at 75°C for 1h) was greater than that of water (cooking at 100°C for 3h) and hydrogen peroxide (cooking at 75°C for 1h) treatments. Due to the great influence of alkaline solution on cork, this study uses three alkali solutions, including potassium

hydroxide (KOH), AHP and ammonium hydroxide (AOH), to analyze their effect on cork properties. The paper described changes in color, volume, hardness, compression resilience ratio, and filtrate components after solvent cooking. The objectives were to investigate the effect of solvent treatment on cork's physical properties and filtrate components. This study also intended to provide insight into cork use and purification.

## MATERIALS AND METHODS

### Materials

Reproduction cork of *Q. variabilis*, supplied by Qinbar Mountain Cork Company was produced in Shaanxi Qinbar mountainous areas in China. It was stored at room temperature for more than six months with an average moisture content of 6%. The cork was processed into 16 mm (axial) × 16 mm (tangential) × > 6 mm (radial) size for volume and compression resilience testing, and 30 mm (axial) × 30 mm (tangential) × > 6 mm (radial) for hardness and color testing.

### Solvent treatments

The cork samples were immersed in three solvents and purified water at 75°C for 60 min. The different concentration solvents were KOH (0.1%, 0.3%, and 0.5%), AHP (0.5%, 1%, and 1.5%) with a pH level between 11.5-12, and AOH (5%, 10%, and 15%). A freeze dryer was used to remove the solvents, and then the samples were air drying for 2 weeks to make the moisture content consistent before and after treatment (the difference is within 1%).

As shown in Fig. 1, the filtrates of the cooked cork samples were collected and were neutralized using HCl ( $6 \text{ mol}\cdot\text{L}^{-1}$ ) to 5.5-6 except the filtrate of AOH treatment.

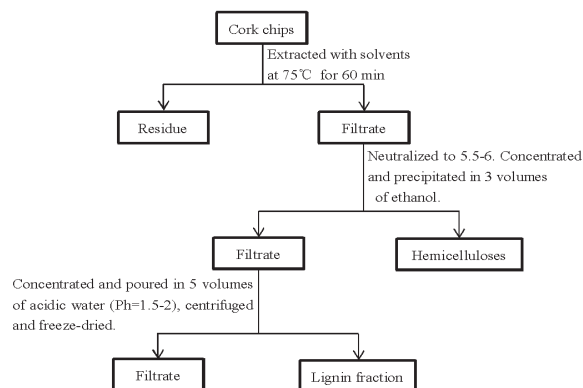


Fig. 1: Schematic illustration of the integrated process.

Then the filtrates were concentrated to 100 mL using a rotary evaporator. After that, the concentrated solutions were dripped into 300 mL ethanol with magnetic stirring. Degraded hemicelluloses were separated by filtering. 150 ml HCL was poured in the filtrates obtained above, which had been concentrated to 50 ml. The degraded lignin precipitated and was isolated using centrifugation and lyophilization.

### Characterization of physical properties of treated cork

Physical properties after different solvents cooking followed methods previously described by Song et al. (2018). Color measurements of uncooked and cooked samples were taken using a colorimeter, SC-80C (Kangguang Inc., Beijing, China). The hardness value of the cork specimens was measured using the Shore A Hardness test (Liaoning Yingkou Inc., China). Measurements of 30 replicates were performed.

The compression resilience of corks was investigated using a universal materials testing machine (CMT5504, SANS Inc., Shenzhen, China). The compression load was parallel to the radial direction of the oak tree. Approximately 50% compression in the radial direction was done at a crosshead speed of 5 mm·min<sup>-1</sup>, and then the loading was removed. The dimension recovery after compression was determined by measuring the residual amount of compression in the squeezing direction immediately. In order to compare resilience ratio of cork after cooking at different times, test was conducted at 15 min and 24 h after pressure release. The compression resilience ratio was calculated using Eq. 1.

$$R = (l_2 - l_1) / l_1 \times 100 \quad (\%) \quad (1)$$

where:  $R$  - the compression resilience ratio (%),

$l_1$  - the sample thickness compressed in half (mm),

$l_2$  - the sample thickness at 15 min and 24 h after pressure release (mm).

### Characterization of filtrates

Analysis of the chemical compositions of hemicelluloses and lignin in the filtrates after cooking treatments was conducted according to the laboratory analytical procedure provided by NREL (Sluiter et al. 2008). Analysis of chemical composition was extracted from the filtrates at concentrations of 0.1% (KOH), 3% (AHP) and 5% (AOH) after cork cooking treatments. For 2D-HSQC spectra, the lignin (50 mg) was dissolved in DMSO-d<sub>6</sub> (0.5 ml), and the Bruker standard pulse program hsqcetgpsi2 was used for HSQC experiments as previously reported (Wen et al. 2013a).

## RESULTS AND DISCUSSION

### Color regions of cork after solvent treatments

$\Delta L^*$  represents the difference in lightness and  $\Delta E^*$  denotes the total color difference between cooked and uncooked samples. From Fig. 2, it can be seen that  $\Delta L^*$  were negative values for the samples in water and three solvent treatments, suggesting that the lightness of cork decreased after cooking.  $\Delta L^*$  of KOH and AOH treated cork was around -20, and that of AHP and water treated was around -5. KOH, AHP and AOH, which present alkaline, hydrolyze part of lignin and result in cork's reduced lightness (Chen et al. 2000). In our previous study, the lightness of cork increased after the embedding H<sub>2</sub>O<sub>2</sub> treatment under the same experiment condition (Song et al. 2018). In this study, the lightness of cork decreased slightly after AHP treatment was probably due to the alkaline effect.

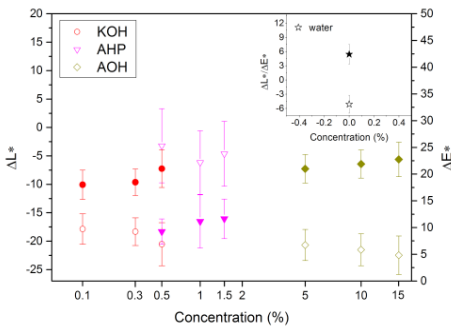


Fig. 2: Change of surface color of cork after treatment in different reagents. The upper corner figure is the color of the purified water treated samples. The hollow and solid symbols are  $\Delta L^*$  and  $\Delta E^*$ , respectively.

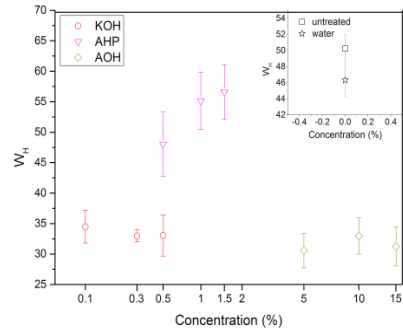


Fig. 3: Change of Hunter whiteness ( $W_H$ ) of cork after treatment in different reagents. The upper corner figure is the  $W_H$  value of untreated and purified water treated samples.

As shown in Fig. 2, the value of the  $\Delta E^*$  changed for all treated cork samples. The effect of alkali on color of cork was great, which can be reflected from the  $\Delta E^*$  value of 11.63 after AHP treated at a lower concentration (1.5%) compared with 10.50 after  $H_2O_2$  treated at a higher concentration (7%) in our previous study (Song et al. 2018). Changes of cork composition, medium conditions, and dissolution of extracts etc. are the factors that cause color variation of cork (Song et al. 2008).

Fig. 3 shows the effect of solvents on Hunter whiteness of cork.  $W_H$  increased as the AHP concentration increased. The rate of the increase with the concentration ranged from fast to slow for  $W_H$  of AHP-treated samples. The effect of water on whiteness of cork was not obvious. KOH and AOH, which were alkaline, reduced the whiteness of cork via hydrolyses of lignin. The effect of high AOH concentration on the whiteness of cork was close to that of low KOH concentration, presumably because the alkalinity of KOH was stronger than that of AOH.  $W_H$  of cork cooked with AHP was higher than that of water, KOH and AOH.  $HO_2^-$ , which is a decomposition product of  $H_2O_2$ , is the main ingredient in bleaching. It breaks conjugated double bonds of chromophoric lignin, resulting in bleaching (Gierer 1990). The bleaching effect of AHP at a lower concentration was still better than that of  $H_2O_2$  with a higher concentration (Wang et al. 2010). Alkalinity can accelerate the decomposition rate of hydrogen peroxide, producing more  $HO_2^-$  with increasing pH and accelerating the oxidative bleaching effect (Ma et al. 2010, Wang et al. 2010).

### Volume changes of cork after solvent treatments

The change of volume between treated and untreated samples is shown in Fig. 4.  $V_0$  and  $V$  represent the volumes of cork before and after reagent treatments, respectively.

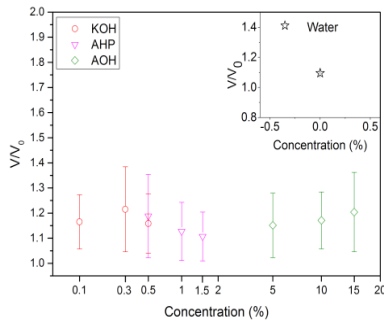


Fig. 4: Effect of reagent treatment on volume change in cork. The upper corner figure is the volume change of purified water treated sample.

The values of  $V/V_0$  of all samples were greater than 1.00, indicating that the sample sizes increased after reagent treatments. The changes of cork volume treated by reagents were larger than that of purified water. Water absorption in the cell wall and reduction of cell wall corrugation after boiling may explain the increase in volume (Rosa et al. 1990, Rosa and Fortes 1993). The surface area and pore volume of the samples treated with alkaline solvents increased due to the partially decomposed microstructure (Zhu et al. 2015a). A loose structure allowed the solvents to enter into the samples more easily, leading to an increase in size. The increase of swelling values indicated that the structure of material was slightly destroyed to some extent (Cui et al. 2015).

**Hardness changes of cork after solvent treatments**

$H_0$  and  $H$  represented the hardness of cork before and after reagent treatment, respectively. The values of  $H/H_0$  were less than 1 in Fig. 5, indicating that the hardness of cork after water and reagents cooking was less than that of untreated samples.

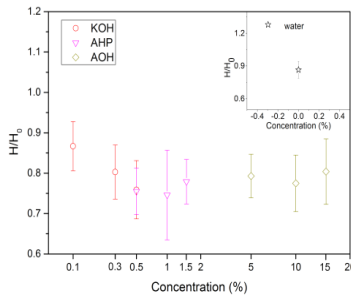


Fig. 5: Effect of reagent treatment on hardness change in cork. The upper corner figure is the hardness of purified water treated sample.

The decrease rates of hardness of cork after the three reagent treatments were higher than that of purified water treatment due to the destruction of cork’s microstructure by the solvents. Hardness decreasing with increased concentration of KOH solution was attributed to the degradation of cellulose and lignin (Obi Reddy et al. 2012, Zhao et al. 2012). Increased alkaline concentration led to greater lignin degradation by cleavage of inner-molecular  $\alpha$ - and  $\beta$ -aryl ether linkages and cellulose depolymerization by peeling and hydrolytic reactions (Zhao et al. 2012).

Although hardness of cork after AHP treatment was lower than that of untreated samples, the hardness slightly increased at a solution concentration of 1.5%.

### Compression resilience changes of cork after solvent treatments

Fig. 6 shows that the compression resilience ratios of cork cooked with water and reagents were less than that of untreated cork. Compression resilience ratios showed downward trends with increasing concentrations in alkaline solution (KOH, AHP, and AOH).

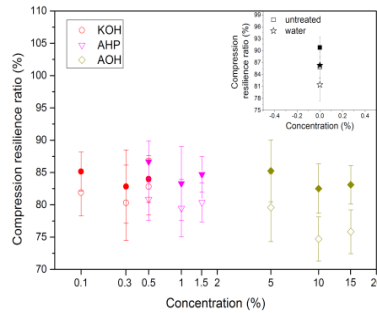


Fig. 6: Effect of reagent treatment on the change of compression resilience ratio of cork. The upper corner figure is the compression resilience ratios of the untreated and purified water treated samples. The hollow and solid symbols are the compression resilience ratios of cork after pressure relief for 15 min and 24 h, respectively.

Cooking promotes crystallization of amorphous areas of cellulose, reducing compression resilience ratios (Gao et al. 2017). Suberin, which determines the compression resilience ratios of cork, also degrades; it is removed after breakdown of the inter-monomeric ester links by alkaline hydrolysis and alkaline trans-esterification (Pereira 2007). The compression resilience ratios of cork treated with AOH were the smallest after 15 min relief, and the resilience was large after 24 h. Samples treated with AHP solution had a moderate compression resilience ratios. The difference in resilience ratios for KOH-treated samples between 15 min and 24 h relief was the smallest. This may be due to the small amount of destruction of suberin and lignin with severe degradation by KOH, whose alkali was the strongest among the reagents in this experiment, resulting in difficult resilience even if the time was longer.

### Component analysis of filtrates after solvent treatments of cork

In Fig. 7, the mass percent of hemicelluloses and water-soluble lignin generally showed an increasing trend with an increase of alkaline solution concentration. The presence of lignin in the filtrates indicated partial degradation of cork lignin, and this is one of the reasons for color change.

The hemicelluloses content in the KOH and AHP filtrates was higher than that of lignin because hemicelluloses are more likely affected by alkali than lignin or  $\alpha$ -cellulose (Obi Reddy et al. 2012). As the concentration increased, the content of hemicelluloses in AHP solution increased. And this may be the reason for the higher hardness of cork treated in AHP at the concentration of 1.5%. Das and Chakraborty (2006) believe the percentage crystallinity index increased with increasing alkali treatment due to the more compact cellulose chain after removing cementing material.

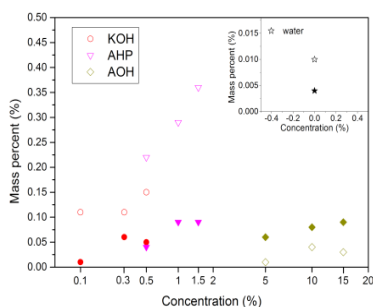


Fig. 7: Mass percents of hemicelluloses and water-soluble lignin extracted from the filtrates. The upper corner figure is the mass percents of the purified water treated samples. The hollow and solid symbols represent hemicelluloses and water-soluble lignin, respectively.

However, the mass percent of hemicelluloses decreased slightly in the AOH solution at 15% concentration, which potentially contributed to the degradation of hemicellulose into small molecules and made them difficult to collect. In AOH solution, mass percent of lignin was higher than that of hemicelluloses. It is likely that destruction of lignin was greater than that of hemicelluloses in AOH. Kim and Lee (2005) demonstrated that AOH removed 75–85% of the total lignin of corn stover and solubilized 50–60% of hemicelluloses but retained more than 92% of the cellulose content. At the same time, water-soluble lignin with a lower molecular weight aggregated with increasing alkalinity that was easier to collect (Zhu et al. 2015a).

Tab. 1: Sugars and uronic acids in hemicelluloses and water-soluble lignin.

	Neutral sugars and uronic acids (%) <sup>a</sup>							Xyl/Ara <sup>c</sup>	Xyl/UA <sup>d</sup>
	Ara <sup>b</sup>	Gal	Glu	Xyl	Man	GluA	GalA		
H <sup>e</sup> KOH	1.16	0.75	0.42	1.82	0.25	1.40	0.03	1.56	1.28
H <sup>e</sup> AHP	1.06	0.67	0.59	2.08	0.15	1.43	0.04	1.97	1.42
H <sup>e</sup> AOH	0.73	0.45	0.35	1.10	0.14	0.73	0.02	1.51	1.47
L <sup>f</sup> KOH	0.06	0.03	0.08	0.03	ND <sup>g</sup>	0.02	ND	/	/
L <sup>f</sup> AHP	0.10	0.03	0.14	0.05	0.02	0.01	ND	/	/
L <sup>f</sup> AOH	0.41	0.40	0.38	0.43	0.15	0.14	0.02	/	/

<sup>a</sup> Chemical composition was extracted from the filtrates at concentrations of 0.1% (KOH), 3% (AHP) and 5% (AOH), respectively, <sup>b</sup> Ara, arabinan; Gal, galactan; Glu, glucan; Xyl, xylan; Man, mannan; GluA, glucuronic acid; GalA, galacturonic acid, <sup>c</sup> Xylan to arabinan ratio, <sup>d</sup> Xylan to uronic acids ratio, <sup>e</sup> Hemicelluloses, <sup>f</sup> Water-soluble lignin, <sup>g</sup> ND, not detected.

The released monomeric sugars and uronic acids from hemicelluloses and water-soluble lignin in the filtrates are listed in Tab. 1. Sugar composition analysis showed that the obtained residual hemicelluloses were rich in xylan (2.08%–1.10%), glucuronic acid (1.43%–0.73%), and arabinan (1.16%–0.73%). The content of mannan (0.14–0.25%) and galacturonic acid (0.02–0.04%) were relatively small. It presented typical hemicellulosic components of glucuronoxylans-type polysaccharides (Sun et al. 2014). Miranda et al. (2013) studied the proportion of monosaccharides in *Q. variabilis* in descending order of glucose (42.8%), xylose (27.5%), arabinose (15.4%), galactose (9.0%), mannose (4.0%), rhamnose (1.2%) (Miranda et al. 2013). This is consistent with the trend of the proportion of water-soluble monosaccharides extracted from three



solvents, in which glucose existed in the form of glucuronic acid. The degree of extraction for hemicelluloses differed based on solvents; it was the highest in AHP extraction, especially xylan, the main component in hemicelluloses. Compared with the other two solvents, the concentration of AOH solvent was high (5%), however, the extraction of hemicelluloses using AOH was the smallest.

Small amounts of carbohydrates were found in water-soluble lignin, and they were also existed in lignin fractions (Zhu et al. 2015b). Mannan, and galacturonic acid were not detected in KOH-treated lignin. The linkages that connected lignin and hemicelluloses may have been destroyed in strong alkali. The weak alkali, such as AOH, made more polysaccharides (types and contents) into water-soluble lignin, suggesting that alkaline strength may be important for the separation of hemicelluloses and lignin. The ratios of xylan to arabinan (Xyl/Ara) and xylan to uronic acids (Xyl/UA) represent the degree of linearity or branching of hemicelluloses. The Xyl/Ara and Xyl/UA were 1.97 and 1.42 for AHP-isolated hemicelluloses, respectively, indicating that the hemicelluloses had fewer side chains and branches.

### NMR spectra analysis

The structure characteristics of water-soluble lignin isolated by KOH and AOH were analyzed using 2D-HSQC NMR, as shown in Fig. 8. In the side-chain region of water-soluble lignin, the linkages and substructures were assigned according to previous literature as noted in Tab. 2 (Wen et al. 2013b, Zhu et al. 2015a, b).

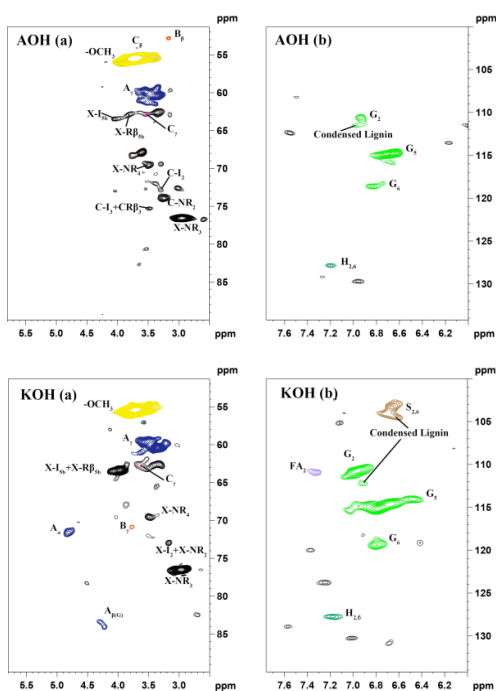


Fig. 8: NMR spectra of 2D lignin. Side-chain region (a), aromatic region (b).

Tab. 2: Assignments of  $^{13}\text{C}$ - $^1\text{H}$  cross-signals in the HSQC spectra of degraded water-soluble lignin fractions from cork (Kim and Ralph 2014, Zhu et al. 2017).

Lable	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm)	Assignments
$\text{C}_{\beta}$	53.7/3.61	$\text{C}_{\beta}$ - $\text{H}_{\beta}$ in phenylcoumaran substructures (C)
$\text{B}_{\beta}$	52.9/3.19	$\text{C}_{\beta}$ - $\text{H}_{\beta}$ in $\beta$ - $\beta$ resinol substructures (B)
$-\text{OCH}_3$	55.6/3.71	C-H in methoxyls
$\text{A}_{\gamma}$	59.5/3.59	$\text{C}_{\gamma}$ - $\text{H}_{\gamma}$ in $\beta$ -O-4 substructures (A)
$\text{C}_{\gamma}$	62.5/3.64	$\text{C}_{\gamma}$ - $\text{H}_{\gamma}$ in phenylcoumaran substructures (C)
$\text{B}_{\gamma}$	71.0/3.80	$\text{C}_{\gamma}$ - $\text{H}_{\gamma}$ in $\beta$ - $\beta$ resinol substructures (B)
$\text{A}_{\alpha}$	71.5/4.81	$\text{C}_{\alpha}$ - $\text{H}_{\alpha}$ in $\beta$ -O-4 units (A)
$\text{A}_{\beta(\text{G})}$	83.9/4.33	$\text{C}_{\beta}$ - $\text{H}_{\beta}$ in $\beta$ -O-4 linked to G/H unit (A)
$\text{S}_{2,6}$	103.6/6.68	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in syringyl units (S)
$\text{G}_2$	111.1/6.98	$\text{C}_2$ - $\text{H}_2$ in guaiacyl units (G)
$\text{G}_5$	114.7/6.71	$\text{C}_5$ - $\text{H}_5$ in guaiacyl units (G)
$\text{G}_6$	118.9/6.80	$\text{C}_5$ - $\text{H}_5$ in guaiacyl units (G)
$\text{H}_{2,6}$	127.7/7.17	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in H units (H)
$\text{FA}_2$	110.7/7.35	$\text{C}_2$ - $\text{H}_2$ in ferulate (FA)

Water-soluble lignin in cork exhibited similar spectral patterns compared to the milled wood lignin in *Eucommia ulmoides* Oliver (Zhu et al. 2015a, b), but there were some notable differences. The aromatic region in the spectra of water-soluble lignin presented basic lignin units (guaiacyl [G], syringyl [S], and p-hydroxyphenyl [H]). Both G ( $\text{G}_2$ ,  $\text{G}_5$ , and  $\text{G}_6$ ) and H units were obtained after KOH and AOH treatments; however, the S unit only appeared in KOH-treated lignin. Meanwhile, the content and condensation degree of the aromatic region obtained by KOH were higher than that of AOH treatment. The contents of the G units were the highest in both KOH-soluble and AOH-soluble lignin, and the milled cork lignin showed that G units accounted for 95% of the total lignin content (Pereira 2007).

$-\text{OCH}_3$ ,  $\text{A}_{\gamma}$ , and  $\text{C}_{\gamma}$  on the side-chain appeared in both KOH-soluble and AOH-soluble lignin.  $\text{C}_{\beta}$  and  $\text{B}_{\beta}$  were tested in AOH-soluble lignin, and  $\text{A}_{\alpha}$ ,  $\text{B}_{\gamma}$  and  $\text{A}_{\beta(\text{G})}$  were tested in KOH-soluble lignin. Differences were found in the side-chain and aromatic regions of lignin from different solvent treatments.  $\text{FA}_2$  at 110.7/7.35, representing  $\text{C}_2$ - $\text{H}_2$  in ferulate, in KOH-soluble lignin was the main family of suberin oligomers (Graça et al. 2015). The difference of compression resilience ration between 15 min and 24 h was small probably due to degradation of suberin by strong alkali.

As can be seen from the 2D-HSQC spectra, water-soluble lignin contained small amounts of carbohydrates, such as xylan internal unit (X-I), xylan non-reducing end unit (X-NR), xylan  $\beta$ -reducing end unit (X-R $\beta$ ), cellulose internal unit (C-I), and cellulose non-reducing end (C-NR). This indicates that the cellulose and hemicelluloses linked with lignin were coprecipitated during the precipitation process of hydrochloric acid. The presence of correlations at 63.2/3.96, 63.1/3.80, 72.8/3.17, 72.8/3.16, 76.3/3.01 and 69.5/3.49 were associated with X-I $_{5b}$ , X-R $\beta_{5b}$ , X-I $_2$ , X-NR $_2$ , X-NR $_3$ , and X-NR $_4$  indicating that carbohydrates precipitated in KOH-soluble lignin were mainly xylan from hemicelluloses (Kim and Ralph 2014). AOH-soluble lignin contained not only xylan, such as X-I $_{5b}$ , X-R $\beta_{5b}$ , X-NR $_3$ , and X-NR $_4$ , but also cellulose compounds including C-I $_2$  (72.9/3.29), CR $\beta_3$  (75.01/3.48), and C-NR $_2$  (73.9/3.21) (Kim and Ralph 2014). For KOH-soluble and AOH-soluble lignin, the amount of reducing-end and non-reducing end of carbohydrates was more than that of internal peaks.

## CONCLUSIONS

1. KOH, AHP, and AOH solvents were used to cook cork samples. After the cooking process, the volume of cork increased and the lightness decreased. The bleaching performance of AHP was better than the other two solvents.
2. The hardness of cooked cork in the solvents of KOH, AHP and AOH decreased compared to uncooked cork. The compression resilience ratio of cork decreases slightly after solvents cooking.
3. The content of hemicelluloses and lignin in the filtrates increased with solvent concentration. Water-soluble lignin contained a small amount of carbohydrate. G unit and H unit lignin were found in the filtrates of KOH and AOH solvent treatments, while S unit lignin was only found in KOH filtrate.

## ACKNOWLEDGMENTS

This research was financially supported by the National Natural Science Foundation of China (No. 31470583) and International Scientific and Technological Cooperation Seed Foundation of Northwest A&F University. The authors also acknowledge the Fundamental Research Funds for the Central Universities, Grant No. 2452017097.

## REFERENCES

1. Alvira, P., Tomas-Pejo, E., Ballesteros, M., Negro, M.J., 2010: Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review. *Bioresour. Technol.* 101: 4851-4861.
2. Balberčák, J., Ihnát, V., Boháček, S., Pažitný, A., Lubke, H., 2018: Chemical processing of waste wood based agglomerates. Part II: Evaluation of properties of fluting liners made of semichemical pulp obtained by an alkaline cooking process. *Wood Research* 63(1): 35-44.
3. Balberčák, J., Ihnát, V., Boháček, S., Medo, P., Lubke, H., 2017: Chemical processing of waste wood based agglomerates. Part I: Evaluation of properties of fluting liners made of semichemical pulp obtained by a mildly alkaline sulphur-free cooking process. *Wood Research* 62(5): 715-726.
4. Chen, Y., Huang, W., Chang, D., Hu, W., 2000: Study on promoting effects of NaOH pretreatment on wood bleaching. *Chem. Ind. For. Prod.* 20: 52-56.
5. Cui, X., Zhao, S., Hu, M., Li, C., Wang, B., 2015: The influence of Tween 20 concentration on biodesulfurization of ground tire rubber by *Sphingomonas* sp. *Chin. J. Appl. Environ. Biol.* 21: 1037-1043.
6. Cumbre, F., Lopes, F., Pereira, H., 2000: The effect of water boiling on annual ring width and porosity of cork. *Wood Fiber Sci.* 32: 125-133.
7. Das, M., Chakraborty, D., 2006: Influence of alkali treatment on the fine structure and morphology of bamboo fibers. *J. Appl. Polym. Sci.* 102: 5050-5056.
8. Ferreira, J., Miranda, I., Şen, U., Pereira, H., 2016: Chemical and cellular features of virgin and reproduction cork from *Quercus variabilis*. *Ind. Crop. Prod.* 94: 638-648.
9. Fortes, M.A., 1993: Cork and corks. *Eur. Rev.* 1: 189-195.

10. Gao, Z., Zhang, Y., Wu, Z., Wang, Y., Li, R., Huang, R., 2017: Effect of pressurized heat treatment on spring-back of surface compressed polar wood. *Chin. Wood Ind.* 31: 24-28.
11. Gierer, J., 1982: The chemistry of delignification. Part I. *Holzforschung* 36: 43-51.
12. Gierer, J., 1990: Basic principles of bleaching part 2: anionic processes. *Holzforschung* 44: 395-400.
13. Gigac, J., Fišerová, M., Stankovská, M., Pažitný, A., 2017: Enzymatic hydrolysis of extruded wheat straw with addition of sodium hydroxide and calcium hydroxide. *Wood Research* 62 (6): 919-930.
14. Graça, J., Cabral, V., Santos, S., Lamosa, P., Serra, O., Molinas, M., Schreiber, L., Kauder, F., Franke, R., 2015: Partial depolymerization of genetically modified potato tuber periderm reveals intermolecular linkages in suberin polyester. *Phytochemistry* 117: 209-219.
15. Kim, H., Ralph, J., 2014: A gel-state 2D-NMR method for plant cell wall profiling and analysis: a model study with the amorphous cellulose and xylan from ball-milled cotton linters. *Rsc. Adv.* 4: 7549-7560.
16. Kim, T.H., Lee, Y.Y. 2005: Pretreatment and fractionation of corn stover by ammonia recycle percolation process. *Bioresource Technol.* 96: 2007-2013.
17. Ma, J., Fan, Y., Wu, R., 2010: Effects of hydrogen peroxide treatment on chromaticity index of the triple *Tomentosa populus*. *Pap. Making* 29: 21-25.
18. Miranda, I., Gominho, J., Pereira, H., 2013: Cellular structure and chemical composition of cork from the Chinese cork oak (*Quercus variabilis*). *J. Wood Sci.* 59: 1-9.
19. Obi Reddy, K., Shukla, M., Uma Maheswari, C., Varada Rajulu, A., 2012: Mechanical and physical characterization of sodium hydroxide treated Borassus fruit fibers. *J. Forest Res.* 23: 667-674.
20. Pereira, H., 2007: *Cork: Biology, Production and Uses*. Elsevier Science, Amsterdam, 1<sup>st</sup> Edition, 346 pp.
21. Pereira, H., 2013: Variability of the chemical composition of cork. *Bioresources* 8: 2246-2256.
22. Pereira, H., 2015: The rationale behind cork properties: a review of structure and Chemistry. *BioResources* 10: 6207-6229.
23. Rosa, M.E., Fortes, M.A., 1993: Water absorption by cork. *Wood Fiber Sci.* 25: 339-348.
24. Rosa, M.E., Pereira, H., Fortes, M.A., 1990: Effects of hot water treatment on the structure and properties of cork. *Wood Fiber Sci.* 22: 149-164.
25. Silva, S.P., Sabino, M.A., Fernandes, E.M., Correlo, V.M., Boesel, L.F., Reis, R.L., 2005: Cork: properties, capabilities and applications. *Int. Mater. Rev.* 50: 345-365.
26. Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D., 2008: Determination of structural carbohydrates and lignin in biomass. Laboratory analytical procedure, Technical Report NREL/TP-510-42618.
27. Song, X., Shangguan, W., Zhang, L., Yuan, Y., Lei, Y., 2018: Effect of different boiling treatments on physical properties of cork from *Quercus variabilis*. *Bioresources* 13: 2411-2423.
28. Sun, S., Cao, X., Li, H., Xu, F., Sun, R., 2014: Structural characterization of residual hemicelluloses from hydrothermal pretreated Eucalyptus fiber. *Int. J. Biol. Macromol.* 69: 158-164.
29. Wang, Y., Zhang, L., Zhang, Z., 2010: Study on the new activator of hydrogen peroxide bleaching. *Light Text. Ind. Technol.* 39: 16-19.
30. Wen, J., Sun, S., Xue, B., Sun, R., 2013a: Quantitative structures and thermal properties of birch lignins after ionic liquid pretreatment. *J. Agr. Food Chem.* 61: 635-645.

31. Wen, J., Sun, S., Xue, B., Sun, R., 2013b: Recent advances in characterization of lignin polymer by solution-state nuclear magnetic resonance. *Mater* 6: 359-391.
32. Zhao, J., Lei, Y., Ma, Z., 2009: Optimizing process parameters of cork expansion treatment. *China Wood Ind.* 23: 31-33.
33. Zhao, X., Zhang, L., Liu, D., 2012: Biomass recalcitrance. Part II: Fundamentals of different pre-treatments to increase the enzymatic digestibility of lignocellulose. *Biofuels Bioprod. Biorefining* 6: 561-579.
34. Zhu, M., Wang, Z., Wen, J., Qiu, L., Zhu, H., Su, Y., Wei, Q., Sun, R., 2017: The effects of autohydrolysis pretreatment on the structural characteristics, adsorptive and catalytic properties of the activated carbon prepared from *Eucommia ulmoides* Oliver based on a biorefinery process. *Bioresource Technol.* 232: 159-167.
35. Zhu, M., Wen, J., Su, Y., Wei, Q., Sun, R., 2015a: Effect of structural changes of lignin during the autohydrolysis and organosolv pretreatment on *Eucommia ulmoides* Oliver for an effective enzymatic hydrolysis. *Bioresource Technol.* 185: 378-385.
36. Zhu, M., Wen, J., Wang, Z., Su, Y., Wei, Q., Sun, R., 2015b: Structural changes in lignin during integrated process of steam explosion followed by alkaline hydrogen peroxide of *Eucommia ulmoides* Oliver and its effect on enzymatic hydrolysis. *Appl. Energ.* 158: 233-242.

SHANGUAN WEIWEI, WANG QINGGUO, YUAN YIDAN, \*SONG XIAOZHOU  
NORTHWEST A&F UNIVERSITY  
COLLEGE OF FORESTRY  
SHAANXI 712100  
CHINA

\*Corresponding author: songxiaozhou@nwfufu.edu.cn

ZHU MINGQIANG  
NORTHWEST A&F UNIVERSITY  
COLLEGE OF MECHANICAL AND ELECTRONIC ENGINEERING  
SHAANXI 712100  
CHINA

