Fractionation and Potential Applications of Components from Microwave Liquefaction of Chromate Copper Arsenate-Treated Wood

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Decommissioned chromate copper arsenate (CCA)-treated wood poles were subjected to a microwave liquefaction process. The liquefied products were separated into cellulosic component, lignin fractions, and spent liquor. Analysis of the distribution of the CCA elements showed that the resulting cellulosic component and lignins were detoxified. Compared with the CCA-treated wood, the fractionated detoxified cellulosic component had become micro-sized and had a higher glucan content, crystallinity, and glucose conversion yield, as well as a larger surface area. Thus, the detoxified cellulosic component has potential as a raw material for biorefinery usage or for cellulosic material reinforced composite production. The constituents, such as glucose, xylose, glycerol, and their derivatives, as well as the metal elements in the spent liquor, are appropriate ingredients for the preparation of antifungal and insect resistant polyurethane foams. The fractionated detoxified cellulosic component and lignin products, in addition to the potential application for the spent liquor in the polyurethane industry, confirmed that the microwave liquefaction process coupled with a fractionation procedure is an environmentally conscious approach for the integrated utilization of decommissioned chromate copper arsenate treated wood.

Keywords: CCA-treated wood; Microwave liquefaction; Detoxify; Recycle

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INTRODUCTION

Chromate copper arsenate (CCA) is an inorganic waterborne wood preservative that has been widely used for approximately 60 years. A wide range of wood products, such as decks, fences, and other residential applications as well as industrial products such as poles, timber, and marine pilings have been treated with CCA. Inevitably, the treated wood is decommissioned and removed from service. The traditional methods for the disposal of treated wood include landfilling and burning. Neither method is profitable or without environmental and liability implications. Landfilling is expected to become costlier and more restricted due to the increased concentration of arsenic as a result from the increased amount of CCA-treated wood accepted into landfills. Since January 1, 2004, the U. S. and Canadian wood preservation industry has voluntarily discontinued the use of CCA-treated wood in residential areas due to the concerns over possible human health impacts (Townsend *et al*. 2005; Kazi and Cooper 2006). The amount of CCA-treated wood destined for landfill disposal is very likely to increase in the future, due to the fear of potential adverse effects from the CCA elements, so proper recycling methods for these materials are greatly needed.

To recycle the CCA-treated wood, it can be reduced into particles or fibers and incorporated into wood-based composites, such as particleboard and wood-plastic composites (Munson and Kamdem 1998; Kamdem *et al*. 2004). However, the application of the CCA-treated wood usually reduces the efficiency of the mechanical properties of the composites, and the sawdust that results from the machine processing releases CCA elements into the air.

To prevent the diffusion of heavy metals into the environment, CCA elements have been removed from treated wood *via* chemical or biological methods prior to its disposal or further recycling (Clausen and Smith 1998; Clausen 2004; Kakitani *et al*. 2006; Kazi and Cooper 2006; Hse *et al*. 2013). Structural panels have been fabricated from remediated CCA-treated wood (Clausen *et al.* 2006). Additionally, CCA-treated wood can be recycled *via* a three-step conversion into chemicals (Hakola *et al*. 2013). Although these two approaches to recycling CCA-treated wood are environmentally friendly, the processes are complex and expensive. Thus, a closed-loop recycling system to utilize decommissioned CCA-treated wood in an economical way is needed.

In previous research, a modified microwave liquefaction process was proposed to fractionate wood cell wall components to make a closed-loop utilization of wood residues. During this process, the woody materials were subjected to a microwave liquefaction process, and then the liquefied products were separated into cellulose fiber fractions, lignin fractions, and biopolyols fractions (Xu *et al*. 2012; Xie *et al*. 2016a). Further investigation confirmed that the cellulose fraction contained valuable resources needed for nanofiber production, and the lignins and biopolyols were also valuable ingredients for the preparation of bio-based polyurethane foams (Xie *et al.* 2015, 2016b). To test the feasibility of this microwave liquefaction process in the detoxification of the CCA-treated wood, decommissioned CCA-treated wood was liquefied *via* microwave for subsequent fractionation and analysis. The aim of this research was to determine the distribution of the metals in CCAs for each fraction and to gather fundamental information on the further use of environmentally friendly cellulosic fraction.

EXPERIMENTAL

Materials

Decommissioned CCA-treated utility poles were obtained from a local utility company (Pineville, LA, USA). The pole was cut into small pieces by a saw machine. After being air-dried, the wood pieces were ground in a Wiley mill. The wood particles that passed through the size 20 mesh sieve and did not pass through the size 40 mesh sieve were collected and oven-dried to a constant weight. All reagents and chemicals were from commercial sources and were used as received.

Microwave Liquefaction and Fractionation

The liquefaction and fractionation processes are illustrated in Fig. 1. The liquefaction of the decommissioned CCA-treated wood was conducted in a Milestone laboratory microwave oven as previously described (Xie *et al.* 2015). The of microwave liquefaction reaction consisted of 2 g of CCA-treated wood particles, 8 g of solvent (a glycerol and methanol mixture), and 0.14 g of sulfuric acid loaded into Teflon vessels with a magnetic stirring bar. The Teflon vessels were placed onto a rotor tray inside the microwave cavity. The temperature was increased from room temperature to 120 °C at a heating rate of 25 °C/min and then kept constant for 5 min.

At the end of the reaction, the vessels were cooled to room temperature, and the liquefied products were vacuum-filtered. The solid components retained on the filter paper, designated as the cellulosic component, were rinsed with methanol and oven-dried at 105 °C. The filtered liquid was vacuum-evaporated to remove methanol, and then distilled water was added. After thoroughly stirring, the mixture was centrifuged at 7000 r/min for 15 min. The supernatant designated as the spent liquor was obtained *via* the removal of water. The precipitate portion designated as the lignin fraction was air dried. The yield was the mass percentage of each fraction to the original weight of the CCA-treated wood.

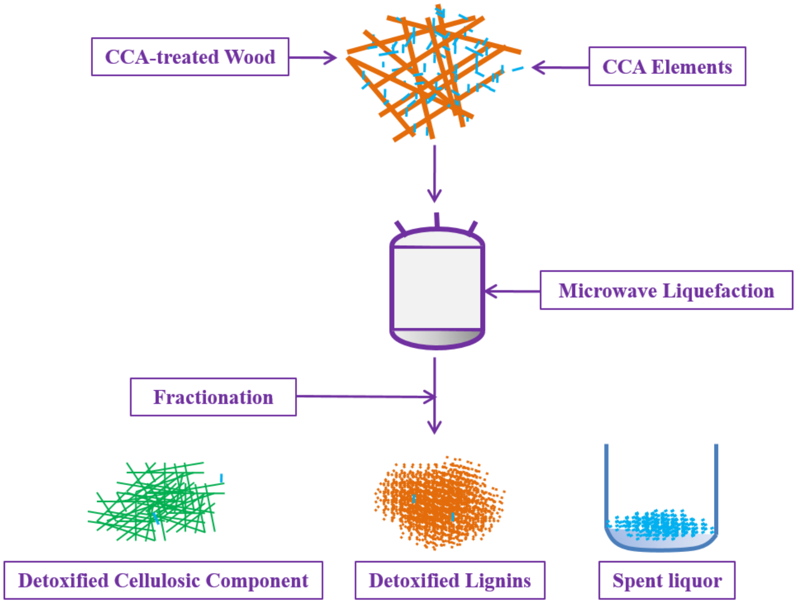

Fig. 1. Schematic of the liquefaction process and the fractionation of components

Determination of Heavy Metals

The heavy metal content of Cu, Cr, and As was determined for each of the three fractions. The samples were subjected to a digest procedure in accordance with the American Wood Protection Association Standard A7-93 (AWPA 2008). After digestion, the samples were diluted with distilled water to a final volume of 25 mL. The heavy metal content was quantified *via* inductive coupled plasma atomic emission spectroscopy (ICP-AES) (PerkinElmer, Inc., Optima 5300DV, Waltham, MA, USA). The weight percentage (wt.%) of the CCA elements in each fraction was determined as the mass percentage of the element in each fraction divided by the total mass of the element in all three fractions. For example, the weight percentage of Cu in the detoxified cellulosic component was calculated with the following formula,

$$WP\% = 100 \times W_f/(W_f+W_l+W_s) \tag{1}$$

where W_f is the mass of Cu in the fiber fraction, W_l is the mass of Cu in the lignin fraction, and W_s is the mass of Cu in the spent liquor.

Chemical Analysis

The acid hydrolysis method was used to determine the chemical compositions of the CCA-treated wood and the detoxified cellulosic component (Sluiter *et al*. 2008). A 0.3 g dry sample was hydrolyzed at 121 °C in 3 mL of 72% sulfuric acid and 84 mL of distilled water for 1 h. The hydrolysis was carried out in an autoclave. The pressure bottle was autoclaved for 1 h at 121 °C. After the sample was cooled down, the mixture was neutralized and filtered. The liquid was analyzed by a high performance liquid chromatography (HPLC; Waters 2695e, Milford, MA, USA) and an Aminex HPX-87p (Bio-Rad, Hercules, CA, USA) at 85 °C with a refractive index detector at 35 °C. The test conditions were as follows: the injection volume was 10 μL, the eluent water was 0.6 mL/min, and the analysis time was 50 min. The solid residue retained after the filtration was oven-dried. The weight of the dried residue was measured, and the Klason lignin content was calculated as the dry weight of the residue to the original weight of the sample (0.3g).

Fourier Transform Infrared Spectra Analysis

The Fourier transform infrared spectra (FT-IR) analysis was performed using a Nicolet Nexus 670 spectrometer (Madison Instruments, Middleton, WI, USA) equipped with a Thermo Nicolet Golden Gate MKII Single Reflection ATR accessory. The data collection was performed with a spectral resolution of 4 cm^{-1} and 32 scans were taken per sample.

X-ray Diffraction

The crystallinity of the CCA-treated wood and the detoxified cellulosic component samples was analyzed by the wide angle X-ray diffraction method (Bruker D 5000, Wittelsbacherplatz, Munich, Germany). The data were generated with a diffractometer using Cu Kα radiation (λ = 1.54 A) at 40 kV and 30 mA over the angular range of 2θ = 5 to 40° and a step time of 2.0 s. A focusing powder diffraction method was applied. The crystallinity index (*CrI*) was determined as follows,

$$CrI\ (\%) = \frac{I_{002} - I_{\mathrm{am}}}{I_{002}} \times 100 \tag{2}$$

where I_{002} is the intensity of the diffraction from the (200) plane at 2θ = 22.1°, and I_{am} is the intensity of the amorphous material taken at 2θ = 18° (French 2014).

SEM Images

The microstructure of the CCA-treated wood and the detoxified cellulosic compoent were observed *via* scanning electron microscopy (SEM, JSM-6110LV, Tokyo, Japan). Test samples were coated with gold prior to analysis.

Enzymatic Hydrolysis

Enzymatic hydrolysis was performed in a 50 mL flask using 30 mL of 0.05 M sodium acetate buffer (pH 4.8) at 48 °C. The flasks were agitated at 150 rpm in a Certomat-R rotary shaker (B-Braun, Melsungen, Germany) for 96 h. The solid portions were added at a concentration of 2.5% (w/v) on a dry basis. The enzyme loading process for the substrate consisted of 18 FPU/g-cellulose for cellulase and 27 CBU/g-cellulose for β-glucosidase. Samples were taken at 48 h, 72 h, and 96 h. The glucose yield was calculated by assuming that the 1 g of fiber present in the solution equaled approximately 1.11 g of glucose.

RESULTS AND DISCUSSION

Fractionation and Heavy Metal Distribution

The microwave liquefied decommissioned CCA-treated wood was separated into three fractions. The weight percentage on a dry basis of each fraction was 48.7%, 20.6%, and 30.0% for the fiber, lignin, and spent liquor, respectively. Figure 1 shows the liquefaction and fractionation processes. As shown in Fig. 2, FT-IR spectroscopy was used to characterize the differences in the chemical structures of the CCA-treated wood and the three fractions.

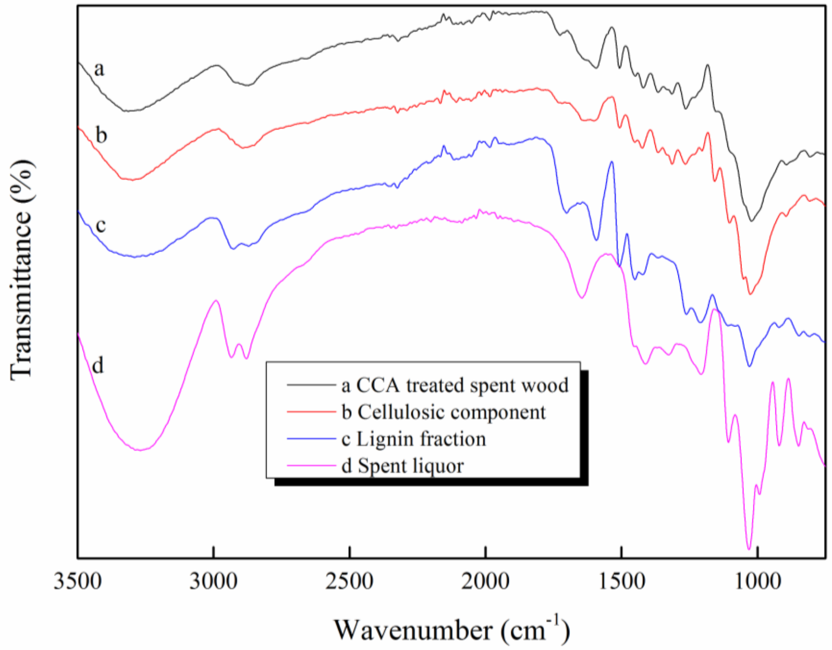

Fig. 2. FTIR spectra of (a) CCA-treated wood, (b) cellulosic component, (c) lignin fraction, and (d) spent liquor

The spectrum of the cellulosic component showed relatively weak bands in relation to hemicellulose (1735 cm^{-1}) and lignin (1596 cm^{-1} and 1506 cm^{-1}) in contrast with the CCA-treated wood, which indicated that the hemicellulose and lignin were liquefied and dissolved in the solvent during liquefaction. The typical bands corresponding to lignins at 1596 cm^{-1}, 1506 cm^{-1}, and 1456 cm^{-1} were observed in spectrum c, which gave evidence that the lignin fraction was mainly composed of lignin derivatives. The hydroxyl group had bands at 3320 cm^{-1}, 1028 cm^{-1}, 1108 cm^{-1}, and 845 cm^{-1} assigned to the carbohydrate derivatives and the glycerol were observed in the spectrum of the spent liquor fraction (spectrum d).

The heavy metal distribution in each fraction is presented in Table 1. More than 90% of the heavy metal remained in the spent liquor, and the weight percentage of As, Cr, and Cu in the cellulosic component was 5.7%, 4.5%, and 4.3%, respectively. Interestingly, the weight percentage of each heavy metal in the lignin fraction was also particularly low; the weight percentage of As, Cr, and Cu in the lignin fraction was 3.2%, 4.9%, and 2.2%, respectively. This result indicated that microwave liquefaction in combination with fractionation could be used to produce detoxified fibers and lignin products.

Table 1. Heavy Metal Distribution in Each Fraction of Microwave Liquefied CCA-treated Wood

Fraction	Cellulosic Component	Lignin Fraction	Spent Liquor
As (%)	5.7	3.2	91.1
Cr (%)	4.5	4.9	90.6
Cu (%)	4.3	2.2	93.5

Physicochemical Characterization of the Detoxified Cellulosic Component

To explore the potential utilizations of the detoxified fibers, the chemical composition, crystallinity, and the microstructures of the detoxified fibers were evaluated. The chemical composition of the CCA-treated wood and the detoxified fibers is shown in Table 2. The detoxified fibers had a higher glucan content than CCA-treated wood; however, the xylan, mannan, and lignin content of the CCA-treated wood was higher than in the detoxified fibers. This result indicated that hemicellulose and lignin were degraded during liquefaction, which resulted in a relative increase in the glucan content. Furthermore, the detoxified fibers were enriched with cellulose, revealing that they can be used as a resource for cellulose material in the manufacturing of cellulosic material reinforced composites.

Table 2. Chemical Composition of the CCA-treated Wood and the Detoxified Cellulosic Component

Sample	Glucan (%)	Xylan (%)	Mannan (%)	Klason Lignin (%)	Ash (%)
CCA-treated Wood	33.6	6.4	11.3	29.7	2.1
Detoxified Cellulosic Component	56.5	2.5	6.6	23.3	1.7

Figure 3 shows the wide-angle X-ray diffraction (XRD) spectra of the CCA-treated wood and the detoxified cellulosic component. One obvious difference in the XRD patterns was that the CCA-treated wood had a crystal intensity at 2θ = 20.9°, 26.7°, 36.6°, and 39.5°. These peaks may indicate the presence of metallic oxides in the CCA preservatives that initially penetrated the wood. However, these peaks disappeared in the XRD spectrum of the detoxified cellulosic component. This result also revealed that the detoxified cellulosic component retained little of the heavy metals. The XRD patterns of the CCA-treated wood and the detoxified cellulosic component displayed peaks at 2θ = 14.9°, 16.1°, 22.1°, and 34.5°, which all corresponded to the typical signatures of cellulose I. In comparison, the XRD spectrum of the detoxified cellulosic component had narrower and more intense peaks (at 2θ = 22.1°) than that of the CCA-treated wood. The calculated crystallinity index value for the CCA-treated wood and the detoxified cellulosic component was 42.7% and 63.1%, respectively. The relatively high crystallinity index value of the detoxified cellulosic component was attributed to their high glucan content. This was due to the degradation of the non-cellulosic materials, such as lignins and hemicelluloses, during the liquefaction process, which was confirmed *via* chemical composition analysis. The high crystallinity property of the detoxified cellulosic component indicated that they are potential raw materials for the preparation of composites with excellent performance.

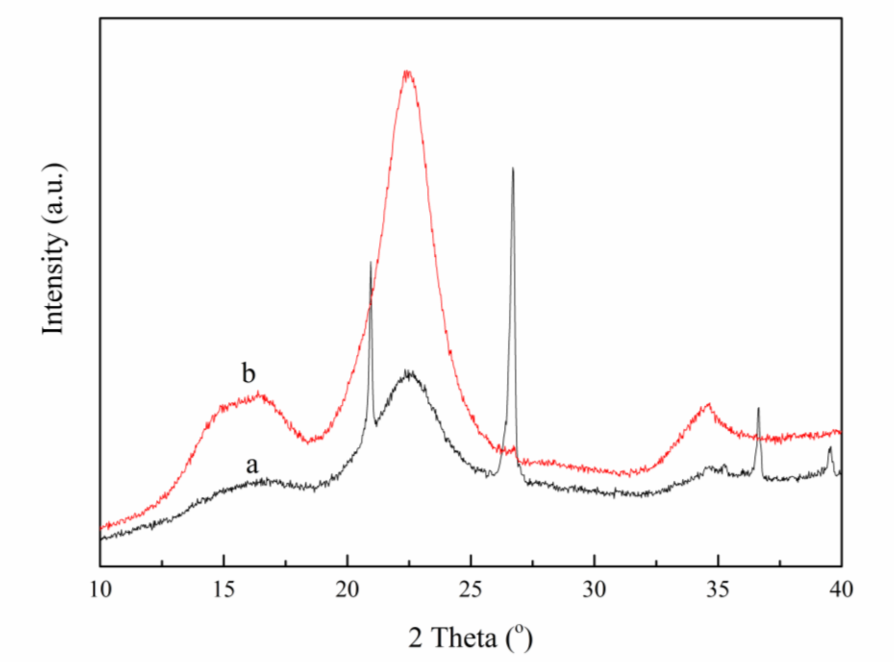

Fig. 3. XRD spectra of (a) CCA-treated wood and (b) detoxified cellulosic component

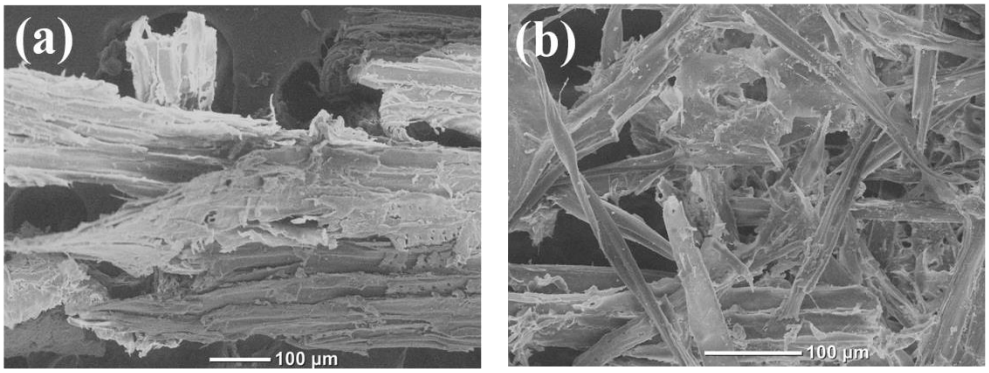

Fig. 4. SEM images of (a) CCA-treated wood and (b) detoxified cellulosic component

Figure 4 shows the SEM images of the CCA-treated wood and the detoxified cellulosic component. The CCA-treated wood particles were composed of large fiber bundles (Fig. 4a). The microstructure of the detoxified cellulosic component showed a significant difference from that of the CCA-treated wood. Figure 4b shows micro-sized individual fibers with a diameter between 15 µm to 50 µm. Damaged fiber cell wall fragments were also observed in Fig. 4b. The individual fibers and damaged fragments observed in the detoxified cellulosic component could be due to the decomposition of the hemicelluloses and lignins that acted as bonding materials in the wood. When compared with the CCA-treated wood, the micro-sized detoxified cellulosic component also presented a large surface area. This characteristic, as well as the lower hemicellulose and lignin content, implied that the detoxified cellulosic component could be more susceptible to an enzyme attack for nanocellulose isolation and biorefinery purposes. Therefore, to verify the feasibility of the usage of detoxified cellulosic component in the production of bioethanol, both the CCA-treated wood and the detoxified cellulosic component were subjected to enzymatic hydrolysis, and the glucose yields with respect to time are presented in Fig. 5.

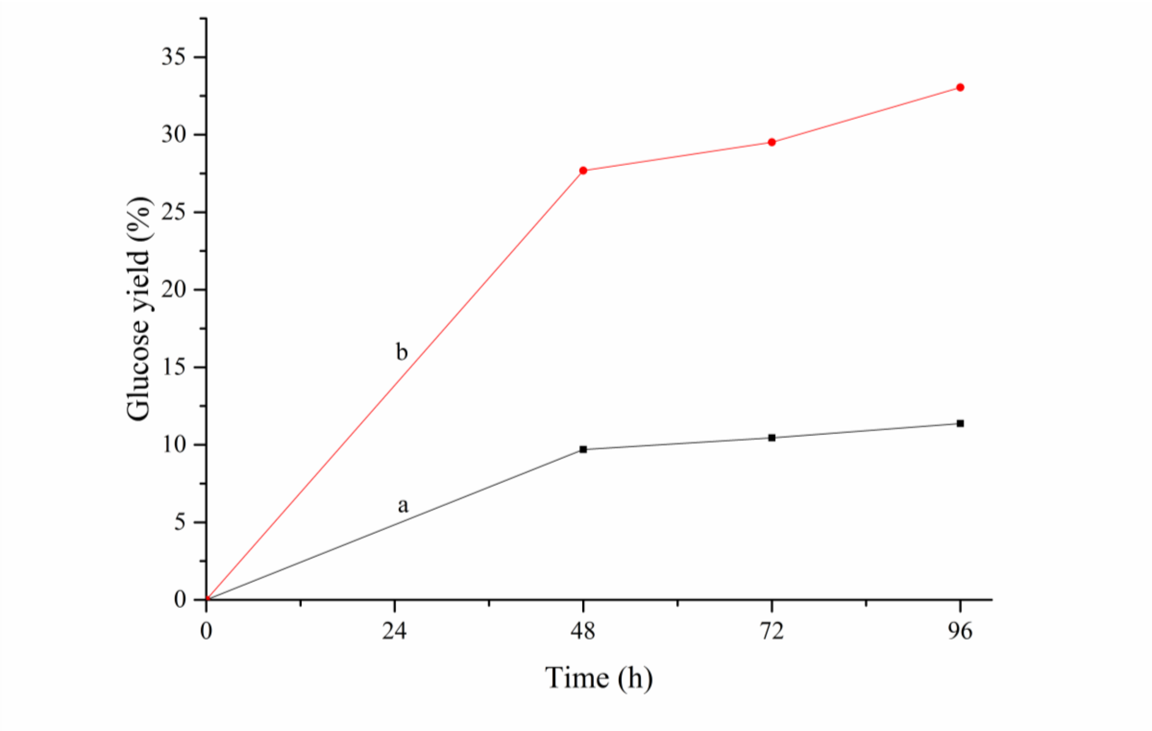

Fig. 5. Comparison in glucose yield of (a) CCA treated wood and (b) detoxified cellulosic component

The glucose yield of the CCA treated wood was 11.4% after 96 h, while the detoxified cellulosic component had a glucose yield of 33.0%, which was almost three times as much as the CCA-treated wood. The enzymatic hydrolysis results confirmed that the glucose yield of the detoxified cellulosic component was higher than that of the CCA-treated wood. However, it was still lower than the yield of the pretreated CCA-treated wood, as reported in previous research (Hakola *et al*. 2013). This was due to the fact a large amount of lignin remained in the fiber cell walls, and it acted as a barrier to the enzyme. Though the lower glucose yield of the detoxified cellulosic component indicated the fibers were not yet ready for use in industrial practice, the large surface area and easy chemical accessibility of the fibers made them a potential raw material for bioethanol production with further proper pretreatment.

Potential Utilization of the Spent Liquor

Though this study focused on the fractionation of the detoxified cellulosic component and their characteristics and applications, the chemical components and potential utilization of the spent liquor were also analyzed to make a closed-loop utilization of the decommissioned CCA-treated wood *via* liquefaction and fractionation processes.

The FTIR spectra analysis indicated that the spent liquor contained enriched hydroxyl groups due to the degradation of the celluloses and hemicelluloses and the presence of glycerol and glycerol derivative blends. Except for the solvent and the heavy metals, the chemical components derived from the wood component in the spent liquor were determined *via* HPLC.

The results showed that the spent liquor contained glucose, xylose, and arabinose; and the concentrations of the glucose, xylose, and arabinose were 12.4 g/kg, 8.47 g/kg, and 6.87 g/kg, respectively. From the chemical analysis of the spent liquor, it could be concluded the spent liquor had great potential as an integrant in the preparation of polyurethane foams *via* providing hydroxyl groups. Since the heavy metals from the CCA treatment remained in the spent liquor, it is possible the synthesized polyurethane foams may possess antifungal and insect resistant abilities.

CONCLUSIONS

1. The microwave liquefied decommissioned CCA-treated wood was separated into three fractions (cellulosic component, lignin fraction, and spent liquor). After liquefaction and fractionation, the CCA elements were primarily distributed in the spent liquor (Cu 91.1%, Cr 90.6%, and As 93.5%).
2. The chemical analysis, FTIR and XRD spectra, and SEM images indicated that detoxified cellulosic component had a higher glucan content, higher crystallinity, and a larger surface area than the decommissioned CCA-treated wood.
3. The detoxified cellulosic component also showed a relatively high glucose conversion yield compared to the CCA-treated wood, which indicated their potential as a resource for the biorefinery industry. The enriched hydroxyl groups in the spent liquor proved the spent liquor could be used as an ingredient in the production of polyurethane foams via providing hydroxyl groups. In addition, the metal elements in the spent liquor could also endow the foams with antifungal and insect resistant ability.

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