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EFFECTS OF ULTRASONIC PRETREATMENT ON THE DRYING CHARACTERISTICS OF *EUCALYPTUS GRANDIS × EUCALYPTUS UROPHYLLA*

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ABSTRACT

In this paper, wood pretreatments were carried out at an ultrasound intensity of 300 W and a frequency of 40 kHz for 60 min, and the ensuing drying process used a temperature of 60 °C. The study analyzed the pretreated wood before and after ultrasonic pretreatment via drying dynamics, electron microscope scanning, and Fourier transform infrared spectroscopy. The results showed that ultrasonic pretreatment successfully improved the effective water diffusivity, decrease the drying time, reduce the amount of extractives on the inner wood pores, and create microchannels in the wood, resulting in improved heat and mass transfer rates. These results indicate that ultrasonic pretreatment is an effective method for the drying of eucalyptus.

KEYWORDS: *Eucalyptus grandis* × *Eucalyptus urophylla*, effective water diffusivity, hydroxyl content, ultrasonic pretreatment.

INTRODUCTION

Due to the continuously increasing depletion of natural forest resources, the development and utilization of woods in plantations is increasing, both domestically and globally. Eucalyptus is a fast-growing and high-yielding tree species which cutting cycle is short, so to some extent it can alleviate the plight of China's timber shortage. However, it is prone to drying defects such as shrinkage during the drying process (Ratti 2001). Its application is very limited; therefore, to improve drying efficiency and quality is of great significance. Wood drying is the most important procedure during the production process of wood products; and energy consumption accounts for about 40% to 70% of the total energy consumption required for wood products (Zhang and Liu 2006). Moreover, the process of drying wood is extremely complex, involving coupled transient mechanisms of heat, mass, and momentum transfer processes, accompanied by physical, chemical, and phase change transformations (Ratti 2001). Conventional drying methods (such as steam treatment or microwave pretreatment) (Kininmonth 1971) are used to dehydrate various timber; However, those methods require large amounts of energy and usually impart significant alterations in product quality and functionality attributes due to exposure to longer drying times or increased temperatures. There is a significant interest to focus on developing innovative drying approaches to accelerate the drying process in order to increase production throughput, while reducing energy consumption (thereby decreasing both environmental and financial costs) without compromising the quality of the endproduct (Zeng 2008). This is important due to a rising consumer demand for high-quality products, coupled with the need for eco-friendly and sustainable processes to maintain competitiveness, while minimizing environmental impact.

Ultrasound technology utilizes mechanical waves at frequencies above the threshold of human hearing (> 20 kHz) (Kadam et al. 2015). This treatment of solutions is a newly emerging technology that offers great potential as an alternative pretreatment technology (Duan et al. 2007, Aversa et al. 2010, Jangam 2010, Mothibe et al. 2010). The vibrating of acoustic waves in materials containing water can induce compression and expansion of the material (the so called "sponge effect"), which leads to the formation of microchannels in the cells. Moreover, the application of ultrasound in liquids can lead to cavitation. Imploding bubbles induce very high and brief local changes in both pressure and temperature, which lead to cell damage (Cárcel 2003, Cárcel et al. 2007, Fan and Rodrigues 2007, Gallego-Juarez 2010, Bussemaker and Zhang 2013). Consequently, heat and mass transfer can be enhanced through streaming within the solution (García-Pérez et al. 2009, Xu et al. 2009, Cárcel et al. 2010, García-Pérez et al. 2010, Zhao and Chen 2011).

The reason chooses eucalyptus as materials is because eucalyptus as an excellent fast-growing tree species has been widely used in pulping and papermaking. However eucalyptus also has the advantages of high density and strength, so it also can use as furniture and decorative materials. While its growth stresses and drying difficulty, which excessive extractives content is one of the main reason, resulting in its applications has been relatively backward, so this article uses environmentally friendly ultrasonic pretreatment which in the field of ultrasonic cleaning has excellent performance, hoping to use ultrasonic waves to open up the path of moisture migration within the wood to speed up the drying process and improve dry quality.

MATERIALS AND METHODS

Sample preparation

The wood (*Eucalyptus grandis* × *Eucalyptus urophylla*) used in this paper was provided by the Guangxi Ushine Home Products Limited Company of China.

All of the samples with the initial moisture content of 95-100% and the dimension of it was 200 x 100 x 20 mm (length, width, thickness) (Zhao et al. 2009). In order to simulate the real process of production as closely as possible, all end cross-sections were blocked by covering them with wax during the drying.

Ultrasonic pretreatment

The ultrasonic pretreatment was carried out in distilled water within an ultrasonic bath (Cheng-Cheng Ultrasonics, Beijing, China, model VGT-2200A). In this experiment, there were 20 specimens in each group, the test samples were treated with ultrasonic of 40 KHz and intensity of 300 W for 60 min. The control group was as dry as the experimental group, but was not subjected to ultrasonic pretreatment. The experiments were performed in triplicate.

Drying procedure

After pretreatment, all samples were placed in a constant temperature and moisture content chamber to reach the same moisture content and then dried at 60° C, the weight of the sample was recorded every two hours. When the moisture content of the specimen reached 12%, then they will be oven dried at 103 ± 2°C (Zhao et al. 2009). The drying rate of the samples can be calculated from the weight changes in the drying process.

Electron microscope scanning

After drying, the specimen randomly selected from different pretreatment conditions and cut into 5 x 5 x 2 mm for scanning electron microscope analysis (SEM, Hitachi S-3400N II, Tokyo, Japan).

Fourier transform infrared spectroscopy analysis

The control group and ultrasonic treated samples were separately ground into wood powder and passed through an 80-mesh screen. The wood powder were mixed with potassium bromide (KBr) pellets with a ratio of 1:100 in weight for FTIR (Tensor 27, Bruker, Germany) analysis. Then, the samples were analyzed with a scanning range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} for 32 scans.

Wood drying properties above and below the Fiber Saturation Point (FSP)

The fiber saturation point is linearly related to the temperature. When the temperature increase by 1°C, it reduced by 0.1%. (Stamm and Loughborough 1935). Thus, the FSP equation could be described as follows:

$$M_{fsp} = 0.3 - 0.001(T - 20) \tag{1}$$

where: M_{fsp} - the fiber saturation point (%),
T - the temperature (°C).

According to Eq. 1, the fiber saturation point is at 26% for a temperature of 60°C.

Effective water diffusivity

The ability of moisture content to move within the wood during the drying process can be represented by the effective water diffusivity. The change in the effective water diffusivity during wood drying is calculated using the following equation (Phoungchandang et al. 2008):

$$\mathrm{MR} = (M - M_e)/(M_0 - M_e) = Aexp(-kt) \tag{2}$$

where: MR - non-dimensional moisture content (%),
M - moisture content at the time t (%),
M_e - equilibrium moisture content (%),
M_0 - initial moisture content at the time t = 0 (%),
k - drying rate constant (s^{-1}),
t - the drying time (s).

Values of MR were plotted in a semi-logarithmic graph against time, thus obtaining an lnMR-t diagram, revealing a linear relationship. The slope of line was a constant of the drying rate defined by Eq. 3:

$$dMR/dt = -k(M - M_e) \tag{3}$$

The linear relationship that was obtained from the lnMR-t diagram enabled the application of Fick's second law of diffusion and the experimental effective diffusion to each specimen. The effective water diffusivity could thus be calculated using the drying rate (K) with the thickness (L) of the specimen according to Eq. 4 (Marinos-Kouris and Maroulis 1995):

$$D_e = KL^2/\pi^2 \tag{4}$$

where: D_e - the water effective diffusion coefficient ($m^2 \cdot s^{-1}$),
L - the specimen thickness (m).

RESULTS AND DISCUSSION

Drying dynamics under different conditions

Drying time under different pretreatment conditions

To estimate the effect of ultrasound on the drying rates of eucalyptus wood, drying dynamic curves were plotted via moisture content versus time (as shown in Fig. 1).

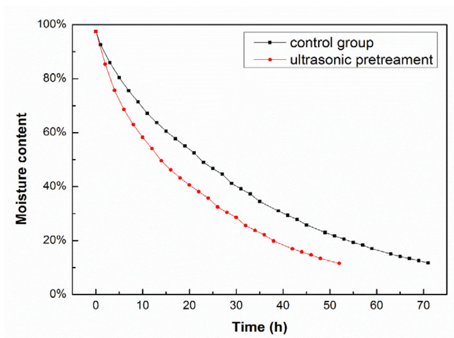

Fig. 1: Drying kinetics of untreated and pretreated samples.

As the result depicted in Fig. 1 show, the drying times of the ultrasonically treated samples were noticeably shorter compared to samples dried without ultrasonic pretreatment. On average, the samples treated with ultrasound only took 52h to dry, reducing the moisture content from 97% to 11% at 60°C. However, 71h were required to dry wood to the same condition without ultrasonic pretreatment. The result were attributed to ultrasonic cavitation, as well as mechanical effects of the sound waves, which can destroys the microstructure of samples and accelerate the movement of water within the wood (Mason 1999, Mason 2001, Priego Capote and Luque de Castro 2007, Esfahani and Azin 2012, He et al. 2016, Zhao et al. 2016).

Effective water diffusivity

Two basic forms of moisture exist in wood: free water and bound water (Salin 2008). Therefore, the drying characteristics of different types of water are very essential for wood drying. Fiber saturation point describe the status when the moisture content at which the cell wall is saturated while the voids are empty (Siau 1995). Thus, considering the drying rates above and below the fiber saturation point during the ultrasonic drying of wood can help us to understand the effect of ultrasound on the drying characteristics of water.

Effective water diffusivity values in wood samples were calculated via Eq. 4. Average values of the effective water diffusivity of control group and ultrasonic pretreatment samples are demonstrated in Tab. 1.

Tab. 1: Effective water diffusivity of the wood of control group and ultrasonic pretreatment samples.

	$De \times 107 (m^2.s^{-1})$	
Drying types	Ultrasound	Control
Moisture content above FSP	9.23	5.28
Moisture content below FSP	8.32	4.06

Ultrasonic pretreatment increased the effective water diffusivity of samples compared to the control group. Subsequent to ultrasonic pretreatment at a frequency of 40 kHz for 60 min, and compared to the control group, the effective water diffusivity of samples increased by 43% and 51% above and below FSP, respectively. This may be due to the cavitation effect of the ultrasonic wave, which causes the rupture of the microbubbles to create localized high temperature and pressure, the cumulative effect resulting in cell damage and microchannels, these will facilitate the movement of water in the drying process. (Simal et al. 1998, He et al. 2013, He et al. 2014, He et al. 2017).

Fourier transform infrared spectroscopy analysis

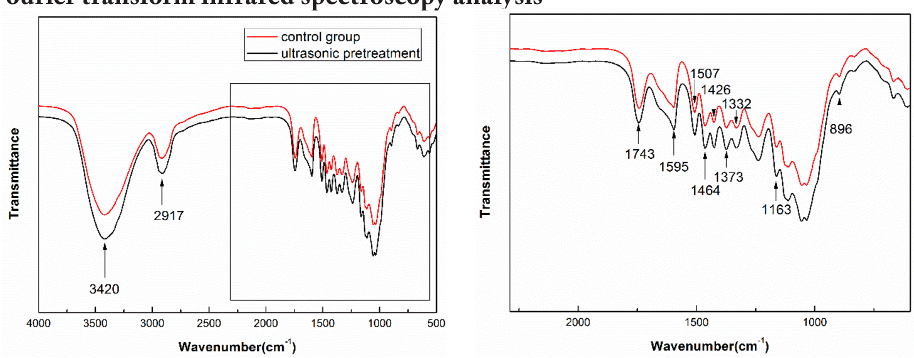

Fig. 2: FTIR spectra of untreated (red) and pretreated (black) samples.

Fourier transform infrared (FTIR) spectroscopy is a nondestructive method for studying the physico-chemical properties of lignocellulosic materials. The FTIR spectra of untreated and ultrasonically pretreated eucalyptus wood are shown in Fig. 2. The spectra of untreated and ultrasonically pretreated eucalyptus wood are dominated by peaks in the region between 3600 and 2800 cm^{-1}, which represent the stretching vibrations of CH and OH, respectively (Alemdar and Sain 2008). The peak at 3420 cm^{-1} increased after the ultrasonic pretreatment, indicating that the hydroxyl group in the ultrasonically pretreated eucalyptus wood had increased. This phenomenon may be explained with the effect of acoustic cavitation and mechanical effect of high frequency ultrasound. Through the cavitation effect, the microbubbles generated within the wood are expanded and busted, these can induce localized micro-jets and strong shock waves, companying with the mechanical effects of fiber to constantly stretching and compressing, causing erosion of the surface and the sonification impact can break the relatively weak interfaces among the fibers, which are bonded to each other mainly via hydrogen bonds (Chen et al. 2011). The peaks at 1595 cm^{-1}, 1507 cm^{-1}, and 1464 cm^{-1} represent the aromatic C=C stretch of aromatic rings and the C-H deformation of lignin, respectively (Sain and Panthapulakkal 2006, Alemdar and Sain 2008, Lionetto et al. 2012). The intensity of these peaks increased in the ultrasonically pretreated eucalyptus wood. This indicates that ultrasound can increase the homolytic cleavage of the phenyl ether β-O-4 and α-O-4 bonds within lignin, as well as the bonds between lignin and hemicellulose. The cumulative effect was lignin released from the connection with others and then re-deposited on the surface (Csoka et al. 2008, Lionetto et al. 2012, Liu et al. 2015). The bands at 1426 cm^{-1}, 1373 cm^{-1}, and 1332 cm^{-1} represent the CH2 bending vibration, CH bending, and OH in plane bending in crystallized cellulose I and amorphous cellulose mixture, cellulose and amorphous cellulose, respectively. The intensities of those peaks are increased in ultrasonically pretreated eucalyptus wood, indicating that the amorphous area of the cellulosic component was more affected by the ultrasonic pretreatment (Colom et al. 2003). The peak at 1743 cm^{-1} is characteristic for an unconjugated carbonyl group, typical for xylan and hemicelluloses (Lionetto et al. 2012). The band at 1163 cm^{-1} was associated with the asymmetrical bridge at the C-O-C stretching for crystallized cellulose. The intensity of those peaks increased in the pretreated samples, however the changes are not significant. The increase of the band at 896 cm^{-1} in the ultrasonically pretreated eucalyptus wood indicates the typical structure of cellulose. These results indicate that ultrasonic effects cause a minor change of the structure of cellulose and hemicellulose due to mechanical and sonochemical effects. This occurred via the cumulative effect of the hydroxyl radicals and shear forces in the hot region around the collapsing bubbles.

Electron microscopic analysis

Fig. 3 shows the scanning electron microscopy micrographs of the samples before and after ultrasonic pretreatment. The SEM photos show a distinct difference in the microstructure of eucalyptus due to ultrasonic pretreatment. Fig. 3a shows eucalyptus wood without ultrasonic pretreatment pits are occluded, only a few microchannels in the membranes. Compared to Fig. 3a, Fig. 3b shows a sample that was treated by ultrasound for 60 min at 40 KHz, some cracks and microchannels emerged on the pits, some of the pit membranes had even ruptured, and the pit aspiration ratio had decreased. Fig. 3c shows samples without ultrasonic pretreatment, where the wood ducts are filled with a large amount of extractives. However, Fig. 3d shows a significant change, as the inner wall of the wood duct had become very smooth, and the amount of extractives decreased greatly. Those phenomena may have been caused by the vibration of acoustic waves, which induced a series of rapid compressions and expansions of the water containing material (the so called “sponge effect”) that may lead to the formation of microchannels in pits. Furthermore, the effect of acoustic cavitation caused by high frequency ultrasound can generate a strong impact force, which can remove surface-attached extractives (Wang 2006).

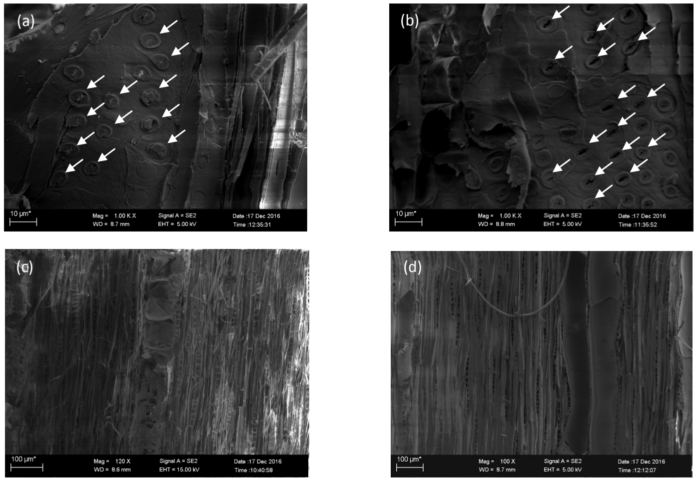

Fig. 3: Photomicrograph of vessels: (a) wood without pretreatment (1000×); (b) pretreatment for 60 min at 40 kHz(1000×); (c) wood without pretreatment (100×); (d) pretreatment for 60 min at 40 kHz(100×).

This ability to reduce extractives and create micochannels and decrease pit aspiration ratio may be the main reason for increasing liquid impregnation after ultrasonic treatment. That indicates that ultrasonic pretreatment offers an effective measure to change the microstructure of wood and therefore, to improve the heat and mass transfer rate of wood.

CONCLUSIONS

The chemical properties and microstructure of eucalyptus prepared both with and without ultrasonic pretreatment were studied. Although the hydroxyl content of the ultrasonic treated samples was increased, while the analysis of the drying time and the effective water diffusivity (Compared to untreated samples, the drying time was reduced by 27% and the effective water diffusivity of samples was increased by 54%) shows that the ultrasonic wave still have an advantage to accelerates the movement of water in the wood during drying, and the ultrasonic effect on the whole structure of the wood is not significant, then the impact on mechanical properties should be small, this subject deserve further study.

SEM analysis shows, ultrasonic pretreatment also reduced the amount of extractives on the inner wood pores and created microchannels on wood cell walls, thus improving the movement of water and decreasing the difficulty of drying. In this way, we can improve the dimensional stability of wood, and broaden the wood application range on fast growing wood species. This paper provides theoretical guidance for the application of fast-growing wood and to improve its value; however, further investigation is required before adoption in large-scale industrial operations.

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