Effects of Extraction Process on the Dried Cell Wall Pore Structure of Messmate Heartwood

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In order to study the effects of a messmate heartwood extraction process on its cell wall pore structure and its drying ability, its nanopore structure was explored after *via* gas adsorption technology. Specifically, the messmate heartwood particles were extracted with methanol, and then the cell wall pore structure of the original and extracted samples were evaluated by N_2 and CO_2 sorption and pycnometer methods, respectively. Overall, compared with the original samples, the cell wall porosity, micropore volume, mesopore volume, BET specific surface area, and specific surface area of the micropores of the extracted messmate heartwoods increased by 2.55%, 0.007 cm^3/g, 0.0014 cm^3/g, 0.24 $m^2 \cdot g^{-1}$, and 21.9 $m^2 \cdot g^{-1}$, respectively. The cell wall pore volume measured *via* the gas adsorption method was smaller than the measurement from the pycnometer method. The results indicated that the presence of extractives made the messmate cell wall have a decreased pore volume and porosity, which may be one of the reasons messmate wood is difficult to dry. Messmate extractives primarily were present in the micropores of the cell wall in the range of 0.4 nm to 0.7 nm. However, gas sorption technology could not detect all the pores in the cell wall of the messmate heartwood sample.

Keywords: Pore structure; Gas sorption method; Pycnometer method; Extractives

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INTRODUCTION

Messmate (*Eucalyptus obliqua* L'Herit.) wood, which is produced in southeastern Australia, has a large commercial volume (Redman *et al*. 2018). However, messmate is also one of the most difficult wood species in Australia to dry, because it easily collapses during the drying process. Its lowest basic density is 630 kg/m^3 (Bootle 1983). One of the reasons why it is difficult to dry is that it has high impermeability and its radial to tangential permeability anisotropy ratio is high, *i.e.*, approximately 10^2 (Redman *et al*. 2012).

Wood drying is the process of moisture removal in wood. Water in wood primarily passes through vessels, tracheids, wood rays (between 15 μm to 400 μm in diameter), pit channels between connecting cells (between 0.4 μm to 30 μm in diameter), and micropores and some mesopores in the cell wall (diameter less than 10 μm) (Yin *et al*. 2015). Among them, the pit channels, micropores, and mesopores in the cell wall are the primary water transfer channels in wood. However, during the process of wood formation, resins, tannins, sugars, and other extractives might be deposited in these pores, blocking the path of water movement, and therefore affecting the drying rate and quality. For example, the deposition of extractives in the pit can cause pit occlusion and hinder the water transfer between cells.

The movement of water is also affected by the presence of extractives in the space between the cell walls. Studies also show that the pores in the cell wall not only affect the drying speed and quality of the wood, but they also play a vital role in the mechanical properties, dimensional stability, wood modification and protection, chemical pulping, and bleaching of wood (Papadopoulos and Hill 2003; Borrega and Kärenlampi 2011). Therefore, further understanding of the wood cell wall pore structure is important to better understand the drying process and its subsequent utilization. Although gas adsorption technology has been used to study the dried cell wall pore structure of wood, it is unknown whether all the pores in the wood cell wall can be detected by this technology.

Wood cell wall structures can be studied *via* direct observation using electron microscopy, *e.g.*, scanning tunnelling microscope (STM), transmission electron microscopy (TEM), high resolution transmission (HRTEM), and atomic force microscopy (AFM). However, these techniques can only be used for qualitative research for wall structure but not the delicate wall pore structure, and can only obtain partial information on the samples due to the small observation area. Gas sorption and pycnometer methods can obtain overall wall pore information of the sample, and the former can also obtain the pore size distribution and specific surface area. Chang *et al*. (2015) used the N_2 adsorption-desorption method to quantitatively test the overall characteristics of the pores in the cell walls of tension and opposite poplar wood, and the corresponding pore structure changes during maturation. Zauer *et al*. (2013) used gas pycnometry to study the influence of the sample preparations on the density and porosity of the cell walls; they found that the measured density and porosity of the cell walls were related to the sample geometry and climatic conditions.

Therefore, the purpose of this paper is to quantitatively characterize the dried cell wall pore structure of messmate wood and in addition to study the effect of the extraction process on the pore structure of the cell walls and drying of messmate. A further goal was to evaluate the effect of gas adsorption technology in exploring its nano pore structure.

EXPERIMENTAL

Materials

Messmate heartwood samples from Australia with a straight texture and no obvious defects were selected. Samples were first kiln dried until the moisture content reached 12% then a section of the wood block was cut and processed into particles (40 mesh particles with diameter less than 0.425 mm and 20 mesh particles with diameter less than 0.85 mm were selected). Some of the particles were used as original samples, and the other particles were extracted with methanol referring to Laboratory Analytical Procedure (LAP) published by National Renewable Energy Laboratory of the U.S. Department of Energy. The extraction time was greater than 10 h at the temperature of 80 °C. The treated wood flour was denoted as the extracted samples.

Methods

The pycnometer method is a classical method proposed by Stamm (1964) to study the cell wall pore structure of wood. A 1-4566-02 type pycnometer (AS ONE Co., Osaka, Japan) was used in this experiment. Water and mineral oil (25 cSt at a temperature of 40 °C) were used as the polar and non-polar displacement fluids, respectively. A 40-mesh size ($<$0.425 mm) absolutely dry control sample and the extracted samples were used in the

test. The cell wall substance-specific volume, cell wall-specific volume, cell wall pore volume, and cell wall porosity were calculated.

In order to test the distribution of the micropores and some mesopores in the cell wall, N_2 and CO_2 isotherm sorption tests were performed on the 20-mesh size original and extracted samples. Two replicates were taken for each gas adsorption test, and each sample weighed 0.5 to 1.5 g. During the N_2 and CO_2 sorption test, the sample was first degassed at a temperature of 60 °C for greater than 12 h. The N_2 adsorption test was carried out in an ASAP2020 HD88 automatic specific surface area and pore size distribution instrument (Micromeritics Instrument Co., Norcross, GA); the temperature was set at 77.4 K, and the relative pressure range was 0.01 to 0.995. The specific surface area was obtained *via* the BET (Brunauer- Emmett-Teller) theory and formula (Brunauer *et al*. 1938), and the pore size distribution and pore volume were calculated *via* the BJH (Barrett-Johner-Halenda) (Barrett *et al*. 1951) method. The CO_2 adsorption test was carried out using a NOVA automatic specific surface area and pore size distribution instrument (Quantachrome Co., Boynton Beach, FL). The test temperature was controlled at a temperature of 0 °C. The sorption time of each sorption point was set to 5 min. According to the density function theory (DFT) and the Grand Canonical Monte Carlo (GCMC), the adsorption branches in the CO_2 isotherm loop were selected for calculation using autosorb-1 software (version 11.04), Quantachrome Co., Boynton Beach, FL).

RESULTS AND DISCUSSION

Analysis of Cell Wall Density and Porosity Using the Pycnometer Method

After the methanol extraction process, the extractive content of the messmate heartwood particles was 6.55%, with a standard deviation of 0.15. Table 1 shows the mean and standard deviation of the cell wall substance-specific volume, cell wall-specific volume, cell wall porosity, and cell wall pore volume of the extracted messmate wood particles samples and the original samples, which were determined using the pycnometer method.

Table 1. Cell Wall Pore Parameters of the Original and Extracted Samples Measured via the Pycnometer Method

Properties	Original Samples (12 Samples)		Extracted Samples (16 Samples)	
	Mean	Standard deviation	Mean	Standard deviation
Cell Wall Substance-Specific Volume (cc/g)	0.663	0.0001	0.658	0.003
Cell Wall-Specific Volume (cc/g)	0.691	0.003	0.704	0.004
Cell Wall Pore Volume (cc/g)	0.028	0.002	0.046	0.003
Cell Wall Porosity (%)	3.99	0.003	6.54	0.004
Note: The original and extracted samples had a 95% confidence interval of 0.026 to 0.029 and 0.044 to 0.048 for the cell wall pore volume, respectively				

Table 1 shows that the cell wall pore volume and porosity of the messmate samples were 0.028 cc/g and 3.99%, respectively. They were lower than the cell wall pore volume and cell wall porosity of Douglas fir wood (0.033 cc/g and 4.8%, respectively), aspen wood (0.031 cc/g and 4.47%, respectively), and western red cedar wood (0.032 cc/g and 4.58%,

respectively) (Shi and Avramidis 2018). The relatively low cell wall pore volume and cell wall porosity had a certain effect on the drying rate, which may be one of the reasons why messmate wood is difficult to dry. The extraction treatment released 2.55% of the cell wall porosity and 0.018 cc/g of the cell wall pore volume. This indicated that there were extractives in the cell wall pores of messmate heartwood. This is not conducive to the removal of moisture in the drying process and may increases the difficulty of drying.

Characteristics of the Gas Isothermal Sorption

Figure 1a shows the CO_2 adsorption-desorption isotherms of the original and extracted messmate samples. The CO_2 adsorption capacity of the extracted samples (6.37 cm^3/g) was significantly higher than the CO_2 adsorption capacity of the original samples (2.30 cm^3/g), *i.e.*, 2.8 times greater than the original samples. From the adsorption curve and desorption curve trends, the CO_2 adsorption isotherm of the original samples was reversible, but hysteresis appeared in the extracted samples, the explanation of which requires further investigation. The N_2 adsorption-desorption isotherm of the extracted samples and the original samples are shown in Fig. 1b. The adsorption capacity rapidly increased at the low relative pressure. At this stage, adsorption primarily occurred in the micropores, which indicated that there was a certain micropore structure in the original samples and the extracted samples. When the P/P_0 ratio exceeded 0.1, the tendency of adsorption capacity continued to increase with a slow increase in relative pressure, which indicated that the multilayer adsorption of mesopores (2 nm to 50 nm) and macropores (greater than 50 nm) had occurred at this stage. When the P/P_0 exceeded 0.8, the amount of N_2 adsorbed rapidly increased again, which indicated that the interaction between the adsorbent and the adsorbate was strong, and the capillary condensation occurred in the macropores. According to the classification of the International Union of Pure and Applied Chemistry (IUPAC) (Sing 1985), the N_2 adsorption isotherms of the original samples and the extracted samples were type II. A type II adsorption isotherm is characterized by the presence of macropores in the adsorbent, which indicated that there were mesopores and macropores in the original and extracted samples.

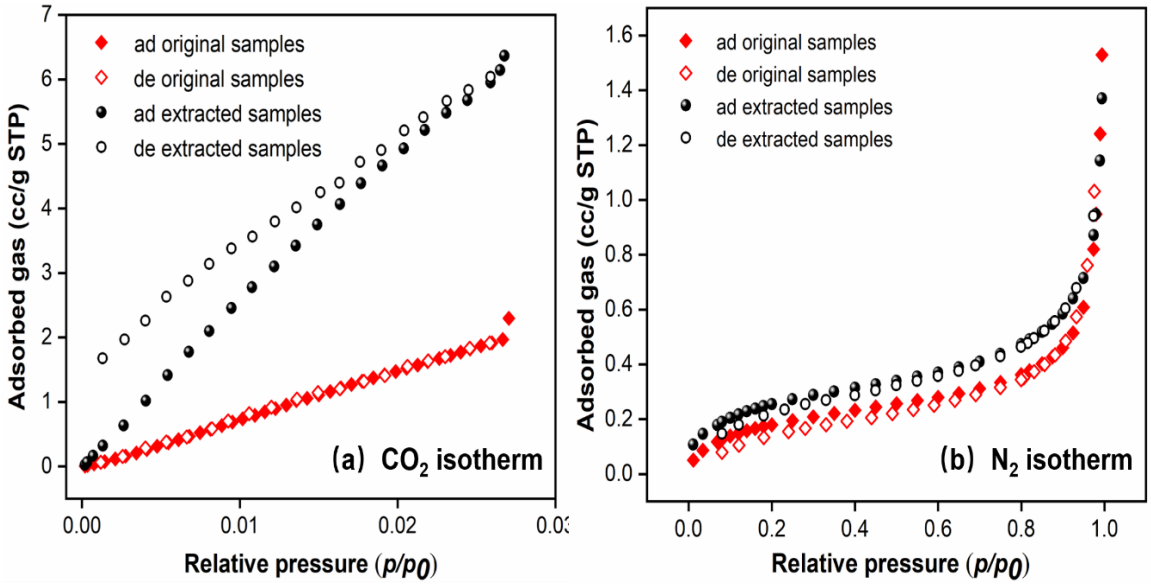

Fig. 1. Adsorption-desorption isotherms of the original and the extracted samples. a) CO_2 isotherm and b) N_2 isotherm

Using the Gas Adsorption Method to Determine the Characteristics of the Cell Wall Pore Structure

As shown in Table 2, after the extraction treatment, the increase in the micropore volume and specific surface area of the extracted samples was much larger than the BHJ and BET. The results showed that the extractives primarily were present in the micropores. In N_2 adsorption tests, the cavity size usually corresponds to the pore size calculated from the adsorption curve, while the pore size calculated from the desorption curve corresponds to the orifice size (Groen and Pérez-Ramírez 2004). Therefore, the pore shape can be obtained from the pore size calculated from the adsorption and desorption curves. According to the average mesoporous pore diameters (D_a and D_d), which correspond to the N_2 adsorption and desorption curves shown in Table 2, the messmate samples before and after extraction all showed chimney-like pores with cavities smaller than their orifices. This pore structure reduces the ability of capillary condensation to a certain extent, which is conducive to water movement.

Table 2. Pore Parameters of the Original and Extracted Samples Measured *via* the Gas Sorption Method

Sample Types	BET Specific Surface Area (m2·g-1)	D_a (nm)	D_d (nm)	BJH volume (cc/g)	Micropore Volume (cc/g)	Micropore Specific Surface Area ($m^2 \cdot g^{-1}$)	Average Pore Diameter (nm)
Original samples	0.69	16.96	19.12	0.002	0.015	40.796	0.600
Extracted samples	0.93	11.89	12.6	0.002	0.022	62.742	0.574
Note: D_a/D_d are the mean mesopore diameter on adsorption /desorption branch of the isotherm							

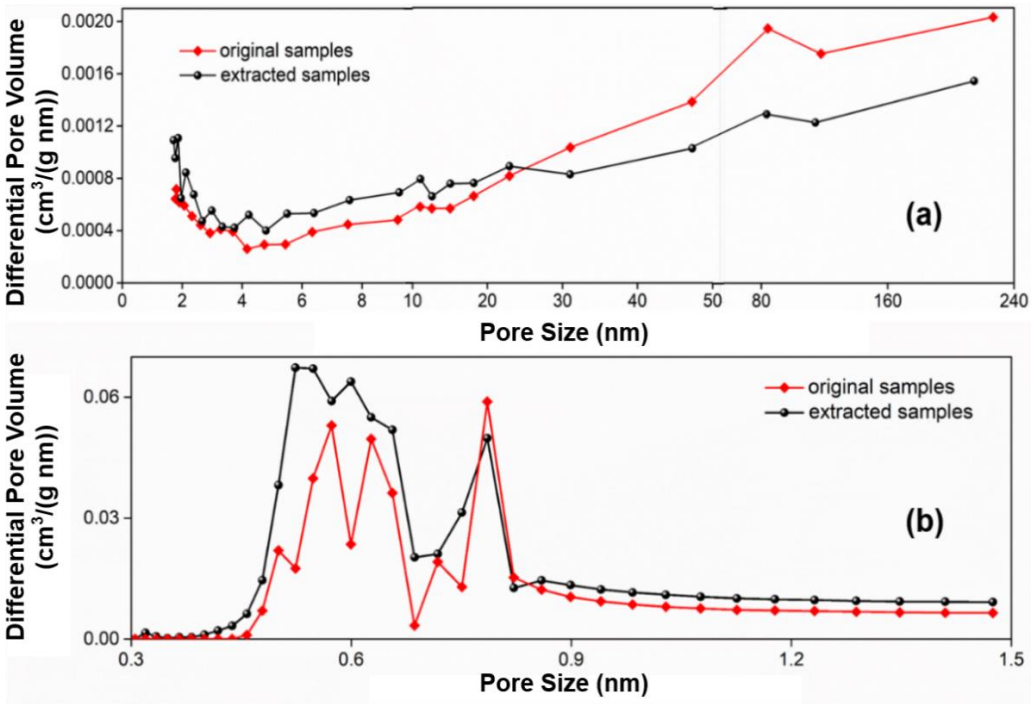

Fig. 2. Pore size distribution of the original and extracted samples: (a) mesopore; and (b) micropore

Figure 2 compares the relationship between the pore size and the pore volume of the messmate samples before and after extraction. Figure 2a shows that the pore volume of the extracted samples was larger than the pore volume of the original samples when the pores were in the range of 1.7 to 23 nm, but smaller when pores were in the range of 31 to 214.7 nm. As shown in Fig. 1b, when the P/P_0 ranged from 0.98 to 1, the N_2 adsorption capacity of the original samples was slightly higher than the adsorption capacity of the extracted samples. This indicated that there were more large pores in the original samples than in the extracted samples. The extraction treatment significantly increased the pore volume of the micropores but decreased the pore volume of a few macropores and some larger mesopores. The specific reasons for the decrease of pore volume in some macropores and some larger mesopores need to be further studied and demonstrated. Figure 2b shows the changes in the pore size distribution of the messmate heartwood samples before and after extraction. After this treatment, the pore volume (ranging from 0.4 nm to 0.7 nm) obviously increased, which further indicated that the messmate extractives primarily affected the micropores ranging from 0.4 to 0.7 nm.

The N_2 adsorption isotherms (Fig. 2a) showed that the pore diameters detected ranged from 1.71 to 226 nm, *i.e.*, primarily mesopores and macropores. According to Zauer *et al.* (2013), most of the pore sizes of dry wood cell walls were within 4 nm, so the larger mesopores and macropores detected on the N_2 adsorption isotherm should be pores located outside the cell wall, *e.g.*, the pores in the pit membranes. Therefore, the total pore volume of the cell wall was calculated from the sum of all the micropores detected by the CO_2 adsorption method and the pores detected by the N_2 adsorption method with a size less than 10 nm.

Table 3. Gas Adsorption Method for Testing the Cell Wall Pore Volume Parameters of the Messmate Samples Before and After Extraction

Samples Types	Mesopore Volume of Cell Walls (cc/g)		Cell Wall Micropore Volume (cc/g)		Total Pore Volume of the Cell Walls (cc/g)
	Sample size	mean	Sample size	mean	mean
Original samples	2	0.0029	2	0.0152	0.0181
Extracted samples	2	0.0043	2	0.0222	0.0265

The average values of the mesopores, micropores, and total pore volume of the cell walls less than 10 nm measured *via* the gas adsorption method are shown in Table 3. The mesopore and micropore volumes of the cell walls, and the total pore volume of the cell walls of the extracted samples were higher than the original samples. The extraction treatment increased the mesopore and micropore volumes of the messmate heartwood cell walls, which indicated that the extractives in the messmate wood occupied part of the cell wall pores, and primarily occupied the micropores in the cell walls.

In general, the results of the gas adsorption procedure showed that the pore volume of the cell walls of the extracted samples were higher than the pore volumes of the original samples. This is similar to the results using the hydrometer method, which indicated that the gas adsorption technology has certain potential in exploring the pore structure of wood cell walls.

Comparison of the Gas Adsorption Method and the Pycnometer Method in Terms of Measuring the Cell Wall Pore Volume

Although gas adsorption technology could detect the changes in the pore structure before and after extraction, it was still doubtful whether it could detect all the pores in the cell walls of the messmate samples. Table 4 shows the total pore volume of the cell walls of the original and the extracted samples calculated *via* the gas adsorption and the pycnometer method, respectively. The V2/V1 indicated that the total pore volume of the cell wall measured *via* the gas adsorption method was smaller than the total pore volume *via* the pycnometer method, which was consistent with the results reported by Shi and Avramidis (2018). The smallest pore diameter measured *via* the CO_2 adsorption test was approximately 0.31 nm and the largest pore size was approximately 1.47 nm, but the increasing trend at the end of the CO_2 adsorption isotherm indicated that the volume of the mesopores was larger. The smallest pore size tested *via* the N_2 adsorption-desorption was approximately 1.77 nm. Therefore, the test results of the gas adsorption method were lower than the results of the pycnometer method, which may be because the pores ranging between 1.47 nm to 1.77 nm and below 0.31 nm were not detected by the gas adsorption method, but were detected via the pycnometer method.

Table 4. Comparison of the Cell Wall Pore Volume of the Original Samples and the Extracted Samples *via* the Gas Adsorption Method and the Pycnometer Method

Samples Types	Cell Wall Pore Volume From the Pycnometer Method (cc/g)			Cell Wall Pore Volume From the Gas Adsorption Method (cc/g)	V2/V1 (%)
	Mean	Standard deviation	95% confidence interval	Mean	
Original samples	0.028	0.002	0.026 to 0.029	0.018	65%
Extracted samples	0.046	0.003	0.044 to 0.048	0.027	58%
Note: V1 is the cell wall pore volume from the pycnometer method and V2 is the cell wall pore volume from the gas adsorption method					

CONCLUSIONS

1. The results of the pycnometer tests showed that the extractives occupied the cell wall pores of the messmate heartwood, which made it have relatively low cell wall pore volume and porosity. This could be one of the reasons why messmate wood is difficult to dry.
2. The results of the gas adsorption tests showed that the micropore, mesopore volume, and total pore volume of the messmate heartwood cell walls increased after extraction, especially the micropore volume (ranging from 0.4 to 0.7 nm. The results showed that the extractives primarily were present in the micropore range (0.4 to 0.7 nm) of pores. Some mesopores and macropores in messmate wood, primarily from the pore structure, were found outside the cell walls.
3. Gas sorption technology has a certain potential to study the pore structure of wood cell walls, but it cannot detect all the pores in the messmate cell walls. A possibly reason

for this is that the micropores in the pore size range of 1.47 nm to 1.77 nm and below 0.31 nm were not detected via this technology.

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