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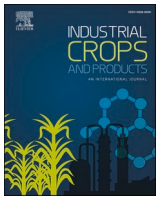

Carbonate pre-treatment of wood for transformative structural applications through densification

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ABSTRACT

This study investigated carbonate pre-treatment of wood followed by densification for producing advanced wood structural materials. Poplar wood blocks of 100 mm long and 20 mm wide with thickness of 10 mm were treated with sodium carbonate with and without sulfide at different carbonate loadings at 150 °C for 30 min. Carbonate effectively removed lignin and hemicelluloses which facilitated subsequent wood densification for improving wood mechanical properties. Comparing with wood pre-treatment using sodium hydroxide, carbonate pre-treatment improved wood yield but achieved similar level of wood mechanical strength. Considering sodium carbonate is the key ingredient of commercial pulping process liquors such as spent pulping liquor (black liquor) and green liquor (an aqueous solution of the dissolved inorganic smelt from the combustion of concentrated pulping spent liquor), the present study indicated that low cost, effective, and cleaner wood pre-treatment can be achieved using spent process liquors rather than fresh and expensive sodium hydroxide (white liquor). Laboratory black liquor was used to pretreat the same poplar wood blocks, the good wood mechanical properties of the treated wood after densification confirmed this hypothesis. The practical significance of the present study is the utilization the residue alkali in spent process liquors rather than fresh NaOH for wood pre-treatment to reduce environmental impact. Furthermore, the spent liquor after wood-pretreatment can be directly feed into commercial pulp mill chemical recovery system to reduce capital and operation cost.

1. Introduction

Wood is inherently a sustainable structural material. Upgrading woody crops such as poplar, planted on marginal land initially intended for bioenergy applications, to structural materials not only has high economic benefits, but also sequestrates and stores carbon to mitigate climate change. However, these woody crops have low density with poor mechanical properties. Wood treatments commonly applied in the wood processing industry can increase end use performance and wood service life. Common wood treatments include thermal (Bourgois et al., 1989; Tillman et al., 1989), preservative (Lebow, 2010) treatments, impregnation (Chen et al., 2014; Dong et al., 2016; Shams et al., 2005) and acetylation (Tarkow et al., 1946; Tullo, 2012). Wood densification through thermal treatment alone has shown to improve wood mechanical strength (Kutnar and Šernek, 2007) especially for those woods with low densities such as fast-growing plantation poplar wood (Fang et al., 2012b). However, pure wood densification including commercial trade names of *Lignostone*, *Lignofol*, and *Staypak* (Kollmann et al., 1975), thermal-hydro-mechanical (THM) densification (Navi and Girardet, 2000), and viscoelastic thermal compression (VTC) process (Kamke and Sizemore, 2008) resulted in moderate improvement in wood properties with limited commercial market share to affect sustainability. Recent studies, however, indicated that in-situ wood chemical delignification can provide the opportunity for wood cell-wall engineering to significantly improve and alter wood properties to produce a variety of products such as super strong wood with outstanding mechanical strength (Song et al., 2018), highly moldable wood with excellent foldability (Song et al., 2017; Xiao et al., 2021), and optically transparent wood for windows and light management in buildings (Li et al., 2019; Mi et al., 2020; Zhu et al., 2016). It is these transformative innovations that can expand wood from traditional utilizations to many market segments as sustainable solutions through market innovations to significantly reduce human carbon footprint. To achieve this goal, a sustainable wood delignification step is critical, which makes the

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present study highly relevant.

Delignification has long been commercially practiced in the pulp and paper industry, however, in-situ wood delignification is very different from wood pulping that uses small wood chips and deconstruct wood into fibers. In-situ wood delignification requires to preserve the wood physical integrity while uniformly treat wood in large dimensions, which is difficult to achieve with significant cost and potential negative environmental impact. For example, it is known that delignification using sulfite (Song et al., 2018) or soda-anthraquinone (soda-AQ) (Liu et al., 2019) adopted in earlier wood delignification studies for cell-wall engineering have major environmental concerns due to difficulties in chemical recovery using sulfite process as well-known in the pulp and paper industry, and carcinogenic potential using AQ process, for example, AQ produced wood fibers have been banned in food packaging production (Hart and Rudie, 2014). Chlorite is routinely used in laboratories to remove wood lignin (Mazumder et al., 2000), while alkaline peroxide is often used to modify/remove residual lignin in wood fibers in the pulp and paper industry. Using peroxide and/or chlorite or chlorite delignification in multiple steps (Li et al., 2017, 2016) to remove a substantial amount of bulk wood lignin, however, is cost prohibitive because of the high chemical dosage and process steps required. Solvent based processes such as organolsolv (Iakovlev and vanHeiningen, 2012; Luterbacher et al., 2014) and acid hydrotropic fractionation (Cai et al., 2020; Chen et al., 2017) have been proven effective in solubilizing lignin and hemicelluloses. These processes were developed to achieve complete separation of wood fibers and/or deconstruction of wood cells, and are not suitable for wood treatment which requires to preserve wood structural integrity for producing structural materials. For example, using maleic acid hydrotropic fractionation for wood delignification resulted in wood with decreased mechanical properties perhaps due to cellulose depolymerization by acid (Wang et al., 2020). Furthermore, chemical recovery to achieve sustainable production has not been demonstrated at large scales using solvent-based processes. Therefore, finding a cost-effective, scalable, and sustainable wood chemical treatment processes that has no adverse effect on the properties of the resultant engineered wood is critically important.

Here we evaluate carbonate, a weak and low cost alkali, as a novel approach to selectively remove lignin and hemicelluloses from wood for subsequent wood densification to produce wood with greater strength and performance. Despite wood treatment using NaOH, a much stronger and more costly alkali, has been successfully demonstrated (Wang et al., 2020), the significance of the present approach is that carbonate is a major component in commercial pulp mill process liquors. Specifically, sodium carbonate (Na_2CO_3) is approximately 40 % of the alkali in pulping spent liquor, referred to as black liquor for its color, with typical Na_2CO_3 concentration of approximately 15 g/L (Clayton et al., 1989). Also, sodium carbonate is approximately 60 % of the alkali in another pulping process liquor often called green liquor in kraft pulp mills for its greenish color from small amounts of iron sulfide present in the solution, with typical Na_2CO_3 concentration of approximately 180 g/L. Green liquor is an aqueous solution of the dissolved inorganic smelt from the combustion of concentrated pulping spent liquor (black liquor). Therefore, both green and black liquors are readily available in commercial pulp mills at low cost, especially black liquor with near zero cost. Using unused residual alkali in side streams of pulp mill black, or green liquors, or mixtures of green and black liquors without using white liquor (fresh liquor for wood pulping containing primarily NaOH), is a cost-effective and scalable approach. Furthermore, the spent liquor from post-wood-treatment can simply be cycled back to a pulp mill chemical recovery system, eliminating additional environmental impacts and the need for an expensive chemical recovery system, leading to a more sustainable and economical process than using fresh alkaline white liquor of NaOH. Because significant delignification is not necessary for producing super strong wood or moldable wood as indicated by earlier studies (Song et al., 2017, 2018; Xiao et al., 2021), it is hypothesized that carbonate treatment is ideally suited for producing super strong wood and moldable wood. The weaker alkalinity of carbonate than NaOH may decrease cellulose degradation, advantageous for producing strong wood. As discuss earlier, wood has long been used as a structural material. Its' inherent renewability and capable of storing carbon have attracted great interest for many structural applications as an alternative sustainable solution to metals. Therefore, the present study aimed at substantially increasing wood utilization to nontraditional markets through sustainable cell wall engineering has significant importance.

2. Materials and methods

2.1. Materials

Poplar wood (*Populus deltoides* Bartr. ex Marsh × *P. nigra* L.) was harvested from Hugo Sauer Nursery, USDA Forest Service, Northern Research Station, Rhinelander, Wisconsin, in December 2018. The logs were hand peeled to remove bark. Wood block samples of 100 mm (longitudinal) by 10 mm (radial) by 20 mm (tangential) were cut from the fresh wood logs. Wood materials within a radius of 10 mm from the center of each wood log were discarded and not used to eliminate the effect of juvenile wood on wood block mechanical properties.

Sodium carbonate (Na_2CO_3) was purchased from Sigma-Aldrich (St. Louis, MO). Pulping spent liquor (black liquor) were collected from laboratory wood delignification at the USDA Forest Products Laboratory.

2.2. Wood treatment using carbonate

Poplar wood samples were dried first to constant weight at 103 ± 2 °C before undergoing hydrothermal and chemical treatment using carbonate. Sulfide free sodium carbonate (Na2CO3) solutions of concentration 0, 60.4, 93.5 g/L were prepared by dissolving appropriate amounts of Na2CO3 in water, corresponding to total alkali (TA) charge (as Na2O) on wood of 0, 10, 15 %. A sulfide containing sodium carbonate solution with Na2S and Na2CO3 concentration of 6.5 and 20.8 g/L, equivalent to TA and sulfidity of 5 % and 30 %, respectively, was also prepared to simulate kraft pulping spent liquor. Wood samples were treated at 155 °C for 30 min using the prepared carbonate solutions at a liquor-to-wood ratio L/W = 3:1 in a 1-L bomb reactor placed in a 21-L rotating wood pulping digester heated by a steam jacket, as described previously (Tian et al., 2011). These treatment runs were denoted as G0 (hydrothermal treatment with no Na_2CO_3), G10 and G15 (sulfide free

Table 1
List of wood chemical treatment and densification conditions.

Samples[1]	Treatment at 155 °C for 30 min with chemical loading (g/L)			Densification at 150 °C for 15 min		Wood thickness (mm)[2]
	Na_2CO_3	NaOH	Na_2S	Stop bar	P (MPa)	
Untreated wood						10.0
G0P1N	0	0	0	No	1	5.0
G10P1N	60.4	0	0	No	1	4.8
G15P1N	93.5	0	0	No	1	4.1
G15P3N	93.5	0	0	No	3	3.7
G15P5N	93.5	0	0	No	5	3.2
G10P1	60.4	0	0	Yes	1	7.1
B5P1	20.8	0	6.5	Yes	1	7.3
BLqP3N	9.6	55.4	0	No	3	3.5
BLqP5N	9.6	55.4	0	No	5	3.1

[1] G*n* stands for pure carbonate solution with total alkali (TA) charge (as Na_2O) on wood *n*%. B5 stands for sulfide containing carbonate solution at TA (as Na_2O) 5 % and sulfidity 30 %. P*n*: stands for pressing at *n* MPa, respectively. N: stands for pressing without the stop bars.
[2] After densification and conditioning.

carbonate treatment), and B5 (low carbonate concentration with sulfide to simulate black liquor) as listed in Table 1. A separate treatment BL was carried out using a laboratory wood pulping spent liquor (NaOH without Na_2S) under the same conditions. The chemical composition of the laboratory liquor was: Na_2CO_3 = 9.6 g/L, NaOH = 55.4 g/L, determined by the SCAN-N 30:85 ABC titration method (SCAN, 1985). This is a laboratory black liquor from a treatment with low wood loading to result in a very high NaOH concentration. After treatment, the samples were washed using tap water several times. The chemical compositions of the treated wood were analyzed.

2.3. Wood chemical composition analysis

Chemical compositions of wood samples were determined by the Analytical Chemistry and Microscopy Laboratory at the USDA Forest Products Laboratory, Madison, WI, USA, using conventional two-step acid hydrolysis, as described previously (Luo et al., 2010). In brief, the carbohydrates in wood samples (Wiley-milled to 20 mesh) were hydrolyzed into monomeric sugars in two steps using sulfuric acid and then analyzed for sugars by ion chromatography (ICS-5000, Dionex) with amperometric detection (HPAEC-PAD). The insolubilized materials were measured gravimetrically and then combusted at 560 °C for 3 h to gravimetrically determine the ash content. The difference between the amounts of ash and the insoluble solids is considered as Klason lignin.

2.4. Wood densification

The treated poplar wood samples were washed with tap water and surface water was removed with paper tower, and then densified while wet in the wood's radial direction right after treatment. As listed in Table 1, wood samples were compressed (Fig. 1) using a heated-platen 12″ X 12″ hydraulic press (Carver model) from an initial thickness of 10 mm at a pressure of 1.0 MPa for 15 min at 150 °C without stop bars. Additionally, G15 wood samples were pressed without stop bars at either 3 or 5 MPa. Furthermore, G10 and B5 samples were pressed using two 8-mm-thick stop bars. The stop bars were used to control the extent of densification. All densified wood samples were labeled according to their treatment and pressing conditions as listed in Table 1. After densification, the wood samples were conditioned in a climate-controlled chamber at 20 °C and a relative humidity of 65 % for two weeks.

2.5. Post-densification thermal fixing treatment

The post-densification thermal fixing treatments of the densified wood samples were conducted at 180 °C for 2 h in a 0.13 m^3 chamber with less than 2 % oxygen content. The chamber was heated via injecting saturated steam (Gao et al., 2018; Wang et al., 2021). After the treatment, the samples were cooled and dried, and the weight changes of samples were recorded.

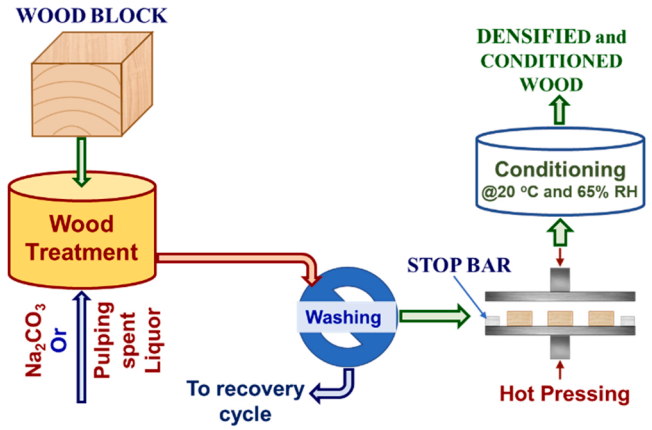

Fig. 1. A schematic flow diagram shows wood treatment, densification, and conditioning.

2.6. Wood characterization

Each wood sample was weighed before and after delignification, densification, and conditioning. Mass loss (ML) by wood treatment and densification was determined as

$$\mathrm{ML} = \frac{m_0 - m_2}{m_0}(\%) \quad (1)$$

where m_0 is the initial mass of the oven-dried sample before delignification and m_2 the mass of the same sample after densification, drying and conditioning. It should be noted that ML were measured after densification while solids yields in Table 2 were measured right after wood treatment before densification.

Wood compression in radial direction had minimal effect in the length and width directions. The compression ratios (CR) immediately after densification CR_1 and after conditioning CR_2 are defined as the percentages of change in wood thickness from its original sample thickness t:

$$\mathrm{CR}_N = \frac{t_0 - t_N}{t_0}(\%) \quad (2)$$

where t_0 and t_N are thicknesses of the initial and densified or densified and conditioned wood samples, with $N = 1$ immediately after densification and $N = 2$ after conditioning. A parameter to characterize wood sample rebound set-recovery (SR_1) or shrinkage (negative value) after conditioning can be expressed as

$$\mathrm{SR}_1 = \frac{t_2 - t_1}{t_1}(\%) \quad (3)$$

Density (ρ) of the samples was calculated after conditioning in a climatic chamber (20 °C, 65 % RH) until no changes in weight. The densification ratio was defined as the density ratio of the densified wood over the original wood, i.e.,

$$\overline{\rho} = \frac{\rho_1}{\rho_0}(\%) \quad (4)$$

Modulus of rupture (MOR) and modulus of elasticity (MOE) were measured by three-point static bending tests using a modified standard procedure described in ASTM D4761–19 (ASTM, 2019) on specimens with dimensions of approximately 100 mm (longitudinal) by 20 mm (tangential) of varied thickness (radial) with a span of 89 mm and a crosshead speed of 5 mm/min using a universal mechanical testing machine (Instron 5869, Grove, PA, USA). Mean and standard deviations of MOR and MOE were calculated from testing results of 10 replicate samples for each set of wood samples as

Table 2
Solid yield and chemical compositions of treated poplar wood along with wood component mass yields (numbers in the parentheses).

Groups	Solids yield (%)	Ash (%)	Klason Lignin (%)	Cellulose (%)	Xylan (%)
Untreated poplar	100	0.1	23.6 (100)	48.4 (100)	18.4 (100)
G0	95.2	0.1	25.0 (100.8)	50.3 (106.1)	17.9 (92.4)
G10	89.0	0.0	19.6 (74.0)	53.3 (105.0)	17.5 (84.3)
G15	86.5	0.0	16.1 (59.1)	56.3 (107.7)	16.5 (77.4)
B5	93.6	0.0	20.7 (82.1)	52.5 (101.3)	17.4 (88.5)

$$\mathrm{MOR} = \frac{3 \times F_{\max} \times l}{2 \times b \times t^2} \tag{5}$$

$$\mathrm{MOE} = \frac{l^3}{4 \times b \times t^3} K \tag{6}$$

where $F_{\max}$ is the peak load, l is the span of supports, b is the width of the sample, t is the thickness of the sample, and K is the slope of the load vs deflection curve between 20 % and 40 % of the maximum load achieved obtained from linear regression.

Wood hardness was characterized by the Brinell hardness test using European Standard EN 1534 (European-Standard, 2020) with minor modifications, similar to that carried out in the literature (Fang et al., 2012a; Gong et al., 2010). Specimens with dimensions 20 mm (longitudinal) by 20 mm (tangential) cut from the densified and conditioned wood blocks were tested using a universal mechanical testing machine (Instron 5896, Grove, PA, USA) with a ball diameter of $D = 3.18$ mm. During testing, the ball was penetrated to a depth $h = 1.60$ mm. At least six replicate samples were tested for each set to calculate mean and standard deviation. The Brinell hardness (H_B) in N/mm^2 was calculated as

$$H_B = \frac{F}{\pi \times D \times h} \tag{7}$$

where F is applied load, D is diameter of the indenter ball, and $h = 1.6$ mm is the measured depth of the indentation at the applied load.

The dimensional stability of bulk wood was measured by using the samples with an area of 20 mm × 20 mm cut from the densified wood after thermal fixing treatment described earlier. The bulk wood was immersed in water for 16 days and then oven-dried. The weight and thickness of all samples were then measured. Water absorption (WA), thickness swelling (TS), and set recovery (SR_w) were calculated according to Eqs. (8–10).

$$\mathrm{WA} = \frac{m - m_d}{m_d} \times 100\% \tag{8}$$

$$\mathrm{TS} = \frac{t - t_0}{t_0} \times 100\% \tag{9}$$

$$\mathrm{SR_w} = \frac{t_r - t_d}{t_0 - t_d} \times 100\% \tag{10}$$

where m and t are the wet weight and thickness of samples after immersion in the water, m_d and t_d are the mass and thickness of oven-dried densified samples before immersion in the water, respectively, t_r is the thickness of water-soaked samples after oven drying, t_o is the thickness of the corresponding raw wood blocks, same as that in Eq. (2).

3. Results and discussions

3.1. Wood component loss by carbonate treatment

The chemical composition of the treated wood along with wood component mass losses are listed in Table 2. Wood solids yields varied with carbonate loading and was greater than 85 % for all the treatments performed. The hydrothermal treatment had the lowest wood mass removal and thus the highest solids yield of 95 %. Lignin and hemicellulose dissolutions ranged from approximately 18–41 % and 12–23 %, respectively, for the samples treated by carbonate. Results clearly show that carbonate treatment had negligible cellulose loss and/or protected cellulose better than NaOH treatment under the same treatment temperature and time reported in literature (Wang et al., 2020). This is important for the resultant wood mechanical strength.

3.2. Wood compression ratio and density

The ML, measured CR, and $\bar{\rho}$ of the wood samples are presented in Table 3. ML of densified wood are very similar to the mass losses right after wood treatment reported in Table 2, suggesting mass loss through densification and drying is negligible.

The CRs for wood samples pressed without the two stop bars were 50–70 %, depending on wood treatment mass loss and pressing pressure. For pressing at 1 MPa, the maximum CR was approximately 60 % from the run G15P1N. CRs were around 26 % for the two samples pressed with stop bars of 8 mm in height during densification at 1 MPa. The compression ratios CR_1 and CR_2 before and after conditioning were approximately the same for all samples.

SR is used to measure potential of set recovery or shrinkage of wood samples after conditioning. For the samples pressed without stop bars, a 1 MPa pressing pressure resulted in a SR of 6 %, higher than the SRs for the two samples pressed at elevated pressures of 3 and 5 MPa. Pressing with stop bars resulted in negligible set recovery after conditioning, perhaps due to the low extent of densification.

Hot-pressing reduced the thickness of wood samples and increased sample density comparing with the density of the control (untreated and unpressed) wood of 0.463 g/cm (Wang et al., 2020). Pressing without stop bars increased wood density by 65–88 % depending on wood mass removal by treatment. A higher mass loss increased or facilitated wood densification. Density was nearly doubled for the wood treated under G15 and pressed under 5 MPa. Density increase was approximately 20 % for the two wood samples pressed with stop bars, slightly lower than those reported previously using NaOH treatment (Wang et al., 2020). The results indicate that any effect of a low mass loss using carbonate treatment can be well compensated by removing stop bars or using a slightly higher pressure in pressing.

3.3. Densified wood physical and mechanical properties

Wood treatment changes the color of wood due to the presence of chromophores in wood lignin as shown in Fig. 2. Overall, the wood color is similar to the brown color of popular commercial wood stains/paints and is acceptable from aesthetic point of view. Detailed quantitative analyses of wood colors were conducted (Table S1).

A series of bending and hardness tests were performed on the control and densified wood samples to evaluate the mechanical properties of densified wood samples. Table 4 shows that MOR, MOE and H_B were all

Table 3
Average values and standard deviations of mass loss, compression ratio, density and porosity of poplar samples treated by carbonate.

Groups	Mass loss (%)	CR_1 (%)	CR_2 (%)	SR_1 (%)	$\bar{\rho}$	ρ (g/cm^3)
Untreated	-	-	-	-	1.00	0.463 ± 0.019
G0P1N	5.2 ± 0.5	52.2 ± 2.3	50.0 ± 2.4	4.8 ± 0.6	1.65	0.765 ± 0.097
G10P1N	11.1 ± 1.4	54.5 ± 0.2	51.8 ± 0.4	6.0 ± 0.7	1.64	0.761 ± 0.033
G15P1N	13.6 ± 2.8	61.7 ± 0.3	59.2 ± 0.3	6.5 ± 0.7	1.88	0.870 ± 0.072
G15P3N	11.5 ± 1.9	63.8 ± 0.9	63.3 ± 0.8	1.5 ± 0.8	1.92	0.891 ± 0.049
G15P5N	10.2 ± 0.5	67.8 ± 3.5	68.0 ± 3.6	-0.7 ± 1.1	2.05	0.953 ± 0.039
G10P1	13.4 ± 1.1	26.6 ± 1.3	29.2 ± 0.8	-3.6 ± 1.2	1.18	0.535 ± 0.021
B5P1	9.7 ± 0.6	26.1 ± 3.7	27.1 ± 3.1	-1.4 ± 0.9	1.24	0.572 ± 0.031
BLqP3N	28.2 ± 8.9	75.4 ± 2.4	71.3 ± 16.2	16.7 ± 3.9	1.84	0.852 ± 0.078
BLqP5N	27.1 ± 8.7	72.4 ± 3.5	71.5 ± 7.3	3.4 ± 0.5	1.77	0.818 ± 0.126

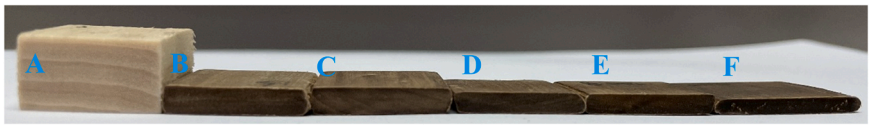

Fig. 2. Photos of untreated poplar wood and densified and conditioned wood samples pre-treated by carbonate. (A) Untreated, (B) G0P1N, (C) G10P1N, (D) G15P1N, (E) G15P3N, (F) G15P5N.

Tablee 4
Bending strength and hardness of densified wood.

Wood samples	ρ (g/cm^3)	MOR (MPa)	MOE (GPa)	H_B (MPa)
Untreated poplar	0.463 ± 0.019	88.5 ± 5.1	6.5 ± 0.8	14.8 ± 2.5
G0P1N	0.765 ± 0.097	109.8 ± 25.7	4.6 ± 1.2	27.8 ± 2.5
G10P1N	0.761 ± 0.033	135.1 ± 16.7	17.0 ± 3.6	37.2 ± 3.9
G15P1N	0.870 ± 0.072	159.6 ± 10.3	24.0 ± 2.8	50.4 ± 4.3
G15P3N	0.891 ± 0.049	140.0 ± 14.0	6.3 ± 0.7	65.7 ± 10.8
G15P5N	0.953 ± 0.039	100.0 ± 12.0	4.8 ± 0.5	27.3 ± 6.2
G10P1	0.535 ± 0.021	102.3 ± 9.6	11.1 ± 1.2	19.4 ± 2.7
B5P1	0.572 ± 0.031	114.8 ± 9.7	11.0 ± 1.0	25.0 ± 4.8

increased by densification. Due to explosive steam release resulting from hot pressing of water-saturated wet wood samples at high pressures, the two sample sets pressed at 3 and 5 MPa resulted in cracks. The G15P5N samples were significantly shattered. Therefore, the data for these samples need to be discerned. Comparing G15P1N with the un-densified, untreated poplar wood, MOR was almost doubled to 160 MPa, while MOE and H_B were increased by over 350 % to 24 GPa and 50 MPa, respectively. It is worth noting that even with defects, the H_B of G15P3N was increased to 65.7 MPa when pressing pressure was increased to 3 MPa. These data are very encouraging for super strong wood floor applications. Comparing G10P1N with G10P1 suggests pressing without stop bars further increased wood mechanical strength due to the higher wood density resulting from removing the stop bars in pressing.

To further illustrate the effectiveness of carbonate treatment, the data in Table 4 were plotted along with literature data from densified wood through NaOH treatment (Wang et al., 2020) and simple thermal densification at high pressures (Fang et al., 2012b). The thermal densification was achieved using steam (140–220 °C) injected from the press to treat wood under a pressure profile of 4.5–9 MPa for 30 min, compared with pressing at a constant pressure of only 1 MPa at 150 °C min for 15 min for the carbonate treated wood samples reported here. The data points from the thermal treatment study (Fang et al., 2012b) shown in Fig. 3 are in the order of increasing density on the x coordinate: unpressed, pressed at 160 °C and pressed at 200 °C. Results clearly indicate that wood bending MOR and MOE were increased with wood density (data points from the defective G15P3N and G15P5N samples with very high densities were omitted), and independent of wood treatment method. However, thermal treatment only achieved a density of 0.73 g/cm^3 for wood veneers 4.3 mm thick even with much higher pressures and being steamed at 220 °C compared to the density of 0.87 g/cm^3 (Table 3) achieved with carbonate treatment (14 % mass loss) of 10 mm thick wood boards pressed only at 1 MPa at 150 °C (Table 2). The data clearly show that much higher density was achieved at moderate pressure of 3–5 MPa for carbonate treated wood samples.

3.4. Thermal-fixing to improve dimensional stability of densified wood

Water absorption (WA), thickness swelling (TS), as well as set recovery (SR_w) of densified wood samples were measured and are used to evaluate wood dimensional stability after soaking in water for 16 days. As listed in Table 5, it appears that hydrothermal treatment which dissolved some hemicelluloses may have slightly decreased WA compared with the untreated wood. Carbonate treatments dissolved lignin and increased WA of subsequently densified wood. When comparing sample G10P with G10N, pressing without stop bars resulted in a lower WA than with stop bars. The WA values listed in Table 5 for the carbonate treated wood are similar to those of unbleached wood fibers of 150 % reported in literature (Luo et al., 2011).

TS of densified wood samples increased with increasing mass loss through thermo-chemical treatment. Also, G10P1N, pressed without stop bars, exhibited a much higher TS compared to G10P1 because the internal stresses introduced during hot-pressing are much higher without the stop bars than that induced with stop bars at a lower compression ratio (Song et al., 2018; Wang et al., 2020). Furthermore, by definition of TS, G10P1N with a much thinner initial thickness will result in a large TS.

The elastic strain energy stored in semi-crystalline microfibrils and lignin of wood is the principal reason for compression set recovery (Higashihara, 2000; Navi and Heger, 2004). SR_w of carbonate treated wood is approximately 25 % as listed in Table 5.

Thermal fixing treatment is the key to improving the dimensional stability of densified wood (Navi and Heger, 2004). Mass losses (ML_f) through thermal fixing was minimal for the four samples tested, as listed in Table 5. Thermal-fixing, substantially reduced thickness swelling (TS_f) by approximately 50–70 % for the samples evaluated when compared with the corresponding samples without thermal fixing. This is despite water absorption values not significantly decreasing. Thermal fixing also significantly decreased set-recovery (SR_{Wf}) by approximately 50–75 % except for the hydrothermally treated sample G0P1N; perhaps this is because G0P1N had a relatively low set recovery even without thermal fixing. The thermal fixing treatment led to the depolymerization of amorphous cell-wall polymers which are believed to be responsible for the spring-back effect in wood, the softening of remaining lignin, and the probable formation of covalent bonds in the deformed position (Chen et al., 2018; Navi and Sandberg, 2012). Additionally, the residual lignin compromises the formability of the cellulose scaffolds in wet conditions (Frey et al., 2019). It was reported that densified wood with alkaline delignification under the same thermal-fixing conditions had a SR_{wf} of 7.5 % (Wang et al., 2021), indicating that thermal fixing treatment had similar fixation effect on densified wood whether pretreated by carbonate or sodium hydroxide.

3.5. Densified wood from chemical treatment using spent pulping liquor

Poplar wood blocks treated by laboratory spent pulping liquor were densified at 3 and 5 MPa. The wood blocks were air dried to moisture content of approximately 10 % to avoid wood damage due to cell rupture by steam formation from hot pressing. The results (Table 6) indicate that spent pulping liquor treatment can effectively prepare wood for densification and achieve significant improvement in wood bending strength, similar to the results from carbonate treatment (Table 4) and NaOH treatment (Fig. 3). For example, the MOR and MOE of BLqP3N treated by spent pulping liquor are similar to G15P3N treated by pure carbonate solution pressed at the same 3 MPa. However, specimens pressed at 5 MPa had decreased bending strength. An earlier study indicated that high alkali charge can reduce the mechanical strength of densified wood as reported previously (Wang et al., 2020), perhaps due to excessive cellulose depolymerization at high alkali dosages. The laboratory spent pulping liquor contains a significant amount of NaOH which may caused excessive cellulose depolymerization to result in decreased mechanical strength of BLqP5N.

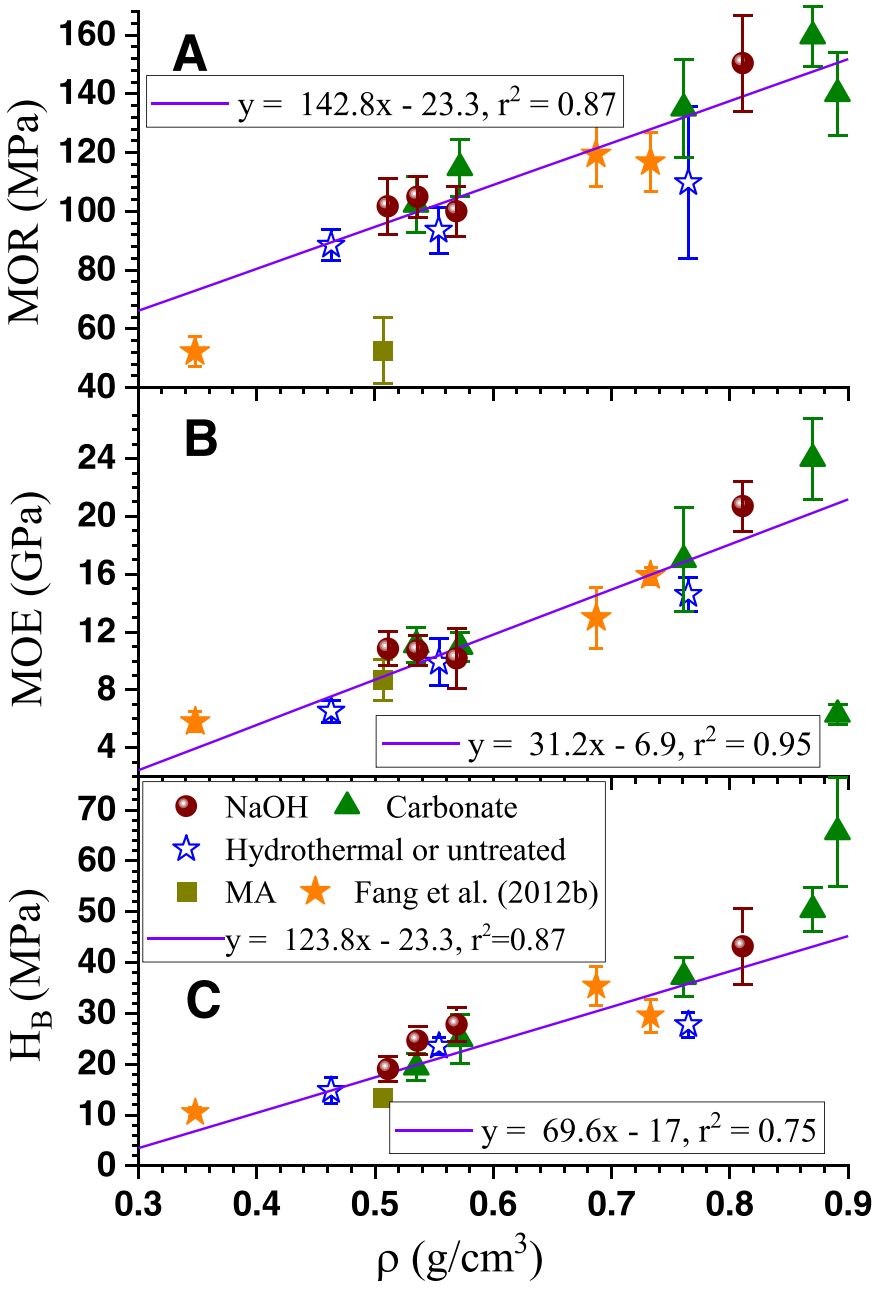

Fig. 3. Comparisons of mechanical properties of different densified woods as a function of wood density from various thermal and chemical treatments.

Table 5
Comparisons of water absorption, radial swelling and set recovery of densified samples treated by carbonate with and without thermal fixing.

Wood samples	WA (%)	TS (%)	SR_w (%)	ML_f (%)	WA_f (%)	TS_f (%)	SR_{wf} (%)
Untreated	111.6	8.3	–				
G0P1N	94.5	66.8	10.4	0.1 ± 0.2	105.3 ± 6.0	38.7 ± 4.4	10.0 ± 2.1
G10P1N	136.4	68.7	29.0	0.0 ± 0.4	137.0 ± 2.4	35.5 ± 1.9	13.5 ± 2.1
G15P1N	146.3	91.1	26.3	0.6 ± 0.1	100.5 ± 2.6	44.7 ± 1.2	6.1 ± 1.0
G15P3N	133.2	76.2	8.9				
G15P5N	143.4	127.0	22.5				
G10P1	166.4	38.6	30.2	1.1 ± 0.5	130.0 ± 1.5	22.1 ± 4.0	15.4 ± 1.5

Table 6
Mechanical bending strength of densified wood blocks.

Wood samples[1]	ρ (g/cm^3)	Bending		HB (MPa)
		MOR (MPa)	MOE (GPa)	
Pristine poplar	0.463 ± 0.02	88.5 ± 5.1	6.5 ± 0.8	14.8 ± 2.5
BLqP3N	0.869 ± 0.093	122.6 ± 28.4	15.1 ± 6.1	
BLqP5N	0.833 ± 0.074	90.7 ± 22.7	9.6 ± 3.6	

[1] P3N, and P5N stand for pressing without stop bars at 3, 5 MPa, respectively.

3.6. *Wood microstructure of densified wood*

Poplar wood vessel elements have thin walls and can be easily deformed under compression (Standfest et al., 2013). Optical microscopic imaging can resolve the deformation of vessel elements as shown in Fig. 4. Comparing with the natural poplar wood (Fig. 4A), the vessel

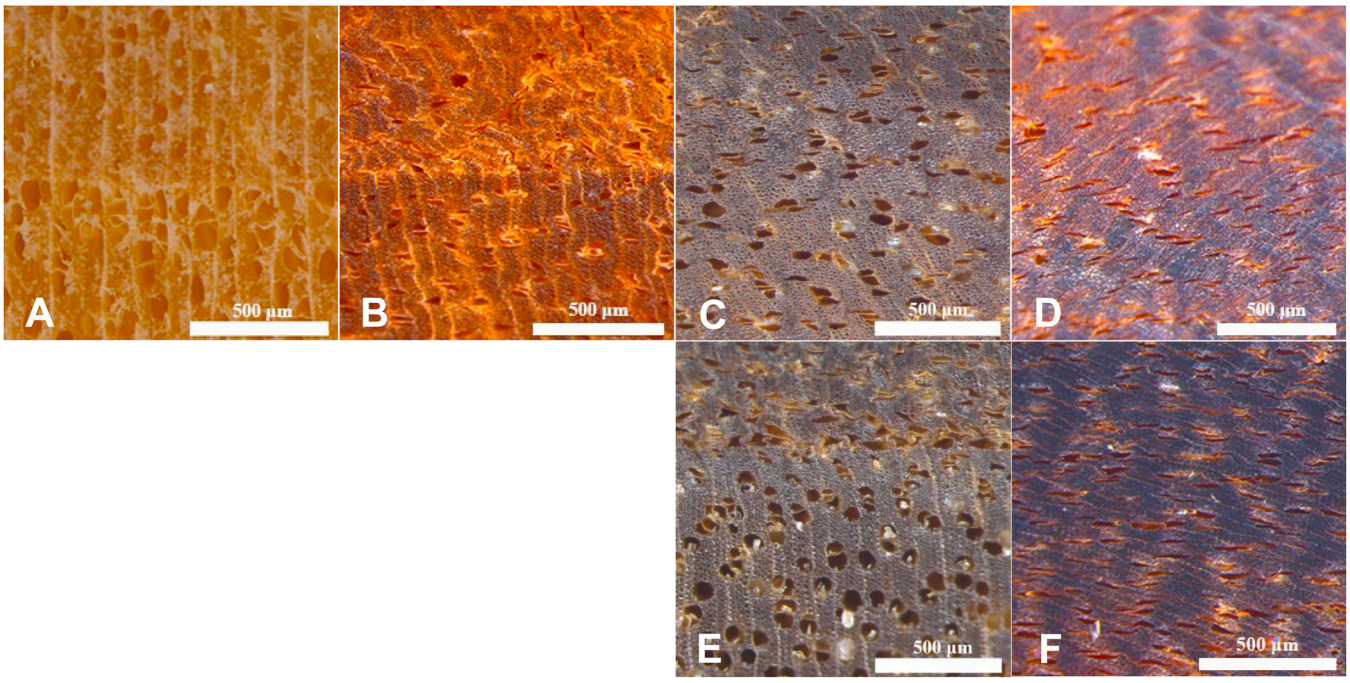

Fig. 4. Optical micrographs of wood sample cross section fiber longitudinal direction. (A) Untreated, (B) G0P1N, (C) G10P1N, (D) G15P1N, (E) G10P1, (F) G15P3N, All scale bars = 500 µm.

elements were deformed to different extent for different treated and densified poplar wood samples (Fig. 4B–F). Pressing the hydrothermal treated wood with the stop bars resulted in vessel element deformation mainly near wood surface (Fig. 4B). Increasing component removal resulted in more collapsing of vessels elements under the same pressure (comparing Fig. 4B with C and D), in agreement with our earlier study (Wang et al., 2020). Removing the stop bar, deformation proceeded deep into the wood (comparing Fig. 4C with E). Increase pressing pressure also further densified the wood (comparing Fig. 4D with F).

SEM imaging showed that thin early wood cells are easier to collapse than latewood (Laine et al., 2014). Since poplar wood has minimal difference between earlywood and latewood cells, a uniform densification is expected in the present study as shown in Fig. 4B–D and F (pressing without stop bars) and in agreement with an earlier study (Standfest et al., 2013). The collapsing of wood cells reduced the void volume in wood and increased wood density to improve its mechanical properties (Fig. 2).

4. Conclusions

Carbonate pre-treatment of wood at approximately 150 °C for 30 min is effective in removal a sufficient amount of wood lignin to lose wood structure for subsequent densification through thermal compression to result in a wood with substantially improve mechanical properties, i.e., bending strength of hardness, for structural applications. The dimensional stability of the densified wood can be improved through post-densification steam treatment. Alkaline wood pretreatment using fresh sodium hydroxide has demonstrated its potential for producing super strong wood for advanced structural applications with subsequent densification. The significance of the present study lies in the fact that carbonate is the major component of spent pulping liquor. Therefore, wood treatment can use spent pulping liquor rather than fresh sodium hydroxide to save chemical recovery processing cost and reduce environmental impact. Results of densified wood pretreated using laboratory pulping spent liquor verified this possibility.

CRediT authorship contribution statement

Wang conducted most of the experiments on carbonate wood treatment, densification, thermal fixing, and part of the mechanical testing. **Simson** and **Gleisner** conducted laboratory spent pulping liquor wood treatment and densification. **Fishwild** and **Begel** conducted mechanical testing of densified wood samples treated by spent pulping liquor. **Zhu** initiated and designed the study.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Co-authors Zhu, Simson and, Gleisner are co-inventors of a US patent application.

Data availability

Data are available under reasonable request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2022.115645.

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