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# Impacts of Process Parameters on VOC Emissions from Treated Poplar Wood with Low Molecular Weight Urea-Formaldehyde Resin

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## ABSTRACT

*Poplar wood was usually impregnated with low molecular weight thermosetting resins to improve its physical and mechanical properties. However, volatile organic compounds (VOCs) and formaldehyde emitted from treated wood have leaded to poor indoor air quality (IAQ). The trends of VOC emissions as a function of the pressing time and pressure factors were mainly investigated in this work. Aldehydes, alkanes and terpenes were the predominant compositions identified in the VOC emissions, although low amounts of ketones and alcohols were also found. With increasing of the pressing time and pressure, weight percent gain (WPG) clearly increased, whereas VOC concentrations increased considerably at the first stage and then began to decrease after a pressing time of 2.5 h at the 43.36 WP level, and after a pressure of 0.95 MPa at the 44.41 WPG level. This showed that VOC emissions from poplar wood impregnated by UF resin were directly influenced by WPG that was affected by process parameters. Therefore, it may be possible to reduce VOC emissions by optimizing the parameters investigated in this work.*

**Key words:** Poplar wood, Impregnation, Volatile organic compound (VOC), Emissions

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## INTRODUCTION

With the decrease of natural forest resources and the implementation of protecting policies, fast-grown plantation wood has replaced natural forest wood as the main material to meet the increasing demand. Due to its characteristics such as low density, poor quality, and weak protection properties, researchers have explored an approach of penetration of low molecular weight resins into wood to improve its physical, mechanical, and biological properties [1-3]. It has been reported that the impregnation of wood with melamine-formaldehyde (MF) resin results in a measurable increase in the modulus of elasticity (MOE) and surface hardness [4]. In another study concerning the impregnation of wood with phenol-formaldehyde (PF) resin, it was found that low molecular weight resin could penetrate cell walls, leading to a clear increase in the dimensional stability and anticorrosion performance [5]. The dimensional stability of wood treated with UF resin improved by 48.5% between 33–35 WPG level, and the MOE of treated samples also increased by 5.62% compared with untreated wood at the 33.8 WPG level [6]. However, low-density wood treated with resin penetration also released formaldehyde and volatile organic compounds (VOCs), resulting in poor indoor air quality (IAQ) [7-8]. VOCs emitted from wood-based materials have caused wide public concern. At present, there have been no studies reported on VOC emissions from poplar wood treated with UF resin.

The aim of this work is to examine the influences of different processing parameters on VOC emissions from treated poplar wood. Species of VOCsemitted from treated poplar wood were determined. Furthermore, it will be discussed whether a sustainable reduction or control of emissions can be achieved by adjusting these parameters.

## EXPERIMENTAL SECTION

A poplar tree (*Populousdavidiana*) was collected from a forest farm in Tieli, Heilongjiang province, China. The age of the tree was 20 years and its diameter at breast height (DBH) was 38.50 cm. Non-deficient, knotless, normally grown (no pitch line, no reaction wood, no decay, and no insect or mushroom damage) wood was cut from the same poplar tree into blocks of300 mm × 100 mm × 20 mm (longitudinal × tangential ×radial), which were dried to 5% moisture content.

A 32% solution of low molecular weight UF resin was produced by an adhesive factory in Jilin province. The molar ratio of urea and formaldehyde was 1.05 and free formaldehyde content was 0.17%. The resin viscosity was 14.5 sec at 20 ℃. The PH value was 8.0. Wood samples were impregnated with the UF resin according to the designed process parameters of the vacuum/pressure method (Table 1). The maximum working pressure and vacuum were 1.50 MPa and -0.1 MPa, respectively. The vacuum pump reached -0.08 MPa within 30 s.

**Tab.1: Vacuum/Pressure Process Parameters of Wood Treated with Resin**

| Experimental group | Process parameters | | |
|---|---|---|---|
| | Pressing time /h | Pressure /MPa | Vacuum time /min |
| Pressing time | 1 / 2.5 / 4 / 5.5 | 0.95 | 30 |
| Pressure | 2.5 | 0.75 / 0.85 / 0.95 / 1.05 | 30 |

Impregnated samples were maintained for 3 days in an air-dry state, dried at a temperature of 60 ℃ for 10 h, and then dried at a temperature of 80 ℃ until the moisture content was approximately 5%. The resin was cured at a temperature of 120 ℃ for 2 h. As soon as the samples cooled down, their edges were sealed with aluminum-coated adhesive tape; they were wrapped tightly in aluminum foil to prevent the release of edges and exposed areas.

## METHODS

Samples were tested in airtight environmental test chambers with a volume of 15 L. Treated woods without drying defects were selected and the loading factor was 4.0 $m^2m^{-3}$. The temperature was 23±0.5℃ in the chambers and VOCs were measured in the outlet port.

Air samples were collected on a Tenax TA at a flow rate of 150±1 mL $min^{-1}$for a period of 20 min, which was a total air volume of 3 L. 200ng of toluene-D8 was injected into each tube as the internal standard. After sampling, the tubes were thermally desorbed with a thermal desorption sampler (TP-5000). They were then characterized and quantified by gas chromatography and mass spectrometry (ThermoFisher DSQⅡ).

Thermo desorption conditions were as follows: desorption temperature, 280℃; desorption time, 5 min; injection time, 1 min; and split ratio, 30:1. A 30 m analytical column (HP-5MS, film 0.25μm, i.d. 0.25 mm) was used in the GC. The temperature program was that an oven temperature of 40 ℃ was maintained for 2 min, raised to 50℃ at a rate of 2℃ $min^{-1}$ and maintained for 4min, increased to 150℃ at a rate of 5℃ $min^{-1}$ and maintained for 4min, and finally raised to 250℃ at a rate of 10℃ $min^{-1}$ to be maintained for 8min. The ion source of MS was EI and its temperature was 230℃. The scan mode was full scan (40–450 amu).The individual VOC was identified by using retention time and a standard mass spectra library with the match quality not less than 90% and quantified based on their response factors derived from the standard curves.

## RESULTS AND DISCUSSION

### Components of VOCs

VOCs from poplar wood impregnated with different process parameters were detected in an airtight chamber after testing times of 24 h, 48 h, and 72 h. Concentration of the total volatile organic compound (TVOC) after 48 h and 72 h were less than 4%. VOCs quickly reached a state of equilibrium in airtight chambers [9]. The method could shorten the testing time and was conducive to comparing the differences of VOC emissions from treated wood with different processes. Table 2 summarized composition and concentration of VOC emissions. Aldehydes, alkanes and terpenes were the predominant compositions identified in the VOC emissions from treated poplar wood with low molecular weight UF resin, although low amounts of ketones and alcohols were also found. The species detected in the VOC emissions did not change with the increase of the pressing time and pressure.

Aldehydes are the most universal compounds in the indoor air of new homes. With respect to low odor thresholds, elevated concentrations of aldehydes can lead to problems with perceived indoor air quality [10]. Straight-chained aldehydes originated from free unsaturated fatty acids degraded through autoxidation [11].Hexanal, nonanal and do decanal were the main components of aldehydes, which accounted for more than 70% of aldehydes. Heptanal, be aldehyde and octanal were also prevalent compounds measured in the VOC emissions from wood products. Baumann [12] detected hexanal, heptanal, bezaldehyde, octanal, nonanal and so on from 53 particleboard and 16 medium-density fiberboard (MDF) samples and He [13] also determined nonanal and decanal from wood chip and MDF, which are similar to the result of this study.

Alkanes emissions, such as nonane, decane, dodecane, tetradecane, and pentadecane, exceeded other composition emissions and accounted for more than 40% in TVOC emissions. Dodecane 2-methyl-tridecane, tetradecane andpentadecane were the main compounds detected in the VOC emissions. The result was similar to the previous studies. Shen [14] measured nonane, dodecane and hexadecane from MDF in a small environmental chamber. Huang [15] tested tetradecane, pentadecane and hexadecane from fiber drying without an adhesive. It indicated that degradation of the wood is probably responsible for the presence of the alkanes. However, no clear source of the alkanes has been identified.

Terpenes are important compounds in the defense against insects and fungi [11]. Terpenes themselves do not cause problems related to indoor environments and human health, but the ozone in indoor air and terpenes such as D-limonene and α-pinene react to the stable products such as aldehydes, peroxides and condensed phase compounds, some of which are sensory eye and airway irritants[16].Tables 2depicted thatα-pinene, 3-Carene and D-limonene were the main components of terpenes and there was no regular change in terpene concentrations after changing the pressing time and pressure. Terpene emissions ranged from 46.20 to 52.09μg m$^{-3}$ (pressing time group) and from 36.55 to 46.68μg m$^{-3}$ (pressure group). The changes do not depend on process parameters butrather on the natural variability of the poplar itself. Terpenes originate from wood extractives, and they are volatile due to their high vapor pressures at ambient temperatures. Consequently, the influence of drying temperature on terpene emissions was more obvious [17].

**Tab. 2: VOC Emissions from Wood Treated with UF Resin at Different Process Parameters**

| Compound | VOC concentrations after the testing time of 24 h / μg m$^{-3}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Pressing time factor / h | | | | Pressure factor / MPa | | | |
| | 1 | 2.5 | 4 | 5.5 | 0.75 | 0.85 | 0.95 | 1.05 |
| Aldehydes | | | | | | | | |
| Hexanal | 21.53 | 40.92 | 37.30 | 32.06 | 23.82 | 25.16 | 32.74 | 24.13 |
| Heptanal | 3.23 | 5.38 | 2.88 | 3.00 | 2.79 | 3.74 | 6.43 | 4.23 |
| Benzaldehyde | 7.01 | 7.18 | 8.55 | 7.42 | 5.63 | 8.53 | 4.94 | 4.61 |
| Octanal | 9.59 | 16.16 | 13.99 | 12.12 | 4.30 | 7.34 | 14.12 | 10.96 |
| Nonanal | 2.83 | 4.43 | 1.89 | 2.09 | 5.34 | 6.28 | 3.48 | 5.44 |
| Dodecanal | 10.06 | 17.29 | 23.93 | 13.20 | 17.08 | 36.42 | 19.14 | 31.30 |
| Decanal | 5.14 | 3.45 | 4.06 | 3.12 | 3.24 | 4.69 | 6.73 | 4.37 |
| Terpenes | | | | | | | | |
| α-Pinene | 34.55 | 35.29 | 23.63 | 34.69 | 26.76 | 28.91 | 29.84 | 27.45 |
| β-Pinene | 0.00 | 5.51 | 3.88 | 3.84 | 0.00 | 3.52 | 5.01 | 3.65 |
| 3-Carene | 10.43 | 11.29 | 18.69 | 10.32 | 6.62 | 4.30 | 8.84 | 7.43 |
| D-Limonene | 3.61 | 0.00 | 0.00 | 2.80 | 3.17 | 2.55 | 2.99 | 3.73 |
| Alkanes | | | | | | | | |
| Decane | 4.60 | 5.20 | 3.78 | 3.28 | 5.65 | 3.38 | 4.98 | 3.90 |
| Nonane | 7.23 | 6.72 | 5.67 | 4.56 | 3.83 | 6.13 | 6.73 | 4.74 |
| Undecane | 10.33 | 9.29 | 10.90 | 12.44 | 10.03 | 12.36 | 11.66 | 9.56 |
| Dodecane | 24.48 | 25.49 | 27.81 | 30.30 | 28.20 | 26.57 | 30.64 | 28.59 |
| Octane,2,3,7-trimethyl- | 11.71 | 15.19 | 9.94 | 11.64 | 10.47 | 15.85 | 16.34 | 12.33 |
| Tridecane, 6-methyl- | 9.64 | 12.12 | 7.56 | 10.66 | 7.72 | 9.36 | 7.34 | 10.36 |
| Tridecane, 4-methyl- | 5.12 | 10.42 | 7.08 | 8.59 | 11.53 | 9.77 | 14.71 | 7.58 |
| Tridecane, 2-methyl- | 12.93 | 18.27 | 11.53 | 12.86 | 12.84 | 15.69 | 20.62 | 16.84 |
| Tridecane, 3-methyl- | 5.34 | 9.72 | 7.13 | 5.09 | 13.08 | 17.48 | 15.43 | 19.02 |
| Dodecane, 2,6,10-trimethyl- | 0.00 | 13.19 | 7.68 | 0.00 | 0.00 | 5.92 | 13.92 | 14.98 |
| Tetradecane | 8.13 | 15.97 | 16.21 | 14.32 | 10.17 | 7.86 | 18.94 | 14.45 |
| Pentadecane | 3.69 | 7.31 | 13.67 | 5.26 | 0.00 | 5.17 | 7.71 | 5.78 |
| Hexadecane | 4.13 | 5.24 | 3.95 | 4.13 | 6.11 | 6.69 | 5.83 | 4.53 |
| Ketones | | | | | | | | |
| Acetophenone | 2.39 | 5.31 | 9.91 | 3.22 | 7.88 | 8.46 | 9.46 | 9.32 |
| 5-Hepten-2-one, 6-methyl- | 2.78 | 6.22 | 4.59 | 4.00 | 5.02 | 5.40 | 3.36 | 0.00 |
| Others | 33.12 | 71.81 | 58.86 | 56.49 | 40.33 | 34.40 | 53.26 | 51.02 |

*ND, not detected; others included 2-Octanol, Naphthalene, Naphthalene, 2-methyl- and Naphthalene, 1-methyl-*

## Pressing Time

Trends in TVOC emission and average WPG along with pressing time were given in Fig. 1. TVOC emissions were clearly affected by pressing time. In general, with an extended pressing time, WPG and TVOC concentrations increased significantly. The values of WPG rose to 67.45% after an impregnation of 5.5 h from 28.05% after an impregnation of 1 h, and simultaneously, TVOC concentrations ranged from 253.6μg m$^{-3}$ after an impregnation of 1 h to 384.37μg $m^{-3}$ after an impregnation of 2.5 h after the testing time of 24 h. However, TVOC concentrations reduced directly to 311.5μg $m^{-3}$ after a pressing impregnation of 5.5 h. The trend of VOC emissions was more obvious after the testing time of 48 h.

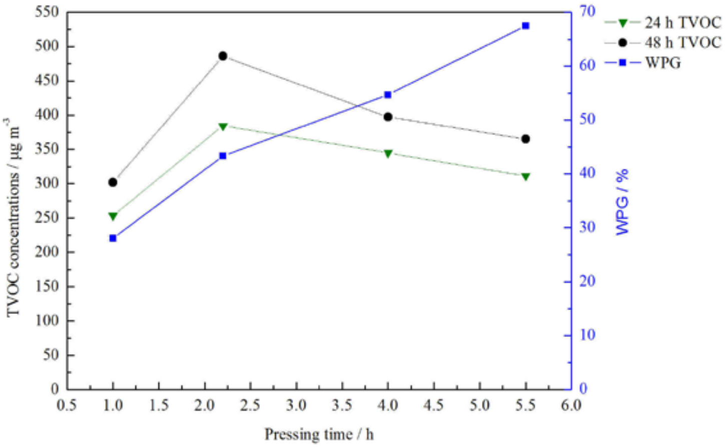

**Fig.1: VOC emissions and WPG at different pressing time**

Therefore, TVOC emissions are directly influenced by the degree of impregnation of low molecular weight thermosetting resin into low-density wood. The degree of impregnation is closely related to the chemical structure of the impregnation compound and the wood structure. Low molecular weight resin is penetrated into hardwood by wood vessels and wood rays. Due to the structure of the hardwood, the impregnating process acts as a multi-stage filtration of the resin. The relatively high molecular weight resin was kept in vessels, and the low molecular weight resin coated the inner surface of the lumina of fiber and parenchyma cells. Only the lower molecular weight resin coated the bulk cell walls of the fiber and parenchyma cells [18] [5]. After curing of the UF resin, the free radicals in wood activated high activity hydroxymethyl groups of the resin filling the voids of cell walls and the inner surface of cell lumina and produced carbonyl (—C=O) instead of hydroxyl (—OH) and other cell wall materials [19-20]. Covalent bonds strengthen cell walls.

An increase in the resin content impregnated into the wood may improve VOC emission levels. This is consistent with the results showing that VOC emission from particleboard was obviously impacted by resin content and with rising resin content, VOC emissions from wood-based panels also increased [21]. However, wood structure is more complicated than wood-based panel resin interface. After the resin content impregnated into wood (WPG) reached 43.36%, the TVOC concentrations began to decrease. This different emission pattern is likely due to the decrease of wood porosity during the treatment of wood with excessive resin. When the resin content reaches a certain value, superabundant resins that deposit in the wood vessels and the surface of the cell walls will lead to blocked vessels and cell wall voids after curing of the resin [22]. Meanwhile, the resin molecules that bulked the cell walls form chemical bonds with hydroxyl groups of the cell wall materials causing the reduction of cell wall voids. Low wood porosity results in a decreasing VOC diffusion coefficient [23], while according to the mass transfer model, diffusion coefficients directly contribute to VOC emissions [24-25]

### Pressure of Impregnation

The same TVOC emission trend as in Fig. 1 was shown in Fig. 2, namely that with elevating pressures and increasing WPG, TVOC concentrations clearly increased to 375.20μg $m^{-3}$ (0.95 MPa and WPG 44.41%) from 271.60μg $m^{-3}$ (0.75 MPa and WPG 30.7%) first and then decreased to 340.3μg $m^{-3}$ when the pressure was 1.05 MPa and WPG was 50.04% (the testing time of 24h). TVOC emissions after the testing time of 48 h were higher than those after the testing time of 24 h, but the emission pattern did not change. It was illustrated that TVOC emissions from treated wood with low molecular weight resin were directly affected by WPG, which was changed by pressures of impregnation. The reason that pressures and WPG affected VOC emissions was the same as that identified in the previous analysis about the impact of pressing time and WPG on VOC emissions. Inflection points of WPG were different in two experimental groups, but they were also above 43%. This showed that when the WPG exceeded a certain value, excess resin impregnation would lead to a reduction of the wood porosity to prevent VOC release.

A comparison of the sample of pressure 0.95 MPa (Fig. 2) with the sample of pressing time 2.5 h (Fig. 1) showed that its TVOC concentration (375.20 and 476.22 μg $m^{-3}$) was nearly the same as that of pressing time 2.5 h (384.37

and 486.03 μg m$^{-3}$) after the testing time of 24 h and 48 h. It showed that experiments had high parallelism. The minor difference of TVOC emissions is due to different resin contents impregnated into the wood. It also showed that TVOC emissions decreased with the reduction of WPG when WPG was less than a certain value (43.36% and 44.41% in this work). WPG is influenced by a comprehensive action of process parameters. The control of VOC emissions is achievable with a reasonable optimization of process parameters. This will be investigated in the next step of the work.

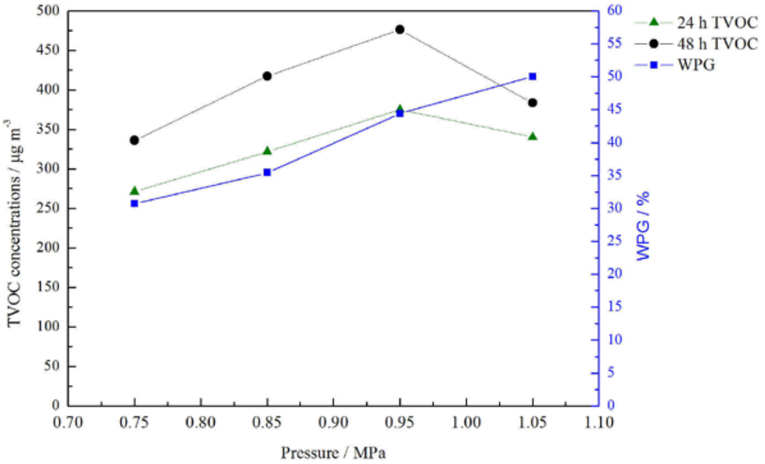

**Fig.2: VOC emissions and WPG at different pressures**

## CONCLUSION

Alkanes, aldehydes, and terpenes were the main components of VOC emissions from wood impregnated with urea-formaldehyde resin. A small amount of ketones and alcohols were also detected. With increasing pressing time and pressure, the WPG of the treated wood increased, and there was also a clear increase in the TVOC concentrations. However, TVOC emissions started to decrease when the WPG continued to rise beyond a certain value (43.36% and 44.41% in this work). Therefore, it is possible that a sustainable reduction or control of emissions can be achieved by adjusting these parameters under the premise of meeting the wood performance and reducing costs.

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