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Effective Extraction of Useful Chemicals during the Compressive Molding of Wood with High-Pressure Steam

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The compressive molding method with high-pressure steam has been developed in our laboratory, as an ecological method to make products from sawdust, leaves and branches, which arise from wood-based industries as waste. By this method, logs can be transformed into squares, and sawdust, leaves or branches into biomass boards. Square timber will widely be used as building materials, and biomass board to be used for weed suppressers or spreading materials on the sidewalk. For example, the board made by this method already has been used at many places, e.g., walking paths in Kenrokuen Garden. In addition, much essential oil mainly terpenoids can also be obtained through this process. It was found that the essential oil contained furfural and 5-hydroxymethyl-2-furfural, which are byproducts from saccharides and hemicelluloses with high temperature steaming. Furthermore a new apparatus was developed by combining a high pressure distillator with the compressive molding apparatus. With this apparatus, the distillation of higher boiling compounds such as sesqui-terpenoids, which are hardly distilled with 100 °C steam was made possible. In the case of operations at several saturated steam pressures (0.4-1.6 MPa) for 60 min, the yields of these compounds increased with steam pressure within the limits of this experiment.
Keywords: compressive molding process, high-pressure steam, distillation, extraction.

1. INTRODUCTION

The compressive molding process has been developed[1-2] in our laboratory. It is used to produce squared timbers[3] from thinnings and biomass boards[4-6] from branches, leaves or sawdust without any adhesives. The squared timbers can be utilized for building material, and the biomass board also can be utilized for weeds suppress boards and so on. In the process of the compressive molding of wood, a sap was arisen (Photo) from cross section of log.

In this paper, the compounds in the sap were detected, and the effective extraction method was developed in various wood-based raw materials. So far, the extractives from wood were mainly obtained by normal steam distillation[7] and the wood after the extraction, that is residue, was used to another way. For example of ordinal methods, the residue converted to the wood-based board with some adhesives, or just burned to obtain the energy etc. There are two problems in traditional ways of thinking like that. One is the environmental pollution if the residues are just burnt and another is these methods have to do two processes. So it takes long time and the cost is raised up. It is difficult to supply widely. Developing this treatment, both compressed wood and extractives are simultaneously obtained from wood-based raw material. Now we are in the face of difficult problem that the increased atmospheric carbon dioxide causes of burning petrol or anything else. Using this treatment, the wood-based and unutilized resources converted to useful material without wasting of time and energy. Most of compounds obtained from wood-based raw material have bioactivity, which are useful for medicines or food additives.

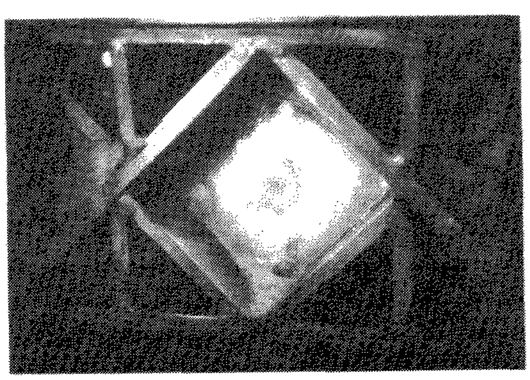


Photo In the process of extraction the sap

2. MATERIALS AND METHODS

2.1. The analysis of the sap extracted by the process of compressive molding of wood

2.1.1. A log of Japanese cedar (*Cryptomeria japonica*)

A log of Japanese cedar (diameter; 127 mm, length; 1.8 m, weight; 18.7 kg) was used as a raw material. After the log was steamed, the process of the compressive molding was performed under 0.2 MPa (=120 ℃) steam pressure. The extracted liquid was moved to the out of the apparatus, and it was obtained in 30min. The liquid was separated into chloroform layer and water-soluble layer. The chloroform layer was separated by preparative TLC on silica gel plate using the mixed solvent of chloroform and methanol (20:1). Each fraction was analyzed by ^{1}H-NMR. The water-soluble layer was freezing dried, and the sample was analyzed the contents of constituent sugars by alditol-acetate method.

2.1.2. A log of White birch (*Betula platyphylla*)

A log of White birch was also used as a raw material. The treatment condition was at 120℃ (=0.2 MPa) for 20 min. Then it dealt with the extracted liquid equal to that method.

2.2. The development and analysis of the steam distillation at a normal pressure after the compressive molding process

A branch and leaves of Japanese cedar were used as a raw material. After the compressive molding process to make biomass boards, the extracted liquid was moved to the out of the apparatus. Then, the extracted liquid was distilled under atmospheric steam pressure (0.1 MPa=100℃)(Fig. 1). In this process, it was separated into two parts, one is the distilled liquid (DST) and the other is the undistilled liquid (UN-DST). Each DST and UN-DST was extracted by diethyl ether. The UN-DST was separated by preparative TLC on silica gel plate using the mixed solvent of ethyl acetate and *n*-hexane (3:2) and analyzed by ^{1}H-NMR. The DST was analyzed by GC-MS.

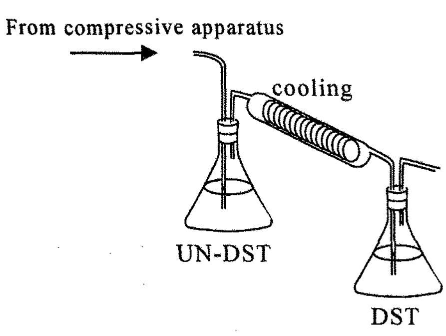


Fig. 1 The steam distillation at a normal pressure after the compressive molding process

2.3. The development and analysis of the steam distillation at a high pressure after the compressive molding process[8]

2.3.1. A branch and leaves of Japanese cypress (*Chamaecyparis obtusa*)

A branch and leaves of Japanese cypress were used as a raw material. After the compressive molding process to make biomass boards, the extracted liquid was collected from compressing part to other part, distiller, in the same apparatus under steam saturated high-pressure (0.4-1.6 MPa). Then, the distilled liquid was passed through the cooling box, and it was collected. (Fig.2). The distilled liquid was extracted with ethyl acetate, and the organic-soluble layer was analyzed by GC, GC-MS.

2.3.2. Sawdust of Western red cedar (*Thuja plicata*)

Sawdust of Western red cedar was also used as a raw material. The treatment condition was under saturated high-pressure (0.4-1.6 MPa) for 20 min. Then it dealt with the extracted liquid equal to that method.

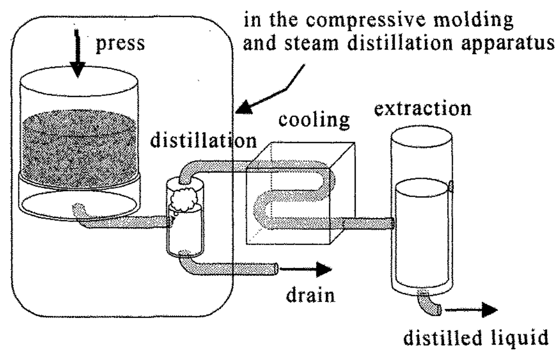


Fig. 2 The compressive molding and high -pressure steam distillation apparatus

3. RESULTS AND DISCUSSION

3.1. The analysis of the sap extracted by the process of compressive molding

3.1.1. A log of Japanese cedar

The result of analyzing by ^{1}H-NMR, vanillin, vanillyl alcohol, coniferyl aldehyde, coniferyl alcohol, *d,l*-pinoresinol, lariciresinol and dihydro dehydro diconiferylalcohol (Fig. 3) were detected with authentic from chloroform layer separated by preparative TLC. The result of constituent sugar by alditol-acetate method was shown in Table 1.

It is considered that these phenolic compounds are lignan derivation or glycoside-lignin monomers that means lignin precursor. The parts of these compounds were deetherified in high saturated steam pressure. It is the main hemicelluloses in softwood that arabinoglucronoxylan and glucomannan. The result of alditol-acetate method was shown that these hemicelluloses were partly converted into monosaccharide. Especially, the content of arabinose was higher. Not only the phenolic compounds but also arabinose which is one of the valuable monosaccaride could be obtained in this process.

3.1.2. A log of White birch

The result of analyzing by ^{1}H-NMR, coniferyl aldehyde, coniferyl alcohol, sinapyl aldehyde and sinapyl alcohol (Fig. 3) were detected with authentic from ethyl acetate layer separated by preparative TLC. These phenolic compounds are also lignin derivation. The result of the contents of constituent sugars by alditol-acetate method was shown Table 2. The water-soluble layer was acidified by hydrochloric acid and refluxed for 5hr. Then, this water-soluble layer was reanalyzed the contents of constituent sugars by alditol-acetate method. It was also shown in Table 2. And this acidic water solution was extracted with ethyl acetate layer. The result of analyzing by ^{1}H-NMR, small amounts of the phenolic compounds were detected. From this result, it was proven that the extracted sap contains oligo-saccharides and glycoside-lignin monomer like syringin or coniferin. Then, they were squeezed by compression, some of them were deethrified into mono- or oligo-saccharides and phenolic compounds.

Table The contents of constituent sugars in extracts from Japanese cedar and White birch

Species	Sugars					
	Ara	Xyl	Man	Gal	Glc	
Japanese cedar	29	9	33	17	12	(%)
White birch	29	8	20	-	42	(%)
	(17)	(13)	(27)	(-)	(43)	(%)

Parentheses denote the after acidic treatment.
Ara; Arabinose, Xyl; Xylose, Man; Mannose, Gal; Galactose, Glc; Glucose.

3.2. The development and analysis of the steam distillation at a normal pressure after the compressive molding process

The result of analyzing by ^{1}H-NMR, 5-hydroxymethyl-2-furfural (5HMF) was mainly detected from N-DST diethyl ether layer separated by preparative TLC. DST was analyzed by GC-MS, *p*-menth-1-en-4-ol and β-elemol (Fig. 3) were detected mainly. From these results, low boiling point compound such as the terpenes which was included in the row material were distilled under normal saturated steam pressure (0.1 MPa), then it was obtained in the DST division, whereas compounds which was difficult to distill like 5HMF under normal saturated steam pressure were obtained in the UN-DST division. Using this process, the compounds could efficiently be separated. However, most of compounds in DST division were sesqui-terpenes, it was supposed that mono-terpenes that have low boiling point were passed through into the atmosphere.

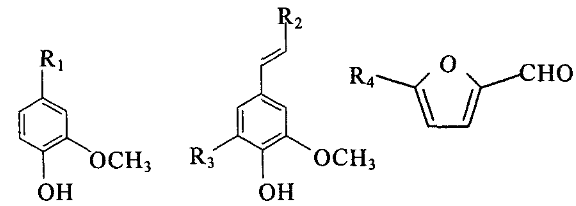
3.3. The development and analysis of the steam distillation at a high pressure after the compressive molding process.

3.3.1. Leaves of Japanese cypress

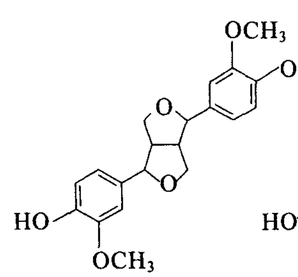
The result of analyzing by GC-MS, funebrene, 3,7,11-trimethyl-dodeca-1,6,10-trien-3-ol and 2,4-diisopropenyl-1-methyl-1-vinyl-cyclohexane (Fig. 3) were detected. It is indicated that this process could be obtain the di-terpens, which were hardly obtained in normal steam distillation so far.

3.3.2. Sawdust of Western red cedar

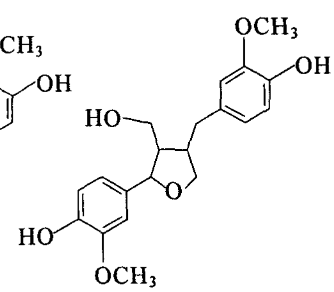
The result of analyzing by ^{1}H-NMR, thujaplicins, thujic acid, furfural and 5HMF were detected, mainly. Especially, it was difficult to distill thujaplicins and thujic acid by normal steam distillation, each components content based on the oven-dried basis was 2.6×10^{-3}% and 7.6×10^{-3}%, respectively. By this method, the best yield in this experiment (0.4 – 1.6MPa steam pressure) was under 1.6MPa steam pressure. These two compounds are obtained 0.69%, 1.32% (oven-dried basis) in the condition, respectively. Even under 1.0MPa steam pressure that was the best condition of biomass board of physical property, these two compounds were obtained 0.27% and 0.44%, respectively. It is considered that the high saturated steam pressure and the squeezing might have significantly influenced the yield.



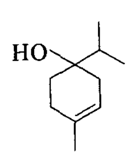
R_1=-CHO Vanillin
R_1=-CH_2OH Vanillyl alcohol
R_2=-CHO R_3=-H Coniferyl aldehyde
R_2=-CH_2OH R_3=-H Coniferyl aldehyde
R_2=-CHO R_3=-OCH_3 Sinapyl aldehyde
R_2=-CH_2OH R_3=-OCH_3 Sinapyl alcohol
R_4=-H Furfural
R_4=-CH_2OH 5HMF



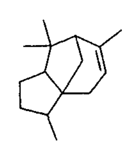
d,l-Pinoresinol



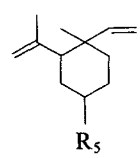
Lariciresinol

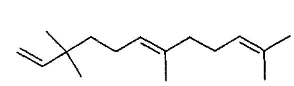


p-Menth-1-en-4-ol



Funebrene





3,7,11-trimethyl-dodeca-1,6,10-trien-3-ol
R_5=-isopropyl-2-ol β-Elemol
R_5=-isopropenyl 2,4-diisopropenyl-1--methyl -1-vinyl-cyclohexane

Fig. 3 The main compounds obtained from wood-based raw material

4. CONCLUSION

In this study, it was proven that the extractives arisen during the compressive molding process of wood-based row material were including many chemicals. Most of them have bioactivity, and expect to be used for medicines or food additives and so on. Further, using this method, the wood itself also could be utilized for new material.

Acknowledgments

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