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conductivity of the carbonization layer is lower than that of the wood material, which is the reason why wardrobes made of paulownia wood are able to protect kimonos from fire.

To reviewer:

Thank you very much for your patience and advice for my manuscript. I revised my paper as your suggestion.

And to reviewer #1, in the line 9 of abstract, I don't think I need to change "radial" to "cross".

Flame retardancy of paulownia wood and its mechanism

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Abstract

Paulownia wood (Pauloumia tomentosa) is a special kind of wood material in that it has especially excellent flame retardancy. Using this property, it has been commonly used to make clothing wardrobes for a long time in Japan. In this research, the flame retardancy of paulownia wood has been verified by heating experiments and cone calorimeter testing. The structure and tissue of the material have been analyzed by scanning electron microscope and other methods. Moreover, the mechanism of the flame retardancy of paulownia wood was analyzed by model experiments and FEM analysis. The result shows that the cell tissue of paulownia wood is very porous and similar to the structure of a honeycomb. It can be easily carbonized when heated. Since paulownia wood contains few lignins, it generates very little combustible gas when heated. Furthermore, when viewed from the radial section, the vessel structure of paulownia wood is very large and independent, compared to cedar wood (Cryptomeria japonica), which has a thin and continuous tracheids structure. Oxygen is not sufficiently supplied in this type of structure found in paulownia wood. Thus, it is difficult to ignite, and only carbonized when heated. Generally speaking, the thermal conductivity of the carbonization layer is lower than that of the wood material, which is the reason why wardrobes made of paulownia wood are able to protect kimonos from fire.

Keywords: Biomaterial, Paulownia wood, Flame retardancy, Microstructure, Fiber, Vessel structure, FEM

1. Introduction

In recent years, an innovative way of thinking came into being, which was to discover the uniqueness and magnificence of organisms, that is, to learn what kinds of conditions and processes are necessary to create them, and to make artificial material with new functions that mimic nature [1]. It turns out to be that a lot of organisms are composed of amazing materials, which are beyond anything imaginable. The properties of their basic materials are not limited by conditions like temperature, pressure and elements, etc [2-6]. Paulownia wood is a special kind of wood material that grows quickly, which is light, soft, and is also excellent for repelling insects, controlling humidity, and for insulation. In Japan, it has been commonly and long used to make wardrobes, the interior material of fireproof safes and other fittings. It has been said that even if a wardrobe made of paulownia wood is charred jet-black due to a fire, a kimono (Japanese clothing) inside is safe.

Previous studies have been done on the carbonization process and the combustibility of wood [7-13]. However, theoretical studies of the flame retardancy of paulownia wood are sparse. In this research, the flame retardancy of paulownia wood has been verified by experiments, and its mechanism was clearly found from the researched structure and tissue of the material. In addition, the relation among the thermal characteristic, structure and physical characteristics are verified by FEM analysis performed in a heating experiment.

2. Evaluation of the flame retardancy of paulownia wood

2.1 Materials

The two kinds of wood boards used in this study are shown in Table 1. The moisture content of air-dried wood of different kinds of wood is almost stable; it changes according to the region and season. The materials were kept indoors for one month, and the moisture content of paulownia wood and cedar wood was found to be 7.96% and 9.20%, respectively. While all of the specific gravity of wood substance is about 1500 $Kg{\cdot}m^{-3}$, the density only varies according to porosity and moisture content [14]. Thus, the porosity of paulownia wood and cedar wood are 82% and 72%, respectively, by calculation.

The thermal conductivity of general wood is in the order of 0.07 to 0.23 $W{\cdot}m^{-1}{\cdot}K^{-1}$[15-16]. In this experiment, the thermal conductivity of the paulownia wood that was used measures 0.101$W{\cdot}m^{-1}{\cdot}K^{-1}$ with comparative apparatus, and the cedar measures 0.100$W{\cdot}m^{-1}{\cdot}K^{-1}$. Although their values are almost identical, the thermal conductivity of the paulownia wood is lowest among all types of wood. The cavities of both materials are very small (on order of 20 to 30μm), heat transfer is not affected by convection. This explains why the thermal conductivity of the two materials is almost equal though the porosity of paulownia wood is 10% larger than that of cedar [17].

2.2 Heating experiment of wood board

A paulownia board and a cedar board (0.085 (W) x 0.085 (D) x 0.012 (H) m^3) were dried in a furnace for 24 hours, so the moisture content of both materials was 0%. Then the paulownia board and cedar board were each put on an aluminum board surface that was heated to 450 degrees Celsius by an electric heater, and their appearance were recorded on video. The varied states of the wood boards upon heating are shown in Figure 1. About 1 minute after the paulownia wood board was put on the aluminum board, a carbonized layer 5mm thick appeared, and that of the cedar wood was only 1mm. Following this, the carbonized layer of cedar wood increased, becoming ash after 30 minutes. Conversely, the carbonization layer of paulownia wood did not turn to ash, though it increased slowly. That is, it is known that although the process of carbonization occurs very fast, the transformation from carbonization layer to ash occurs very slowly in paulownia wood.

To reduce the influence of air flow resultant from the cedar wood warping upon heating, another experiment was done in which a wire mesh was suspended 5mm from the aluminum surface. The wood boards were then placed on the wire mesh, and a heating experiment was performed as above. The results showed a similar tendency from those obtained in the previous experiment.

2.3 Evaluate on cone calorimeter test

To evaluate the combustion characteristics of the paulownia wood quantitatively, a cone calorimeter testing with ISO5660 was done. The testing involves a constant radiant heat being irradiated onto the surface of the sample, and then the sample would ignite with a burner. During testing, the following parameters were determined: time to sustained ignition, mass loss rate, heat release rate, average heat release rate, peak of heat release rate, total heat release, specific extinction area, CO and CO_2 yields etc. The sample of 0.08 (W) m x 0.085(D) m x 0.02 (H) m was tested at a heat flux of $50 kW\cdot m^{-2}$.

By studies in the cone calorimeter, Mikkola proposed that the carbonization speed v ($m\cdot s^{-1}$) equals the mass decrease speed m'' ($kg\cdot m^{-2}\cdot s^{-1}$) divided by density ρ ($kg\cdot m^{-3}$) [18-21].

$$v = \frac{m''}{\rho} \tag{1}$$

Figure 2 shows the time-weight curves. Using this data and equation (1), the carbonization speed of paulownia wood and cedar wood is 2.93 x $10^{-5} cm\cdot s^{-1}$ and 1.96 x $10^{-5} cm\cdot s^{-1}$ respectively. This means paulownia wood is easily carbonized, about 1.5 times than cedar wood. Moreover, each of the cedar wood samples is 100.85 $kW\cdot m^{-2}$ and 99.30 $MJ\cdot m^{-2}$ against 86.98 $kW\cdot m^{-2}$ for the average heat release rate and 53.69 $MJ\cdot m^{-2}$ at the total heat release of paulownia wood.

Thus, the characteristic of paulownia material in that it easily carbonizes and hardly ignites was experimentally confirmed through heating experiments and cone calorimeter testing.

3. Microstructure of paulownia wood

Figure 3 shows the microstructure models of paulownia and cedar wood. Their SEM micrographs are shown in Figure 4. The structure elements of paulownia wood are vessel, fiber, parenchyma and ray. The vessel of paulownia wood is larger; its size being about 150 to 350μm. The bigger vessels are gathered in the area of the annual ring, and others are distributed in other areas uniformly. The structure of paulownia wood is ringed porous wood, but it has the tendency of diffuse porous wood. The fiber's shape in paulownia wood is similar to the structure of a honeycomb; its thickness is only 1μm, its diameter only 25 to 45μm. Parenchyma is developed well around the vessel. The cell wall of parenchyma is thinner than that of fiber. This is one of the reasons for the light weight quality of paulownia wood [22]. Cedar is a typical conifer. 97% is constructed with tracheids. Tracheids are distributed almost uniformly, and are 30 to 50μm in diameter, with a cell wall thickness of 3μm. The feature is that tracheids of earlywood are bigger and thinner while latewood is smaller and thicker. SEM micrographs in the radial section were shown in (c) and (f) of Figure 4. Viewing from a radial section, the vessel structure of paulownia wood is very big and independent, compared to the cedar wood, which has a thin and continuous tracheids structure.

4. Mechanism of easily carbonization

The reason paulownia wood easily carbonizes is that it has a big and independent vessel structure of thin cells regarding its microstructure and it low density regarding its physical property.

First, it can be explained by thermal diffusivity (α). It is known that the specific heat (C) of wood is shown by the equation (2), regardless of tree kind or density. The thermal diffusivity is given by the equation (3). So, the specific heat for (C) of paulownia wood and cedar wood were almost equal. Because the density (ρ) of cedar wood is 1.6 times greater than that of paulownia wood, the thermal diffusivity (α) of paulownia wood is larger. This shows why paulownia wood is easily carbonized.

$$C = 0.266 + 0.00116t \tag{2}$$

$$\alpha = \lambda / C\rho \tag{3}$$

Where t is temperature, λ is thermal conductivity.

$$\lambda_2 = \lambda_1 \left\{ 1 - (1.1 - 0.98\gamma_0) \frac{t_1 - t_2}{100} \right\} \tag{4}$$

Where λ_1 and λ_2 are the thermal conductivity on the temperature of t_1 and t_2, γ_0 is the specific gravity of oven-dried wood.

Next, evaluation of the carbonization simulation in terms of physical properties was done. A paulownia board (0.08 (W) x 0.08 (D) x 0.02 (H) m^3) was put on aluminum board surface and heated by an electric heater as shown in Figure 5. Its changes were recorded on video. The inside temperature of paulownia board at intervals of 5mm in the direction of depth were measured with a thermocouple. That is, the temperature of the heated side is T1, the temperature of the center is T3, the temperature of the top is T5, and the temperature at 5mm and 15mm from the heated side are T2 and T4. The results are shown in Figure 6, and the broken line is the temperature of 280 degrees. About 20 minutes after heating, a carbonization layer appeared which increased with heating. After about 60 minutes it increased to 6mm.

In Figure 6, we observed the inside temperature to increase to slightly over 280 degrees. This occurred because the thermal conductivity of the carbonization layer is low. The place that became 280 degrees is about 6mm from heated side. These results are similar to those of observed.

Corresponding to the heating experiment, a 2-dimensional model was made using ANSYS as the FEM system, and then carbonization analysis was done. The material properties, such as thermal conductivity, specific heat, and density were given as a function of temperature. The carbonization temperature of wood is about 280 degrees, so below 280 degrees, the thermal conductivity and the specific heat of paulownia wood were given by empirical formula (4) of Kollmann and empirical formula (2) of Dunlap. Additionally, over 280 degrees, the material properties were given by carbon, that is thermal conductivity of 0.074 $W \cdot m^{-1} \cdot K^{-1}$ and specific heat of 0.84 $kJ \cdot kg^{-1} \cdot K^{-1}$. The density was discerned by the result of DTA-TA analysis.

A 2-dimensional nonlinear transient heat conduction analysis was done under the above-mentioned analysis conditions, and the temperature of the experiment was specified. The part (black color) which had a temperature of over 280 degrees was set as the carbonized layer. The carbonization simulation is shown in (b) of Figure 7. Figure 8 shows the result, and the broken line is the temperature of 280 degrees.

The carbonized simulation of FEM analysis is in close agreement with the data obtained by the experiment. That is, a carbonized layer had appeared after 20 minutes, and the carbonized layer was increased to 6mm in thickness after 60 minutes. The temperature of T2 of FEM analysis is not consistent with the experiment because the material properties suddenly changed at 280 degrees. However, other temperatures are almost correspondent with the experiment.

Furthermore, considering the microstructure of paulownia wood, another FEM analysis was done. A model with big and independent cavities and a model with thin continuous cavities were made. Each model was then analyzed with transient heat conduction on flow fields. The results showed that the inside temperature of the model with big and independent cavities easily rose, and subsequently easily carbonized.

5. Mechanism of low flash point

5.1 Combustion condition of wood

While heating wood, the moisture will first vaporize at about 100 degrees, then from 220 to 260 degrees hemicellulose will decompose, then from 240 to 350 degrees cellulose will decompose, and finally lignin will decompose at 280 to 500 degrees [14]. The combustible gas like CO, H_2, and CH_4 is generated in the pyrolysis of wood. When these gases mix with air and then become concentrated, combustion occurs.

The combustion condition of wood is dependent on the following two variables: (1) The concentration of combustible gas that is mixed by the pyrolysis products and air to ignite must be reached. (2) The energy for combustible gas to ignite must be supplied [11]. In the above experiments, the energy for combustion was the same because of the same heating conditions. So, we surmise that the combustion condition (1) is responsible for the difference in the combustion of the two materials.

5.2 Factors that influences combustion

Chemical composition analysis and elementary composition analysis are shown in Table 2. The elementary composition of wood is mainly carbon (C), hydrogen (H) and oxygen (O), with carbon accounting for over 40% of the composition. The result shows the lignin in paulownia wood is 5% lower than in cedar wood. Lignin is a hydrophobic aromatic compound that is most commonly derived from wood and is an integral part of the cell walls of plants [4]. Lignin makes up about one-quarter to one-third of the dry mass of wood. It has been reported that the more lignin wood contains, the more calories and gas can be generated from the wood [23]. Thus, the amount of lignin is related to the retardancy of paulownia wood. It is also clarified by cone calorimeter testing that the average heat release rate and the total heat release of paulownia wood are both lower than that of cedar wood. Gas chromatography analysis in heating the wood is shown in Figure 9. The result shows that a lot of furan, butanamine and acetic acid were generated in the paulownia wood, though in the cedar wood, there was a lot of alkane. Alkane is often called methane hydrocarbon. There are two kinds of alkane generated from cedar wood, petane (C_5H_{12}) and hexane (C_6H_{14}). Petane is included in petroleum, and hexane is a common constituent of gasoline. Furan (C_4H_4O) is an aromatic heterocyclic organic compound, produced when wood is distilled. That is, it is clear that the combustible gas generated from cedar wood is more than that of paulownia wood.

Moreover, the difference in the microstructure of the two materials is an important factor. That is, the vessel structure of paulownia wood is very big and independent, compared to cedar wood, which has a thin and continuous tracheids structure. In order to gain insight into the influence of structure on combustion, the following experimental model was devised.

5.3 Heating experiment of model

Two kinds of models as in Figure 10 were made of corrugated paper. One model (150 (W) x 200 (D) x 84 (H) mm) was lain with sixteen sheets of corrugated paper one on top of another, and then stocked with paste and called the model of cedar. The other model was cut into four parts evenly in depth based on the model of the cedar, and then each part was pasted by corrugated paper and called the model of paulownia. Thus, the cavities of the cedar model are continuous, but in the paulownia model they are independent. These two models were heated by a heater from room temperature, and the temperatures of the heating and the surface of the model were also measured. The heater and the model were put into a chamber, and the smoke generated upon heating was gathered with a pipe.

In the experiment, the model of cedar burned at 62 minutes after heating. Conversely, the experimental model of paulownia would end at the same time, and did not burn to the same extent. The states at 50 and

60 minutes by heating are shown in Figure 11. The results show that although there is no difference between the temperatures on the surface of the two models, the cedar model burns more easily than the paulownia. The corrugated paper that had not carbonized of the paulownia and cedar models are 10 and 7 layers after 50 minutes, and those which remained were 7 and 4 layers after 60 minutes, respectively. That is, the state of the paulownia model after 60 minutes by heating was similar to the cedar model after 50 minutes. Therefore, the model of the independent cavity structure is more difficult to burn than that of the continuous cavity structure. It proved that the oxygen is not sufficiently supplied in a structure such as that found in paulownia wood, and the concentration of combustible gas necessary for ignition is hardly being reached.

Conclusion

The characteristic of paulownia material that it easily carbonizes and hardly ignites was experimentally confirmed through heating experiments and cone calorimeter testing. Moreover, the mechanism of flame retardancy of paulownia wood is elucidated by the analysis of its material structure, composition, model combustion experiments and FEM analysis. It was determined that the cell tissue of paulownia wood is very porous, similar to the structure of a honeycomb. It becomes easily carbonized when heated. Because paulownia wood contains few lignins, it generates very little combustible gas when heated. Furthermore, Oxygen is not sufficiently supplied in the large and independent vessel structure of paulownia wood, compared to cedar wood, which has a thin and continuous tracheids structure. Thus, it is difficult to ignite, and only carbonizes when heated. Generally speaking, the thermal conductivity of the carbonized layer is lower than that of the wood material, which is the reason why a wardrobe made of paulownia wood can protect the kimono from fire. It appears that the result may be more suitable for future work in developing flame resistant material or noncombustible material.

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Reference

1. J. ODA, Journal of the Japan Society of Mechanical Engineers, 99(1996) 177.
2. J. ODA et al., JSME international journal. Series A, 49(2006) 390.
3. M. KITAGAWA and P. LI, Journal of Materials Science, 39(2004) 6855.
4. J. ODA et al., Transactions of the Japan Society of Mechanical Engineers, Series A, 64(1998) 2217.
5. J. ODA et al., Transactions of the Japan Society of Mechanical Engineers, Series A, 63(1997) 431.
6. J. ODA, Transactions of the Japan Society of Mechanical Engineers, Series A, 46(1980) 997.
7. J. STEJSKAL, Journal of Applied Polymer Science, 103(2007) 24.
8. CE BYRNE and DC NAGLE, Carbon, 35(1997) 259.
9. A. KURIYAMA, Bulletin of the Forestry and Forest Products Research Institute, 304(1979) 7.
10. A. ELFASAKHANY, XS BAI, in Proceedings of Progress in Computational Fluid Dynamics 6 (2006) p.188.
11. T. HARADA, Bulletin of the Forestry and Forest Products Research Institute, 378(2000) 1.
12. KW RAGLAND, Bioresource Technology, 37(1991) 161.
13. S. ISHIHARA, Journal of the Japan Wood Research Society, 35(1989) 775.
14. M. HUSHITANI et al., Physics of Wood (in Japanese), (Buneido 1985) p.198.
15. M. SUZUKI, Wood Industry, 35(1980) 162.
16. S. SHIDA and M. OKUMA, Journal of the Japan Wood Research Society, 26(1980) 112.
17. S. MOCHIZUKI and A. MURATA, Fundamentals of Heat Transfer (in Japanese), (Nissin 1994) p.123.
18. V. BABRAUSKAS and WJ PARKER, Fire and Materials, 11(1987) 31.
19. V. BABRAUSKAS, Fire and Materials, 8(1984) 81.
20. S. ISHIHARA, Journal of the Japan Wood Research Society, 35(1989) 775.
21. E. MIKKOLA, in proceedings of the Third International Symposium on Fire Safety Science, (1991) p.547.
22. S. HIRAI, Encyclopedia of trees (in Japanese), (KANAE Syobou 1980) p.1.
23. T. OKAMURA, Master’s Thesis, Graduate School of Engineering, Kochi, (2005) p.22.

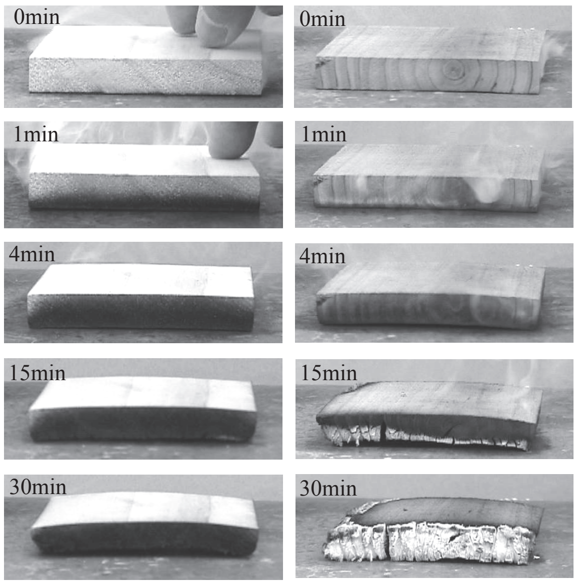
Table 1 Materials used in the experiment.

	Measure of radial section	Thickness	Annual ring width	Density
Paulownia	0.5m x 0.5m	0.012m, 0.024m	0.019m	270 $Kg \cdot m^{-3}$
Cedar	0.09m x 0.8m	0.012m	0.005m	430 $Kg \cdot m^{-3}$

Table 2 Results of composition analysis.

	Cellulose	Hemicellulose	Lignin
Paulownia	45%	25%	29%
Cedar	49%	16%	34%
	C	H	O
Paulownia	43.76%	5.81%	50.43%
Cedar	47.98%	6.03%	45.99%

Fig.1 Appearance of heating wood board.



(a) Paulownia (b) Cedar

Fig.2 Time-weight curves at 50kW·m^{-2}of heat flux.

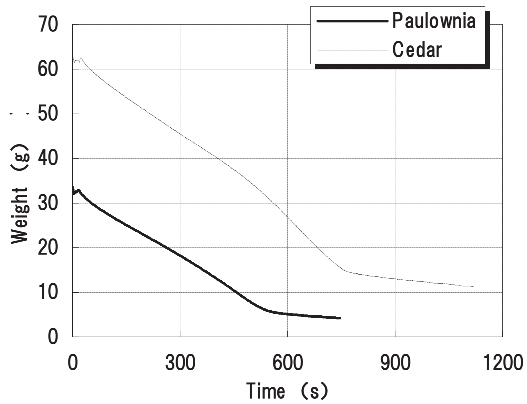
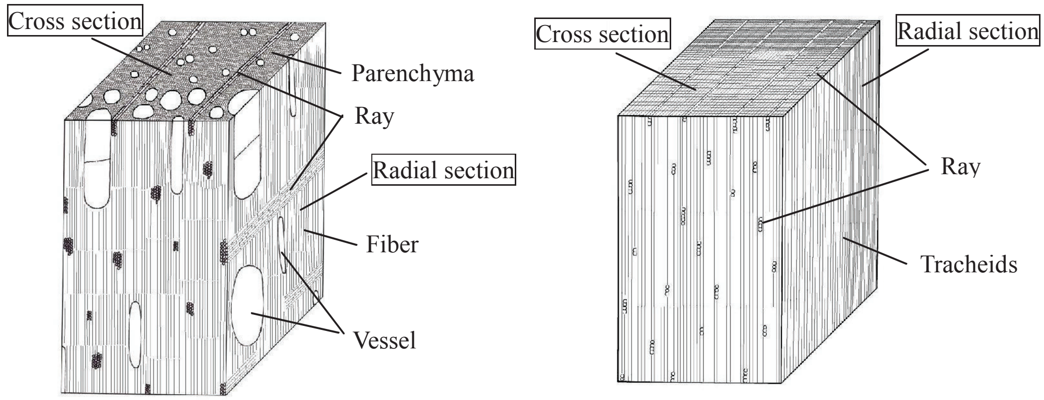
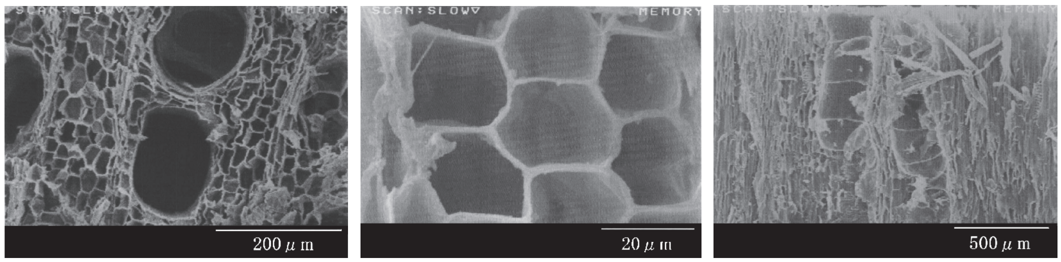


Fig.3 Model of micrographs of the wood.

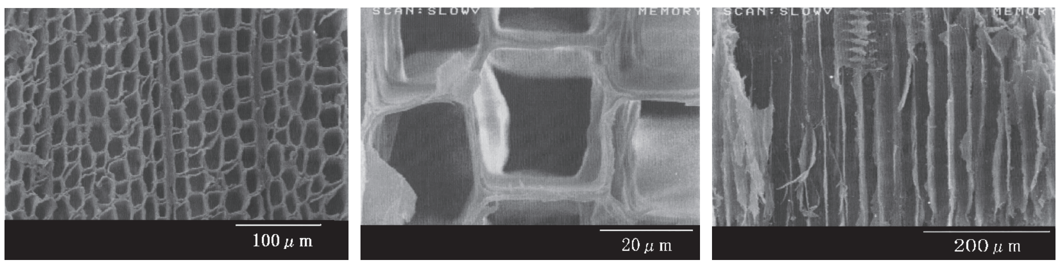


(a) Paulownia (b) Cedar

Fig.4 SEM micrographs of the wood.



(a) Cross section of Paulownia (b) Cross section of Paulownia (c) Radial section of Paulownia



(d) Cross section of Cedar (e) Cross section of Cedar (f) Radial section of Cedar

Fig.5 Appearance of heating experiment.

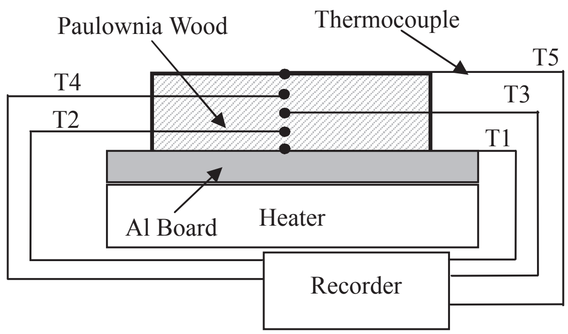


Fig.6 Temperature of heating experiment.

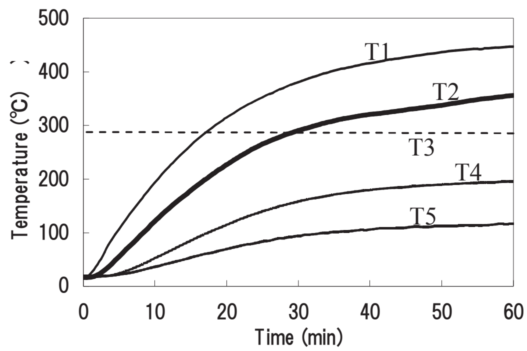
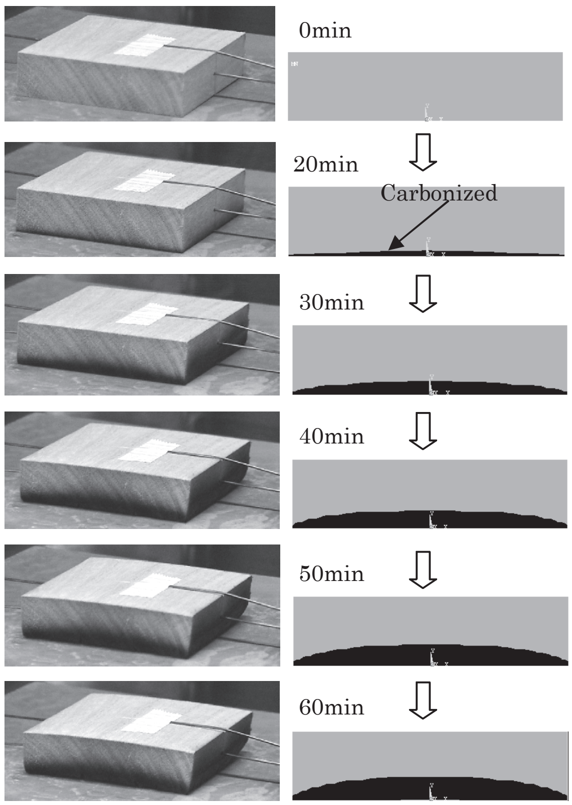


Fig.7 Result of the heating experiment and FEM analysis of paulownia wood.



(a) Experiment (b) Analysis

Fig.8 Temperature of paulownia wood by FEM analysis.

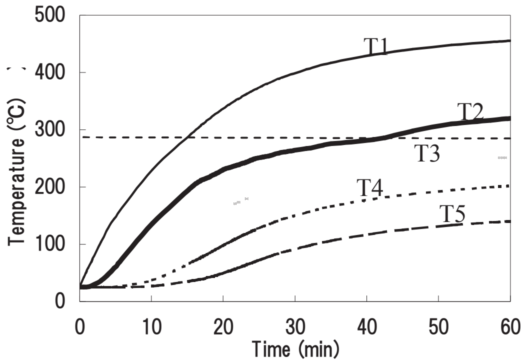
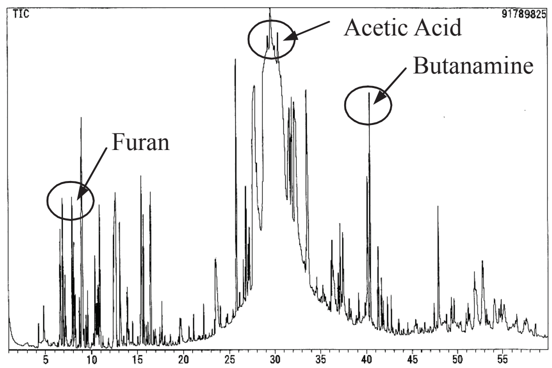
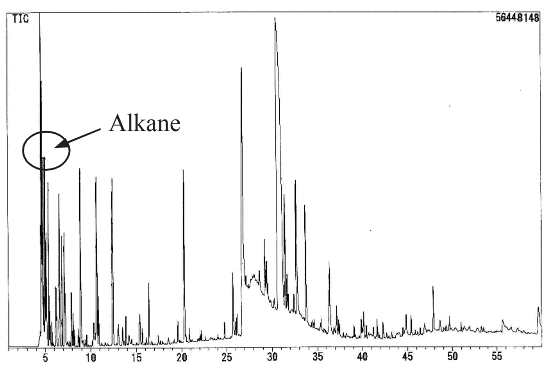


Fig.9 Gas chromatography analysis upon heating the wood.

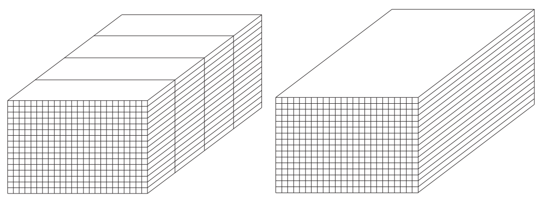


(a) Paulownia



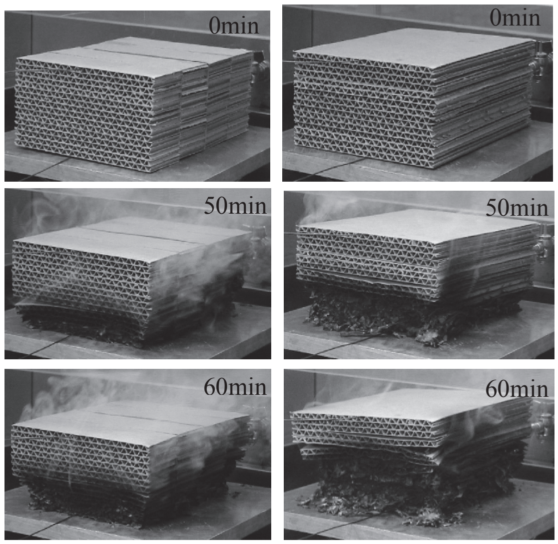
(b) Cedar

Fig.10 The model of wood made of corrugated paper.



(a) Model of Paulownia (b) Model of Cedar

Fig.11 The result of heating the model.



(a) Model of Paulownia (b) Model of Cedar