

論文 (Original Article)

Formation of Stable Charcoal Layer Coating the Wooden Material Surface by the Application of Tannin-Charcoal Suspensions

OHARA Seiji^{1)*}, FUJII Tomoyuki²⁾ and AKITSUKI Katsufumi³⁾

Abstract

The object of this study is to develop an easy method by which wood charcoals can be fixed on the surface of wooden materials. Thus, tannin-charcoal suspensions were prepared by mixing powder of wood charcoals with several kinds of tannin aqueous solutions and submitted to the coating experiments on sugi (*Cryptomeria japonica* D. Don) plywood. We concluded the following. When the plywood was coated with tannin-charcoal suspension prepared using 70% acetone aqueous extractives from either the husk of cacao beans or the bark of sugi, the charcoal powder could not be fixed on the surface of plywood after air-drying. On the other hand, the fixation of charcoal was observed on uses of 70% acetone aqueous extractives from the *Acacia mangium* bark and also of commercial Quebracho. Furthermore, the elimination of charcoal on dropping of water was not observed when purified condensed tannins from the bark of *A. mangium* were used. It was also found that the ratio of tannin to charcoal more than 1/5 (w/w) was needed to form a stable charcoal layer on the plywood which is not eliminated even on dropping of water. SEM observations of the charcoal-tannin layer indicated that charcoal powder elements were fixed tightly by tannin network. Above findings will contribute to the production of wooden materials bearing the various useful functions of both wood charcoal and tannins.

Key words : fixation of charcoal powder, tannin-charcoal suspension, condensed tannins, polyphenolics, sugars, liposoluble components, SEM

Introduction

Wood charcoal has a long history as a material for fuels. Recently, it has been utilized also for materials for filtration and adsorption in the chemical industry (Ishihara, 1996). Sugi (*Cryptomeria japonica* D. Don, Taxodiaceae) wood carbonized at 1000°C can effectively remove mercury from aqueous solutions (Pulido et al., 2001). A charcoal that was produced by carbonizing sugi sapwood at 600°C and following steam-activating at 850 °C for 50 min can also remove chloroform from drinking water (Abe et al., 2001). Recently, there have been many useful functions of wood charcoals demonstrated, some of which are the abilities to regulate the humidity of a room, to adsorb formaldehyde, to deodorize ammonia, and to shield electromagnetic waves (Abe et al., 1998, Saito et al., 2000, Honma et al., 2000, Ide et al., 1992). Therefore, the utilization of wood charcoals as materials for the improvement in housing environment will be considerably extended if they are easily fixed on various wooden materials. However, the utilization of them for this purpose is actually restricted because it is difficult to form a charcoal layer on the surface of wooden materials.

In this study, tannin-charcoal suspensions were

prepared by mixing wood charcoals with several kinds of tannin aqueous solutions and applied to coating with a brush on the surface of sugi plywood. After air-drying, the fixation of wood charcoals on the plywood was examined. As wood charcoal has a black color, a plywood will be occasionally needed to be overlaid when it is applied for interior wooden materials. On such occasions, certain water-soluble adhesives are used conveniently. Therefore, it is also an important factor that the charcoal powders are not eliminated on dropping of water. Thus, it was also examined whether wood charcoal layers formed were eliminated or not on dropping of water to the plywood. Furthermore, microscopic study was done in order to investigate the morphology of wood charcoals fixed in the tannin-charcoal layer.

Materials and Methods

Plant materials

The husk of cacao (*Theobroma cacao* L., Sterculiaceae) bean was provided by Lotte Co. Ltd, Japan. Bark of sugi was collected from fresh trees grown in Ogawa, Ibaraki Prefecture, in March 2001. Bark of *Acacia mangium* Willd (Leguminosae) was collected in

原稿受付：平成 15 年 7 月 30 日 Received July 30, 2003 原稿受理：平成 15 年 11 月 26 日 Accepted Nov. 26, 2003

* Department of Forest Chemistry, Forestry and Forest Products Research Institute (FFPRI), 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan; e-mail: oharas@ffpri.affrc.go.jp

1) Department of Forest Chemistry, Forestry and Forest Products Research Institute (FFPRI)

2) Research Planning and Coordination Division, Forestry and Forest Products Research Institute (FFPRI)

3) Biocarbon Research Institute Inc.

Penang, Malaysia in 1999. These samples were air-dried and ground with a Willey mill to pass an 80-mesh sieve.

Preparation of extractives

The milled samples obtained from *T. cacao*, *C. japonica*, and *A. mangium* were extracted with 70% acetone aqueous solution at room temperature for two days, and the extractives were recovered by filtration. Acetone was removed on a rotary evaporator, and the aqueous solutions were freeze-dried to give the corresponding 70% acetone aqueous extractives (T-AWE, C-AWE and A-AWE, respectively). Quebracho, which is a tannin powder obtained by spray-drying of a hot water extract from the wood of *Schinopsis* species grown in South America, was purchased from Fuji Chemical Industries Co., Ltd., Japan.

Total polyphenolics in extractives

Determination of total polyphenols in extractives was carried out based on the Folin-Ciocalteu method with a slight modification (Julkunen, 1985). Test solutions were prepared by dissolving 10 mg of T-AWE, C-AWE, A-AWE and Quebracho in 100 ml of methanol, respectively. A 0.5-1 ml aliquot of each test solution was taken to a flask and methanol concentrated to dryness. The residue was dissolved in 2 ml of water and transferred to a 10-ml measuring flask. One milliliter of Folin-Ciocalteu phenol reagent (Kanto Kagaku Corporation, Tokyo, Japan) was added, and the flask vigorously shaken. Immediately, 5 ml of 20% sodium carbonate solution was pipetted, the mixture made up to 10 ml with water, and then shaken thoroughly again. After 20 min the absorptivity of the mixture was measured at 735 nm. The working curve was determined using catechin as a standard sample.

Total sugars in extractives

Total sugars in extractives were measured according to the phenol-sulfuric acid method (Dubois et al., 1956) with a slight modification. Test solutions were prepared by the same procedure as for polyphenolics. A 1-2 ml aliquot of each test solution was taken to a flask and methanol concentrated to dryness. The residue was dissolved in 10 ml of water, transferred to a centrifuge tube, and then 10 ml of 1% lead acetate solution was added. After 20 min, centrifugation was made at 18,000 rpm for 20 min. To 2 ml of the supernatant, 0.05 ml of 80% phenol aqueous solution and 5 ml of concentrated sulfuric acid were added. After 35 min, centrifugation was made at 3,500 rpm for 5 min, and the absorptivity of the supernatant was read at 490 nm. The working curve was determined using glucose as a standard sample.

Determination of liposoluble components in xtractives

Five grams of T-AWE, C-AWE, A-AWE and Quebracho were extracted repeatedly with *n*-hexane using a Soxhlet apparatus for 8 hr, respectively. The content of liposoluble components was determined as the difference in dry weights of the samples before and after the extraction.

Preparation of purified condensed tannins

Six grams of A-AWE were dissolved in 600 ml of water and extracted 4-5 times with ethyl acetate. The water-soluble portion was freeze-dried, then dissolved in 50% methanol aqueous solution, and applied to a Sephadex LH-20 column. The column was eluted with 50% methanol until the eluate was clear, and then eluted with 50% acetone aqueous solution to recover approximately 35-40% of the A-AWE as an purified condensed tannin (Ohara et al., 1995).

Wood charcoal

Wood charcoal was produced at Intan Prime Company (Djakarta, Indonesia) by carbonizing the sawdust of rubber-wood (*Hevea brasiliensis*, Euphorbiaceae) at 400 °C using a batch-type charcoal furnace (downdraft). A steam-based activation method was used to form multiple micropores in the charcoal (Abe et al., 2001) as follows. The charcoal was inserted in a rotary kiln that was heated to 1000 °C. Keeping the temperature at 1000 °C, steam and air were introduced into the kiln for 20 min, then the kiln was cooled. The wood charcoal obtained was ground to powder and passed through a 200-mesh sieve. Specific surface area was determined from nitrogen adsorption isotherms using the Nihon Bell Belsorp 28-5A (Osaka, Japan), and was calculated from BET plots in the relative pressure range of 0.01-0.15 (Abe, 1992).

Preparation of tannin-charcoal suspension

Tannin aqueous solutions were prepared in the following manner. Four extractives (T-AWE, C-AWE, A-AWE and Quebracho) were independently dissolved in 50 ml of water so as the final polyphenol concentrations to be 5.0% (W/V). As for the purified condensed tannin from A-AWE, 1.0, 1.5, 2.0, 2.5 and 3.0 g of the sample was dissolved in 50 ml of water to prepare the 2.0, 3.0, 4.0, 5.0 and 6.0% (W/V) aqueous solutions. The control was 50 ml of water instead of the sample solutions. Wood charcoal powder (10 g) was mixed with 50 ml of each tannin aqueous solution in a 100-ml flask, and the flask vigorously shaken. The obtained tannin-charcoal suspension was submitted to the following coating experiments.

Coating of tannin-charcoal suspension on plywood

A sugi plywood was coated with the tannin-charcoal suspension using a brush. After sufficient air-drying, the tannin-charcoal layers on the plywood were examined on their stability against rubbing by a finger. It was also examined whether the wood charcoal was eliminated again when water was added dropwise on the charcoal layer.

Scanning electron microscopy

Some of charcoal powder was transferred on the surface of carbon adhesive tape attached to a brass stub, a sample holder for scanning electron microscopy (SEM), coated with Pt-Pd (80:20) in an ion-sputter coater for 3 min at the condition of 1.5 KeV and 15 mA, then observed with a scanning electron microscope (Jeol JSM-840, Tokyo, Japan).

A piece of the charcoal-tannin layer prepared with purified tannin was peeled off carefully of the plywood, fractured by bending, and fixed on one end of a copper tape set on a SEM stub. It was also coated with Pt-Pd in the same condition as for charcoal powder and observed in a SEM. The orientation of the sample was arranged by bending the copper tape so as to obtain suitable positions for the observations either of the surfaces or the cross section within a SEM.

Results and Discussion

Chemical compositions of extractives

Results of quantitative analyses of polyphenolics, sugars and liposoluble components in extractives are shown in Table 1. T-AWE and C-AWE contained a relatively large amount of liposoluble components (22.2 and 39.9%, respectively), while A-AWE and Quebracho contained a very small amount (0.87 and 0.58%, respectively). It is well known that cacao husk contains about 10% lipids (Chung, 2002). Also, it is reported that the bark of *C. japonica* contains various diterpenes such as phyllocradanol, ferruginol and 6,7-dehydroferruginol (Ashitani et al., 2001). Therefore, it is reasonable that T-AWE and C-AWE contain a large amount of liposoluble components, which were determined as *n*-hexane extracts in this study. A-AWE and Quebracho contained 32.3 and 47.8% polyphenolics, respectively, whereas T-AWE and C-AWE did much less (7.2 and 10.3%, respectively). As to the total sugar contents, there were not so large differences as were in the liposoluble components and in the total polyphenolics among four extractives. However, A-AWE and Quebracho contained about 5-8 times more polyphenolics than sugars, while T-AWE and C-AWE contained both approximately equally.

Table 1. Analytical data of T-AWE^{a)}, C-AWE^{a)}, A-AWE^{a)} and Quebracho^{b)}

Extractives	Total polyphenolics (%) ^{c)}	Total sugars (%) ^{c)}	Liposoluble components (%) ^{c)}
T-AWE	7.2	13.2	22.2
C-AWE	10.3	6.0	39.9
A-AWE	32.3	4.3	0.87
Quebracho	47.8	10.2	0.58

^{a)}T-AWE, C-AWE and A-AWE are 70% acetone aqueous extractives from *T. cacao*, *C. japonica* and *A. mangium*, respectively.

^{b)}Commercial product. ^{c)}% of the oven-dried extractives.

Fixation of charcoal on plywood

Specific surface area of the wood charcoal used in this study was 973 m²/g. Results of the coating experiments using tannin-charcoal suspensions prepared by mixing with several tannin aqueous solutions are shown in Table 2. Different results were obtained depending on the tannin materials used in the preparation of suspensions. In the control without tannins, the charcoal powder was easily removed when the surface of charcoal layer on a plywood was rubbed by a finger. The tannin-charcoal layers using T-AWE and C-AWE were also not fixed on the plywood surfaces, either. Because both T-AWE and C-AWE contained a large amount of liposoluble components, no homogeneous suspensions were prepared, which is assumed to be the reason why the fixation on the plywood was not sufficient. Sugi plywood which was coated with the tannin-charcoal suspension using A-AWE and then air-dried, is shown in Fig.1. In this case the charcoal was fixed on the plywood surface forming a stable tannin-charcoal layer. The similar result was also obtained when the tannin-charcoal suspension using Quebracho was applied. The high fixation ability of tannin-charcoal layer using A-AWE and Quebracho can be explained by the fact that both A-AWE and Quebracho contain only a slight amount of liposoluble components contrary to T-AWE and C-AWE. Even in those cases, however, a part of charcoal powders was eliminated when water was added dropwise on the charcoal layer. On the other hand, when the tannin-charcoal suspension using a 5.0% aqueous solution of the purified condensed tannin from A-AWE was applied, the elimination of charcoal on dropping of water was not observed at all. In the process of purification of A-AWE employed in this study, sugar components are mainly removed (Ohara et al., 1995, Makino et al., 2002). Therefore, the presence of sugar components in the tannin materials is assumed to cause the elimination of charcoal powders on dropping of water.

The coating experiments were made on the purified tannin solutions ranging in concentrations from 2.0 to 6.0 % (W/V). Stable tannin-charcoal layers were formed on the surfaces of plywood only when 4.0-6.0 % (W/V)

tannin solutions were used, while they were not when the 2.0-3.0 % (W/V) solutions were used. Therefore, it is concluded that the ratio of tannin to charcoal more than 1/5 (W/W), as 10 g of charcoal is suspended in 50 ml of tannin solution, is needed to form a stable tannin-charcoal layer on plywoods.

Above findings will contribute to the production of new wooden materials bearing the various useful functions of wood charcoal. In addition, the wooden materials will be endowed with some functions of condensed tannins such as formaldehyde adsorption ability and antitermite activity (Ohara et al., 2003, Ohmura et al., 2001). However, the purification of tannin is necessary to form the stable charcoal layer that is not eliminated even on dropping of water. Therefore, the development of an efficient method for a large scale purification of condensed tannins is required for the application of tannin-charcoal suspensions to the improvement in housing environment.

Table 2. Fixation of wood charcoal on sugi plywood in the coating experiments using tannin-charcoal suspensions prepared by mixing with several tannin aqueous solutions.

Tannin samples	Fixation of charcoal on plywood	Elimination of charcoal on dropping of water
Control ^{a)}	Not fixed	n.t. ^{e)}
T-AWE ^{b)}	Not fixed	n.t. ^{e)}
C-AWE ^{b)}	Not fixed	n.t. ^{e)}
A-AWE ^{b)}	Fixed	Eliminated
Quebracho ^{c)}	Fixed	Eliminated
Purified tannins ^{d)}	Fixed	Not eliminated

^{a)}50 ml of water was used instead of tannin aqueous solution.

^{b), c)} See footnotes in Table 1.

^{d)}Condensed tannins purified from A-AWE. ^{e)}not tested.

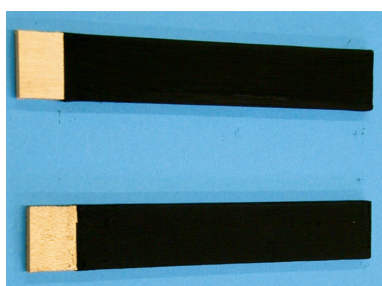


Fig. 1. Sugi plywoods that were coated with the A-AWE-charcoal suspension and air-dried.

A-AWE: see footnote in Table 1.

SEM observations of charcoal layer

Charcoal powder was composed of small elements mostly shorter than 100 μm in length and narrower than 10 μm in width (Fig.2a). Each of those powder elements was predominantly a part of a fiber wall and infrequently a part of the aggregate of fibers or ray parenchyma cells

remaining the original shape and occasionally illustrating a pit structure, and the fractured surfaces were more or less flat with sharp edges (Fig.2b).

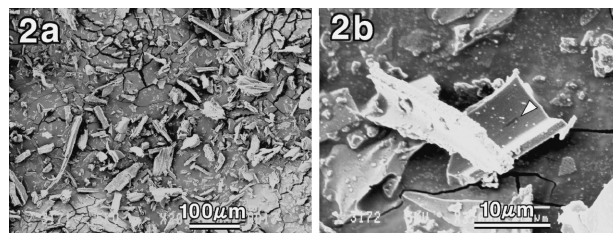


Fig. 2. SEM micrographs of the charcoal powder fixed on a carbon adhesive tape.

2a: Elements were small in size showing some variation.

2b: Most elements were fractured parts of fiber walls showing flat surfaces and sharp edges. Occasionally, cell wall sculptures such as pits (arrow head) were observed.

The tannin-charcoal layer using the purified tannin showed porous structure (Fig.3a). The surface facing to the plywood showed linear components composing a network structure (Fig.3b). Those linear components are assumed to be derived from tannin material, because such substance was not observed in the charcoal powder, which was one of two materials used for the tannin-charcoal layer. On the fractured surface, charcoal powder elements were observed in the conjugates with linear elements, and the powder elements were covered with a thin layer comprising network of linear elements which made the original shape such as sharp edges obtuse (Fig. 3c and 3d). These observations lead to the conclusion that charcoal powder elements are fixed tightly by tannin network.

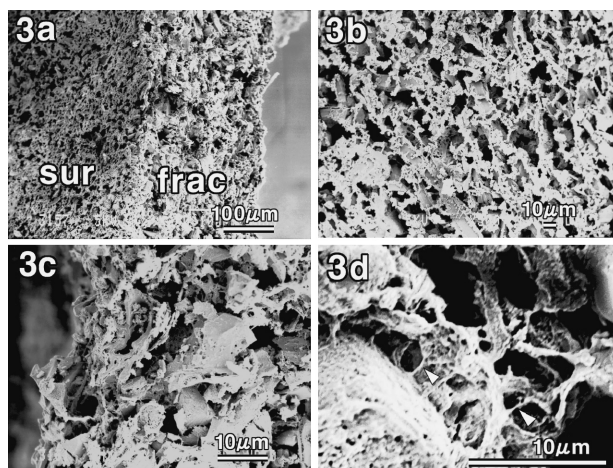


Fig. 3 SEM micrographs of a fragment of the tannin-charcoal layer.

3a: At a low magnification, the surface facing to the plywood (sur) and the cross-sectional fractured surface (frac) were shown

3b: In the surface facing to the plywood, linear structure composing a network roughly in the same plane was observed.

3c: Enlargement of a part of Fig.3a.

3d: A linear network (arrow heads) was connecting and covering elements of wood charcoal powder as a thin layer.

Conclusion

Tannin-charcoal suspensions prepared by mixing wood charcoal powder with four extractives (T-AWE, C-AWE, A-AWE and Quebracho) and condensed tannins purified from A-AWE were submitted to the coating experiments on sugi plywood. The charcoal powder was not fixed on the surface of plywood, when the tannin-charcoal suspensions using T-AWE and C-AWE were applied, probably due to the high content of liposoluble components. The charcoal powder was well fixed on uses of A-AWE and Quebracho, which contained much less liposoluble components, but it was not stable against water. The water resistance was achieved by the use of condensed tannins purified through the removal of sugars from A-AWE. In the tannin-charcoal layer formed on the surface of plywood, charcoal powder elements were fixed tightly by tannin network.

Acknowledgements

This work was supported in part by the Integrated Research Program for Effective Use of Biological Activities to Create New Demand (Bio Renaissance Program) from the Ministry of Agriculture, Forestry and Fisheries of Japan. We thank Ms. Saori Kudo and Ms. Junko Miyazaki for their assistance in extracting and purifying condensed tannins.

References

- Abe, I. (1992) Reliability of bet surface area of activated carbon, *Chemistry Express*, **7**(1), 97-100.
- Abe, I., Iwasaki, S., Iwata, Y., Kominami, H. and Kera, Y. (1998) Relationship between production method and adsorption property of charcoal, *TANSO*, **1998** (185), 277-284.
- Abe, I., Fukuhara, T., Maruyama, J., Tatsumoto, H. and Iwasaki, S. (2001) Preparation of carbonaceous adsorbents for removal of chloroform from drinking water, *Carbon*, **39**, 1069-1073.
- Ashitani, T., Ujike, M., Nagahama, S., Ueno, T. and Sakai, K. (2001) Characterization of Sugi (*Cryptomeria japonica*) bark extracts, *Mokuzai Gakkaishi*, **47** (3), 276-281.
- Chung, B.Y. (2002) Development pattern of secondary cell walls and their chemical characteristics of cacao (*Theobroma cacao* L.), doctoral thesis (Tokyo University).
- Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F. (1956) Colorimetric method for determination of sugars and related substances, *Anal. Chem.*, **28** (3), 350-356.
- Honma, S., Sano, Y., Kubota, M., Umehara, K. and Komazawa, K. (2000) Chemical structure and ammonia adsorption ability of Todomatsu (*Abies sachalinensis*) wood carbonized in nitrogen and air atmospheres, *Mokuzai Gakkaishi*, **46** (4), 348-354.
- Ide, I., Ishihara, S., Kawai, S., Yoshida, Y., Nakaji, M. and Takamatsu, A. (1992) Fire-resistant carbon-board materials II, Fire endurance, electromagnetic shielding, and sound insulation performances of particleboards overlaid with graphite-phenolic spheres, *Mokuzai Gakkaishi*, **38** (8), 777-785.
- Ishihara, S. (1996) Recent trend of advanced carbon materials from wood charcoals, *Mokuzai Gakkaishi*, **42** (8), 717-723.
- Julkunen-Tiitto, R. (1985) Phenolic constituents in the leaves of northern willows: Methods for the analysis of certain phenolics, *J. Agric. Food Chem.*, **33**, 213-217.
- Makino, R. and Ohara, S. (2001) Efficient extraction method of bark tannins, Abstracts of the 51st annual meeting of the Japan Wood Research Society, Tokyo, p.379.
- Ohara, S. and Yanagi, K. (1995) Polyphenols in *Salix* species I. Polyphenols from the bark of *Salix rorida* Lackschewitz, *Mokuzai Gakkaishi*, **41** (4), 406-413.
- Ohara, S. and Yoshikawa, M. (2002) Formaldehyde adsorption ability of tannin-charcoal retaining kraft pulp sheets. Abstracts of the 52nd annual meeting of the Japan Wood Research Society, Gifu, p.363.
- Ohmura, W. and Ohara, S. (2000) Improvement of antitermitic activities of catechin by combination with heavy metals, *Holzforschung*, **54** (5), 457-460.
- Pulido-Novicio, L., Kurimoto, Y., Aoyama, M., Seki, K., Doi, S., Hata, T., Ishihara S. and Imamura, Y. (2001) Adsorption of mercury by sugi wood carbonized at 1000°C, *J. Wood Sci.*, **47**, 159-162.
- Saito, Y., Mori, M., Shida, S. and Arima, T. (2000) Formaldehyde adsorption and desorption properties of wood-based charcoal, *Mokuzai Gakkaishi*, **46** (6), 596-601.

合板表面へ塗布したタンニン・木炭微粉懸濁液による木炭層の形成と耐水性

大原 誠資^{1)*}・藤井 智之²⁾・秋月 克文³⁾

要 旨

木炭微粉を木質材料表面上に固定化する簡易な方法を開発することを本研究の目的とする。木炭と種々のタンニン水溶液を混合して激しく攪拌後、スギ合板へ塗布し、風乾後の木炭の合板表面上への固定化状況を観察することにより、以下の結果を得た。カカオハスク及びスギ樹皮抽出物水溶液を木炭と混合した場合には、木炭微粉は合板上へ固定化されなかった。一方、アカシアマンギウム樹皮抽出物及び市販のケブラチョ水溶液を用いた場合には、木炭微粉の合板表面への固定化が認められた。さらに、精製アカシアマンギウムタンニンをを用いた場合には、木炭が合板表面に固定化されただけでなく、形成された木炭層に水を滴下した時にも木炭の脱離が起こらなかった。水滴下時にも脱離しない安定な木炭層を形成するには、精製タンニンの木炭に対する比率（重量比）を 1/5 以上にする必要があった。合板表面上に固定化された木炭微粉は、タンニンの網状構造中にしっかりと組み込まれて木炭層を形成していた。これらの結果は、木炭とタンニン双方の機能を有する機能性木質材料の製造の可能性を示唆するものである。

キーワード：木炭微粉の固定化、タンニン・木炭微粉懸濁液、縮合型タンニン、ポリフェノール類、糖類、脂溶性成分、走査電子顕微鏡

* 森林総合研究所樹木化学研究領域 〒305-8687 茨城県つくば市松の里1 e-mail: oharas@ffpri.affrc.go.jp

1) 森林総合研究所樹木化学研究領域

2) 森林総合研究所企画調整部

3) (株)バイオカーボン研究所