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Polycyclic Aromatic Hydrocarbon Generation Behavior in the Process of Carbonization of Wood

**D. Nakajima · S. Nagame · H. Kuramochi ·
K. Sugita · S. Kageyama · T. Shiozaki · T. Takemura ·
F. Shiraishi · S. Goto**

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Abstract PAH generation behaviors in carbonization were compared, using cypress, chestnut, and bamboo as samples. Generation of tarry matter was almost completed by the time the temperature reached 400°C, while generation of PAHs continued until the temperature reached 1,000°C. The weight of tarry matter per unit sample weight was large with bamboo, while the amount of PAHs was large with cypress. Of the 15 types of PAHs measured this time, the largest amount collected was fluorene, followed by phenanthrene and anthracene. The amount of PAHs generated accounted for 6×10^{-6} to 16×10^{-6} of the weight of the wood samples.

Keywords PAH · charcoal · fluorene · tarry matter

Efforts to fully reuse and recycle various waste materials, regarding them as resources, are essential in the coming recycling society. Those resources include wood waste such as construction waste and lumber from thinning. Wood waste materials are currently recycled in Japan as construction materials, raw materials for particle boards and paper, mulching materials for suppressing weed and providing nutrients, compost, fuel, materials for charcoal, and animal feed. Of those, charcoal is used for various applications, including as a sorbent, moisture or soil conditioner, and snow-melting agent. In addition, pyroligneous acid generated in the process of carbonization can be used for horticulture. Thanks to these advantages, the use of charcoal is increasing. On the other hand, gaseous components generated during the process of carbonization have been reported to have mutagenicity (Nakajima et al. 2004), causing concern about air pollution and other ill effects. In addition, it is generally known that incomplete combustion of organic substances generates polycyclic aromatic hydrocarbons (PAHs), so PAHs may also be generated in the carbonization process. Although there have been some reports on the generation of PAHs in thermal decomposition and gasification (Scheidl et al. 1991; McGrath et al. 2001, 2003; Morf et al. 2002; Pimenta et al. 1998), there has been little research on the amount of PAHs generated in the carbonization process (R-Poppi and Santiago-Silva 2002). The pyrolysis technique, which heats organic substances under anoxic conditions to decompose them into inorganic gases or low-molecular hydrocarbons, is used for energy utilization in most of the cases. On the other hand, a major purpose of carbonization is to obtain charcoal, which can be used for various purposes as stated above, and conditions for carbonization vary. Although thermal decomposition occurs around 600°C, approximately 850°C at the highest (R-Poppi and Santiago-Silva 2002), the

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D. Nakajima (✉) · H. Kuramochi · S. Kageyama ·
F. Shiraishi
National Institute for Environmental Studies, 16-2 Onogawa,
Tsukuba, Ibaraki 305-8506, Japan
e-mail: dnakaji@nies.go.jp

S. Nagame · T. Takemura
Tokyo University of Science, 1-3 Kagurazaka, 162-8601 Tokyo,
Shinjuku, Japan

K. Sugita
Dia Analysis Services Inc, 8-5-1 Thu-o, Ami, Ibaraki 300-0332,
Japan

T. Shiozaki
Japan Environmental Sanitation Center, 10-6 Yotsuyakami- cho,
Kawasaki-ku, Kawasaki, Kanagawa 210-0828, Japan

S. Goto
Azabu University, 1-17-71 Fuchinobe, Sagamihara, Kanagawa
229-8501, Japan

carbonization temperature is set in a wider range, from as low as 400°C to over 1,000°C. To help suppress the generation of PAHs in the process of carbonization of wood, PAH generation behaviors in carbonization were compared in this study, using cypress, chestnut, and bamboo as samples. The ultimate carbonization temperature was set to 400, 600, 800, and 1,000°C and maintained at that level for one hour for carbonization.

Materials and Methods

Japanese Hinoki cypress (*Chamaecyparis obtusa*), Japanese chestnut (*Castanea crenata*), and Moso bamboo (*Phyllostachys pubescens*) were used as dry test samples. Cypress and chestnut were cut into rectangular solids of 1 cm × 1 cm × 2 cm, while bamboo was cut into 1 cm × 1 cm sections before use. All of the samples were taken from the trees planted in Ibaraki Prefecture and grown in an environment where no chemical agents such as herbicide were used nearby. The samples were dried before use. Water content of each sample before carbonization was approximately 7%. Deuterated PAH16 component solution (ES-2528, CIL) was used as an internal reference material, which was added when PAH quantitative analysis was conducted using a gas chromatograph mass spectrometer (GC–MS). Toluene, ethanol, acetone, and hexane, all of which were for testing residual agricultural chemicals (Wako Pure Chemical Industries Ltd.), as well as anhydrous sodium sulfate (special grade by Nacalai Tesque) were also used.

Figure 1 outlines the carbonization gas collecting apparatus used. A nitrogen gas inlet was installed at the muffle furnace (FUW242PA, Toyo Engineering Works), with which the temperature rise program could be set. The nitrogen gas tube was connected to a corrugated tube within the furnace, which allowed nitrogen gas to stay for a long time within the furnace to prevent the nitrogen gas coming from outside (99.99%) from causing the temperature of the test samples to decrease. The corrugated tube was then connected to a silica tube, into which test samples were placed. One end of the silica tube was made to protrude from the top of the muffle furnace to outside, and a glass tar trap was placed over the protrusion. The tar trap was then connected to another corrugated tube, into which cooling water at –10°C was fed. To prevent the gas components liquefied by cooling from returning to the silica tube within the muffle furnace, they were made to fall along the wall down to the bottom of the tar trap. Five impingers containing acetone (for testing residual agricultural chemicals, Wako Pure Chemical) cooled down with ice were connected in series, in the stage following the corrugated tube for cooling. Test samples of approximately 2 g were placed in a 20 mm-dia. and 280 mm-long silica tube and heated while nitrogen gas was fed (at 10 mL/min) for carbonization (rate of temperature increase: 10°C/min). The carbonization temperature was set to 400, 600, 800, and 1,000°C. Once the set temperature was reached, the furnace was kept at that temperature for 1 h, and then allowed to cool. After the furnace had cooled down, all the parts including connecting tubes were washed with acetone, and the collected solution was then mixed with the acetone within the impingers to prepare 50 mL of solution. One milliliter of this solution was put in an 8-mL vial, which had been dried in a desiccator overnight, condensed under the nitrogen gas flow, dried within the desiccator overnight, and then weighed to calculate the amount of tarry matter.

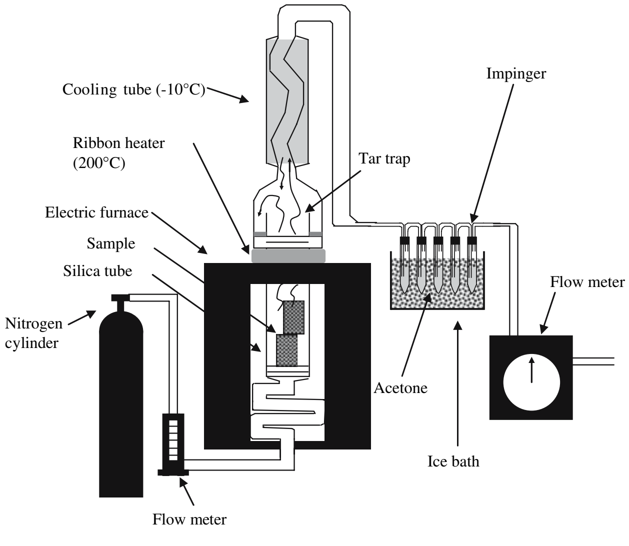

Fig. 1 Carbonization gas and tarry matter collecting apparatus

A differential thermal scale (WS-002 SYSTEM, Bruker AXS) was used for differential thermal analysis of wood samples. The samples of 1 mg were measured in the temperature range from room temperature to 1,000°C. The temperature was increased at the rate of 20°C/min, and helium was used as atmospheric gas.

One milliliter of acetone solution containing tarry matter was put aside, and 1 mL of the internal reference solution (concentration: 0.2 µg/mL each), 5 mL of water, and 1 mL of hexane were added to it and mixed. The solution was left to stand, and then the hexane phase was batched off. One milliliter of acid (1 N H_2SO_4) was added to the hexane phase that had been batched off, they were mixed, and then the mixture was left to stand. The obtained supernatant was dehydrated using anhydrous sodium sulfate, and measurement was made using a GC-MS (5973/6890, Agilent Technologies). BPX-5 (30 m, 0.25 mm i.d., 0.30 µm) was used as a column, helium (He) was used as carrier, and

1 μL sample was fed by the splitless method. The temperature at the inlet was set to 300°C, and the temperature rise conditions of the furnace were set as follows: the temperature was kept at 50°C for 2 min, increased from 50 to 185°C at the rate of 15°C/min, further increased up to 310°C at the rate of 5°C/min, and then maintained for 5 min. The temperature of the ion source was set at 260°C, and determination was made in the SIM mode. Of the 16 PAHs to be measured by the EPA method 8310, the amount of 15 PAHs, excluding naphthalene, were measured this time. Table 1 lists the retention time of each compound and the mass number of target ion.

Results and Discussion

Differential thermal analysis of wood is a method of measuring the reduction of weight of samples resulting from thermal decomposition that occurs while the samples are heated under anoxic conditions. These conditions are similar to those of carbonization, and therefore the analysis is helpful in assessing the carbonization process. Therefore, differential thermal analysis of cypress, bamboo, and chestnut was conducted first. Figure 2 summarizes the results obtained. With each of the three samples, the weight started to decrease around 250°C, and the reduction of the weight ceased by the time the temperature was increased to 400°C. Then, although a slight decrease was found when the temperature was increased to 600°C, almost no decrease was observed while the temperature was increased from 600 to 800°C and from 800 to 1,000°C. Based on this result, the lowest carbonization temperature was set at 400°C in this study, and three other settings were selected in the range up to 1,000°C in steps of 200°C.

Table 1 Retention time and the target ion of compounds measured by GC/MS

Compounds	r.t. (min)	m/z
Acenaphthylene	11.56	152
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Fluorene	12.94	166
Phenathrene	15.41	178
Anthracene	15.58	178
Fluoranthene	19.50	202
Pyrene	20.38	202
Benz[*a*]anthracene	25.55	228
Chrysene	25.70	228
Benzo[*b*]fluoranthene	30.19	252
Benzo[*k*]fluoranthene	30.26	252
Benzo[*a*]pyrene	31.48	252
Indeno[1,2,3-*cd*]pyrene	35.59	276
Benzo[*ghi*]perylene	36.47	276
Dibenz[*a,h*]anthracene	35.71	278

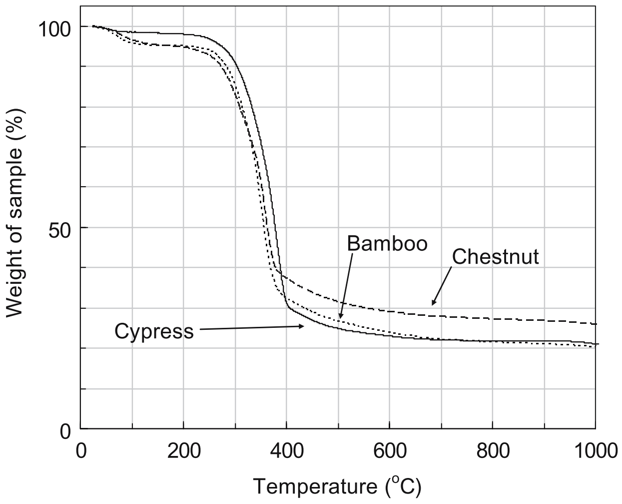

Fig. 2 Result of TG measurement of wood samples

The weight of tarry matter contained in the gas generated by carbonization was then examined. Figure 3 presents the weight of tarry matter collected using the three samples, namely, cypress, chestnut, and bamboo, in units of mg per weight of the samples before carbonization (mg/g sample). Of the three types of wood samples compared this time, the weight of tarry matter collected was slightly heavier with bamboo, but no clear difference was found between chestnut and cypress. The amount of tarry matter generated when the maximum temperature was set at 600°C tended to be larger than that collected when it was set at 400°C, but almost no difference was found between 600, 800, and 1,000°C. Tarry matter of 33 mg was collected per 1 g of bamboo when it was carbonized at 400°C,

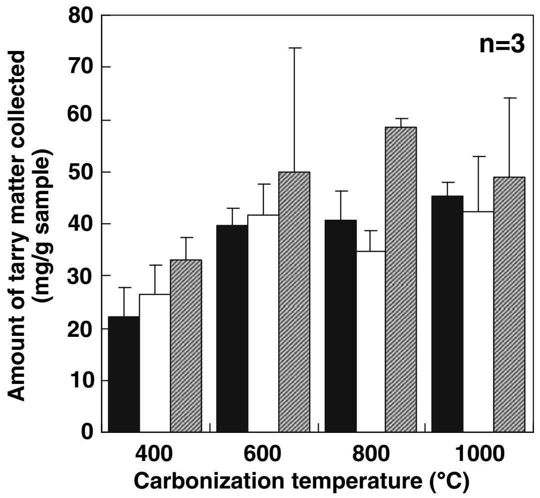

Fig. 3 Relation between carbonization temperature and weight of tarry matter collected. ■ Cypress, □ Chestnut, Bamboo

while 49 mg was collected at 1,000°C. Organic substances that attached to the interior of the tar trap were collected using acetone, and the solution obtained was condensed, dried, and the weight of solidified substance was measured. Consequently no highly volatile substances were contained.

The weight of charcoal generated by carbonization was then examined. Figure 4 lists the weight of charcoal obtained in the ratio to the unit weight of the samples before carbonization (mg/g sample). Almost no difference was found in the ratio of weight of charcoal generated to that of the sample among the three samples. At the carbonization temperature of 400°C, the weight of charcoal generated per 1 g of sample weight varied from 330 mg (cypress) to 370 mg (chestnut). On the other hand, when the carbonization temperature was set at 600°C, approximately 280 mg of charcoal was generated with all of the samples. At 800°C, the value varied from 260 to 270 (mg/g sample), and at 1,000°C, it varied from 240 to 250 (mg/g sample). As shown by these results, the higher the carbonization temperature, the larger the reduction of weight due to carbonization, but the change in weight reduction was small at 600°C and higher, which was contrary to the case in which tarry matters were collected (Fig. 3). On the other hand, the weight of component recovered (tarry matter weight plus charcoal weight) accounted for 30.3%–39.3% of the weight of raw sample (cypress), 30.9%–43.6% (chestnut), and 32.3%–41.4% (bamboo). To be specific, when bamboo was carbonized at 1,000°C, the weight loss due to carbonization was approximately 750 mg per sample of 1 g, but only 50 mg was recovered as tarry matter. It was found that approximately 70% was decomposed into inorganic gases or low-molecular organic compounds, which cannot be collected with this equipment, even if the moisture content of approximately 7% was taken into consideration.

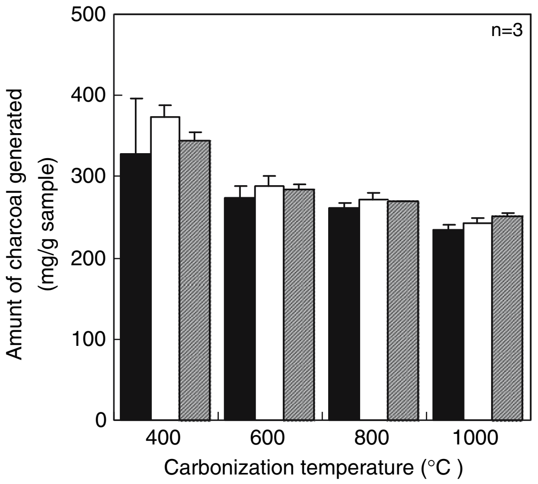

Fig. 4 Relation between carbonization temperature and weight of charcoal. ■ Cypress, □ Chestnut, Bamboo

Prior to studying the generation of PAHs through carbonization, the PAH collection efficiency of the collecting apparatus shown in Fig. 1 was checked as follows: Cypress, chestnut, and bamboo were carbonized at 1,000°C; tarry matter attaching to the silica tube, tar trap, cooling tube, glass tube, and five impingers was collected separately using acetone; and the amount of PAHs contained in each was measured. When cypress was carbonized, the tar trap collected 4.7 µg of PAHs (sum total of 15 components measured this time) per 1 g of sample before carbonization, which was the highest amount of all. The second largest amount, 4.3 µg, was collected with the cooling tube, but almost none was collected with other parts. The tar trap and the cooling tube collected approximately 98% of the total PAHs collected. The amount of collected PAHs decreased as the PAHs traveled through the silica tube, where they were generated, toward the impingers, the end of the equipment, where only 0.02% of the total amount was collected. These results confirmed that generated PAHs were trapped within the cooling tube or the tar trap while being cooled down in the cooling tube. The equipment was thus found to have sufficient PAH collection performance. Meanwhile, charcoal obtained by the carbonization gas collection test was ground in a mortar, and a part of it was extracted by the Soxhlet extraction method for 16 h. The PAH content in the charcoal was measured using toluene and ethanol mixed at the volume ratio of 3:7 as solvent (Nakajima et al. 2004). The amount of PAHs obtained by the test (total of 15 components) was 0.08–0.11 (µg/g sample) with cypress, 0.06–0.12 (µg/g sample) with chestnut, and 0.08–0.15 (µg/g sample) with bamboo. These amounts accounted for only 2% of the total weight collected as tarry matter. No clear difference was found in the amount of PAHs in charcoal between the three types of samples.

Figure 5 presents the ratio of components (15 PAH components in tarry matter) at each of the carbonization temperatures. Although no significant difference was found in composition itself depending on the difference of carbonization temperature, the amount of PAHs generated increased as the temperature was increased. Of the 15 types of PAHs measured this time, the largest amount collected was fluorene, followed by phenanthrene and anthracene. As molecular weight increased, the amount of PAHs generated tended to decrease, except for acenaphthylene and acenaphthene, which had the lightest molecular weights of the 15 components measured this time, 152 and 153, respectively, but generated smaller amounts of PAHs than fluorene and phenanthrene, whose molecular weights were 166 and 178, respectively. The total amount of the 15 PAHs measured this time was 16 µg per 1 g of the sample before

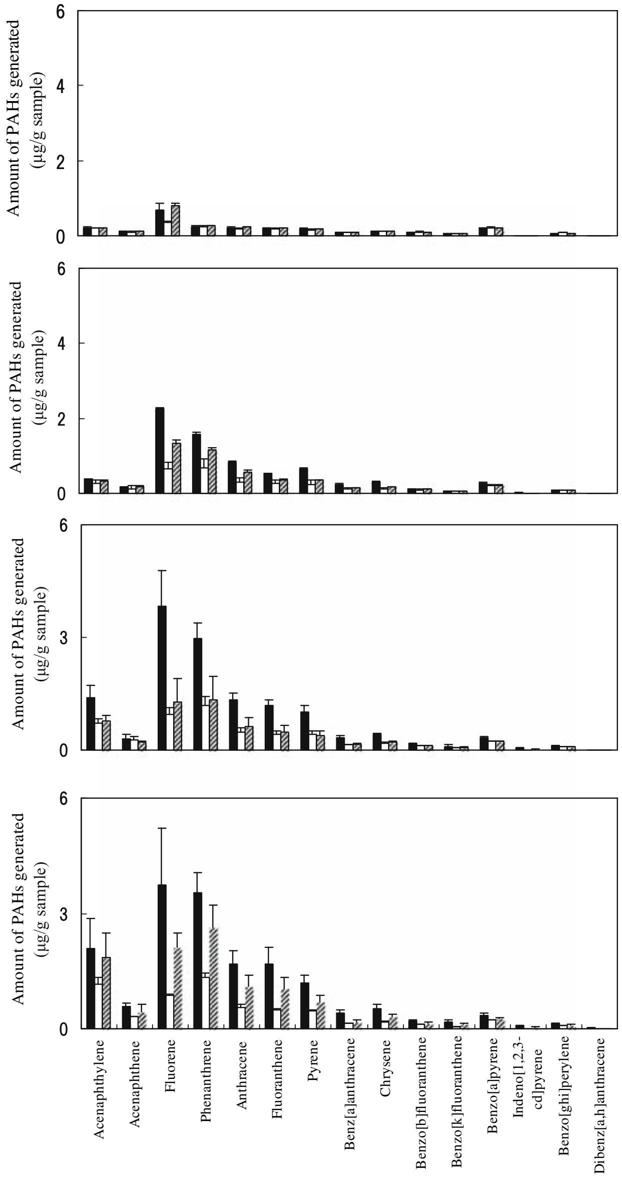

Fig. 5 Relation between carbonization temperature and PAHs generated (n = 3). ■ Cypress, ☐ Chestnut, Bamboo

carbonization (cypress), 6 µg (chestnut), and 11 µg (bamboo), or 0.35 µg/mg, 0.14 µg/mg, and 0.22 µg/mg, respectively in terms of unit tarry matter weight. The weight of tarry matter per unit sample weight was large with bamboo, while the amount of PAHs was large with cypress. Further examination is required to find the cause of this phenomenon.

This study showed that there is a difference between tarry matter and PAH generation behaviors. Generation of tarry matter was almost completed by the time the temperature reached 400°C, while generation of PAHs continued until the temperature reached 1,000°C. The amount of PAHs generated accounted for 6×10^{-6} to 16×10^{-6} of the weight of the wood samples. Of the 15 types of PAHs measured this time, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene, and dibenzo[*a,h*]anthracene are known to have mutagenic properties (IARC 1983). Among them, BaP is classified in group 1 (Carcinogenic to humans) in the list created by the International Agency for Research on Cancer (IARC), and dibenzo[*a,h*]anthracene is classified in group 2A (Probably carcinogenic to humans). Naphthalene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, chrysene, and ideneo[1,2,3-*cd*]pyrene are classified into group 2B (Possibly carcinogenic to humans) (IARC 1983). Our research confirmed that PAHs associated with those carcinogenic substances were generated as a result of carbonization. The experiment conducted this time confirmed that BaP of approximately 0.5 µg was generated from 1 g of raw sample (at 600°C). Based on this result, the weight of BaP generated in the production of 1 kg of charcoal is calculated to be 2 mg. It is therefore essential that strict measures be taken to collect BaP in actual charcoal manufacturing sites to protect the health of workers and local residents.

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