J Wood Sci (2003) 49:248–254

ORIGINAL ARTICLE

Masahiro Ota · Hoque M. Mozammel

Chemical kinetics of Japanese cedar, cypress, fir, and spruce and characterization of charcoal

Received: February 13, 2002 / Accepted: July 12, 2002

Abstract Thermogravimetric and differential thermal analyses techniques have been applied to investigate the thermal degradation characteristics and chemical kinetics of Japanese cedar, cypress, fir, and spruce. The decomposition of the components could be modeled by an Arrhenius kinetic expression. The kinetic parameters were extracted from the thermogravimetric data using least-squares techniques. The heating rates used for the analyses were 10°, 5°, and 0.33°C/min; and the activation energy and reaction order of the above woods were 7.54, 8.39, 2.87, and 7.88 kJ/mol and 0.71, 0.64, 0.44, and 0.63, respectively. Finally, carbonization was done to produce charcoal from these woods under various operating conditions, and the charcoal was characterized in respect to yield, heating value, electrical conductivity, and X-ray diffraction. The quality of the charcoal from fir was the best among the four types of wood. The charcoal produced is inferior to binchotan (white charcoal) in respect to electrical conductivity and crystalline structure.

Key words Thermogravimetry · Kinetic parameters · Carbonization · XRD

Introduction

Carbonized woods have a wide range of applications in various sectors. It is used as fire- and sound-resistant material and electromagnetic shields.[1] Wood-based carbonized materials from unused or waste wood are sought as environmental cleaning products and as a raw material for carbon.[2] Cedar powder carbonized at various temperatures can remove heavy metals such as cadmium, lead, zinc, and mercury.[3–5] Wood charcoal also adsorbs unwanted components such as metal and organic compounds in an aqueous system.[1] Of the total charcoal consumption in Japan, 21% is produced domestically and 79% imported.[6] Because of the rise in the utilization of charcoal for nonfuel uses as well as the use of white charcoal for commercial use and charcoal for leisure use, domestic demand is expected to continue to rise.

Pulido-Novicio et al.[2] evaluated the adsorptive properties of wood charcoal from Japanese cedar and discussed the mechanism of its adsorptive function in relation to the physical and anatomical characteristics of wood after carbonization. Nishimiya et al.[7] analyzed the chemical structure of wood charcoal by Fourier-transform infrared spectroscopy, X-ray diffraction, and photoelectron spectroscopy. Hirata[8] reported thermogravimetric and differential thermal analysis (TG/DTA) results for cellulose, wood, lignin, xylon, and glucomannan up to 500°C at a heating rate of 1°C/min. Ishihara[9] studied the effect of temperature on the qualities of charcoal, but few have discussed the effects of pressure and time along with the analysis of pyrolysis gas.

The purpose of our study was to produce a quality charcoal such as binchotan from waste wood and wood residues. The current study is the first step in determining the kinetic parameters of Japanese cedar, cypress, fir, and spruce up to 1000°C at various heating rates. It examined the effects of temperature, pressure, and carbonization time on the quality of charcoal. X-ray diffraction (XRD) analysis was undertaken to check crystal formation. Pyrolysis gas components at 500°–1000°C were also analyzed.

Materials and methods

Sample preparation

Wood samples of Japanese cedar (*Cryptomeria japonica*), cypress (*Chamaecyparis obtusa*), fir (*Abies firma*), and spruce (*Picea jezoensis*) were used for thermogravimetric analysis and charcoal production. A 50 mm long sample was cut from long wood bars (width 30 mm, 15 mm thick) of different types. The wood samples were kept in desiccators

---

M. Ota (✉) · H.M. Mozammel
Department of Mechanical Engineering, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan
Tel. +81-426-77-2715; Fax +81-426-77-2701
e-mail: ota-masahiro@c.metro-u.ac.jp

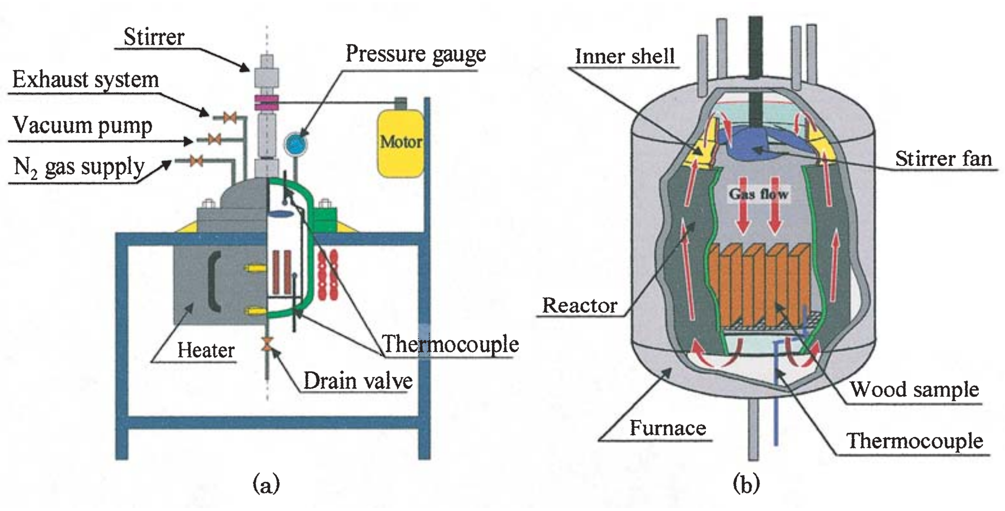


Fig. 1. **a** Experimental setup for carbonization. **b** Inner view of the furnace

to prevent them from absorbing moisture. The moisture content of the wood was determined before charcoal production.

Thermal decomposition

Thermogravimetric and differential thermal analyses (TG/DTA) were carried out using the Seiko TG/DTA300 instrument, taking samples in a platinum sample container. Runs were carried out at heating rates of 10°, 5°, and 0.33°C/min under a nitrogen environment (N_2 flow 200 ml/min) at atmospheric pressure. The wood samples were heated to a final temperature of 1000°C. The thermogravimetric weight loss curve (TG, %) and the derivative weight loss curve (DTG, %/min) were recorded as a function of temperature and time.

Bench scale pyrolysis

The experimental setup (Fig. 1) consisted of a furnace divided into two parts (upper and lower) connected by eight bolts. A circular gasket of cobalt between the two parts made the furnace leakproof. A SUS316 inner shell (220 mm diameter, 300 mm height) inside the furnace held the wood samples. The upper portion of the furnace held the pressure regulating valve, vacuum system, stirrer along with a belt connected with the motor, water cooling line for the stirrer, N_2 gas supply system, and pyrolysis gas/liquid exhaust system. The electrical heater and drainage valve were located in the lower portion. The heating rate could be varied by changing the supplied voltage and with a temperature controller.

Results and discussion

TG/DTA

Figure 2 shows the TG, DTG, and DTA curves of four types of wood at a heating rate of 10°C/min. Two-stage weight loss was observed. For example, the initial decomposition of fir occurred at 41°–126°C, representing 7.90% weight loss. This represents the moisture content of the wood. Similarly, the moisture contents of cedar, cypress, and spruce can be obtained from the TGA curve; their values were 6.84%, 6.45%, and 6.97%, respectively. The initial decomposition temperature increased with the increase in heating rate, which may be due to the increased temperature difference between the analyzer and the sample with the increase in heating rate. Rapid decomposition of the samples occurred around 267°–386°C (cedar), representing a 54.30% weight loss with 25.56% of the weight of final solid residue (Table 1). This zone may be referred to as the active pyrolysis zone because of the high decomposition rates (per unit time) observed. In Table 1 it is seen that the residual weight ratios for cedar and fir are higher than those for cypress and spruce. This may be due to the higher ash contents of cedar and fir (about 6%–7%) in comparison with cypress and spruce (less than 1%).

Based on the overall shape of the TGA curve, it was decided to fit the thermogravimetric data to an Arrhenius equation of the form presented by Goldfarb et al.[10]

$$-\frac{dW}{dt} = Ae^{-E/RT}(W)^n$$

where $W = \frac{W - W_f}{W_o - W_f}$; A is the preexponential factor (min^{-1}); E is the activation of energy (J/mole); R is the universal gas constant (8.3 J/mol K); T is the absolute temperature (K); n is the order of the reaction (dimensionless); t is the time (min); w is the weight of the sample at time t; w_f is the weight of the residue; and w_0 is the initial weight of the sample.

Using the expression for dimensionless weight, W, the above equation can be linearized in the form

$$\log\left[-\frac{1}{w_o - w_f}\frac{dw}{dt}\right] = \log A - \frac{E}{2.3RT} + n\log\left[\frac{w - w_f}{w_o - w_f}\right]$$

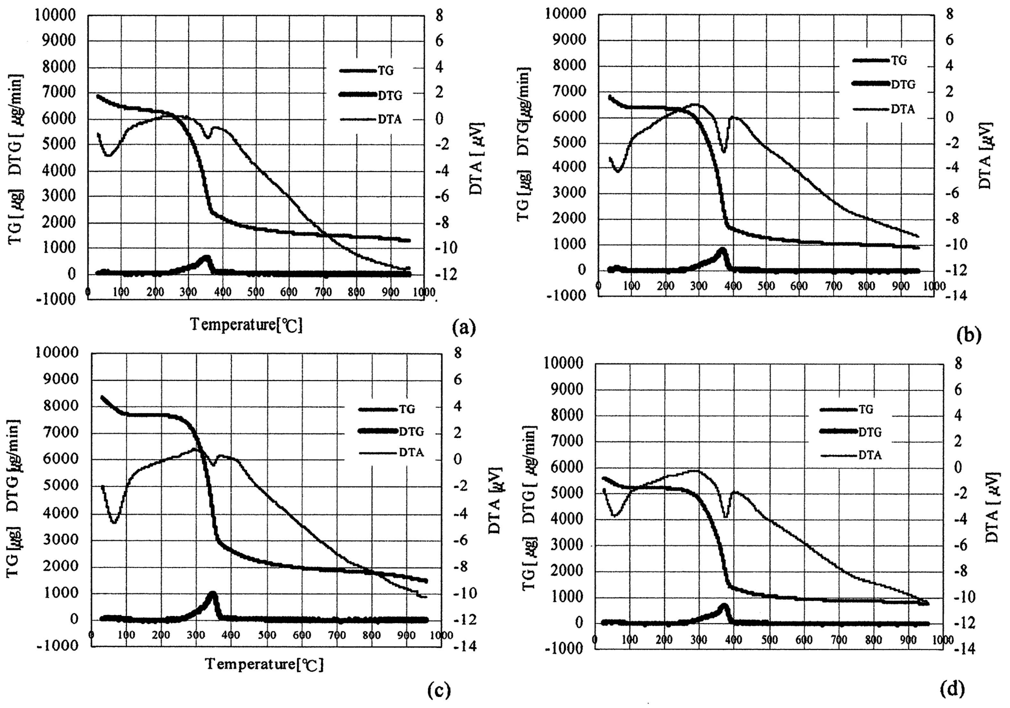
Table 1. TGA and kinetic parameters of various woods at 10°C/min

Wood	Active zone			Residual weight ratio[a] (%)	Kinetic parameters		
	Temp range (°C)	D rate (%/min)	Total D (%)		Log*A*	Activation energy (kJ/mol)	Order of reaction
Cedar	267–386	4.71	54.30	25.56	−1.12	7.54	0.71
Cypress	288–407	5.50	64.50	18.92	−1.19	8.39	0.64
Fir	275–383	5.31	55.43	25.82	−1.81	2.87	0.44
Spruce	289–408	5.56	64.22	18.90	−1.19	7.88	0.63

D, decomposition; TGA, thermogravimetric analysis

[a] Residual weight ratio is at 500°C

Fig. 2. Thermogravimetric/differential thermal analyses (*TG/DTA*) curves for cedar (**a**), cypress (**b**), fir (**c**), and spruce (**d**) at a heating rate of 10°C/min. *DTG*, differential thermogravimetric



This equation is then of the form

$$z = a + bx + cy$$

where

$$z = \log\left[-\frac{1}{w_o - w_f}\frac{dw}{dt}\right]$$

$$x = \frac{1}{2.3RT}$$

$$y = \log\left[\frac{w - w_f}{w_o - w_f}\right]$$

and a is $\log A$; b is $-E$; and c is n.

A least-squares technique can now be used to specify values of $\log A$, $-E$, and n that give the best fit to the proposed mathematical model. The results of the least-squares technique for the four types of wood are presented in Table 1.

The DTA curve expresses thermal energy liberated or absorbed during the decomposition process per unit of time. The downward movement of this curve shows the endothermic reaction, and the upward movement shows the exothermic reaction. The nature of the DTA curves for cypress and spruce are almost identical, with similar peak temperatures and residue ratios. Similarly, identical DTA curves are found for cedar and fir. However, the height of the peaks (downward) for cypress and spruce are greater than those for cedar and fir. This energy consists of the heat of evolution and the heat of reactions. The greater heights (energy) of the down peak of cypress and spruce mean that more pyrolysis reactions occur during this period, leaving less residual.

Figure 3 shows the variation in the DTG curves for spruce at heating rates of 10°, 5°, and 0.33°C/min and a heating rate of 5°C/min up to 270°C and then 0.92°C/min, similar to that used for charcoal production in the furnace. Two peaks were observed on the DTG curves corresponding to the two-stage weight loss on the TG curves (spruce). The first peak represents the evaporation of moisture from the wood, and the second peak represents the reactions contributing to the formation of volatile gases. For example, on the DTG curve at 10°C/min where the stages are more clearly visible, the first peak is observed at 61°C and the second peak at 373°C. In addition to the distinct peaks, a peak-like shape may be observed at different temperatures as a number of reactions occur owing to the presence of cellulose, hemicellulose, or lignin in the woods. For example, prior to formation of the main peak at 373°C, a small peak is formed at 325°C. The peak of the DTG curve shifts toward a higher temperature with the increase in heating rate. DTG peaks occur at 365° and 373°C for heating rates of 5° and 10°C/min, respectively. This may be explained by the same factor that caused the increase in initial decomposition temperature at the higher heating rate. At heating rates of 5° and 0.33°C/min, the first peak is not clearly visible. It is clear from the figures that wood with a higher residual weight ratio has a maximum rate of evolution of volatile matters at comparatively lower temperatures. For example, the DTG peaks for cypress and spruce are at 372° and 373°C, respectively, but those for cedar and fir are at 345° and 347°C, respectively.

Pyrolysis product analysis

A number of experiments have been undertaken to produce charcoal by changing the operational parameters. The effects of temperature, pressure, and time on the yield and quality of charcoal have been studied. Experiments were carried out at temperatures of 350°, 400°, and 500°C with various combinations of pressures (100, 400, and 600kPa) and times (24, 48, and 96h).

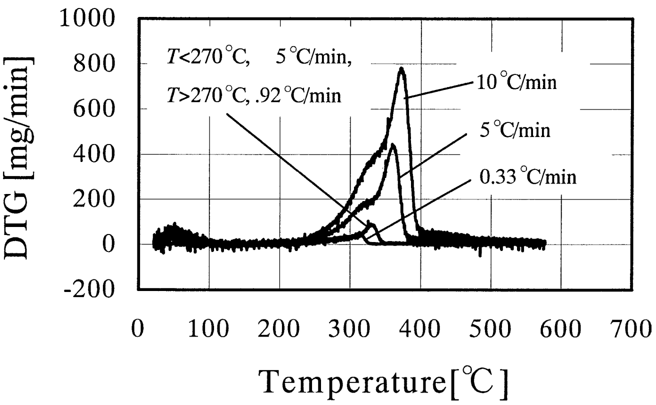


Fig. 3. Differential thermogravimetric (*DTG*) curves for spruce at 0.33°C/min, 5°C/min up to 270°C and then 0.92°C/min, 5°C/min, and 10°C/min

It is seen from the experimental data that the yield of charcoal from different types of wood decrease with the increase in carbonization temperature. This may be due to the fact that, with the increase in carbonization temperature, more cellulose decomposes to tar through depolymerization, and less cellulose decomposes to dehydrocellulose, which then reacts further to give char and gases.[11] In addition, as the temperature is raised, a larger proportion of volatile matter is being driven off. As a result, the charcoal produced has a higher carbon content. The effects of temperature on the yield (a combination of volatile matters, carbon, and ash) are shown in Fig. 4. With the increase in pressure, the vaporizing (or evolution, as the case may be) tendency of wood components decreases. As a result, the charcoal yield from wood increases, but the charcoal consists of more volatile matter. The opposite scenario is seen with an increase in carbonization time, as the volatile matter has enough time to escape. The effects of pressure (Fig. 5) and time (Fig. 6) on the yield of charcoal are not as effective as that of temperature.

The heating value for charcoal mainly depends on the fixed carbon. The heating value increases with the increase in carbonization temperature as the amounts of fixed carbon in charcoal increases with the temperature. For example, the heating value of charcoal from fir is 28950kJ/kg at 350°C but is 34610kJ/kg at 500°C (Table 2).

The electrical conductivity (reciprocal of electrical resistance) of charcoal depends on its carbon crystals, shape, size, and regularity, among other factors.[12] Normally, the electrical resistance of charcoal is expressed as a power of 10 and has the unit Ωcm. The most popular charcoal, binchotan, has an electrical resistance that amounts to zero[13] ($10^0\,\Omega$cm) (i.e., high electrical conductivity). As the temperature increases with constant pressure and time, the charcoal has lower electrical resistance (6.5–8.0 at 500°C, >9.0 at 350°C). This is depicted at the tops of Figs. 4–6. Among the four types of wood, the best quality charcoal in terms of electrical resistance appears to be fir (5.5).

Reheated charcoal shows good conductivity. Samples of charcoal from fir were reheated in a muffle furnace at 925°C for 1h. The electrical resistance was 1.0 (earlier it was 5.5), which is close to that of binchotan. The effect of the carbonization time and pressure on electrical conductivity was not as severe as that observed with a change in temperature.

Table 2. Heating values for charcoal under various operating conditions

Experimental conditions	Heating value (kJ/kg)				
	Cedar	Cypress	Fir	Spruce	Binchotan
350°C/0.1Mpa/24h	30779	30799	28950	31251	
400°C/0.1Mpa/24h	32099	31409	30770	31188	
500°C/0.1Mpa/24h	35409	34943	34610	35948	
500°C/0.4Mpa/24h	34539	35857	34160	35496	30443
500°C/0.6Mpa/24h	35049	35639	32490	36195	
500°C/0.1Mpa/48h	34889	35295	33080	35443	
500°C/0.1Mpa/96h	34009	35169	31750	34988	

Fig. 4. Effect of temperature on the yield and quality of charcoal

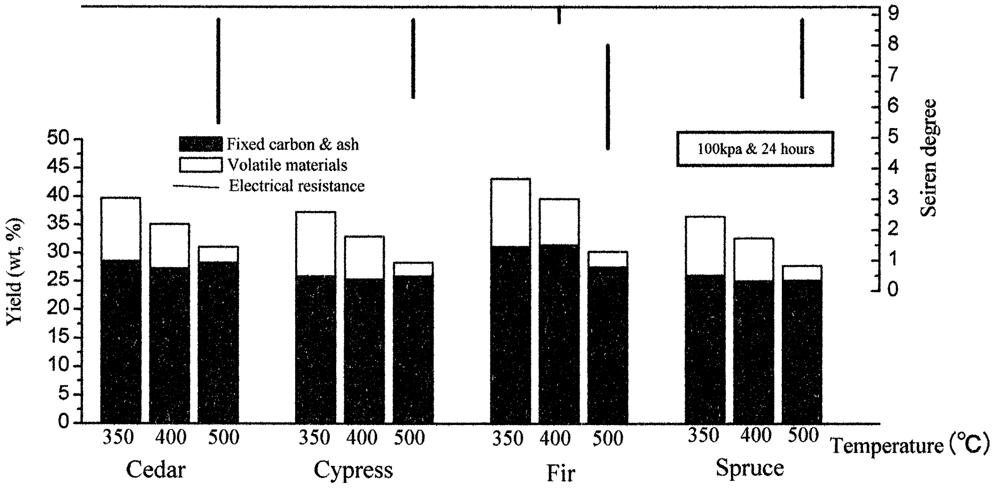


Fig. 5. Effect of pressure on the yield and quality of charcoal

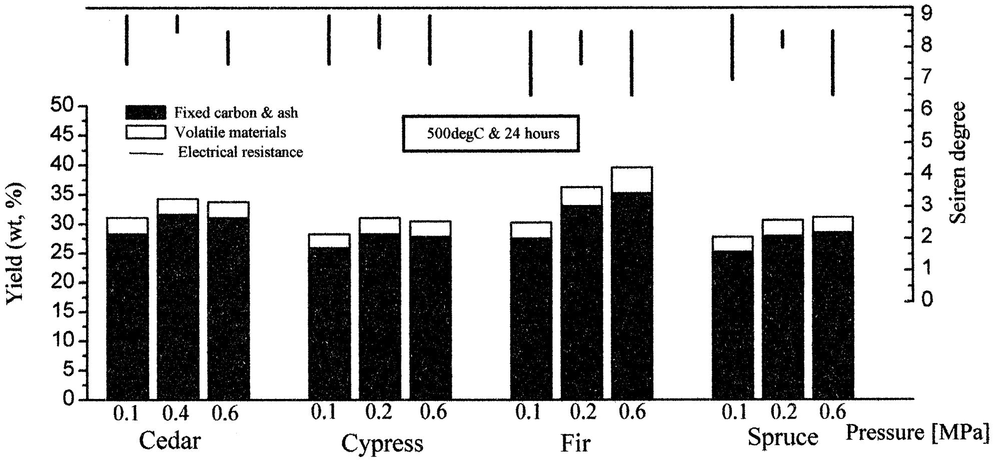
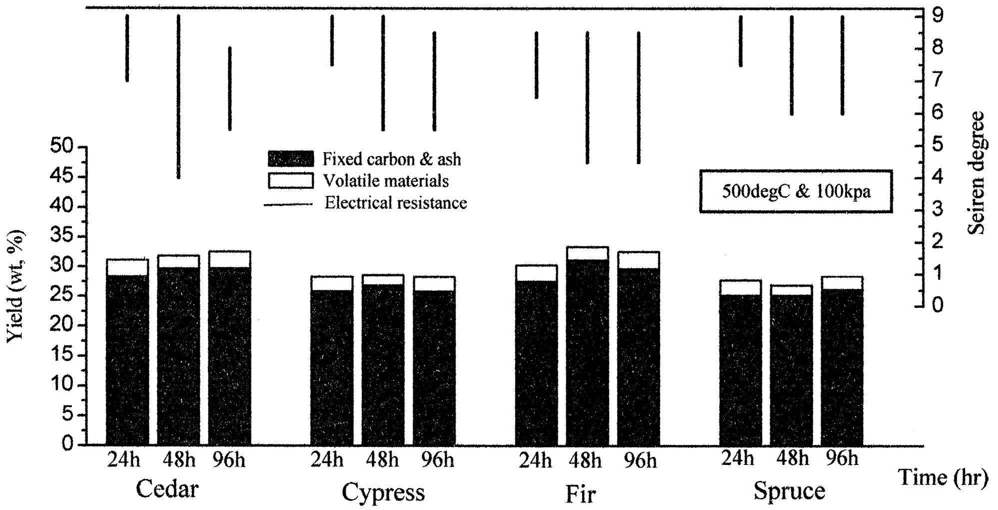


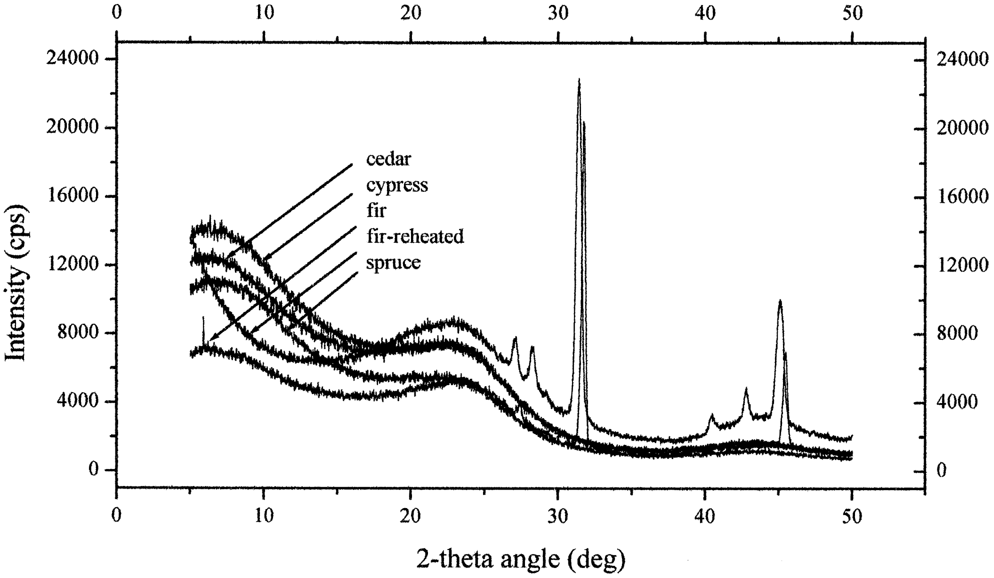
Fig. 6. Effect of time on the yield and quality of charcoal



The results of XRD of four types of wood are shown in Fig. 7. An M21X machine (MAC Science Co.) with the following parameters was used: X-ray tube, copper; wavelength of X-ray 1.54056Å6; electricity 300mA; voltage 40kV; and 2θ angle 5.0°–50°.

The humps in the data for spruce, cypress, and cedar suggest the presence of amorphous or poorly crystalline phases. In theory, pure amorphous material would give no hump at all and would not reveal its presence easily by XRD, except perhaps by helping to raise the background

Fig. 7. X-ray diffraction (XRD) of charcoal produced from cedar, cypress, fir, and spruce at 500°C. XRD of fir charcoal reheated at 925°C for 1 h



level. Fir shows two sharp peaks, at $2\theta = 31.18°$ and 45.50° (i.e., crystal formation occurs). This result confirms that the electrical conductivity of fir is better than that of other types of wood under consideration. In the case of reheating, more carbon crystals form, with sharp peaks appearing at various locations in the XRD graph. It results in a higher value for electrical conductivity. The results of reheating fir charcoal at 925°C for 1 h are also shown in Fig. 7.

Pyrolysis gas is analyzed by a Shimadzu 14B gas chromatograph, and the results of cedar at 500°, 750°, and 1000°C are shown in Fig. 8. At particular temperatures the gas is collected at 0, 20, 40, 60, 90, 120, and 150 min. It is seen from the gas chromatograph results that at lower temperatures (<500°C) the gas is composed mainly of CO and CO_2, as the bonding energy between carbon-carbon and carbon-oxygen is much lower than that of carbon-hydrogen. At about 750°C, gas composition is dominated by CH_4 due to a methane formation reaction. At 750°–1000°C, H_2 dominates. This increase in H_2 can be explained by the water-gas reaction, water shift reaction, and methane steam reforming reaction.

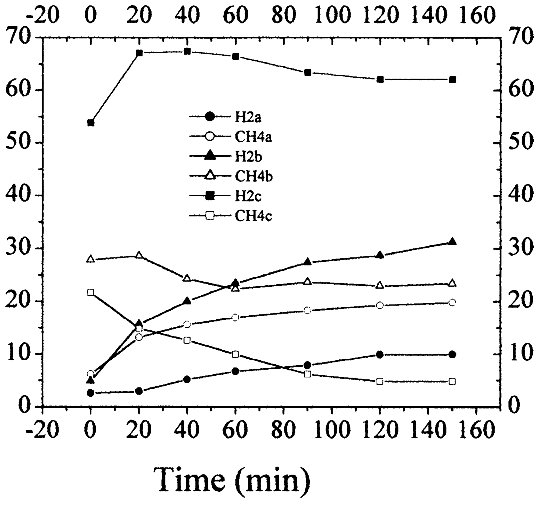


Fig. 8. Gas compositions of Japanese cedar pyrolysis at various temperatures. The time is recorded after the furnace reaches a specific temperature. *a*, *b*, and *c* show the gas compositions at pyrolysis temperatures of 500°, 750°, and 1000°C, respectively

Comparisons with TG results

It is seen from the TG graphs in Fig. 2 that the residual weight ratios of cedar, cypress, fir, and spruce at 500°C were 25.56%, 18.92%, 25.82%, and 18.90%, respectively. The residual of TGA is nothing but the charcoal in the case of carbonization, as the analysis is carried out in an inert atmosphere. The charcoal yields from the above woods at 500°C, 100 kPa, and 24 h were 30.27%, 28.32%, 31.11%, and 27.78%, respectively. In both cases, fir has the highest yield and spruce the lowest. Variations in the residual weight ratio of the TG analysis and charcoal yield of the experimental process are due to the variations in the amount of sample taken and the differences in heating rates. The particle size for TG analysis is too small owing to the weight limitation of the system. Increasing the particle size of the solid feed results in higher char and heating values of the pyrolysis gas. This may be due to the fact that pyrolysis tar produced inside a reacting particle must find its way to the gas surrounding the particle by diffusing through a hot layer of char. Inside this layer the tar may be subject to cracking. Thus the char and gas yield may increase as the length of the diffusion path of the tar is increased (i.e., with greater feed particle size). During charcoal production in the furnace a tremendous pressure rise is observed between 300° and 350°C, representing a high rate of pyrolysis reaction. This phenomenon can be detected at the same temperature ranges in the TG results for these woods.

Acknowledgment The authors express their gratitude to Professor Yoshida of Applied Chemistry in Tokyo Metropolitan University for performing the TG/DTA in his laboratory and for his valuable suggestions about the analyses.

References

1. Ishihara S (1996) Recent trend of advanced carbon material from wood charcoals. Mokuzai Gakkaishi 42:717–724
2. Pulido-Novicio L, Hata T, Kurimoto Y, Doi S, Ishihara S, Imamura Y (2001) Adsorption capacities and related characteristics of wood charcoals carbonized using a one-step or two-step process. J Wood Sci 47:48–57.
3. Pulido-Novicio L, Hata T, Kajimoto T, Imamura Y, Ishihara S (1999) Removal of mercury by carbonized wood materials from aqueous solutions of different types of mercury compounds. Resources Proc J 66(1):3–8
4. Pulido-Novicio L, Hata T, Kajimoto T, Imamura Y, Ishihara S (1998) Removal of mercury from aqueous solutions of mercuric chloride using wood powder carbonized at high temperature. Wood Res 85:48–55
5. Pulido-Novicio L, Hata T, Imamura Y, Ishihara S, Kajimoto T (1998) Removal of mercury and other metals by carbonized wood powder from aqueous solutions of their salts. J Wood Sci 44:237–243
6. Trade statistics (1998) http://www.mof.go.jp/english/1c015f1e.htm, Ministry of Finance, Japan
7. Nishimiya K, Hata T, Imamura Y, Ishihara S (1998) Analysis of chemical structure of wood charcoal by X-ray photoelectron spectroscopy. J Wood Sci 44:56–61
8. Hirata T (1995) Kinetics of pyrolysis of wood and cellulose. Mokuzai Gakkaishi 41:879–886
9. Ishihara S (1999) Wood charcoal as functional carbon materials. J Soc Mater Sci 48:473–482
10. Goldfarb J, McGuchan R, Meeks AC (1968) Kinetic analysis of thermogravimetry. Part II. Programmed temperatures. Air Force Materials Laboratory, Wright-Patterson AFB, Ohio, ARML-TR-68-181
11. Bhattacharya SC, Shrestha RM (1990) Bio-coal technology and economics. RERIC, AIT, Bangkok
12. Migita N (1968) Wood chemistry. Kyoritsu Publishing, Tokyo, p 61
13. Japanese National Institute of Forestry (1973) Handbook of wood industry (in Japanese). Maruzen, Tokyo, p 916