

Production of aromatic compounds  
and functional carbon materials  
by pulse current pyrolysis of woody biomass

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## General introduction

### 1 Background

The development of technologies for obtaining useful chemical substances from sources other than fossil resources has received worldwide attention. In particular, there is a need for the production of feedstock chemicals from abundant wood biomass. Pyrolysis is an important technology involving the quick and efficient conversion of biomass materials to chemicals. Pyrolysis of wood biomass generates viscous pyrolysis oil [1-3] and char with unique properties like surface properties and pore characteristics [2-6] within extremely short time periods. The potential application of pyrolysis oil as a source of raw materials for chemical products as well as for fuel has been mentioned elsewhere [1, 7]. Collection and utilization of both char and pyrolysis oil are also necessary for the efficient production of useful chemical substances. Hence, precise control over pyrolysis conditions and the use of an optimal catalyst are necessary to selectively promote the pyrolysis reaction. Selective conversion of wood biomass to useful chemical substances by pyrolysis is the key to satisfy these requirements.

Optimization of pyrolysis conditions is necessary for expanding the applicability of pyrolysis. The preparation of pyrolysis products with the required characteristics using pyrolysis by the pulse current heating method was investigated in past research. Shape-controlled porous carbon materials with micro-, meso-, and macropores were successfully prepared from Japanese cedar wood meal using this heating method, and the characteristic

physical properties of these carbons were evaluated [8]. The pulse current heating method has many advantages such as low power consumption, extremely short times for pyrolyzing biomass, easy control of pyrolysis temperature and atmosphere using a computer, flexibility in choosing a wide range of pressures, possibility of continuous production, and feasibility of industrial-scale production [9]. Kurosaki et al. reported the conditions for pyrolysis using the pulse current heating method, wherein the current was raised to 2000 A at 10 V for 10 s and then decreased to 800 A at 4 V in order to attain an optimized processing temperature of 800 °C at a heating rate of 50 °C/s [8]. Hata et al. used a higher heat treatment temperature of 2490 °C, which was maintained by raising the current to 1400 A at 4.2 V [10].

Elucidating the composition and characteristics of the pyrolysis products obtained using the pulse current heating method is necessary in order to take full advantage of this technology. Reducing energy consumption and production cost is possible by the simultaneous production and collection of pyrolysis oil and char. Pyrolysis oils of various kinds, and with varying compositions, have recently been obtained at certain pyrolysis temperatures [1, 3, 6]. Improving the pyrolysis conditions is necessary to enable the production of more useful components and the development of selective liquefaction technology. Such an improvement is also required for the production of char. The production of composite materials from inorganic compounds [10, 11], and the conversion of biomass into porous materials [8, 10] at relatively high temperatures using pulse current pyrolysis methods have been discussed previously. Prior studies have focused on the synthesis

of materials containing acidic functional groups by conventional pyrolysis techniques at relatively low temperatures and investigated the ammonia adsorption properties [12, 13]. The application of this technology has also been considered for the functionalization of char. The production of both pyrolysis oil and char in one step is expected to result in better production efficiency and the formation of useful chemicals and functional char, in addition to improving the composition of the pyrolysis oil produced by the pulse current heating system.

The effects of the reactor temperature and the addition of catalyst on the product distribution and product characteristics under atmospheric pressure were investigated in this study. Precise determination of product distribution, pyrolysis oil composition, and functionalization of the pyrolysis char is essential for practical large-scale application of such a system. Japanese cedar wood meal, Todo-fir wood meal, and rice husk were used for pyrolysis in this study, since these raw material wastes are easily obtained. Japanese cedar is one of the most important species used in forest products in Japan, and it contributes to 53% of the total volume of sawn lumber of all wood species [14]. Todo-fir has huge accumulation volume in Hokkaido. Rice husks are estimated to be produced about 2 million ton of per year domestically [15]. The development of a suitable manufacturing technology is necessary for the effective use of biomass. The effects of pyrolysis temperature on wood biomass were analyzed using gas chromatography/mass spectrometry (GC-MS), Fourier-transform infrared (FT-IR) and Raman spectroscopy, transmission electron microscope (TEM), electron diffraction

(ED), and elemental analysis. Product distributions at a given processing temperature were determined for samples obtained with equipment that can afford pyrolysis oil and char simultaneously in the temperature range 300–800 °C. Pyrolysis oil compositions and chemical structures of aromatic compounds were characterized at each pyrolysis temperature. A relationship between the chemical structural changes of the char and increasing pyrolysis temperature was considered. The characteristic properties of ammonia adsorption capacity were also investigated.

## **2 Objectives**

The objectives of the present study are characterization of products obtained by pyrolysis of wood biomass to develop the technology for selectively obtaining useful chemical substances from sources other than fossil resources. The details of the investigations are outlined as follows.

In Chapter 1, the effects of varying pyrolysis conditions on the product distribution and product characterization under atmospheric pressure were investigated. The effects of pyrolysis temperature on woody biomass were analyzed using GC-MS, FT-IR and raman spectroscopy, and elemental analysis.

In Chapter 2, the effect of the pyrolysis condition of char obtained in air and nitrogen atmosphere on these chemical structure and adsorption behavior were investigated to clarify the mechanism of ammonia adsorption on char.

In Chapter 3, the influence of catalyst conditions was studied on the

characterization of char and pyrolysis oil used in the pyrolysis with pulse current heating. Iron oxides, titanium oxide and zeolite (ZSM-5) were used as catalysts. The effects of catalysts on wood biomass were analyzed using GC-MS, TEM and ED.

In Chapter 4, the composition of pyrolysis products obtained from rice husks, Todo-fir, and cellulose were examined as a part of the investigation on utilization of pyrolysis products from biomass. These compositions were then compared for studying the selective conversion of biomass to useful chemical substances by pulse current heating. The different effects of each ingredient in the raw materials on the products were studied by investigating the relation between the pyrolysis temperature and the compositions.

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# **Chapter 1. Production of aromatic chemicals and ammonia adsorbent by pulse current pyrolysis of woody biomass**

## **1.1 Introduction**

Pyrolysis is an important technology involving the efficient conversion of biomass materials to chemicals in a short time. Pyrolysis of wood biomass generates viscous pyrolysis oil [1-3] and char with unique properties [1, 4-6] within extremely short times. Pyrolysis employing the pulse current heating method can be applied to satisfy these requirements in the selective conversion of wood biomass to useful chemical substances. The optimization of pyrolysis conditions is necessary for improving the applicability of this heating method in the production of pyrolysis oil and char with the required characteristics.

Clarifying the composition and characteristics of the pyrolysis products obtained using the pulse current heating method is necessary in order to take full advantage of this technology. Decreasing the energy consumption and the cost of production is possible with the simultaneous production and collection of pyrolysis oil and char. The pyrolysis oils of various kinds and with varying compositions can be obtained at certain pyrolysis temperatures recently. The selective liquefaction technology is expected to occur by controlling the manufacturing conditions for producing more useful components. Prior studies have investigated the synthesis of materials containing acidic functional groups and their ammonia adsorption properties using

conventional pyrolysis techniques at lower temperatures [7, 8] and the application of this technology has also been considered for the functionalization of char. The production of both pyrolysis oil and char in one step is expected to result in benefits such as better production efficiency, synthesis of useful chemicals, and functional char in addition to improved composition of the pyrolysis oil produced by the pulse current heating system.

The effect of reactor temperature on the product distribution and product characteristics under atmospheric pressure was investigated in this chapter. Japanese cedar wood meal was used for pyrolysis in this chapter, since its raw material waste is easily obtained. The effects of pyrolysis temperature on wood biomass were analyzed using GC-MS, FT-IR, Raman spectroscopy, and elemental analysis. Product distributions at a given processing temperature were determined for samples obtained with equipment that can prepare pyrolysis oil and char simultaneously in the range of 300–800 °C. Pyrolysis oil compositions and the chemical structures of aromatic compounds were characterized at each pyrolysis temperature. A relationship between the chemical structural changes of the char as a function of increasing pyrolysis temperature was elucidated. Characteristic properties of ammonia adsorption capacity were also clarified.

## **1.2 Materials and methods**

### ***1.2.1. Pyrolysis of woody meal with pulse current heating***

Sapwood meal obtained from 30 year old Japanese cedar (*Cryptomeria japonica*) was obtained from Wakayama Prefecture and was used as a

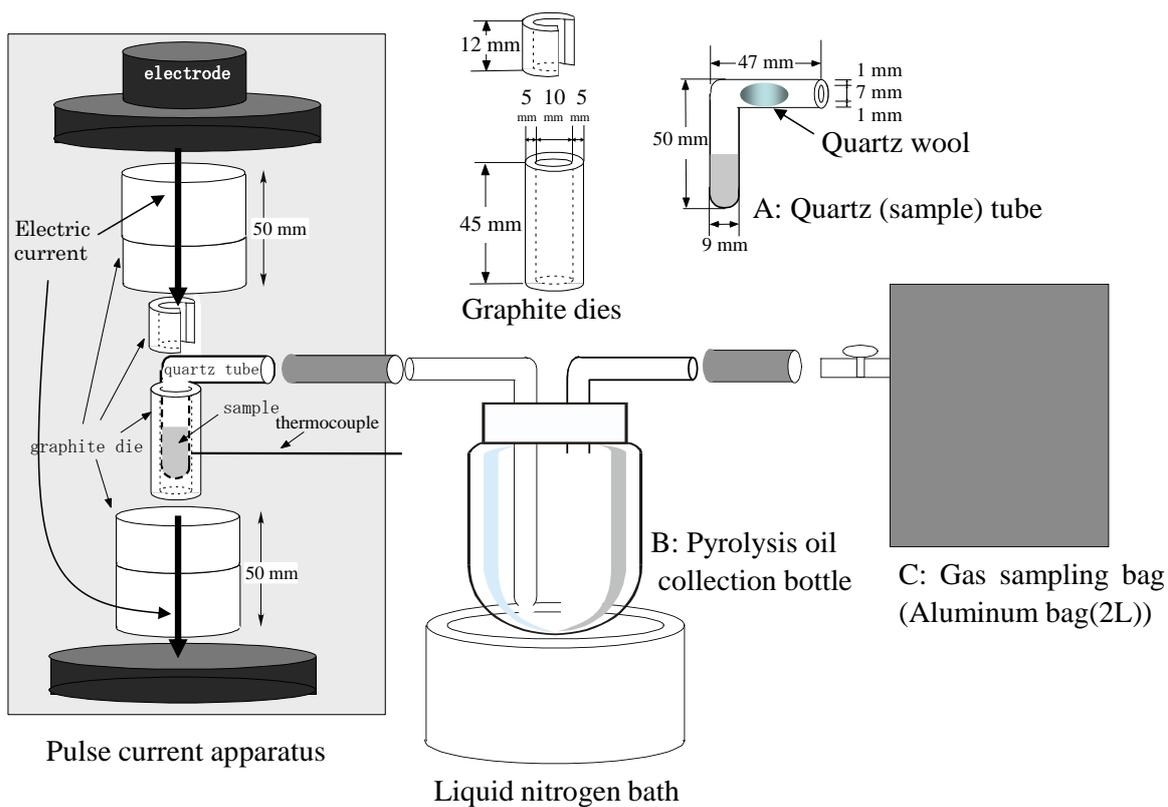


Fig. 1.1 Apparatus and method of collection of pyrolysis products: (A) graphite dies and quartz (sample) tube; (B) pyrolysis oil collection bottle; (C) gas sampling bag (aluminum bag (2 L))

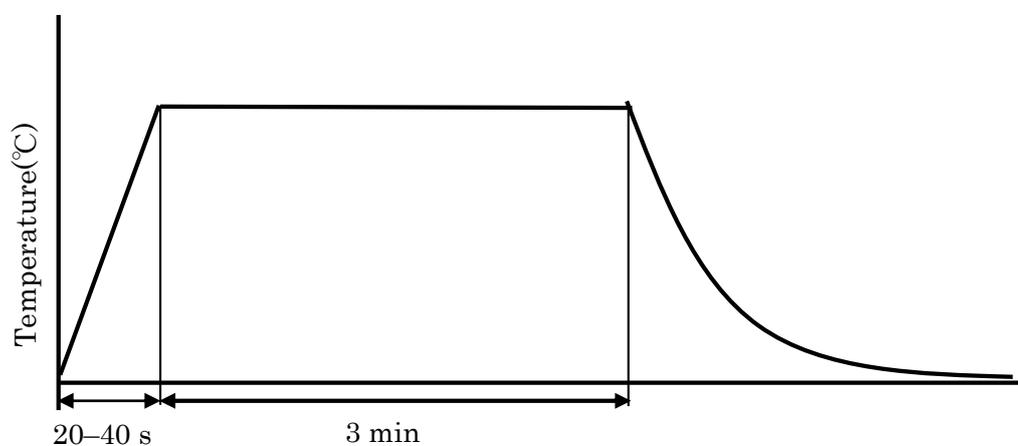


Fig. 1.2 Heating pattern of pyrolysis with pulse current apparatus.

Pyrolysis using pulse current apparatus  
at 300–800 °C for 3 min.

lignocellulosic biomass raw material. The average particle size of the wood meal ground by ball milling was approximately 21  $\mu\text{m}$ . The apparatus used for pyrolysis with pulse current heating incorporating a graphite mold [9], in which a quartz tube (Fig. 1.1 (A)) with the powder sample was inserted, was heated, as shown in Fig. 1.1. A woody powder sample (150 mg) was pyrolyzed under the heating conditions as follows. Pyrolysis was conducted at temperatures of 300  $^{\circ}\text{C}$ , 400  $^{\circ}\text{C}$ , 500  $^{\circ}\text{C}$ , 600  $^{\circ}\text{C}$ , 700  $^{\circ}\text{C}$ , and 800  $^{\circ}\text{C}$ . The heating rate and pyrolysis time were decided by referring to the report by Carlson et al. [10], in which the pyrolysis time and heating rate were 3 min and 15–20  $^{\circ}\text{C}/\text{s}$ , respectively, in order to obtain both pyrolysis oil and char effectively (Fig. 1.2). The reactor temperature was monitored using a thermocouple (Fig. 1.1). A small hole (1 mm i.d.), which did not cause any interruption to the given current, was drilled to insert the thermocouple through a graphite die.

The sample powder in the apparatus (Fig. 1.1) was pyrolyzed by electric heating. The current was raised to 700–950 A at 12–16 V for a few seconds to attain a heating rate of 15–20  $^{\circ}\text{C}/\text{s}$ , and then decreased to 200–450 A at 2–4.5 V, in order to maintain the sample at the reactor temperature. The wood meal sample was expected to be pyrolyzed with radiant heat and heat conduction efficiently by transmitting the quartz tube which was put into the graphite die. The quartz tube, collection bottle, and gas sampling bag (Fig. 1.1 (C)) were connected and constituted a closed system. An L-shaped quartz tube (Fig. 1.1 (A)) helped direct the volatiles produced by pyrolysis to the collection bottle without disturbing the electric current. The liquid fraction with the

volatilized pyrolysis oil components obtained from pyrolysis was cooled with liquid nitrogen for recovery and collected in a washing tube, as shown in Fig. 1.1 (B). The volatiles trapped inside the quartz tube and connector were washed with acetone and then analyzed quantitatively and qualitatively as pyrolysis oil. The solid fraction trapped inside the quartz tube was also collected by washing and filtering. Char samples were quantified by drying and weighing. The ash content of the Japanese cedar wood meal was determined according to the standard published procedure (Japanese Industrial Standard (JIS) M8812) [11].

### ***1.2.2. Characterization of char***

Elemental composition of carbon (C), hydrogen (H), and nitrogen (N) content in the wood meal and the char was determined using a CHN analyzer (MT-5, YANAKO, Japan). Oxygen (O) content was calculated by difference. The amount of ammonia adsorbed by the char was evaluated using the weight percent of N obtained by elemental analysis. The char was suspended in 2.0% aqueous solution of ammonia and kept at 20 °C for 72 hours, then filtered and washed with water until the filtrate became neutral. FT-IR spectra of the wood meal and the char were recorded in the transmission mode in the 4000–400  $\text{cm}^{-1}$  wavenumber range using a FT/IR-4200 spectrophotometer (Jasco, Japan). Dried KBr was used to prepare pellets from the char, with a pure KBr disc used as the background. Raman spectra of the pyrolyzed samples were recorded at room temperature using an inVia Raman spectroscope (Renishaw, UK) equipped with an air-cooled charge-coupled device (CCD) detector. An

argon laser ( $\lambda = 785 \text{ nm}$ ) was adopted as the excitation source. The laser was focused ( $\sim 1 \text{ }\mu\text{m}$  in diameter) with a power of less than 1 mW on the sample surface in order to prevent irreversible thermal degradation. Backscattered Raman spectra were measured in the  $1000\text{--}1800 \text{ cm}^{-1}$  region. The wavenumber was calibrated using the  $520 \text{ cm}^{-1}$  line of a silicon wafer.

### ***1.2.3. GC-MS analysis of pyrolysis oil***

GC-MS and semiquantitative analysis of chemical components in the pyrolysis oils were performed on a GC-MS QP-5050A instrument (Shimadzu, Japan). Tetracosane was used as an internal standard. A DB-5 capillary column was used ( $30 \text{ m} \times 0.25 \text{ mm}$  in diameter, film thickness  $1.0 \text{ }\mu\text{m}$ , Agilent, USA). The injector temperature was  $280 \text{ }^\circ\text{C}$ . The oven temperature was programmed to increase from  $30 \text{ }^\circ\text{C}$  to  $240 \text{ }^\circ\text{C}$  (5 min hold) at a rate of  $14 \text{ }^\circ\text{C}/\text{min}$ , and then from  $240 \text{ }^\circ\text{C}$  to  $310 \text{ }^\circ\text{C}$  (18 min hold) at a rate of  $30 \text{ }^\circ\text{C}/\text{min}$ . High-purity helium was used as the carrier gas with a flow rate of  $40.3 \text{ mL}/\text{min}$ . Splitless mode was used for injection. The components were identified from the obtained total ion chromatogram (TIC) by the Kovats Index method [12-20] and a mass spectral library. Peak areas from the TIC were examined for a semiquantitative analysis.

## **1.3 Results and discussion**

### ***1.3.1. Product distribution and reactor temperatures of wood meal with pulse current heating***

The ash content of the Japanese cedar wood meal sample used in this

study was 0.3%. The heating rate as well as the reactor temperature are important factors, which have a major effect on the yield of pyrolysis oil and char. Graham et al. showed the relationship between product distribution and heating rate. In their study, char was obtained as the main product at heating rates less than 10 °C/s, oil at heating rates ranging from 10 to 1,000 °C/s, and gas at heating rates greater than 1,000 °C/s [21]. The heating rate in the present study was set to 15–20 °C/s and residence time was 3 min by referring to the paper by Carlson et al. [10]

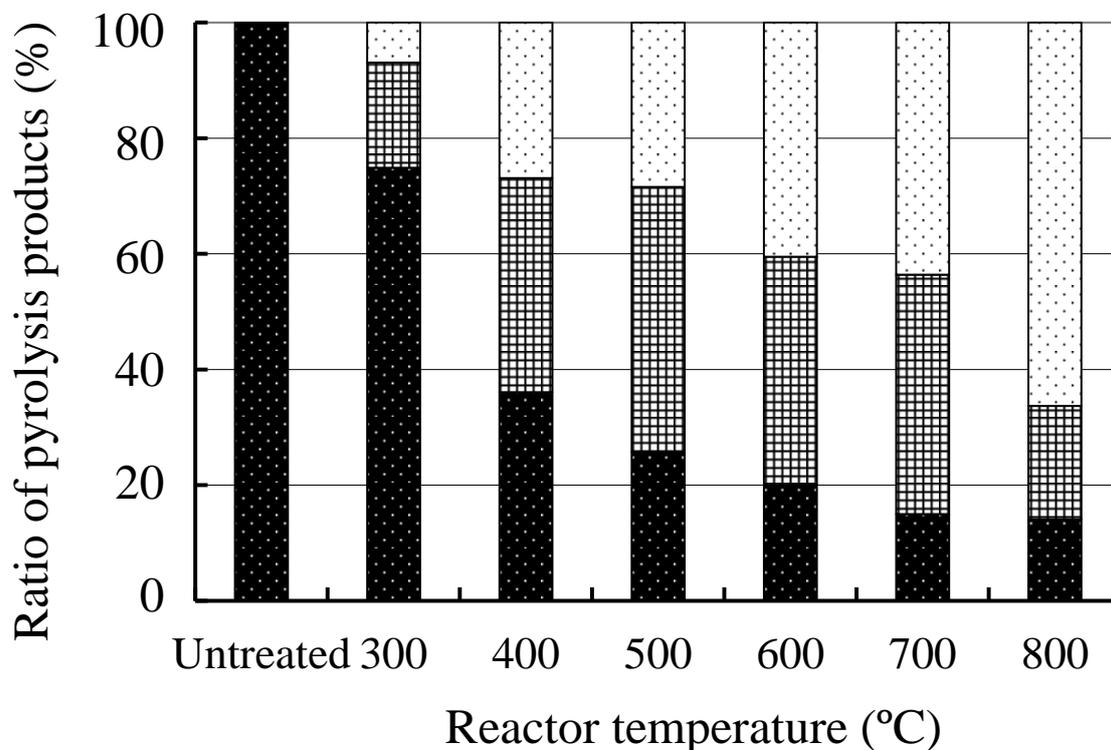


Fig. 1.3 Product distribution at various reactor temperature for Japanese cedar.

Legend:  : Gas,  : Pyrolysis oil (liquid),  : Solid (char)

The yields of both pyrolysis oil and char were consistent with expectations and agreed with the previous reports [22-24]. The pyrolysis oil yield increased with the reactor temperature in the range of 300-500 °C, and decreased from 600 °C to 700 °C, finally reaching 20% at 800 °C, as shown in Fig. 1.3. The maximum yield of pyrolysis oil was obtained between the temperatures of 400 °C and 700 °C. The yields decreased drastically at temperatures less than 400 °C. However, the decrease in yields was more gradual at temperatures greater than 700 °C. The yield of char decreased drastically at reactor temperatures of 300–400 °C and then decreased gradually to reach about 14% at 800 °C. The yields of pyrolysis oil processed at 400–700 °C were determined to be 37–46%, which were slightly lower than the values reported by fast pyrolysis methods using a fluidized bed. In contrast, the char yields at processing temperatures of 400–700 °C were 15–36%, which were comparatively higher than the yields of char obtained in fast pyrolysis. Controlling the reactor temperature is important for obtaining useful chemical substances with high yields, as evident from the observed relationship between the reactor temperature and pyrolysis oil/char yields.

### ***1.3.2. Properties and functions of char***

#### ***1.3.2.1. Elemental composition***

Table 1.1 shows the elemental compositions of the raw material and chars obtained from Japanese cedar wood meal. As can be seen from the data, the weight percentage of C increased while those of O and H decreased along

with decreasing char yields especially at reactor temperatures of 300–500 °C. The temperature for obtaining the elemental compositions of products by pyrolysis with pulse current heating was much lower than that in conventional pyrolysis, as the total pyrolysis time influences the chemical reaction during pyrolysis. The elemental compositions and yields of the pyrolysis residue showed almost the same values at 700 °C and 800 °C, while the composition ratios varied with an increase in carbon content between 300 and 700 °C. The reactor temperature at which a similar char composition ratio was obtained via pyrolysis with pulse current heating was higher than the temperature used in conventional pyrolysis by 100 °C [8]. The compositions of char pyrolyzed at 300 °C, 400 °C, 500 °C, 600 °C, and 700–800 °C using pyrolysis with pulse current heating were close to those observed in the ranges of 190–260 °C, 310 °C, 310–400 °C, 400–500 °C, and 500–700 °C, respectively, in conventional pyrolysis [8].

Table 1.1 Results of elemental analysis of char obtained from Japanese cedar wood meal pyrolyzed in the temperature range of 300 - 800 °C

	Reactor temperature (°C)						
	Untreated	300	400	500	600	700	800
H (%)	6.1	5.9	4.9	3.9	3.3	2.7	2.3
C (%)	49.3	53.7	70.2	75.0	81.5	87.7	87.0
N (%)	0.0	0.1	0.2	0.2	0.2	0.3	0.4
O <sup>a</sup> (%)	44.5	40.3	24.7	20.8	15.0	9.3	10.3
Char (%)	100.0	74.9	36.1	25.7	20.1	15.0	14.1

a: by difference

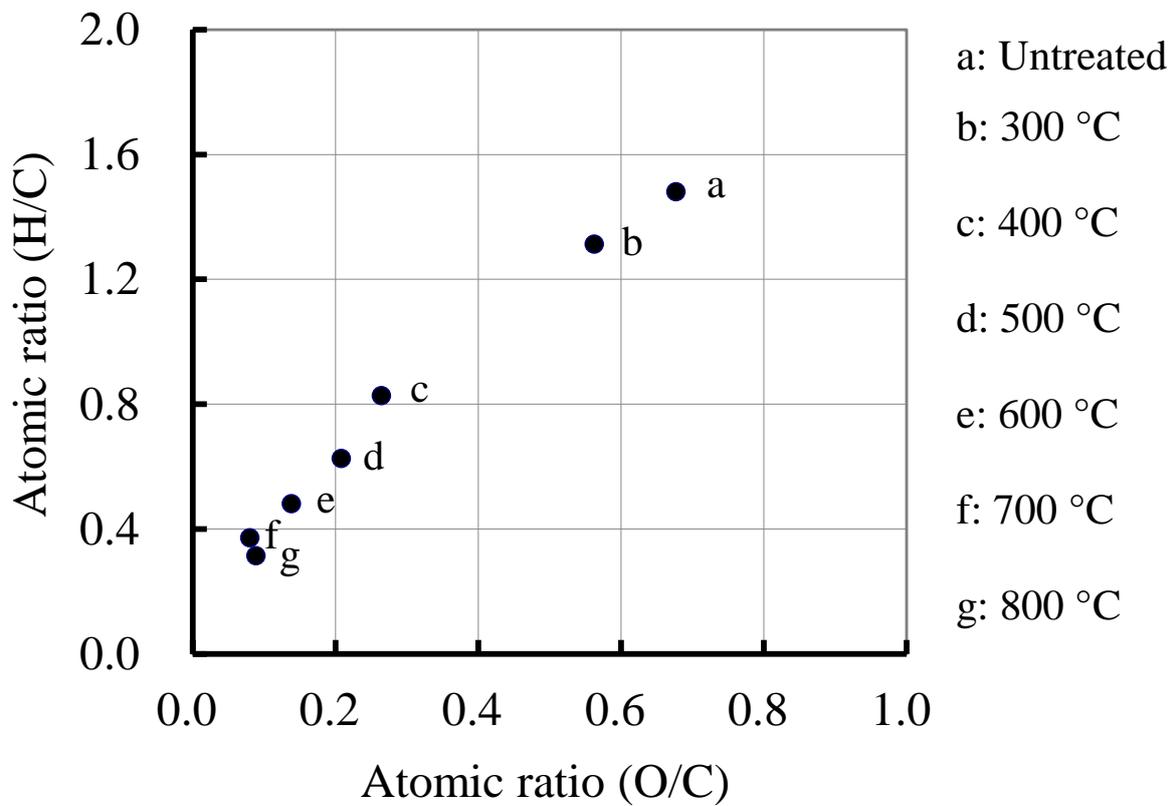


Fig. 1.4 Van Krevelen diagram for char obtained from Japanese cedar wood meal pyrolyzed in the temperature range of 300–800 °C.

Figure 1.4 shows a van Krevelen diagram obtained by plotting the H/C versus O/C atomic ratios of char, which were measured by the CHN analyzer. The curve is useful for following the decomposition reactions taking place during pyrolysis, such as dehydration, decarboxylation, and dehydrogenation, by evaluating the directions of the curves. Each thermal decomposition process during pyrolysis with pulse current heating occurred at reactor temperatures that were 100 °C lower than the corresponding temperatures in conventional slow pyrolysis as follows. Dehydration, decarboxylation, and demethanization were suggested to progress at 300–400 °C, followed by aromatization, in conventional pyrolysis of Japanese cedar [8]. Elimination of functional groups, dehydrogenation, and condensation/polycyclic aromaticization progressed at 400–500 °C [8]. The hexagonal network planes of the graphitic structure were believed to form via condensation of polycyclic aromatic structures mainly by dehydrogenation above 500 °C [8].

#### *1.3.2.2. FT-IR analysis*

The effects of reactor temperature on the chemical structure of Japanese cedar wood meal residue were studied next. The results of FT-IR spectroscopy are depicted in Fig. 1.5. Spectral changes before and after pyrolysis suggested the disappearance of absorptions attributable to oxygen functional groups in char and aromatization of polysaccharide components (e.g., cellulose) at 600 °C, 700 °C, and 800 °C, while no significant spectral changes were observed in the spectra for chars obtained at 300 °C. A decrease in absorption around 3400 cm<sup>-1</sup> attributed to the hydroxyl group (O–H) bond

stretching vibration, a decrease in the absorption around  $2900\text{ cm}^{-1}$  due to the aliphatic C–C bond stretching vibration, and an increase in the absorption due to aromatic C=C bond stretching vibrations at  $1595\text{ cm}^{-1}$  were observed at reactor temperatures from  $400\text{ }^{\circ}\text{C}$  to  $500\text{ }^{\circ}\text{C}$ , suggesting a decrease in the number of hydroxyl groups by dehydration and aromatization of the multi-sugar components present in the wood meal.

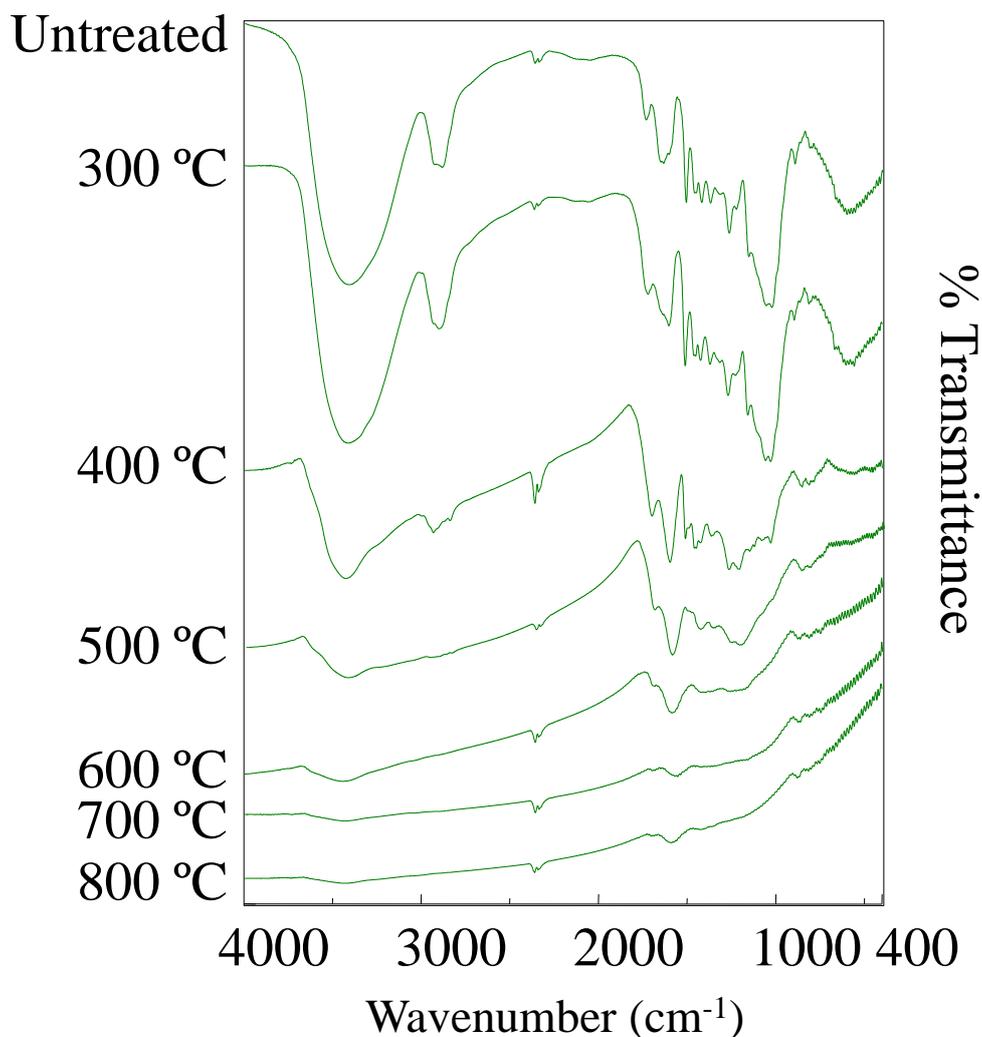


Fig. 1.5 FT-IR spectra of char obtained from Japanese cedar wood meal pyrolyzed in the temperature range of  $300\text{--}800\text{ }^{\circ}\text{C}$ .

Reactor temperatures were lower compared to those used in conventional slow pyrolysis by about 100–200 °C, in order to obtain chemical composition of char similar to those as shown in Chapter 2. The reason for this result is that fewer reactions involving chemical structural changes could occur because of shorter pyrolysis times in pyrolysis with pulse current heating compared to conventional pyrolysis, as mentioned before. The influence of heating conditions on the chemical structure of char was remarkable, especially at 300–400 °C.

### *1.3.2.3. Raman spectral analysis*

Raman spectroscopy was performed by focusing on the changes in absorption of the D- and G-bands to gain information on the structural change in carbon and graphitization with increased reactor temperatures. We noted minimal chemical structural changes in the char during pyrolysis from 400 °C to 800 °C. The amount of amorphous components in chars obtained by pyrolysis with pulse current heating can be evaluated from the G- to D-band ratio (G/D), where the G-band absorption peak originating from the graphitic structure of sp<sup>2</sup> hybridized carbons with lattice vibration appears at 1590 cm<sup>-1</sup> and the D-band absorption peak originating from amorphous carbon appears at 1350 cm<sup>-1</sup>. The absorptions attributed to the D- and G-bands became clearer by increasing the reactor temperatures from 400 °C to 800 °C. The G/D ratio [25], I<sub>1580</sub>/I<sub>1360</sub> varied from 0.98 to 1.03, and no further significant changes were observed at different reactor temperatures. Previous reports have correlated the aromatic character of pyrolysis products to the

presence of absorption peaks in Raman spectra corresponding to D- and G-bands in char pyrolyzed at 700–900 °C and at 600–900 °C by fast pyrolysis [26, 27].

#### *1.3.2.4. Ammonia adsorption capacity*

The effects of reactor temperature on ammonia adsorption capacities in the liquid phase were examined to evaluate the functionalization of char obtained by pyrolysis of Japanese cedar with pulse current heating. The amount of ammonia adsorbed by the char was evaluated using the weight percent of N obtained by elemental analysis. The amount of ammonia adsorption increased at reactor temperatures from 300 °C to 500 °C and then decreased from 600 °C to 800 °C, as shown in Fig. 1.6. The maximum ammonia adsorption was found for the char pyrolyzed at about 500 °C. The formation of acidic functional groups and its relation to ammonia adsorption capacities in carbonized wood have been previously reported for conventional slow pyrolysis processes at approximately 300 °C as shown in Chapter 2. The maximum amount of ammonia adsorption was obtained at approximately 300 °C, as elimination of acid functional groups occurred above 400 °C [7, 8].

Minimal changes in the chemical structure during heating were observed in the FT-IR spectrum of wood meal by pyrolysis with pulse current heating at 300 °C, as very few acidic functional groups were generated, while adsorption peaks corresponding to residual oxygen functional groups were observed in the char by pyrolysis with pulse current heating at 500 °C, as shown in Fig. 1.5. The difference between the reactor temperature for acid

functional group formation and elimination and that required for maximum ammonia adsorption, was due to the difference in pyrolysis time between pyrolysis with pulse current heating and conventional slow pyrolysis. The chemical structure of char is considered to be the main factor influencing ammonia adsorption capacities. The char obtained by pyrolysis at 500 °C was determined to possess both carboxyl and hydroxyl groups, suitable for ammonia adsorption in the present study.

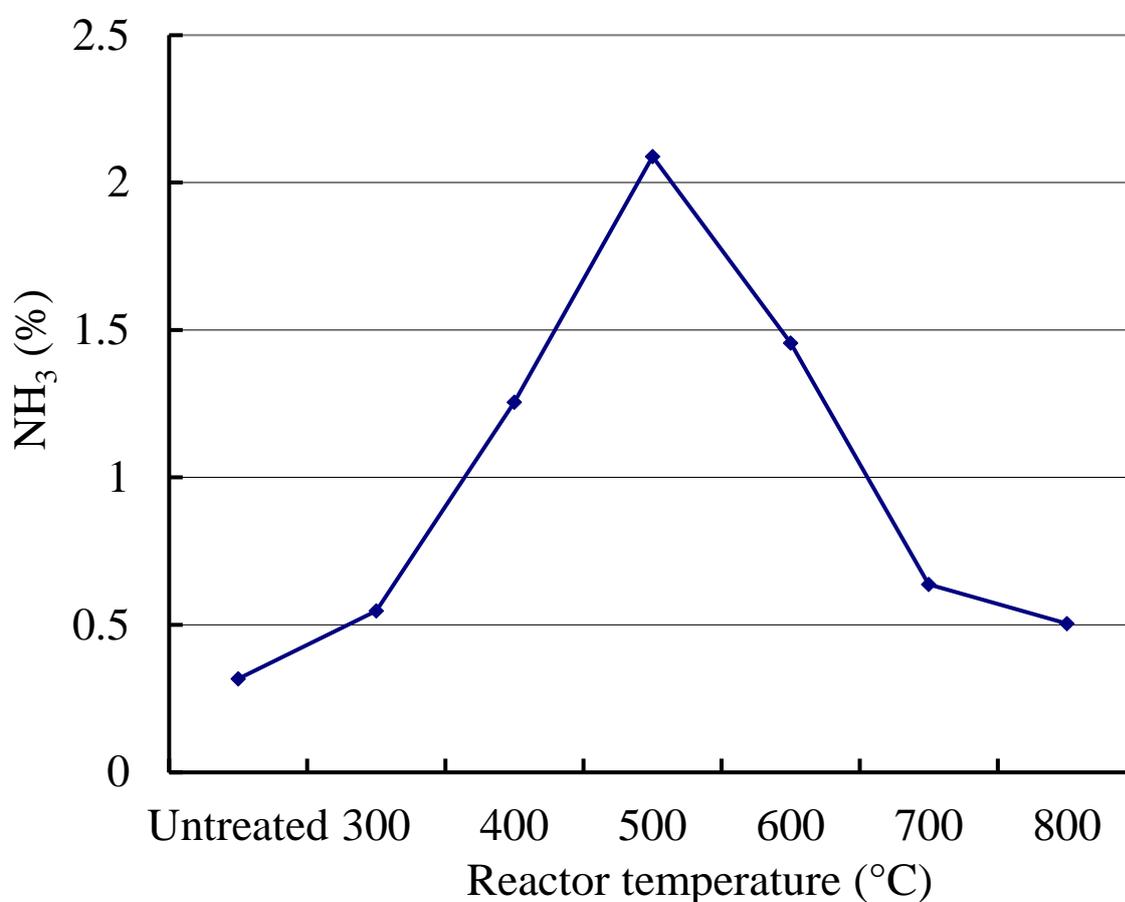


Fig. 1.6 Adsorption of ammonia on the char obtained from Japanese cedar wood meal pyrolyzed in the range of 300–800 °C.

The ash content of chars was not considered to affect the capacity of ammonia adsorption for the following reason. The char obtained at 800 °C exhibited the lowest ammonia adsorption, although the ash content under this condition were higher compared to those obtained under other pyrolysis conditions. In addition, the ash content of the wood meal raw material was 0.3%, as described in the previous section. Therefore, the ash contents of the chars obtained at 500 °C and 800 °C were speculated to be 1.2% and 2.0%, respectively, from each yield and these ash content values were considered to be too small to affect the capacity of ammonia adsorption.

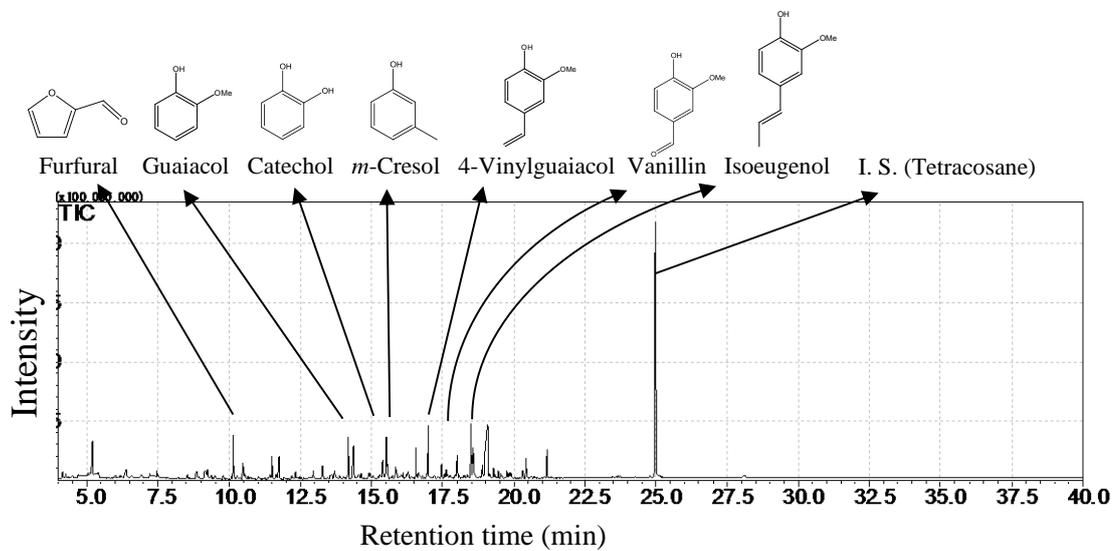
### ***1.3.3. Compositions of pyrolysis oil***

The composition of pyrolysis oil tended to change with the reactor temperatures employed. Aromatic compounds containing oxygen functional groups were observed in the pyrolysis oil obtained at reactor temperatures of 400–500 °C, and aromatic/polycyclic aromatic hydrocarbons were obtained in the pyrolysis oil at 800 °C, in agreement with a report describing the influence of reactor temperature on the chemical properties of pyrolysis oil [28, 29]. Aromatic compounds originating mainly from lignin were observed at pyrolysis temperatures between 500 °C and 800 °C, as shown in Table 1.2, and Fig. 1.7. Compounds with oxygen functional groups, such as isoeugenol and 4-vinylguaiacol, were observed in the pyrolysis oil pyrolyzed at 500 °C. In contrast, for the pyrolysis oil pyrolyzed at 800 °C, those components were detected in only minimal amounts, while more aromatic and polycyclic aromatic hydrocarbon species, such as naphthalene and anthracene, were

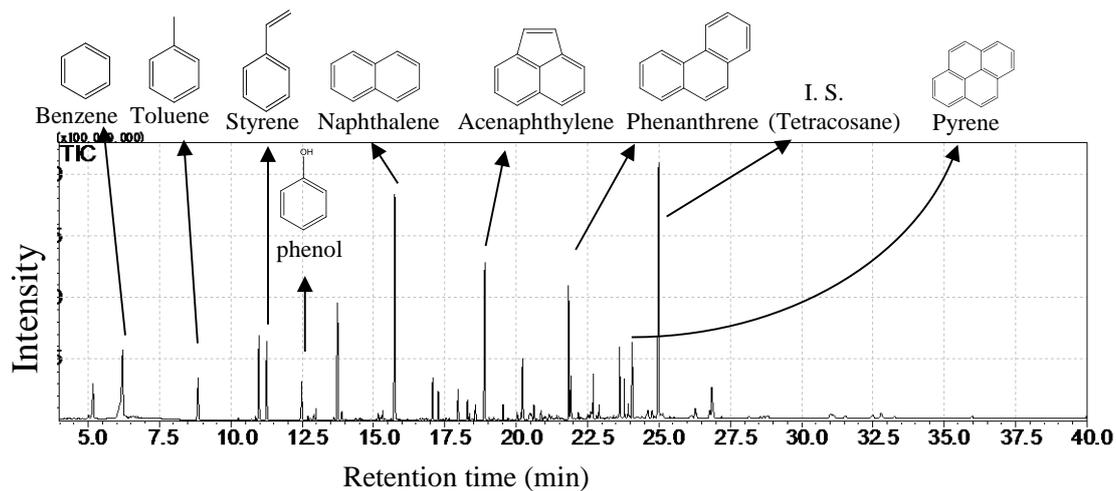
observed. This result suggested that aromatic compounds in pyrolysis oil condensed into polycyclic aromatic hydrocarbon species at temperatures around 800 °C, as described by Elliott et al. [29].

Table 1.2 GC-MS semiquantitative analysis of pyrolysis oil components obtained from Japanese cedar wood meal pyrolyzed at 500 °C and 800 °C.

Retention time (min.)	Pyrolysis oil pyrolyzed at 500 °C area/I. S, area	Pyrolysis oil pyrolyzed at 800 °C area/I. S. area
6.21 Benzene	-	0.63
8.85 Toluene	-	0.18
10.14 Furfural	0.12	-
10.97 Ethynylbenzene	-	0.26
11.25 Styrene	-	0.24
12.48 Phenol	-	0.12
13.74 1-Propynylbenzene	-	0.50
14.19 Guaiacol	0.11	-
15.40 Catechol	0.09	-
15.57 <i>m</i> -Cresol	0.16	-
15.77 Naphthalene	-	0.95
17.07 Methyl-naphthalene	-	0.12
17.45 Eugenol	0.04	-
17.95 Biphenyl	-	0.10
18.00 Vanillin	0.08	-
18.49 Isoeugenol	0.12	-
18.89 Acenaphthylene	-	0.59
20.22 <i>o</i> -Biphenylenemethane	-	0.24
21.84 Phenanthrene	-	0.37
21.91 Anthracene	-	0.14
24.05 Pyrene	-	0.29
25.00 Internal Standard (Tetracosane)	1.00	1.00



Pyrolyzed at 500 °C



Pyrolyzed at 800 °C

Fig. 1.7 Total ion chromatogram (TIC) of pyrolysis oil obtained from Japanese cedar wood meal pyrolyzed at 500 °C and 800 °C by GC-MS.

Only small amounts of levoglucosan were detected. Furfural, on the other hand, was detected as a component of the pyrolysis oil obtained from hemicellulose in Japanese cedar pyrolyzed at 400–800 °C. Patwardhan et al. reported that the yields of levoglucosan dropped remarkably in the presence of small amounts of alkali metals and alkaline earth metals in pyrolysis oil obtained from the fast pyrolysis of cellulose [30]. The ash content of Japanese cedar wood meal sample was 0.3% as mentioned before. In addition, Okada et al. reported on the amount of inorganic elements such as Na (28 ppm), K (1,300 ppm), Rb (2.2 ppm), Mg (92 ppm), Ca (530 ppm), Mn (0.85 ppm), and Cl (22 ppm) contained in the xylem of Japanese cedar wood [31-32]. The above result suggests that the composition of pyrolysis oil obtained from wood meal is affected by inorganic salts, in a manner similar to that previously reported [30].

The characteristic ammonia adsorption property was found in the pyrolysis products (char) obtained with pulse current heating method. On the other hand, similarities in product distribution and the composition of pyrolysis oil were found between the pyrolysis products generated with the fluidized bed reactor and with the pulse current heating method. The product distribution resulting from fast pyrolysis in a fluidized bed reactor conducted under similar heat treatment conditions and pyrolysis time, was similar to those obtained in this study, although the feedstock species were different [33,34]. A similar trend was observed in the composition of the pyrolysis oil obtained by Mohan et al. [28]. The heating rate in this study was remarkably

faster than that of slow pyrolysis, and slightly slower than that of fast pyrolysis in a fluidized bed reactor. Therefore, the pyrolysis oil was obtained with higher yields with the pulse current heating method compared to that with slow pyrolysis. Pyrolysis oil and char were obtained simultaneously, which is not easy in slow pyrolysis. Shortening of the pyrolysis time along with an improvement in the property of the pyrolysis oil and energy efficiency are expected with the pulse current heating method utilized in this study.

#### **1.4 Summary**

The production of chemicals and functional materials from renewable biomass resources has received considerable interest. In this chapter, we have applied rapid pyrolysis by pulse current heating for this purpose. Japanese cedar wood was pyrolyzed at various temperatures by pulse current heating, and the compositional and structural changes in the degraded products were characterized using GC-MS, FT-IR, Raman spectroscopy, and elemental analysis. We found that ammonia was adsorbed on the char obtained by the pyrolysis at 500 °C and observed a sharp dependence of the adsorptivity on the pyrolysis temperature. Under this condition, phenolic compounds such as guaiacol, catechol, 4-vinyl guaiacol, and vanillin were produced as the major components of the pyrolysis oil. Deoxygenation proceeded linearly as a function of the pyrolysis temperature and that pyrolysis at 800 °C produced aromatic hydrocarbons such as naphthalene, acenaphthylene, anthracene, and pyrene along with the current platform chemicals such as benzene, toluene, and styrene. The functionality of residual char as an ammonia

adsorbent and the co-production of aromatic chemicals can be highlighted as a new process designed for efficient usage of woody biomass.

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## **Chapter 2. Effects of chemical structure and pyrolysis conditions on the ammonia adsorption capacity of char**

### **2.1 Introduction**

As it is possible to impart a variety of properties to wood charcoal by controlling the pyrolysis conditions during its production, wood charcoal can be used in a number of applications such as fuel, soil improvement, electromagnetic shielding material, and environmental cleaning; further assessment of its performance is underway [1]. The performance of wood charcoal, when used as an adsorbent, depends on its surface properties, mainly on the specific surface area and chemical structure. The specific surface area could be improved by activation, and the chemical structure could be improved by varying the pyrolysis temperature, atmosphere, and time. In Chapter 1, the functionality of residual char as an ammonia adsorbent was described as a new process designed for efficient usage of woody biomass. The investigation on the relationships between the pyrolysis conditions and its adsorption property, chemical structure was required for more effective preparation of ammonia adsorbent.

Wood material obtained by relatively low-temperature pyrolysis, such as at temperatures below 400 °C, contained a large number of acidic functional groups on its surface [2], thus improving the ability to adsorb basic substances such as ammonia [3] or heavy metals [4]. The contribution of the acidic functional groups on the activated carbon surface, obtained by oxidation, to the adsorption in gas or liquid phase and the effect of solvent

vapor on the adsorption characteristics have been reported previously [5–7]. Oka et al. conducted the oxidation of peat humic acid in the gas and liquid phases and reported the reactivity of the resulting acidic functional groups to ammonia [8]. Therefore, the adsorption of ammonia can be increased by conducting some oxidation treatment to increase the number of acidic functional groups during pyrolysis. Herein, we report the difference in the chemical structure of wood charcoal obtained below 400 °C in the presence or absence of oxygen, and its effect on the adsorption of ammonia. The effect of the atmosphere during pyrolysis on the adsorption abilities of wood charcoal from Hinoki (*Chamaecyparis obtusa*) and Japanese oak (*Quercus mongolica*) were studied by Abe et al. [9]. In this report, the adsorption properties of the charcoal obtained in the temperature range 400–1000 °C under nitrogen and air atmosphere were considered. Although pyrolysis under a nitrogen and air atmosphere have been reported, the resulting chemical structure has been rarely reported. In particular, the relationship between the pyrolysis conditions near 300 °C and the adsorption ability of the resulting charcoal has been rarely reported.

In this chapter, we report the chemical structure of Todo-fir charcoal and the relationship between its ammonia adsorption ability and production conditions for application as a wood adsorbent. The findings on the effect of the acidic functional groups produced during the conventional pyrolysis system under oxygen atmosphere on the adsorption of bases such as ammonia are reported here.

## **2.2 Materials and methods**

### ***2.2.1 Raw material***

Todo-fir (*Abies sachalinensis*) fiber and powdered cellulose were used for pyrolysis. The Todo-fir fiber used here was obtained by the steam defibration of Todo-fir chips at 0.84 MPa pressure for 6 min using pressurized double disk refiner (PDDR). Commercially available cellulose (CF-11, Whatman, USA) was used.

### ***2.2.2 Pyrolysis***

Five grams of air-dried material was placed in a porcelain crucible and covered with a lid, and the char was prepared using an air-tight box-type electric furnace (Tokai Denki, Japan). The rate of increase in temperature was 0.3 °C/min, and after maintaining 100 °C for 1 h and 250–400 °C for 2 h, the char was allowed to cool naturally. For determining the effect of atmosphere and particularly the effect of the presence of oxygen on the properties of the product, the study was conducted in the presence and absence of nitrogen. The resulting Todo-fir char was pulverized using a vibration ball mill TI-100 (HEIKO, Japan), and the fraction of 100 mesh or below was used for various investigations. Commercially available chromatography-grade activated carbon (Wako Pure Chemical Industries, Japan) and activated carbon for ammonia were used as the references.

### ***2.2.3 Elemental analysis***

The elemental analysis of the char was conducted using a CHN corder

MT-3 (YANACO, Japan). The weight of the sample analyzed was 2 mg. The oxygen (O) content was calculated by difference.

#### ***2.2.4 Fourier transform-infrared analysis***

The Fourier transform-infrared (FT-IR) spectra were obtained by the KBr tablet method using a FT-IR spectrophotometer FT/IR-8900 (JASCO, Japan). The weight of the sample used for the analysis was 1 mg.

#### ***2.2.5 Boehm's method***

Following the Boehm method [10], the amount of acidic functional groups was determined from the quantity of alkali adsorbed by the char sample. Approximately 0.2 g of the sample was suspended in 20 mL aqueous solutions of 0.1 N sodium hydroxide (NaOH) and sodium bicarbonate ( $\text{NaHCO}_3$ ), kept undisturbed at 25 °C for 196 h, and then filtered. After washing with water until the filtrate became neutral, the filtrate was titrated with an aqueous solution of 0.1 N HCl. The amounts of NaOH and  $\text{NaHCO}_3$  adsorbed were determined as the total acidic functional groups and strongly acidic functional groups, respectively. The IR spectrum of the char after the alkali adsorption was obtained to examine the change in the chemical structure of the char.

#### ***2.2.6 Ammonia gas adsorption test***

The adsorption isotherm at 40 °C was obtained using a gas sorption analyzer OMNISORP 100 (Beckman Coulter, USA), and the ability of the char

for adsorbing ammonia was evaluated. The IR spectrum of the char after the ammonia adsorption was obtained, and the change in the chemical structure of the char was examined.

## **2.3. Results and discussion**

### ***2.3.1 Yield and chemical composition of char***

The effect of the presence or absence of nitrogen during the pyrolysis was compared based on the yield and elemental analyses. The relationship between the Todo-fir pyrolysis temperature and the yield and elemental composition is shown in Table 2.1.

Under nitrogen atmosphere, the yield decreased significantly in the range 200–300 °C; however, the yield did not decrease significantly in the range 300–400 °C. On the other hand, under air atmosphere, the yield decreased significantly, slightly linearly in the temperature range 200–400 °C. This trend was quite similar to the various patterns of the thermogravimetric curves obtained earlier under nitrogen and air atmosphere [11,12]. This was attributed to the increase in the rate of the weight loss due to the presence of oxygen in the pyrolysis stage in the case of cellulose-based material [13,14]. Accordingly, the relationship between the atmosphere and yield may be attributed to the presence of oxygen in the nitrogen in the pyrolysis apparatus used in this study.

The elemental analysis (Table 2.1) showed no drastic change in the content of various elements in the char obtained under nitrogen atmosphere. With increasing temperature, the carbon content gradually increased,

whereas the oxygen and hydrogen contents gradually decreased. On the other hand, under nitrogen atmosphere, noticeable changes in the carbon and oxygen contents of the char was observed near 300 °C. Compared to the char prepared under air atmosphere, higher carbon and lower oxygen contents were observed. When compared to the van Krevelen diagram (Fig. 2.1) [15],

Table 2.1 Results of elemental analysis of Todo-fir wood char.

	Reactor temperature (°C)						
	Untreated	250	275	300	325	350	400
Todo-fir wood and char (in nitrogen)							
Yield (%)	-	87.82	72.95	52.11	46.88	42.81	39.21
H (%)	6.17	5.61	5.35	4.8	4.69	4.34	3.73
C (%)	49.85	53.86	58.48	70.33	72.58	74.58	76.9
O <sup>a</sup> (%)	43.91	40.36	35.98	24.7	22.56	20.92	19.2
N (%)	0.07	0.17	0.19	0.17	0.17	0.16	0.17
Todo-fir wood and char (in air)							
Yield (%)	-	63.16	48.03	44.34	38.89	26.58	15.07
H (%)	6.17	3.96	2.8	2.61	2.44	2.39	2.63
C (%)	49.85	57.02	60.74	61.17	61.33	62.76	64.25
O <sup>a</sup> (%)	43.91	38.87	36.3	36.06	36.08	34.64	32.79
N (%)	0.07	0.15	0.16	0.16	0.15	0.21	0.33

a: by difference

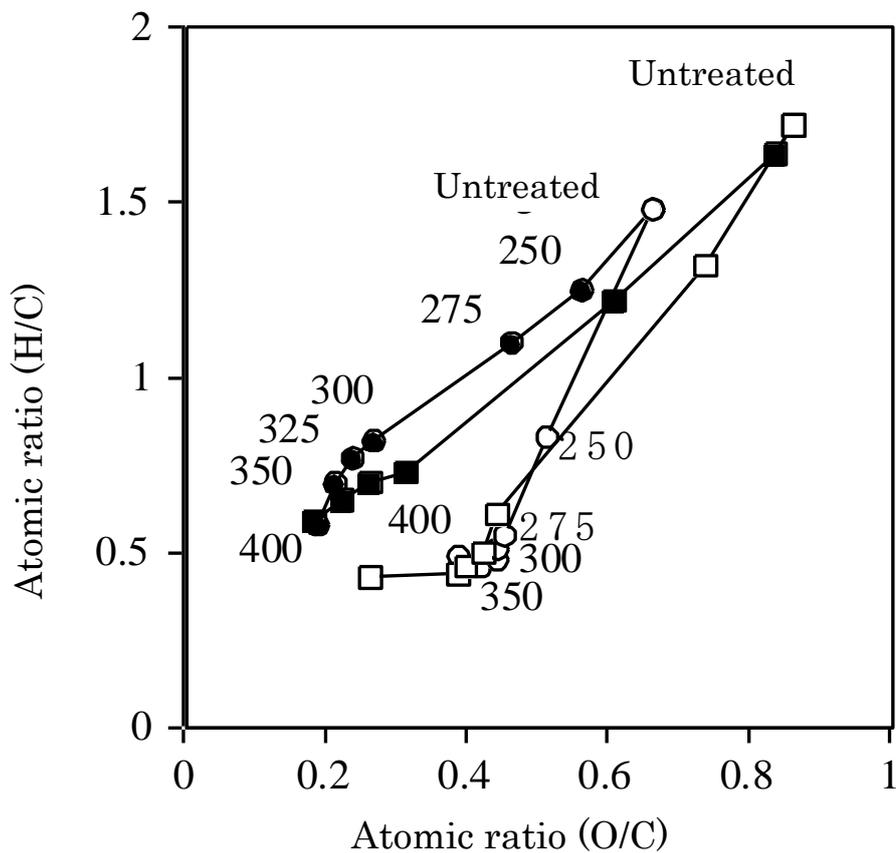


Fig. 2.1. Van Krevelen diagram for char obtained from Todo-fir and cellulose.

- Legend:
- :Todo-fir char (in nitrogen),
  - :Todo-fir char (in air),
  - :Cellulose char (in nitrogen),
  - :Cellulose char (in air).

the effect of the atmosphere during the pyrolysis on the changes in the chemical composition of the product became clearer. Under a nitrogen atmosphere, the dehydration up to 275 °C and the decarboxylation and decarbonylation in the range 275–400 °C have been reported [15–17]. Under

air atmosphere, in the range 200–300 °C, the O/C ratio decreased gradually; however, the H/C ratio decreased significantly, indicating demethanation and the progress in dehydrogenation. Moreover, in the range 300–400 °C, the O/C ratio decreased, while the H/C ratio did not change, indicating decarboxylation. This is because of the gradual reduction in the O/C ratio due to the noticeable formation of oxygen-containing functional groups, such as carboxylic acid groups, in the range 200–300 °C and reduction only in the O/C ratio in the range 300–400 °C because of their sudden removal. In the pyrolysis under air atmosphere, the cellulose char also showed similar properties as Todo-fir char, such as the significant reduction in the H/C ratio despite a gradual decrease in the O/C ratio in the range 200–300 °C.

### ***2.3.2 Chemical structure of char***

The effect of the presence or absence of nitrogen on the chemical structure of the char was compared by the alkali adsorption and IR analyses.

The results of the alkali adsorption test for Todo-fir wood and cellulose char are shown in Fig. 2.2. In the case of Todo-fir char, although a distinct maximum value in the quantity of NaHCO<sub>3</sub> adsorbed was not observed in the sample obtained under nitrogen atmosphere, the quantity of NaOH adsorbed shows the maximum value at 300 °C. In the case of the sample obtained under air atmosphere, convex-shaped curves were obtained for the NaOH and NaHCO<sub>3</sub> adsorptions, showing the maximum values near 300 °C. In the case of cellulose char, the quantities of NaOH and NaHCO<sub>3</sub> adsorbed showed the peaks 300 °C under each atmosphere. In other words, under each atmosphere,

both the quantity of total acidic functional groups and strongly acidic functional groups showed the maxima near 300 °C and decreased with pyrolysis temperature. Depending on the pyrolysis atmosphere, however, the details differed. Thus, in the case of char obtained under nitrogen atmosphere, strongly acidic functional groups were almost absent. In contrast, in the case of the char obtained under air atmosphere, their proportion was high, and the quantity of total acidic functional groups was significantly higher than that in the case of the char obtained under nitrogen atmosphere. This was in agreement with the trend of the formation and removal of the oxygen-containing functional groups according to the difference in the atmosphere, as determined by the elemental analyses. Further, the existence of oxygen at the time of pyrolysis affects not only the yield and chemical composition, but also the chemical structure, particularly the strongly acidic functional groups.

When the quantities of alkali adsorbed as shown in Fig. 2.2 were compared, a distinct peak 300 °C was observed in the case of cellulose char, while in the case of Todo-fir, no such distinct peak was observed. Further, at the pyrolysis temperature 250 °C, the quantity of alkali adsorbed in the case of Todo-fir char was higher than that in the case of cellulose char. This is probably mainly because of the presence of hemicellulose because the pyrolysis of hemicellulose may have started at a lower temperature than cellulose; however, in that case, there was a higher possibility for the formation of acidic functional groups because of the similar behavior as the pyrolysis of cellulose. From the results of the changes in the chemical structure after the pyrolysis of filter paper and pulp reported by Kuriyama

[17], the carbonyl groups formed during the change in the chemical structure due to the pyrolysis of wood at 180–260 °C may have originated from hemicellulose. The peak for the maximum value of the amount of alkali adsorbed, similar to the case of Todo-fir pyrolysis, may be attributed to the effect of physical factors such as the fibrous structure or assembly with hemicelluloses and lignin in the wood.

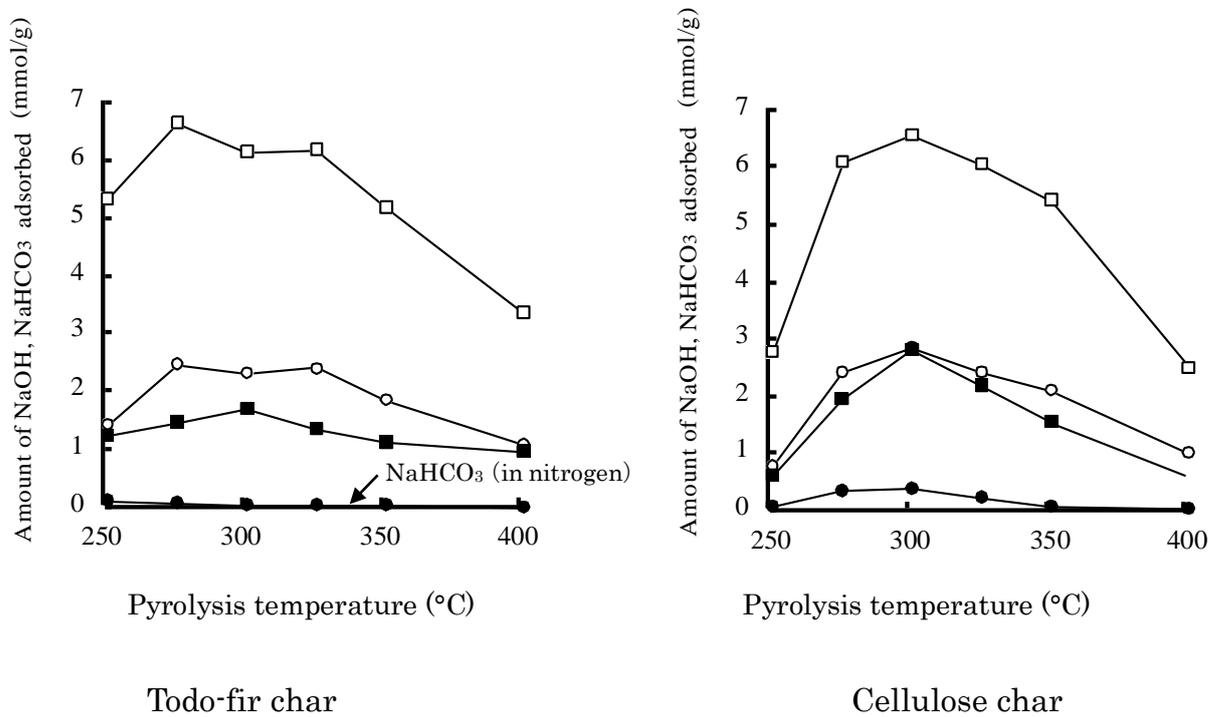
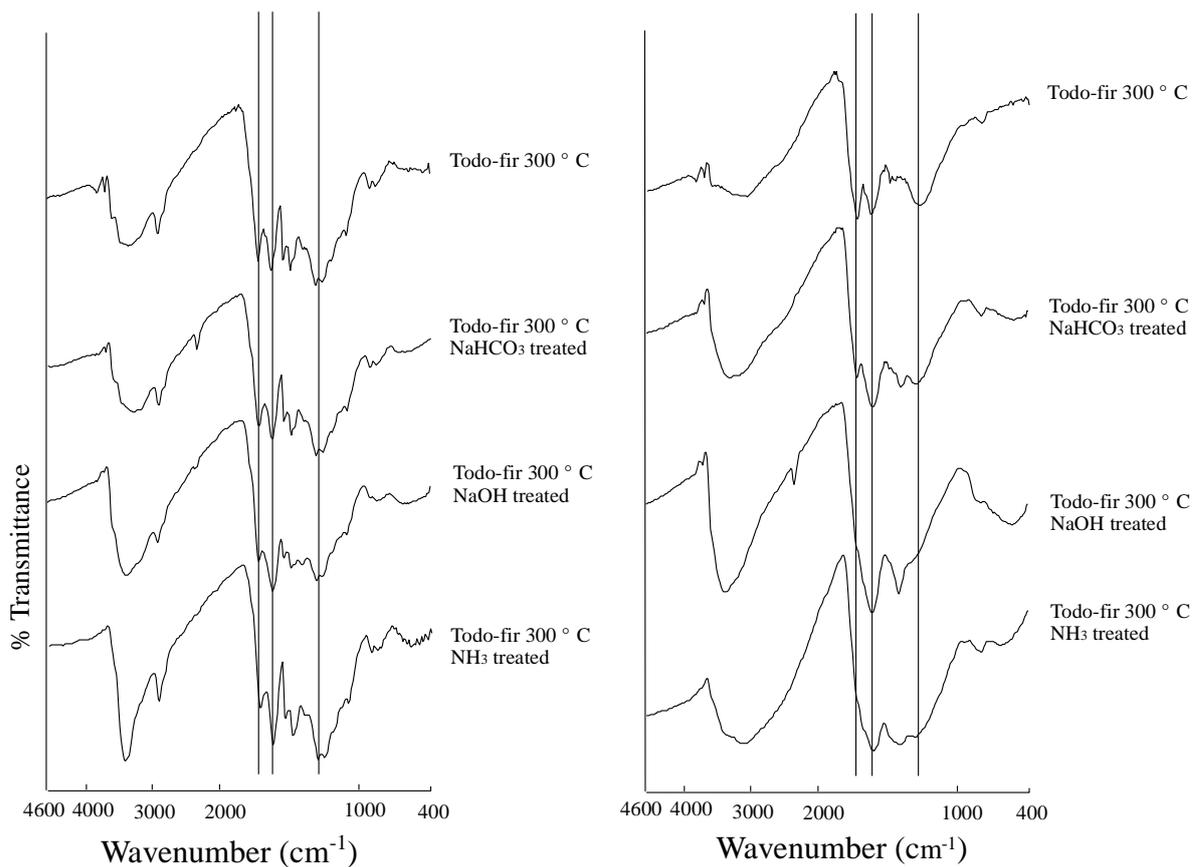


Fig. 2.2 Relationship between pyrolysis temperature and amount of NaOH and NaHCO<sub>3</sub> adsorption of Todo-fir wood char and cellulose char.

Legend: □: NaOH (in air), ○: NaHCO<sub>3</sub> (in air),  
 ■: NaOH (in nitrogen), ●: NaHCO<sub>3</sub> (in nitrogen).



(a) Pyrolyzed in nitrogen

(b) Pyrolyzed in air

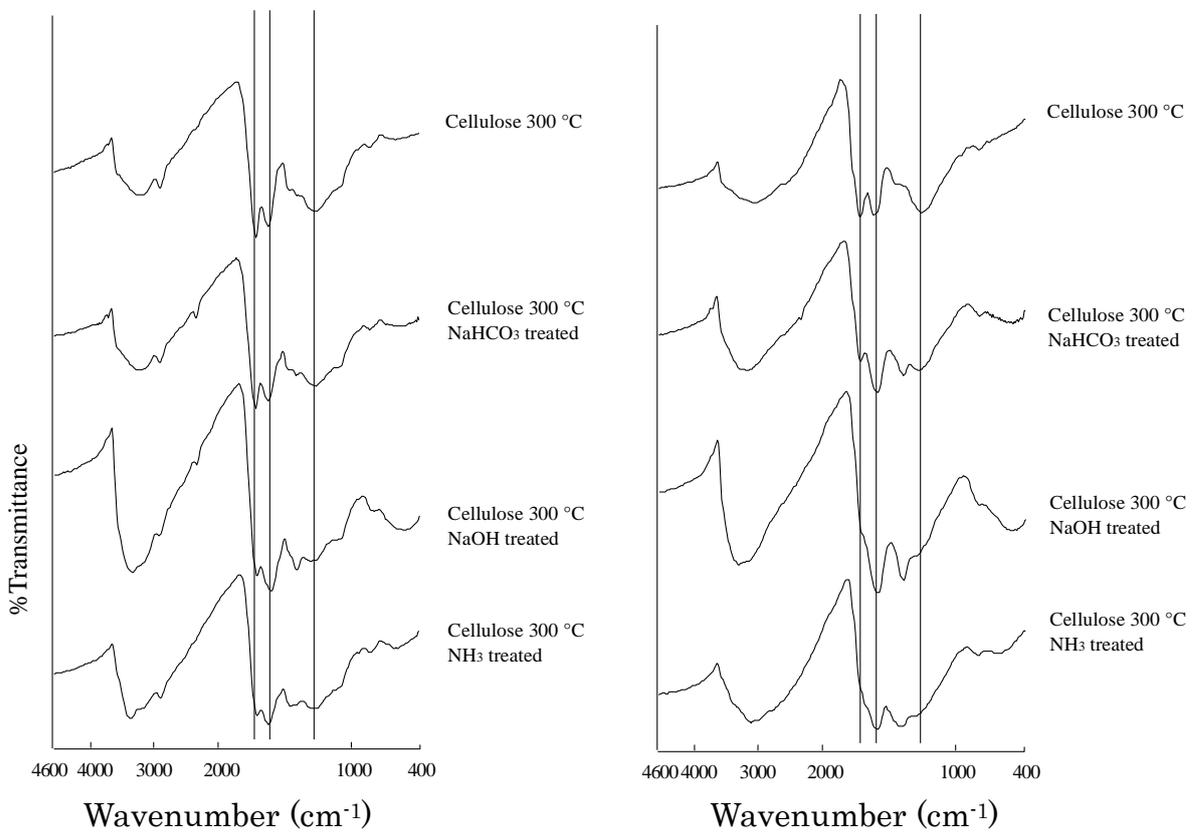
Fig. 2.3. FT-IR spectra of Todo-fir char.

The difference in the chemical structure because of the atmosphere in the case of Todo-fir (300 °C) was compared based on the IR spectra (Fig. 2.3): (a) shows the spectrum of the char under nitrogen atmosphere and (b) shows that under air atmosphere. Each uppermost step represents the non-treated sample, and steps 2, 3, and 4 represent the spectra after treating the char obtained under each atmosphere with 0.1 N NaHCO<sub>3</sub>, 0.1 N NaOH, and

ammonia gas. In the spectra obtained for the chars obtained from each atmosphere, the absorption peaks at 1700 and 1600  $\text{cm}^{-1}$  may be attributed to the C=O groups and aromatic ring, respectively; however, the following results were different. First, the spectrum of the char obtained under air atmosphere showed a broad absorption peak at 3100  $\text{cm}^{-1}$  attributed to carboxylic acid group (Fig. 2.3 (b) uppermost step). On the other hand, in the case of the char obtained under nitrogen atmosphere, the absorption peak 3100  $\text{cm}^{-1}$  was relatively weak (Fig. 2.3(a) uppermost step). A comparison of the spectra after the adsorption of  $\text{NaHCO}_3$  showed that in the char obtained under air atmosphere, a major portion of the absorption peak, which was thought to be originated from the C=O groups, disappeared. In contrast, in the case of the char obtained under nitrogen atmosphere, the absorption peak remained (Fig. 2.3 (a), (b) second step). The absorption at 1700  $\text{cm}^{-1}$  in the case of the char obtained under air atmosphere was mainly attributed to the lactone and carboxylic acid groups, and that in the case of the char obtained under nitrogen atmosphere was mainly attributed to the carbonyl group. The difference became clearer in the change in the spectrum containing weak acidic groups after the NaOH adsorption treatment (Figs. 2.3(a) and 2.3(b), step 3). In the case of the char obtained under air atmosphere, the absorption 1700  $\text{cm}^{-1}$  disappeared, and the absorption 1600 and 1400  $\text{cm}^{-1}$  increased simultaneously, indicating the Na salt formation. However, in the case of the char obtained under nitrogen atmosphere, only a slight change was observed.

The results of the FT-IR analysis (Fig. 2.4) for the cellulose char were also similar; in particular, the spectrum of the char at 300 °C showed almost

similar characteristics as those for Todo-fir char. Moreover, the spectra after the adsorption of NaOH and NaHCO<sub>3</sub> showed a similar change as that in the case of Todo-fir char. The changes in the case of Todo-fir char occurred 300 °C; however, at this temperature range, the formation of carbonyl and carboxylic acid functional groups due to the pyrolysis of cellulose has been reported [17,18]. This indicated that the treatment under air atmosphere was effective for forming acidic functional groups.



(a) Pyrolyzed in nitrogen

(b) Pyrolyzed in air

Fig. 2.4. FT-IR spectra of cellulose char.

### ***2.3.3 Ammonia adsorption capacity***

The ammonia adsorption isotherm for Todo-fir char is shown in Fig. 2.5. Under nitrogen atmosphere, the ability for the adsorption of ammonia increased with increasing temperature in the range 250–400 °C. The results showed that the correlation between the ability for the adsorption of ammonia and the quantity of acidic functional groups was high irrespective of a complete agreement between them. The reason for this may be attributed to the variation in the affinity of different types of acidic functional groups towards ammonia. The ability of the char obtained under air atmosphere to adsorb ammonia was the highest at 300 °C, resulting in a peak at 300 °C. The ammonia adsorption ability of the char near 300 °C greatly exceeded those for the two varieties of activated carbon used as the reference. Further, in the temperature range 250-400 °C, the ammonia adsorption ability for the char obtained under air atmosphere was more than that for the char obtained under nitrogen atmosphere.

The change in the chemical structure of Todo-fir char and cellulose char after the adsorption of ammonia was studied by IR spectra (Figs. 2.3 and 2.4). In both the cases, the absorption peak near 1700  $\text{cm}^{-1}$  disappeared in the char obtained under air atmosphere, and the absorption peak near 1600 and 1400  $\text{cm}^{-1}$  increased, indicating the formation of ammonium salt. In contrast, in the case of the char obtained under nitrogen atmosphere, a clear change was not observed, indicating that the acidic functional groups generated in the char obtained under air atmosphere reacted with ammonia and improved the adsorption ability. The adsorption ability of Todo-fir char to ammonia was

greatly influenced by the pyrolysis temperature and atmosphere during the heating. Thus, the char obtained under air atmosphere effectively introduced acidic functional groups on its surface and improved the adsorption ability for ammonia.

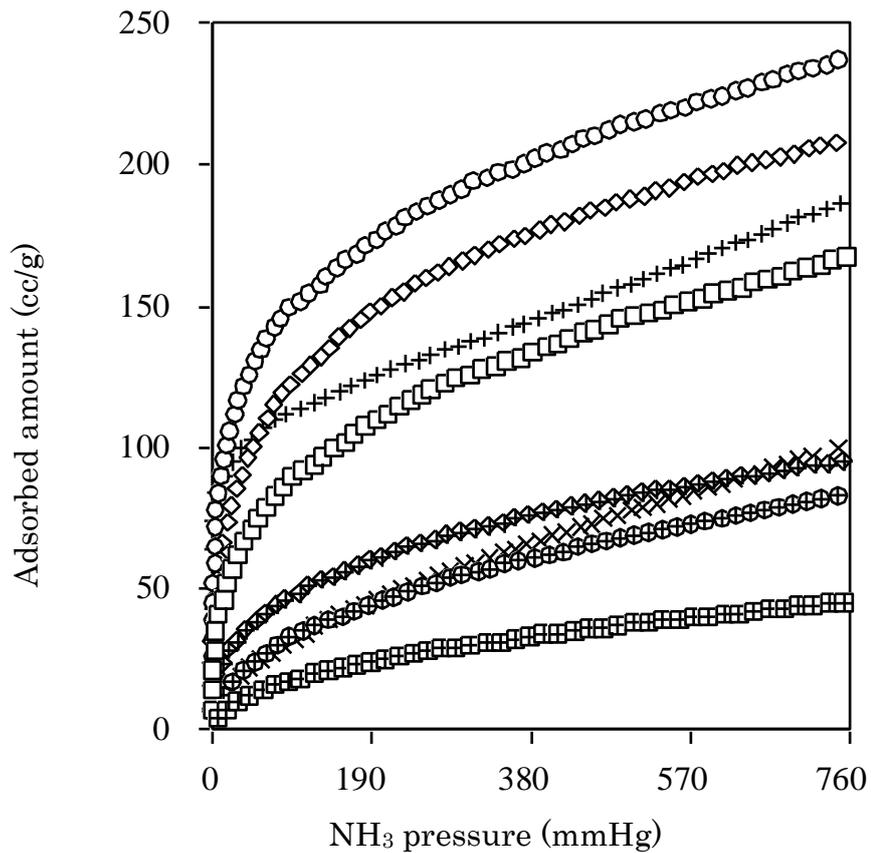


Fig. 2.5. Adsorption isotherms of ammonia on Todo-fir char.

Legend: □ :250 °C in air,    ○ :300 °C in air,    ◇ :400 °C in air,  
 ■ :250 °C in nitrogen, ⊕ :300 °C in nitrogen, ⊕ :400 °C in nitrogen,  
 + :activated carbon for NH<sub>3</sub>    × :activated carbon.

## 2.4 Summary

The cellulose and fibers of Todo-fir wood were pyrolyzed at 250-400 °C for 2 hours under an air or nitrogen atmosphere for investigation of the relationships between the pyrolysis conditions of the char and its adsorption behavior and chemical structure. The results obtained were as follows:

(1) The char of Todo-fir wood and cellulose obtained under an air atmosphere adsorbed noticeably higher amounts of ammonia and alkali than the charcoal obtained under a nitrogen atmosphere. The adsorption of alkali and ammonia showed that the optimum pyrolysis temperature for Todo-fir wood and cellulose was 300 °C in air. (2) The Fourier transform infrared spectra of Todo-fir wood and cellulose char showed the formation of noticeably higher amounts of carboxylic acid and lactone functional groups in the charcoal obtained under an air atmosphere. (3) The char obtained from Todo-fir wood and cellulose under an air atmosphere had higher H and O contents and a lower C content, as determined by elemental analysis. Presumably, dehydration, dehydrogenation, and carboxylation occurred below 300 °C under an air atmosphere. (4) The char obtained from cellulose showed similar behavior as the charcoal obtained from Todo-fir wood.

Thus, the pyrolysis of wood under air is effective for the formation of acidic functional groups on its surface, rendering it a suitable ammonia adsorbent. The reaction for the formation of acidic functional groups is mainly based on the pyrolysis of cellulose.

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## **Chapter 3. Effect of catalytic pyrolysis conditions using pulse current heating method on pyrolysis products of woody biomass**

### **3.1 Introduction**

Biomass pyrolysis is the thermal degradation of lignocellulose in the absence of oxygen to form charcoal, pyrolysis oil, and gaseous fuel products. Depending on the operating conditions, biomass pyrolysis can be subdivided into slow and fast pyrolysis, of which, the latter has been receiving a lot of attention as it maximizes pyrolysis oil production [1-2]. One of the most important methods to improve the quality of pyrolysis oil is the addition of heterogeneous catalysts during biomass pyrolysis [3]. In Chapter 1, the functionality of the residual char and the co-production of aromatic chemicals were reported as a new process designed for efficient usage of woody biomass with using pulse current heating. Pyrolysis conditions for effective preparation of ammonia adsorbent were described in Chapter 2. Subsequently, the investigation about the effect of the catalyst conditions on the characterization of pyrolysis oil and the composition of the char was required for producing specific aromatic compounds at lower temperatures and functional carbon composite.

Pyrolysis employing the pulse current heating method can be applied to catalyzed pyrolysis technology for the production of useful substances from wood biomass [4–10]. A judicious choice of catalysts and the use of optimal pyrolysis conditions make it possible to produce more useful chemical feedstocks in a selective manner. The applicability of pyrolysis oil in fuels,

chemicals, and functional materials has been proposed in previous studies describing catalytic pyrolysis processes [11-12]. Torri et al. reported the effects on the carbon yield of products in the pyrolysis of pine sawdust at 500 °C, using of 31 types of catalysts, including zeolite ZSM-5, TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub> [13]. Lu and co-workers reported the effects of six different metal oxides, including TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>, on the composition of pyrolysis oil obtained from poplar wood at 600 °C using Py-GC/MS [14] and detected PAH (polycyclic aromatic hydrocarbon) compounds. On the other hand, only a few studies have been conducted on the effects on the liquefaction in pyrolysis of wooden biomass at 800 °C using titanium oxide and iron oxide, while investigations about the effects of catalysts on the composition of the oil from the pyrolysis at 500-600 °C have been reported. The selective production of useful substances can be achieved by modifying and improving the properties of pyrolysis oil as a consequence of the synthesis conditions employed. An increase in the composition ratio of aromatic hydrocarbons in pyrolysis oil was reported [15-16] when zeolite and some metal oxides were present in biomass during the pyrolysis process. Furthermore, we expect a reduction in the energy required for the production of pyrolysis oil if fuel or functional materials can be produced from pyrolysis oil at lower temperatures with the aid of catalysts.

Catalytic graphitization is one chemical process from which the physical properties of char formed during pyrolysis originate. Partial graphitization is known to occur during pyrolysis of organic matters when conducted in the presence of iron oxide, titanium oxide, nickel compounds, or other materials.

The following two mechanisms are recognized to operate in catalytic graphitization [17]: (1) dissolution–precipitation and (2) carbide formation. Low-temperature graphitization occurs in graphitizable carbon; the efficient catalytic action of transition-metal elements and their oxides affect the crystallization of carbon [18–19]. Tan et al. reported about the graphitization process of fir powder with iron oxide at 900 to 1,600 °C [20]. Although not an example wood biomass, Parker suggested that Fe<sub>2</sub>O<sub>3</sub> was the most effective toward needle coke (or petroleum coke) graphitization in their examination of iron catalysts, such as FeO, α-Fe<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> [21]. Similar effects are expected in pyrolysis using the pulse current heating method. The effects of the catalytic reactions employing titanium oxide or iron oxide, which have different graphitization mechanisms, on the microtexture of char, produced from wood biomass pyrolysis at 800 °C by using a pulse current heating method, are of interest in understanding the process of microstructural change in wood during pyrolysis.

Some reports have characterized the char obtained from woody biomass/metal-oxide mixtures by pyrolysis with a pulse current heating system [4, 22]. On the other hand, the benefits like efficiently production, useful chemicals, and functional char are expected by producing of both pyrolysis oil and char in one step and the composition of pyrolysis oil produced by the pulse current heating system. Characterization of char and pyrolysis oil, obtained from pyrolysis by the pulse current heating method, is necessary to clarify the influence of catalytic conditions on product composition. We also determined product distributions at a given processing temperature. In this

chapter, Japanese cedar wood meal was used for pyrolysis since its raw material waste can be obtained easily. Japanese cedar is one of the most important species in Japan for use as forest products and wood biomass [23], as described in Chapter 1. The catalysts iron (II, III) oxide ( $\text{Fe}_3\text{O}_4$ ), titanium (IV) oxide ( $\text{TiO}_2$ ), and zeolite ZSM-5, which have different mechanisms of graphitization, were examined. We also analyzed the chemical components of liquefaction and characterized the microtexture of the pyrolysis residue obtained at 500 and 800 °C using these catalysts.

## 3.2. Materials and methods

### 3.2.1. Raw material and catalysts

Sapwood meal ground by a ball mill from Japanese cedar (*Cryptomeria japonica*) wood from Wakayama prefecture with age of 30 was used as a raw material.  $\text{Fe}_3\text{O}_4$  (powder, Wako Pure Chemical Industries, Japan),  $\text{TiO}_2$  (anatase-type powder, Kishida Chemical, Japan), and zeolite ZSM-5 (CVB 3024E, Nominal Cation Form: Ammonium, Zeolyst International, USA) were used as catalysts.  $\text{Fe}_2\text{O}_3$  (powder type),  $\alpha\text{-Fe}_2\text{O}_3$  (powder type), and FeO (powder type), all obtained from Wako Pure Chemical Industries, Japan, were used as catalysts. Wood meal and catalyst powders were mixed in a weight ratio of 1:1 (w/w). Wood meal and catalyst powder were mixed in a 1:1 (w/w) ratio. The apparatus used for pyrolysis by pulse current heating incorporates a graphite mold in which a quartz tube containing the powdered sample is inserted and heated by conducting an electric current through the graphite mold as shown in Chapter 1. For comparison, a woody powder sample (100

mg) was pyrolyzed under the heating conditions as shown in Fig. 1.1.

### ***3.2.2. Pyrolysis with pulse current heating method***

The sample powder in the apparatus (Fig. 1.1) was pyrolyzed by electric heating. Pyrolysis experiments were conducted at temperature of 500 °C and 800 °C and the pyrolysis time of 3 min, the heating rate of 15–20 °C/s. The choice of heating rate and pyrolysis time were based on a previous report by Carlson et al. [16]. The heating pattern used for the pyrolysis experiments is shown in Fig. 1.2. The heating rate was set to 15–20 °C/s in order to obtain both pyrolysis oil and char effectively. The quartz tube, collection bottle, and gas-sampling bag were arranged in a closed system as shown in Fig. 1.1.

### ***3.2.3. TEM analysis of char***

The chars obtained by catalytic pyrolysis were analyzed using TEM (2010F, JEOL, Japan). Selected area electron diffraction (SAED) was taken in addition to imaging.

### ***3.2.4. GC-MS analysis of pyrolysis oil***

GC-MS analyses and semiquantification of pyrolysis oil chemical components were performed on a QP-5050A GC-MS (Shimadzu, Japan) as shown in Chapter 1. The components of pyrolysis oil were determined from the obtained total ion chromatogram (TIC) using the Kovats retention index method [24-32] and a mass spectral library. Peak areas from TIC plots were examined for semiquantification.

### 3.3 Results and discussion

#### *3.3.1. Product distribution*

First, we examined the effects of catalyst addition on product distribution during pyrolysis by the pulse current heating method. The changes in composition ratios of the products obtained from wood meal are shown in Figs. 3.1 (a) and 3.1 (b). The differences of the yield of pyrolysis products were not so remarkable among pyrolysis conditions with and without catalyst. Pyrolysis oil and char yields of 37–46% and 16–23%, respectively, were obtained at a processing temperature of 500 °C, although both these yields decreased with the addition of catalyst. Pyrolysis oil and char yields of 22–35% and 14–18%, respectively, were obtained at 800 °C. Similar yields of products were obtained by catalyst addition in this experiment and almost no decrease in the yields of pyrolysis oil and char was observed.

The effects of catalyst addition on product distribution were investigated by comparing the results obtained in this case to those obtained in the absence of catalysts. The reaction time and addition of catalysts such as ZSM-5, titanium oxide, and iron oxide had little influence on product distribution. At 800 °C, the yield of pyrolysis oil and char with catalyst addition was independent of the type of catalyst except that the yield of pyrolysis oil increased slightly when ZSM-5 was used as the catalyst. Possible reasons for this include: (i) the secondary reaction of pyrolysis oil and char did not occur on catalyst addition at 800 °C, (ii) the ratio of catalyst to wood

meal was 1:1, and (iii) the amount of added catalyst was not as high as that used by Carlson et al. [16], who reported that the carbon yield of oxygenated species decreased, and that of hydrocarbon, CO, and CO<sub>2</sub> gas increased with the catalyst (ZSM5) to glucose ratio from 9:1. The yield of pyrolysis oil was considered to be kept the same level as oxygenated species decreased while aromatic hydrocarbons increased. The effects of catalyst addition on the decomposition of oxygenated compounds and polycyclic aromatic hydrocarbon production are already known [33, 34]. A similar tendency was observed for pyrolysis conducted at both 500 and 800 °C. Consequently, the addition of catalysts had little effect on the char yield.

The effects of iron oxides (Fe<sub>2</sub>O<sub>3</sub>, FeO, and α-Fe<sub>2</sub>O<sub>3</sub>) addition on product distribution in pyrolysis by the pulse-current heating method were examined. The changes in the composition ratios of obtained products from wood meal are shown in Figs. 3.2 (a) and 3.2 (b) (pyrolysis at 500 and 800 °C, respectively). Differences in the yields of products were not apparent in the presence or absence of catalyst. Pyrolysis oil and char yields of 38–52% and 25–29%, respectively, were obtained at 500 °C processing, although both the yields of pyrolysis oil and char decreased with addition of catalyst. Pyrolysis oil and char yields of 28–39% and 18–19% were obtained at 800 °C. This decline in pyrolysis oil and char yield was not recognized in progress of the gasification accompanying catalyst addition. A certain yield could thus be obtained by catalyst addition in this experiment and almost no decrease in the yield of pyrolysis oil and char was observed.

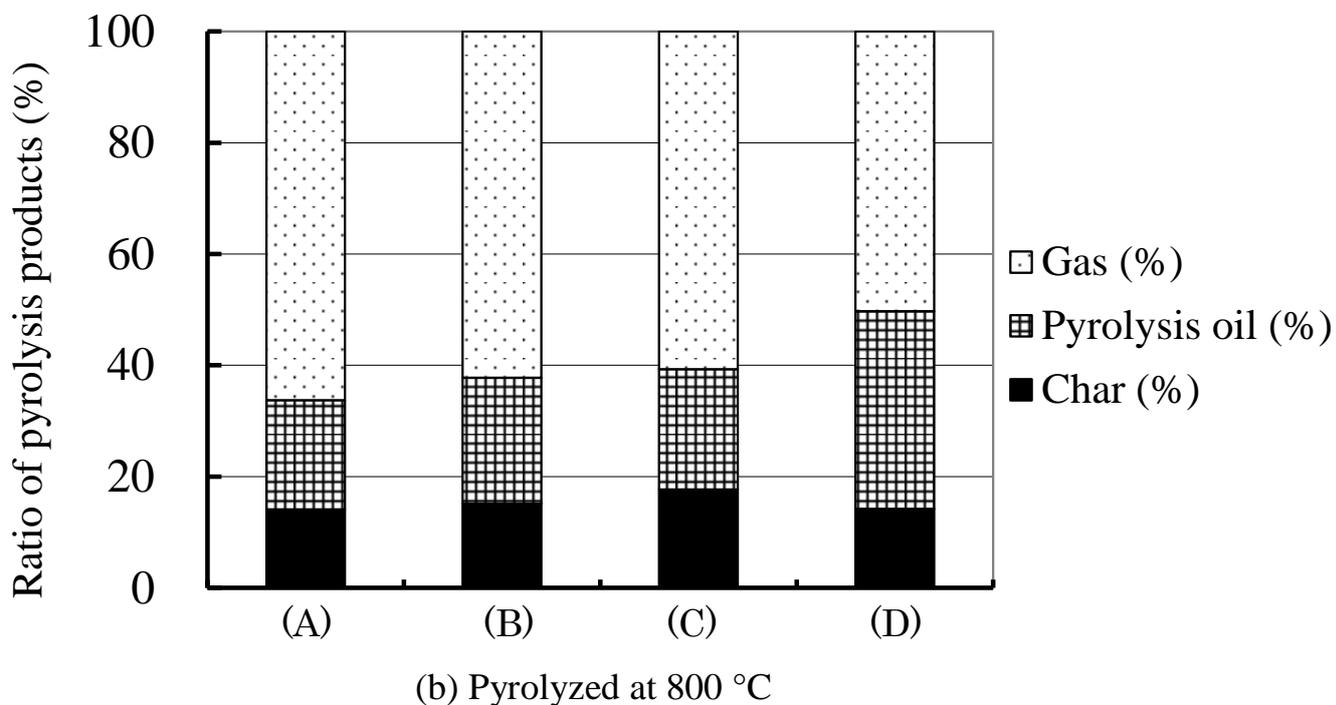
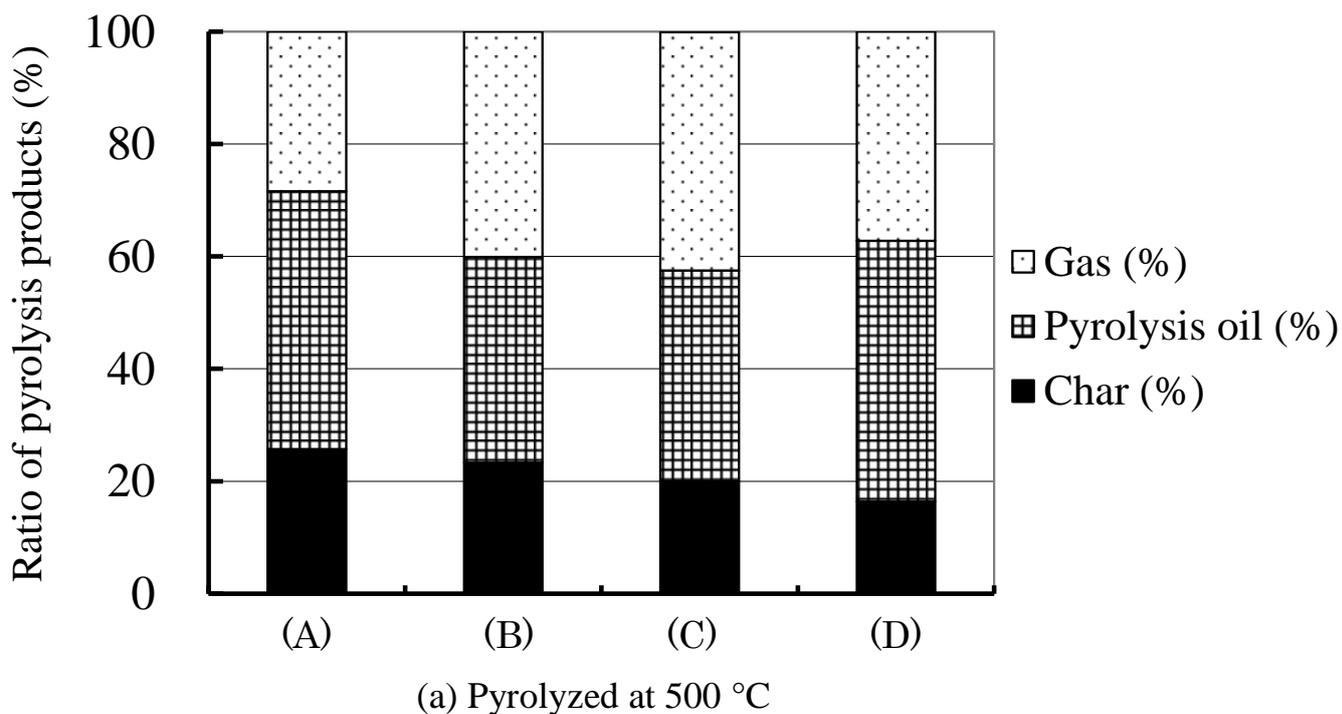
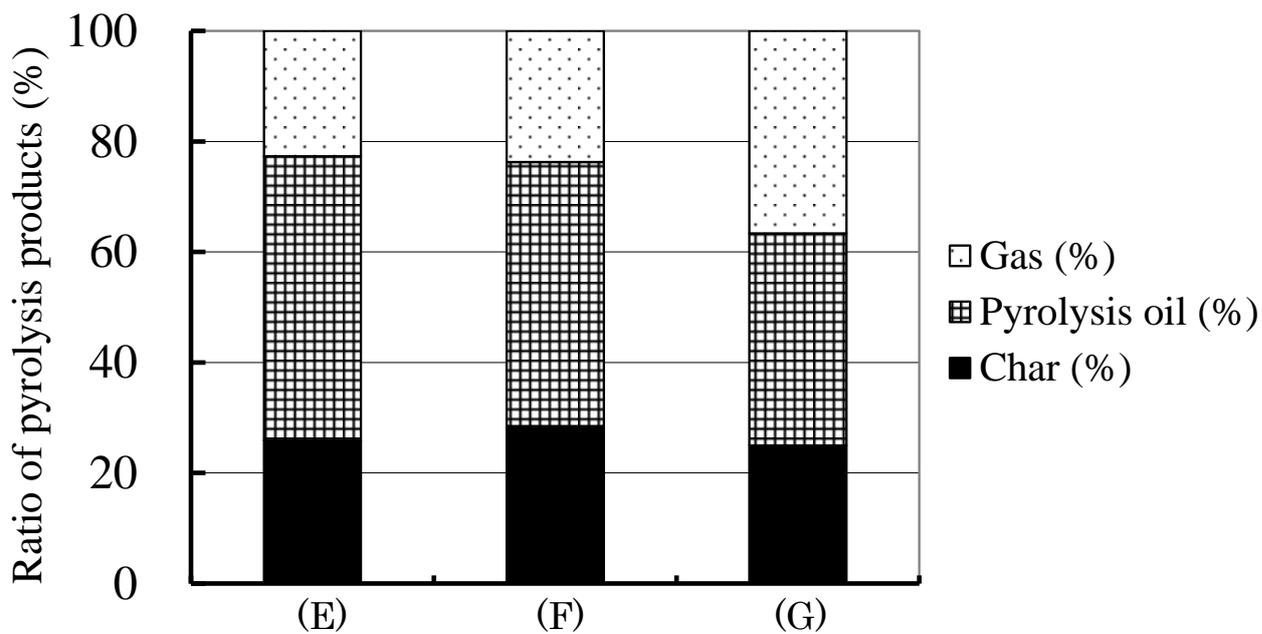
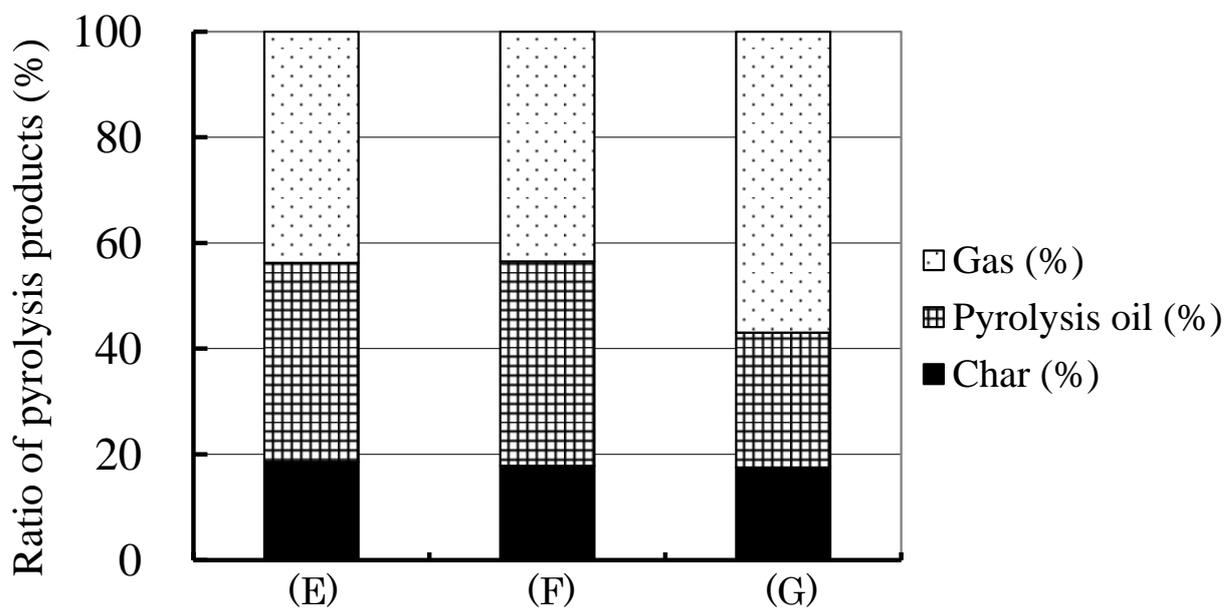


Fig. 3.1 Product distribution of pyrolysis products obtained from Japanese cedar wood meal/catalyst (1:1 w/w) mixtures pyrolyzed at 500 °C (a) and 800 °C (b): (A) Japanese cedar wood meal, (B) Wood meal/ $\text{Fe}_3\text{O}_4$  mixture, (C) Wood meal/ $\text{TiO}_2$  mixture, (D) Wood meal/ZSM-5 mixture.



(a) Pyrolyzed at 500 °C



(b) Pyrolyzed at 800 °C

Fig. 3.2 Product distribution of pyrolysis products obtained from Japanese cedar wood meal/catalyst (1:1 w/w) mixtures pyrolyzed at 500 °C (a) and 800 °C (b): (E) Wood meal/ $\text{Fe}_2\text{O}_3$  mixture, (F) Wood meal/ $\alpha\text{-Fe}_2\text{O}_3$  mixture, (G) Wood meal/ $\text{FeO}$  mixture.

### ***3.3.2. TEM analysis of char***

Pyrolysis residues obtained at 800 °C were examined with TEM and SAED. The results of analysis of wood meal, wood meal/ Fe<sub>3</sub>O<sub>4</sub> (1:1 w/w), wood meal/TiO<sub>2</sub> (1:1 w/w), and wood meal/ZSM-5 (1:1 w/w) pyrolyzed at 800 °C are shown in Figs. 3.3, 3.4, 3.5, and 3.6, respectively. TEM and SAED analysis indicated the coexistence or dissolution of amorphous carbon and iron oxide in the wood meal/ Fe<sub>3</sub>O<sub>4</sub> sample pyrolyzed at 800 °C in Fig.3.4), which were not observed in the pyrolysis residue of Japanese cedar wood meal pyrolyzed without catalyst at 800°C in Fig. 3.3. From these results, state of pyrolysis residue of the wood meal/ Fe<sub>3</sub>O<sub>4</sub> sample pyrolyzed at 800 °C was considered to be in relation to a process of catalytic graphitization. Consequently, as expected, the pyrolysis with pulse current heating process conducted at 800 °C with Fe<sub>3</sub>O<sub>4</sub> addition contributed to changes of char in physical properties. The phenomenon of coexistence or dissolution was more evident at the interface of carbon and oxides in the case of added Fe<sub>3</sub>O<sub>4</sub> shown in Fig.3.4 than in the case of added TiO<sub>2</sub> in Fig.3.5.

The results of analysis of wood meal/Fe<sub>2</sub>O<sub>3</sub> (1:1 w/w), wood meal/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (1:1 w/w), and char/ FeO (1:1 w/w) pyrolyzed at 800 °C are shown in Figs. 3.7, 3.8, and 3.9, respectively. TEM imaging indicated the formation of a micro graphite layer in the wood meal/Fe<sub>2</sub>O<sub>3</sub> (1:1 w/w) sample pyrolyzed at 800 °C (Fig. 3.7). From ED analysis, a diffraction pattern suggesting the existence of a micro graphite layer was also observed (Fig. 3.7). Fe<sub>2</sub>O<sub>3</sub> addition was therefore considered to be effective for graphitization as noted by the observation of the micro graphite layer around the catalyst,

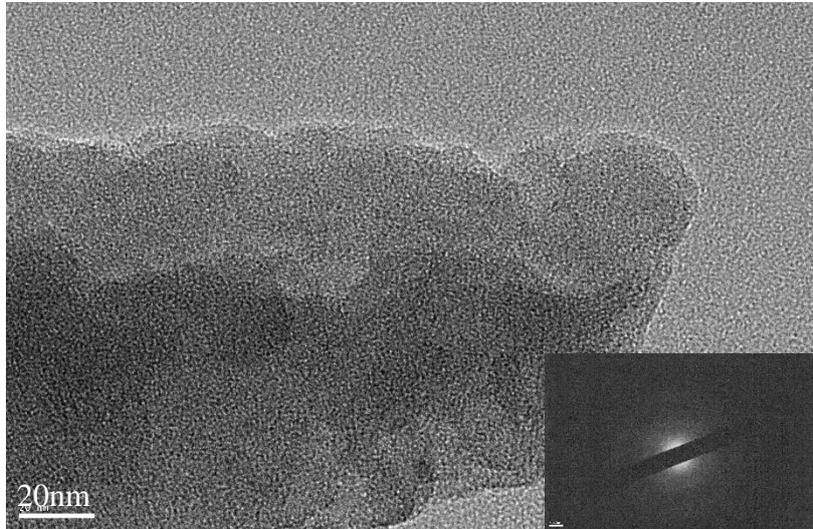


Fig. 3.3 TEM image and SAED of char obtained from Japanese cedar wood meal pyrolyzed at 800 °C.

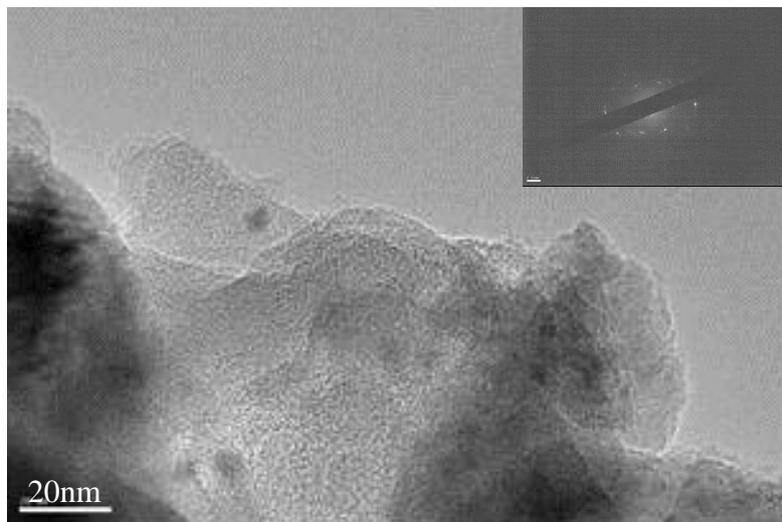


Fig. 3.4 TEM image and SAED of char obtained from mixture of Japanese cedar wood meal/ $\text{Fe}_3\text{O}_4$  (1:1 w/w) pyrolyzed at 800 °C.

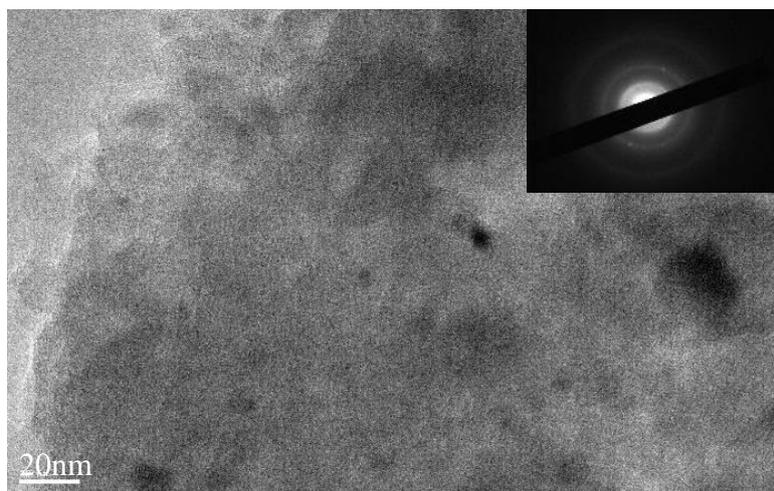


Fig. 3.5 TEM image and SAED of char obtained from mixture of Japanese cedar wood meal/  $\text{TiO}_2$  (1:1 w/w) pyrolyzed at 800 °C.

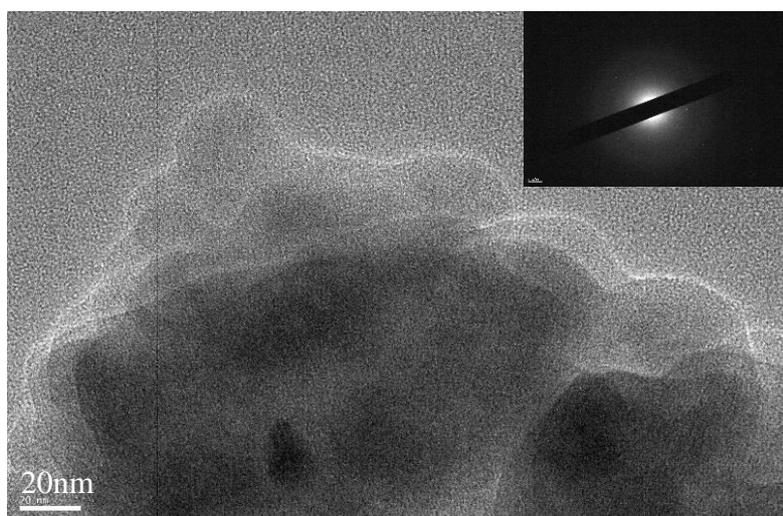


Fig. 3.6 TEM image and SAED of char obtained from mixture of Japanese cedar wood meal/ zeolite (ZSM-5) (1:1 w/w) pyrolyzed at 800 °C.

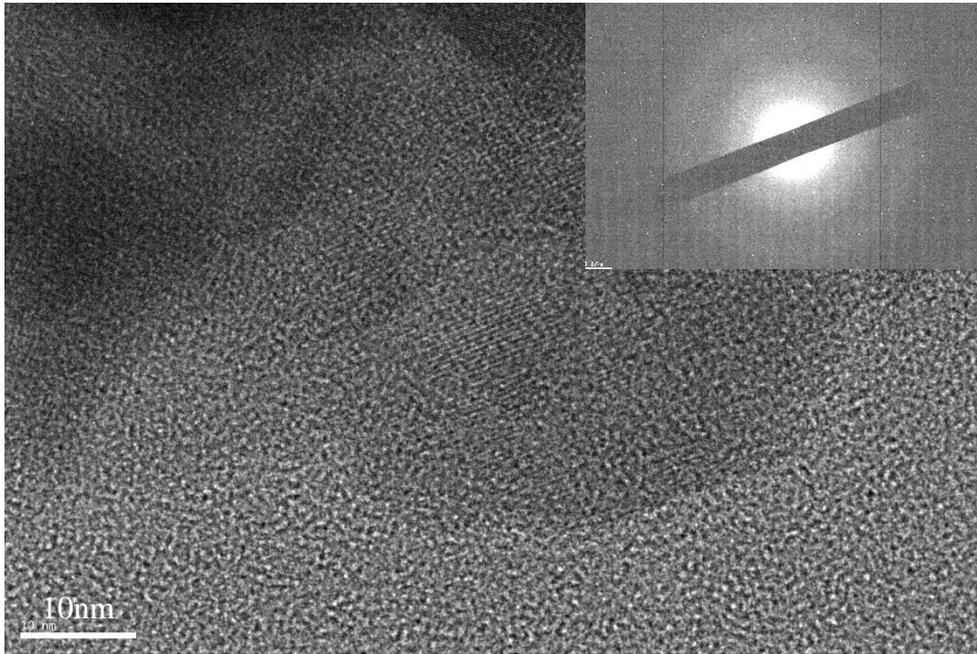


Fig. 3.7. TEM image and SAED of char obtained from mixture of Japanese cedar wood meal/ $\text{Fe}_2\text{O}_3$  (1:1 w/w) pyrolyzed at 800 °C.

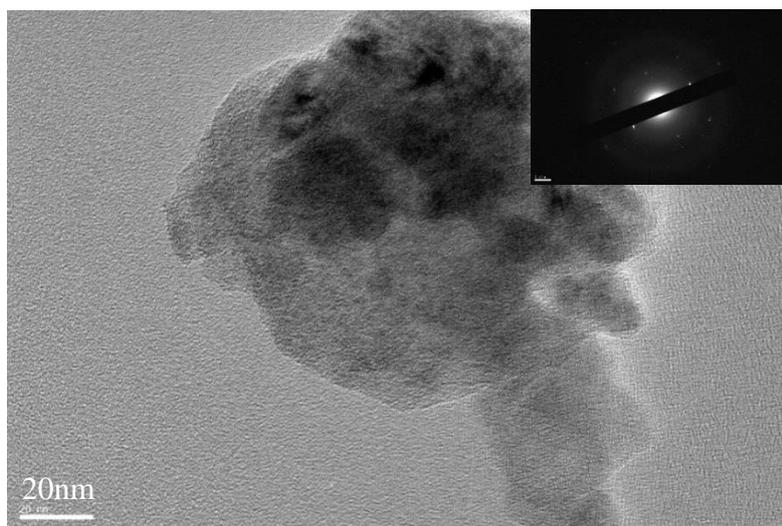


Fig. 3.8. TEM image and SAED of char obtained from mixture of Japanese cedar wood meal/ $\alpha$ - $\text{Fe}_2\text{O}_3$  (1:1 w/w) pyrolyzed at 800 °C.

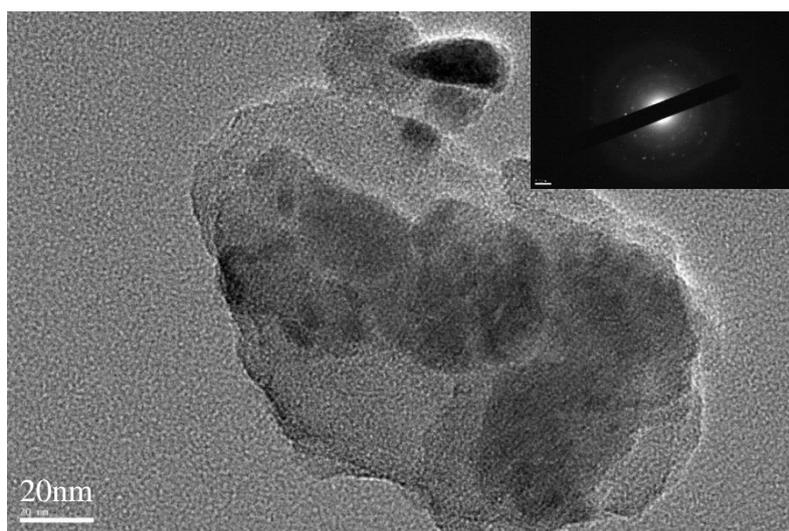


Fig. 3.9 TEM image and SAED of char obtained from mixture of Japanese cedar wood meal/  $\text{FeO}$  (1:1 w/w) pyrolyzed at 800 °C.

### *3.3.3. Composition of pyrolysis oil*

The composition of pyrolysis oil was found to change drastically on catalyst addition compared to results obtained from wood meal pyrolysis in the absence of catalysts. More polyaromatic hydrocarbons (PAHs) were observed in the pyrolysis oil of the Japanese cedar sample at 500 °C with the three kinds of catalyst. The composition ratios of specific aromatic hydrocarbons, including naphthalene, tended to increase at 800 °C. Compounds with oxygen functional groups, such as isoeugenol, vanillin, furfural, and 4-vinylguaiacol, were previously reported to be present in the pyrolysis oil obtained from wood meal pyrolyzed without a catalyst at 500 °C. Aromatic hydrocarbons (benzene, toluene, naphthalene, etc.) and phenols (phenol, cresol) were identified in the pyrolysis oil obtained from both the wood meal/Fe<sub>3</sub>O<sub>4</sub> (1:1 w/w) and wood meal/TiO<sub>2</sub> (1:1 w/w) samples pyrolyzed at 500 °C, while the ratio of compounds with oxygen functional groups decreased relatively (Table 3.1 and Fig. 3.10). A similar tendency was shown in the pyrolysis oil from the wood meal/ZSM-5 (1:1 w/w) sample pyrolyzed at 500 °C (Table 3.1 and Fig. 3.10), although the results were not as remarkable as those for the wood meal/Fe<sub>3</sub>O<sub>4</sub> and wood meal/TiO<sub>2</sub> samples. From the above results, catalyst addition during pyrolysis at 500 °C was considered to be effective in increasing aromatic hydrocarbon content in the resulting pyrolysis oil.

Many kinds of aromatic compounds with oxygen functional groups were included in the pyrolysis oil obtained from wood biomass by pyrolysis at 500 °C, and the amounts of aromatic hydrocarbon or polyaromatic compounds

increased at 700 to 800 °C from previous reports [12, 35]. Each catalyst was considered to be effective in obtaining pyrolysis oil with similar compositions when conducting pyrolysis at higher temperatures, and the yield of each pyrolysis oil did not remarkably decrease; consequently, an increase in aromatic hydrocarbon yield and reduction in pyrolysis energy was achieved. These results are in good agreement with previous reports on the increase in aromatic hydrocarbon yields under pyrolysis conditions using zeolite catalysts [16, 36].

Table 3.1 GC-MS semiquantitative analysis of pyrolysis oil components obtained from Japanese cedar wood meal/catalyst (1:1 w/w) mixtures pyrolyzed at 500 °C.

Retention time (min.)	Pyrolysis oil	Pyrolysis oil	Pyrolysis oil	Pyrolysis oil
	Japanese cedar wood meal [10]	mixture with Fe <sub>3</sub> O <sub>4</sub>	mixture with TiO <sub>2</sub>	mixture with ZSM-5
	area/I. S. area	area/I. S. area	area/I. S. area	area/I. S. area
6.21 Benzene	-	0.32	0.27	-
8.85 Toluene	-	0.24	0.16	-
10.14 Furfural	0.12	0.11	0.07	0.04
10.97 Ethynylbenzene	-	0.03	-	-
11.25 Styrene	-	0.18	0.13	-
12.48 Phenol	-	0.73	0.64	0.28
13.62 <i>o</i> -Cresol	-	0.29	0.30	0.14
13.74 1-Propynylbenzene	-	-	-	-
13.90 <i>p</i> -Cresol	-	0.57	0.48	0.26
14.19 Guaiacol	0.11	0.04	-	-
15.40 Catechol	0.09	0.20	0.17	0.17
15.57 <i>m</i> -Cresol	0.16	0.04	-	-
15.77 Naphthalene	-	0.51	0.82	0.17
17.07 Methyl-naphthalene	-	0.18	0.19	-
17.45 Eugenol	0.04	0.07	-	-
17.95 Biphenyl	-	-	0.06	-
18.00 Vanillin	0.08	0.04	-	-
18.49 Isoeugenol	0.12	0.05	0.04	-
18.89 Acenaphthylene	-	0.12	0.30	-
20.22 <i>o</i> -Biphenylenemethane	-	-	-	-
21.84 Phenanthrene	-	0.05	0.16	-
21.91 Anthracene	-	-	-	-
24.05 Pyrene	-	-	-	-
25.00 Internal standard (Tetracosane)	1.00	1.00	1.00	1.00

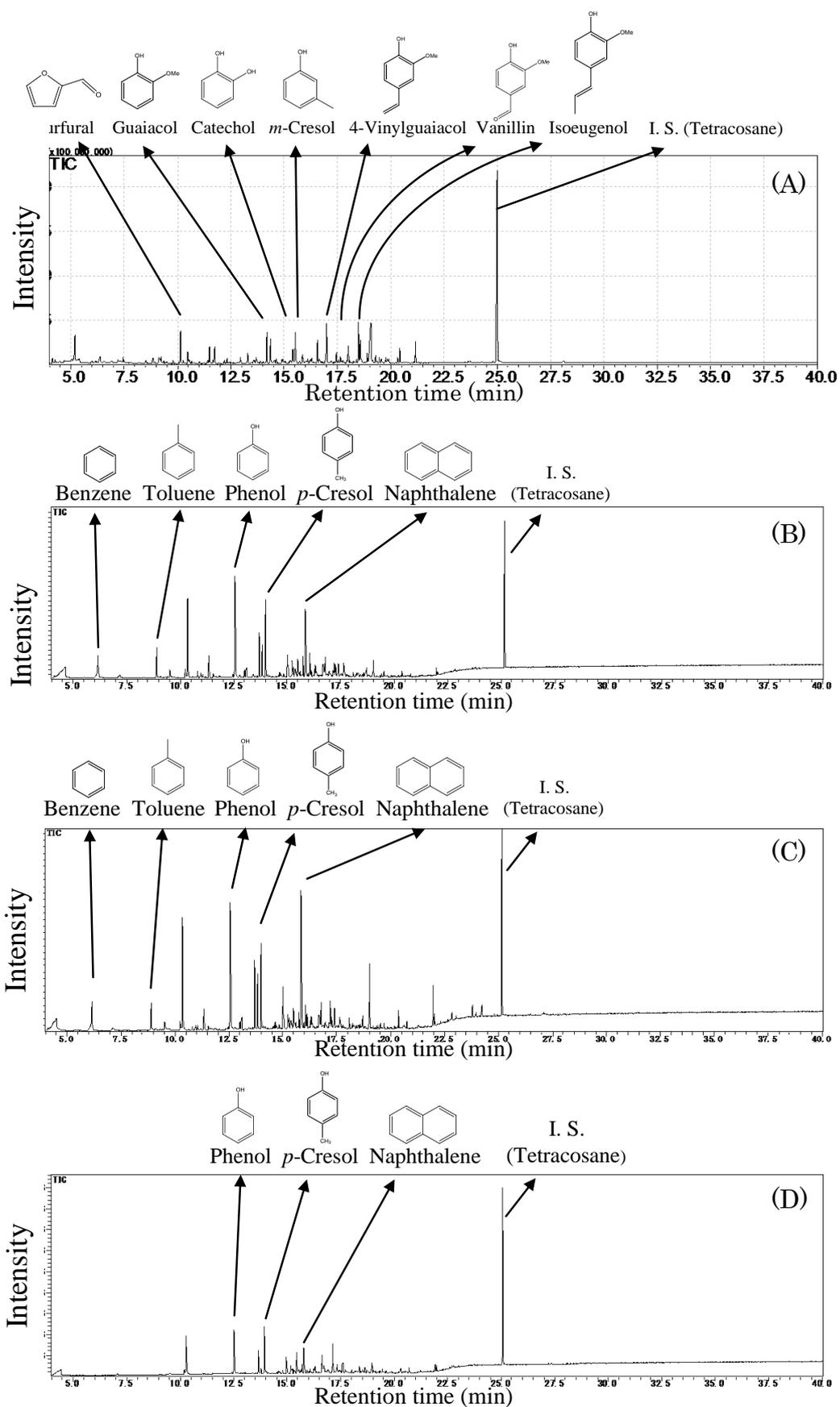


Fig. 3.10 TIC of pyrolysis oils obtained from of Japanese cedar wood meal/catalyst (1:1 w/w) mixtures pyrolyzed at 500°C: (A) without catalyst, (B) Fe<sub>3</sub>O<sub>4</sub>, (C) TiO<sub>2</sub>, (D) ZSM-5

Table 3.2 GC-MS semiquantitative analysis of pyrolysis oil components obtained from Japanese cedar wood meal/catalyst (1:1 w/w) mixtures pyrolyzed at 800 °C.

Retention time (min.)		Pyrolysis oil	Pyrolysis oil	Pyrolysis oil	Pyrolysis oil
		Japanese cedar wood meal	mixture with Fe <sub>3</sub> O <sub>4</sub>	mixture with TiO <sub>2</sub>	mixture with ZSM-5
		area/I. S. area	area/I. S. area	area/I. S. area	area/I. S. area
6.21	Benzene	0.63	0.21	0.25	0.04
8.85	Toluene	0.18	0.03	0.01	0.06
10.14	Furfural	-	-	-	-
10.97	Ethynylbenzene	0.26	-	0.02	-
11.25	Styrene	0.24	0.03	0.01	-
12.48	Phenol	0.12	0.14	-	0.28
13.62	<i>o</i> -Cresol	-	0.03	-	0.14
13.74	1-Propynylbenzene	0.50	-	-	-
13.90	<i>p</i> -Cresol	-	0.07	-	0.22
14.19	Guaiacol	-	0.07	-	0.19
15.40	Catechol	-	-	-	0.18
15.57	<i>m</i> -Cresol	-	-	-	-
15.77	Naphthalene	0.95	1.15	0.61	0.47
17.07	Methylnaphthalene	0.12	0.04	0.02	0.27
17.45	Eugenol	-	0.03	-	-
17.95	Biphenyl	0.10	-	0.01	0.09
18.00	Vanillin	-	0.07	-	-
18.49	Isoeugenol	-	0.11	-	-
18.89	Acenaphthylene	0.59	0.65	0.41	0.36
20.22	<i>o</i> -Biphenylenemethane	0.24	-	-	-
21.84	Phenanthrene	0.37	0.24	0.12	0.05
21.91	Anthracene	0.14	0.05	-	0.14
24.05	Pyrene	0.29	0.19	0.24	-
25.00	Internal standard (Tetracosane)	1.00	1.00	1.00	1.00

The weight ratios of many components decreased in pyrolysis oil obtained from both wood meal/Fe<sub>3</sub>O<sub>4</sub> (1:1 w/w) and wood meal/TiO<sub>2</sub> (1:1 w/w) samples pyrolyzed at 800 °C, whereas the weight ratio of some PAHs (such as naphthalene) increased (Table 3.2, Fig. 3.11). Aromatic hydrocarbons such as benzene, toluene, and naphthalene were mainly detected in pyrolysis oil obtained from wood meal pyrolyzed in the absence of catalyst at 800 °C. Since similar yields of pyrolysis oil were obtained (Figs. 3.1, 3.2) in both catalyzed and uncatalyzed pyrolysis processes, the pyrolysis of biomass with pulse current heating using a suitable amount of catalyst was expected to generate specific aromatic compounds in higher ratios.

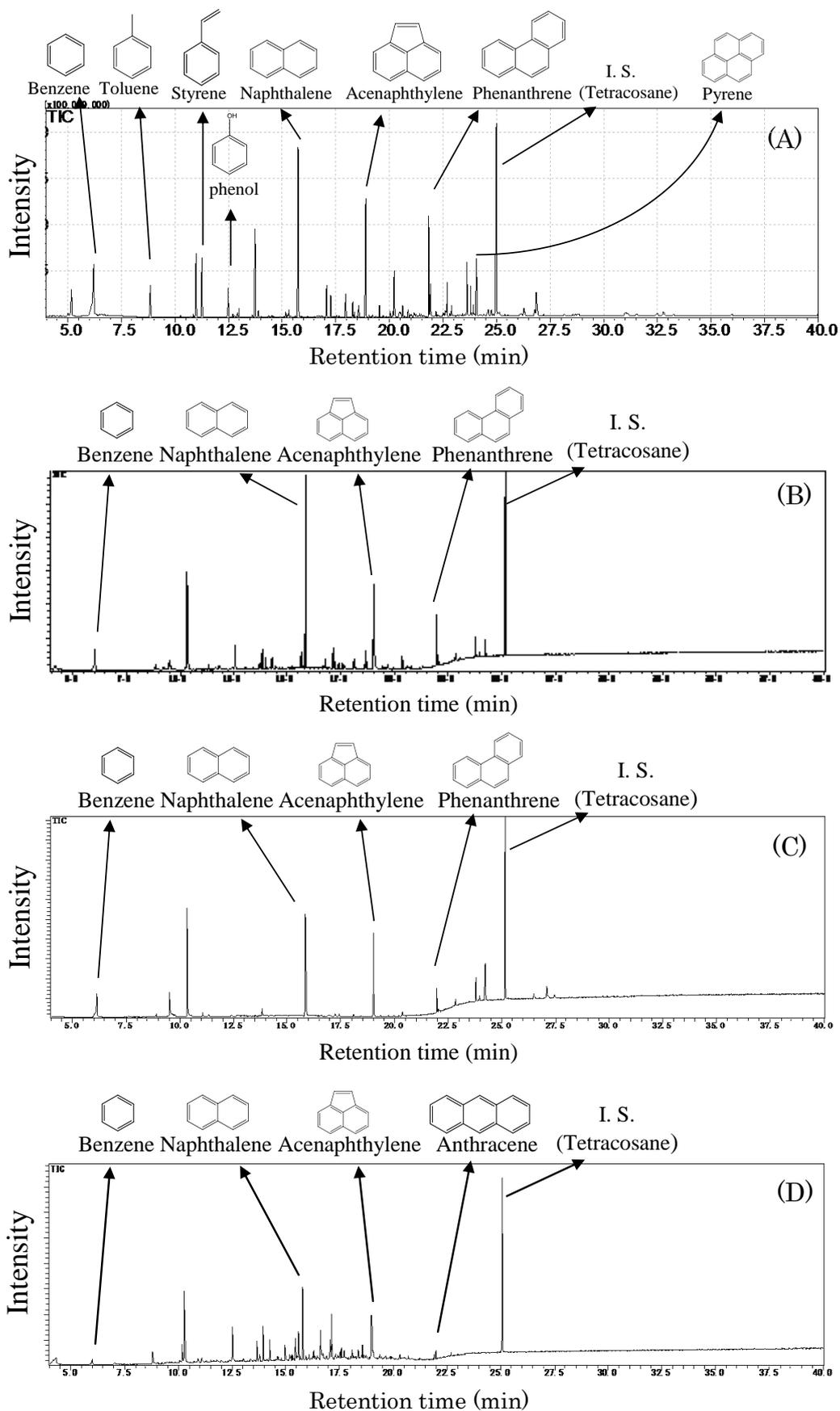


Fig. 3.11 TIC of pyrolysis oils obtained from of Japanese cedar wood meal/catalyst (1:1 w/w) mixtures pyrolyzed at 800°C: (A) without catalyst, (B) Fe<sub>3</sub>O<sub>4</sub>, (C) TiO<sub>2</sub>, (D) ZSM-5.

Aromatic hydrocarbons such as benzene, toluene, and naphthalene were detected in the pyrolysis oil obtained from the wood meal/ZSM-5 (1:1 w/w) sample pyrolyzed at 500 °C; phenol, cresol, catechol, and guaiacol were also detected. The weight ratio of PAHs increased in the pyrolysis oil obtained from wood meal/ZSM-5 sample pyrolyzed at 800 °C, and pyrolysis oil composition showed a similar tendency to that obtained from wood meal/Fe<sub>3</sub>O<sub>4</sub> and wood meal/TiO<sub>2</sub> samples. From these results, pyrolysis using biomass with an adequate amount of catalyst is expected to yield specific aromatic compounds in a higher content, as a similar yield of pyrolysis oil was obtained from catalytic pyrolysis of the wood meal/ZSM-5 (1:1 w/w) sample at 800 °C, compared to pyrolysis without catalyst.

The composition ratio of pyrolysis oil changed drastically with iron oxide addition compared to results obtained from wood-meal pyrolysis without catalysts. Compounds with oxygen functional groups, such as isoeugenol, vanillin, furfural, and 4-vinylguaiacol, were observed in the pyrolysis oil obtained from wood meal pyrolyzed without a catalyst at 500 °C. Aromatic hydrocarbons (benzene, toluene, naphthalene, etc.) and phenols (phenol, cresol) were also obtained in the pyrolysis oil derived from wood meal/FeO (1:1 w/w) pyrolyzed at 500 °C, while the formation rates of compounds with oxygen functional groups relatively decreased (Table 3.3 and Fig. 3.12). A tendency similar to that for the wood meal sample treated without catalyst was shown in the pyrolysis oil from wood meal/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (1:1 w/w) and wood meal/Fe<sub>2</sub>O<sub>3</sub> (1:1 w/w) samples pyrolyzed at 500 °C (Table 3.3 and Fig. 3.12). From the above results, the influence of catalyst (FeO) addition on the

pyrolysis process at 500 °C is considered to be effective in increasing aromatic hydrocarbon content in the obtained pyrolysis oil.

Many kinds of aromatic compounds with oxygen functional groups were identified in the pyrolysis oil obtained from wood biomass by pyrolysis with pulse-current heating at 500 °C, and the contents of aromatic hydrocarbons, or polyaromatic compounds, increased at 700 to 800 °C from previous reports [12, 35]. Each catalyst was found to be effective in obtaining pyrolysis oils of similar compositions at higher temperatures, and the yields of pyrolysis oil with each catalyst did not remarkably decrease.

Table 3.3 GC-MS semiquantitative analysis of pyrolysis oil components obtained from Japanese cedar wood meal/catalyst (1:1 w/w) mixtures pyrolyzed at 500 °C.

Retention time (min.)	Pyrolysis oil	Pyrolysis oil	Pyrolysis oil
	mixture with Fe <sub>2</sub> O <sub>3</sub>	mixture with $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	mixture with FeO
	area/I. S. area	area/I. S. area	area/I. S. area
6.21 Benzene	-	-	0.08
8.85 Toluene	-	-	0.13
10.14 Furfural	0.09	-	-
10.97 Ethynylbenzene	-	-	-
11.25 Styrene	-	-	0.12
12.48 Phenol	0.06	0.03	0.48
13.62 <i>o</i> -Cresol	0.07	0.10	0.25
13.74 1-Propynylbenzene	-	-	0.21
13.90 <i>p</i> -Cresol	0.10	0.07	0.40
14.19 Guaiacol	0.26	0.16	-
15.40 Catechol	-	0.05	0.28
15.57 <i>m</i> -Cresol	0.58	0.57	-
15.77 Naphthalene	-	-	0.40
17.07 Methylnaphthalene	-	-	-
17.45 Eugenol	0.11	0.10	-
17.95 Biphenyl	-	-	-
18.00 Vanillin	0.17	0.19	-
18.49 Isoeugenol	0.46	0.39	-
18.89 Acenaphthylene	-	-	0.09
20.22 <i>o</i> -Biphenylenemethane	-	-	-
21.84 Phenanthrene	-	-	-
21.91 Anthracene	-	-	-
24.05 Pyrene	-	-	-
25.00 Internal standard (Tetracosane)	1.00	1.00	1.00

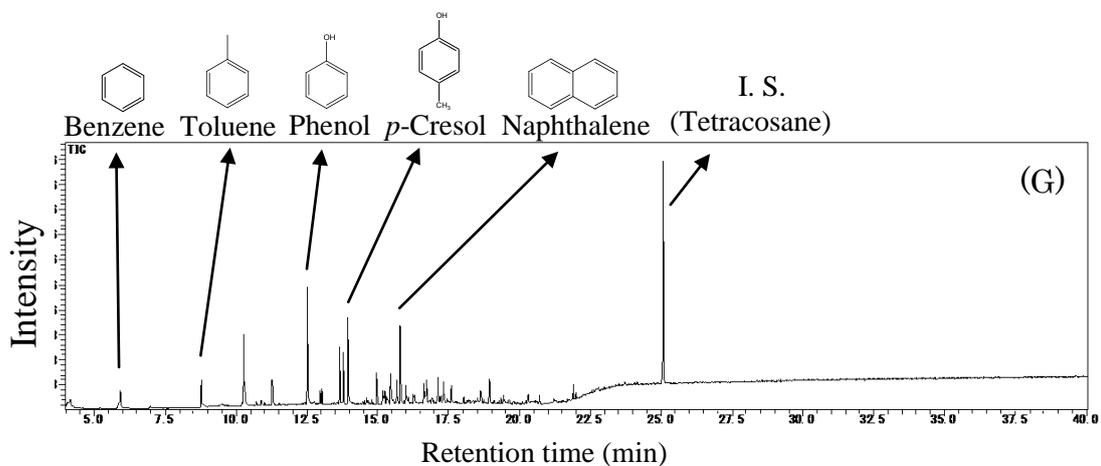
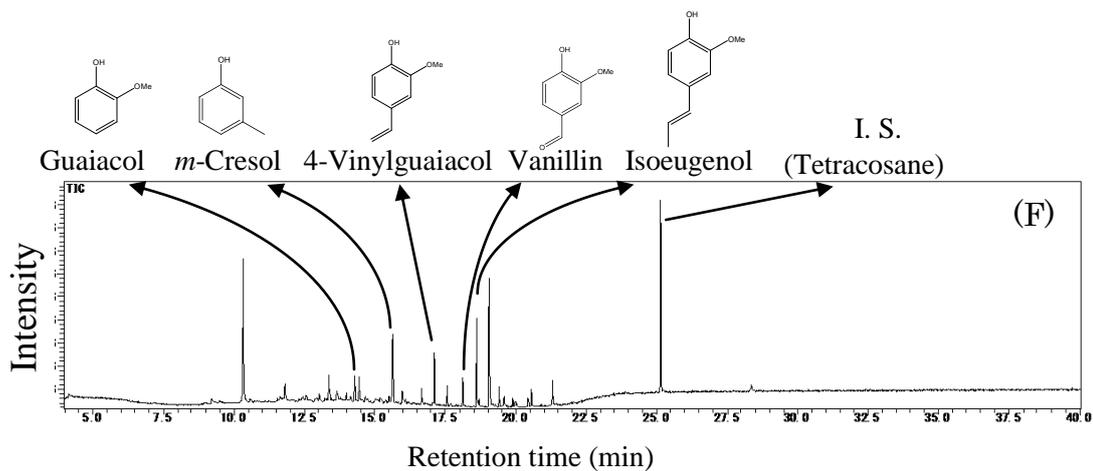
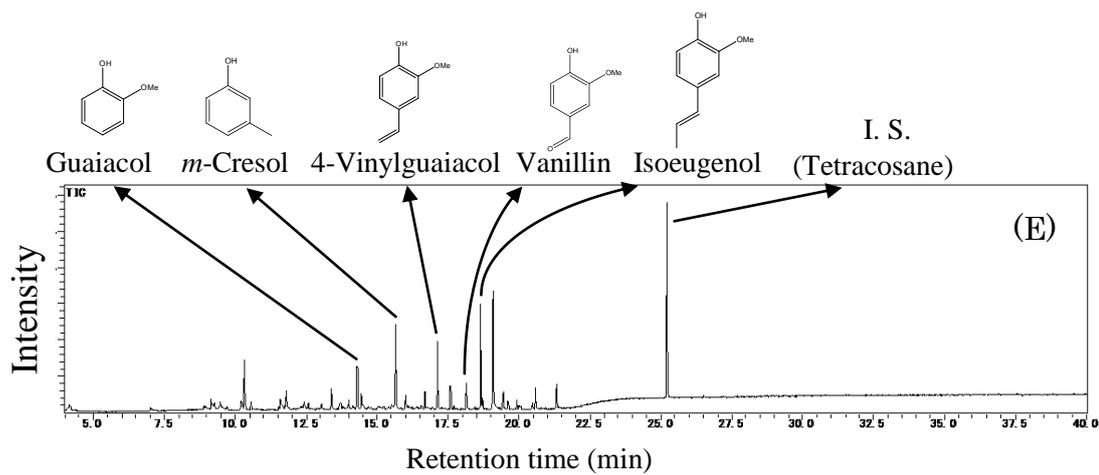


Fig. 3.12 TIC of pyrolysis oils obtained from Japanese cedar wood meal/iron oxide (1:1 w/w) mixtures pyrolyzed at 500°C: (E) Fe<sub>2</sub>O<sub>3</sub>, (F) α-Fe<sub>2</sub>O<sub>3</sub>, (G) FeO.

Therefore, the yield of aromatic hydrocarbons was increased and a reduction in energy requirements was realized. The composition ratios of many components were decreased in pyrolysis oils obtained from wood meal/FeO (1:1 w/w) and wood meal/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (1:1 w/w) samples pyrolyzed at 800 °C, whereas the ratios of some aromatic hydrocarbons (such as naphthalene) increased (Table 3.4 and Fig. 3.13).

Table 3.4 GC-MS semiquantitative analysis of pyrolysis oil components obtained from Japanese cedar wood meal/catalyst (1:1 w/w) mixtures pyrolyzed at 800 °C.

Retention time (min.)		Pyrolysis oil	Pyrolysis oil	Pyrolysis oil
		mixture with Fe <sub>2</sub> O <sub>3</sub>	mixture with $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	mixture with FeO
		area/I. S. area	area/I. S. area	area/I. S. area
6.21	Benzene	0.18	1.18	0.08
8.85	Toluene	0.23	0.45	0.08
10.14	Furfural	-	-	-
10.97	Ethynylbenzene	-	0.05	-
11.25	Styrene	0.14	0.28	0.07
12.48	Phenol	0.66	0.36	0.17
13.62	<i>o</i> -Cresol	0.23	-	-
13.74	1-Propynylbenzene	-	0.52	0.21
13.90	<i>p</i> -Cresol	0.57	0.14	-
14.19	Guaiacol	-	-	-
15.40	Catechol	-	-	-
15.57	<i>m</i> -Cresol	-	-	-
15.77	Naphthalene	0.18	1.29	0.66
17.07	Methylnaphthalene	0.07	0.12	0.10
17.45	Eugenol	-	-	-
17.95	Biphenyl	-	0.07	0.08
18.00	Vanillin	-	-	-
18.49	Isoeugenol	-	-	-
18.89	Acenaphthylene	-	0.47	0.41
20.22	<i>o</i> -Biphenylenemethane	-	0.15	0.19
21.84	Phenanthrene	-	0.29	0.41
21.91	Anthracene	-	0.07	0.13
24.05	Pyrene	-	0.14	0.29
25.00	Internal standard (Tetracosane)	1.00	1.00	1.00

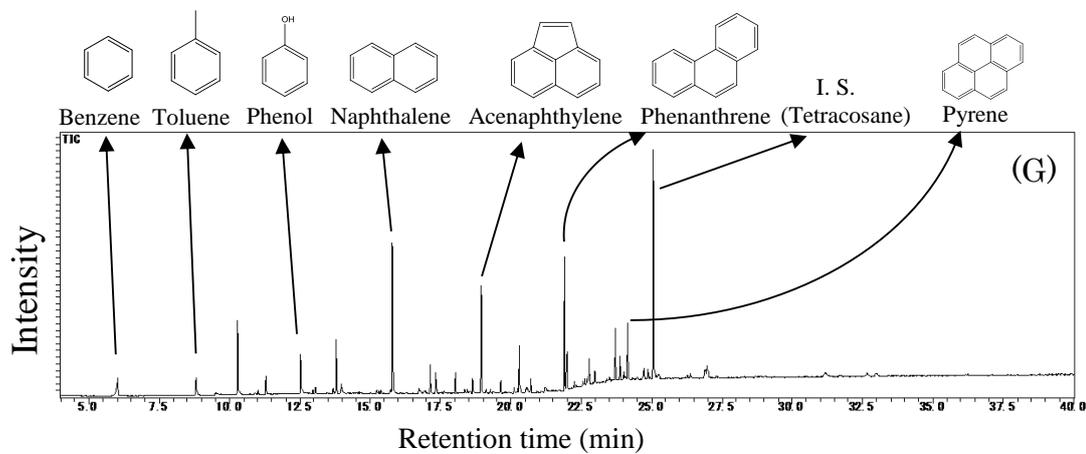
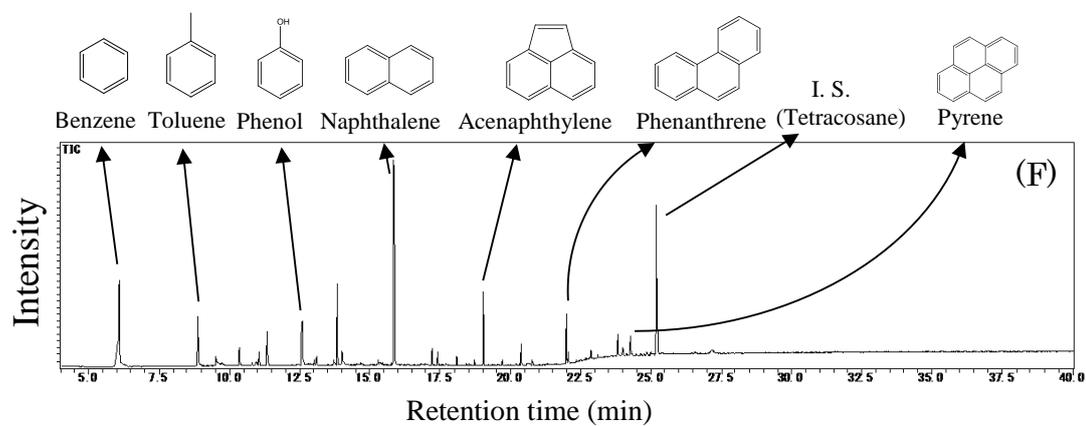
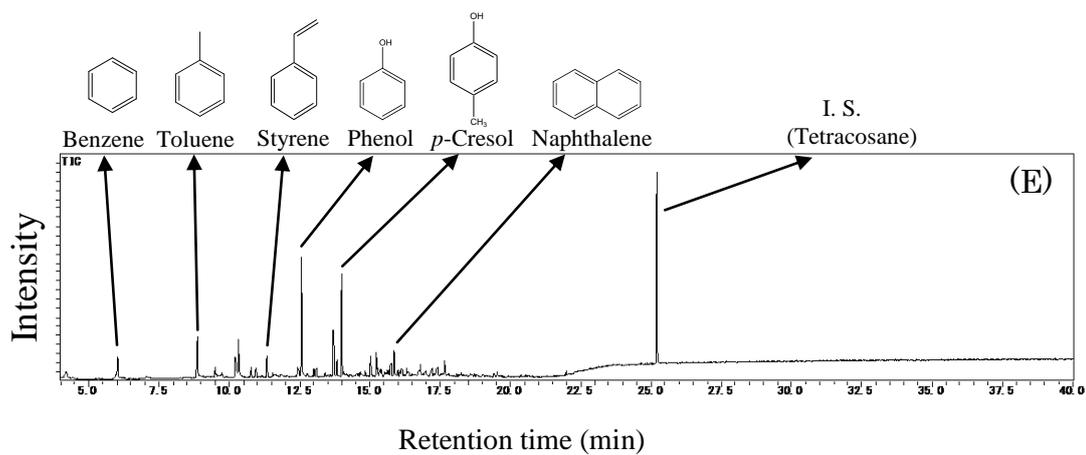


Fig. 3.13 TIC of pyrolysis oils obtained from Japanese cedar wood meal/iron oxide (1:1 w/w) mixtures pyrolyzed at 800°C: (E)  $\text{Fe}_2\text{O}_3$ , (F)  $\alpha\text{-Fe}_2\text{O}_3$ , (G)  $\text{FeO}$ .

Aromatic hydrocarbons (benzene, toluene, naphthalene, etc.) were mainly detected in pyrolysis oil obtained from wood meal pyrolyzed in the absence of catalyst at 800 °C. Since similar pyrolysis oil yields were obtained by catalytic pyrolysis compared to pyrolysis without a catalyst (Figs. 3.3 and 3.4), the pyrolysis of biomass using pulse-current heating and an adequate amount catalyst is anticipated to provide specific aromatic compounds in higher composition ratios. Aromatic hydrocarbons (such as benzene, toluene, and naphthalene) were detected in the pyrolysis oil from wood meal/FeO (1:1 w/w) pyrolyzed at 500 °C, while phenol, cresol, catechol, and guaiacol were also detected. Some of the ratios of aromatic hydrocarbons (such as naphthalene) increased in the pyrolysis oil obtained from wood meal/FeO (1:1 w/w) pyrolyzed at 800 °C, a similar tendency observed for pyrolysis oil obtained from wood meal/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (1:1 w/w). Since a similar yield of pyrolysis oil was obtained from both catalytic and non-catalyzed pyrolysis at 800 °C with the wood meal/FeO (1:1 w/w) sample, the pyrolysis of biomass with pulse-current heating using an adequate amount of catalyst is expected to provide specific aromatic compounds in higher content.

In this chapter, the formation of aromatic hydrocarbons was observed during pyrolysis at 500 °C, and the formation of PAHs, such as naphthalene and phenanthrene could be increased by carrying out pyrolysis at 800 °C in the presence of catalysts. Pyrolysis oil compositions were affected by the addition of catalysts such as iron oxides, titanium oxides, and zeolite ZSM-5. The promotion of PAH production and its catalytic effect of iron oxide at 600 °C and The production of hydrocarbon increased slightly and The effect of

deoxygenating of pyrolysis vapor was low by using titanium oxide as reported by Lu et al. [14]. The catalytic effect of zeolite ZSM-5 on fast-pyrolysis oil compositions were reported for the decomposition of oxygenated compounds, producing aromatic hydrocarbon, and polycyclic aromatic hydrocarbon by Carlson [16], Bridgwater [33], Zhang et al. [34]. The effect of these catalysts on production of aromatic hydrocarbon and PAH promoted the decomposition of oxygenated constituents during pyrolysis under a pulse current heating. The amount of polycyclic aromatics, especially, increased with iron oxide addition.

### **3.4 Summary**

The influence of catalysts on the compositions of char and pyrolysis oil obtained by pyrolysis of wood biomass with pulse current heating was studied. The effects of catalysts on product compositions were analyzed using GC-MS and TEM. The compositions of some aromatic compounds changed noticeably when using a metal oxide species as the catalyst. The coexistence or dissolution of amorphous carbon and iron oxide was observed in char pyrolyzed at 800 °C with Fe<sub>3</sub>O<sub>4</sub>. Pyrolysis oil compositions changed remarkably when formed in the presence of a catalyst compared to that obtained from the uncatalyzed pyrolysis of wood meal. We observed a tendency toward an increase in the ratio of polyaromatic hydrocarbons in the pyrolysis oil composition after catalytic pyrolysis at 800 °C. When iron oxides and TiO<sub>2</sub> were used as catalysts, the composition ratio of aromatic hydrocarbon compounds such as naphthalene was shown to increase, even at

a processing temperature of 500 °C. Pyrolysis of biomass using pulse current heating and an adequate amount of catalyst is expected to yield a higher content of specific polyaromatic compounds.

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## **Chapter 4. Production of aromatic compounds and carbon composite obtained by pyrolysis of unutilized biomass using pulse current heating method**

### **4.1 Introduction**

Viscous pyrolysis oil, char, and gas are obtained by the fast pyrolysis of woody biomass. The development of functional materials from pyrolysis oil or char is important for building a low carbon society. The application of pyrolysis oil as fuel and as raw materials for chemical products have been proposed [1, 2] in the report on the characteristics of pyrolysis products using catalysts. In Chapter 1, 2, and 3, the effects of the pyrolysis and catalyst conditions of woody biomass on pyrolysis products were described for producing of aromatic compounds and functional carbon materials.

Pyrolysis using pulse current heating has advantages in producing functional products, reducing energy consumption, and producing porous carbon compared to a conventional pyrolysis system. Pulse current heating provides a high amount of energy for samples in a short time, wherein a pulse current is applied directly to a graphite die, and heat is generated in the die simultaneously. Current and voltage corresponding to pyrolysis temperature were reported by Kurosaki [3] and Hata [4], and the design of the system along with a practical example were reported by Kikuchi et al. [5].

Char obtained by pyrolysis with pulse current heating has some useful characteristics. For example, Kurosaki et al. reported the controlling of the mesopore diameters in the sample [3, 6]. Kajimoto et al. reported the durability of char over atomic oxygen; this char was prepared from lignin for

potential application in space [7, 8]. Hata et al. prepared a cathode catalyst with non-platinum and with nitrogen-doped carbon pyrolyzed from cellulose [9, 10].

Furthermore, the following studies on producing pyrolysis oil with carbon under pulse current heating were reported. The relation between pyrolysis conditions and the chemical structure of char, ammonia adsorption capacity, and partial graphitization with catalyst addition were reported with respect to the characteristics of pyrolysis products from Japanese cedar (Chapter 1 and 3). The catalytic effect on the composition ratio of some aromatic hydrocarbons, like naphthalene, from Japanese cedar in pyrolysis oil obtained at 800 °C was described in Chapter 3.

Inorganic constituents in plants are considered to be another factor that affects the composition of a fast-pyrolysis product, in addition to basic components in raw materials, pyrolysis conditions, and the addition of catalysts. The effect of inorganic constituents in small amounts in plants also plays an important role, as the inorganic constituents influence the compositions in products obtained by fast pyrolysis [11, 12]. Useful substances can be selectively produced through a better understanding of the mechanism of the catalytic reaction of inorganic constituents in the pyrolysis products obtained from biomass in high yield.

About 2 million ton of rice husks per year are estimated to be produced domestically [13]. Todo-fir has an accumulation volume of 211,781,000 m<sup>3</sup> in Hokkaido, of which utilization and developing value added products from its thinned timbers are important [14]. The development of manufacturing

technology is necessary for the effective use of biomass. Okutani et al. [15] reported that domestic rice husks contain more than 90% SiO<sub>2</sub>, 0–1% K<sub>2</sub>O, CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>O, and TiO<sub>2</sub>; inorganic constituents affect the compositions in pyrolysis products. Furthermore, Genieva et al. [16] mentioned the possibility of using Si compounds, such as Si/C compounds or SiO<sub>2</sub>, in rice husks and its carbonized products as well as the potential application of rice husks as raw materials of SiC, ceramics, silicon compounds, and composites.

In this chapter, the composition of pyrolysis products obtained from rice husks, Todo-fir, and cellulose were examined as a part of the investigation on utilization of pyrolysis products from biomass. These compositions were then compared for studying the selective conversion of biomass to useful chemical substances by pulse current heating. The different effects of each ingredient in the raw materials on the products were studied by investigating the relation between the pyrolysis temperature and the compositions.

## **4.2. Materials and methods**

### ***4.2.1. Raw material***

Rice husks, a variety of “*hoshinoyume*,” and Todo-fir wood from Hokkaido prefecture with an age of 20 were ground by ball milling to a particle size of less than 500 μm; they were used as raw materials of lignocellulosic biomass. CF-11 cellulose powder (Whatman, USA) was used. The water content of rice husks, Todo-fir, and cellulose was 8.9%, 8.4%, and

4.3%, respectively. The ash contents of raw materials were determined according to the Japanese Industrial Standard (JIS) M8812.

#### ***4.2.2. Pyrolysis with pulse current heating***

The apparatus used for pyrolysis was a pulse current heating apparatus with a graphite die [3-6], in which a quartz tube inserted with the sample powder was heated, as mentioned in Chapter 1 and 3. Powder samples of 150 mg were pyrolyzed under the following heating conditions: pyrolysis temperatures of 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C; and pyrolysis time and heating rate of 3 min and 15–20 °C/s, respectively. The heating rate and pyrolysis time were referred to the report by Carlson et al. [17], in which both pyrolysis oil and char were obtained effectively. The temperature during pyrolysis was monitored using a thermocouple inserted into a drilled small hole with 1 mm i.d. in the graphite die, which did not interrupt the applied current.

The liquid fraction of volatilized pyrolysis oil was cooled with liquid nitrogen for the recovery and collection in a washing tube. The volatiles trapped inside the quartz tube and connector were washed with acetone and then analyzed quantitatively and qualitatively as pyrolysis oil for each experiment. The solid fraction trapped inside the quartz tube was also collected by washing and then filtered. Char samples were quantified by weighing after drying.

#### ***4.2.3. Elemental analysis of char***

The elemental contents of carbon (C), hydrogen (H), and nitrogen (N) of the rice husks, wood meal, cellulose, and char were determined using a CHN analyzer (MT-5, Yanako Co., Japan). The oxygen (O) content was calculated by difference.

#### ***4.2.4. GC-MS analysis of pyrolysis oil***

The semiquantitative analysis of pyrolysis oils was performed with a GC-MS QP-5050A instrument (Shimadzu, Japan), where tetracosane as an internal standard and a DB-5 capillary column (30 m × 0.25 mm in diameter, film thickness 1.0 μm, Agilent technology, USA) were used as shown in Chapter 1 and 3.

### **4.3. Results and discussion**

#### ***4.3.1. Product distribution and pyrolysis temperature of rice husks, wood meal, and cellulose using pulse current heating***

The effect of pyrolysis temperature, using pulse current heating, on the distribution of pyrolysis products, such as gas, pyrolysis oil, and char, was studied for rice husks, Todo-fir, and cellulose (Figs. 4.1-4.3). At each processing temperature, high ash contents and char yields were found for the rice husks pyrolysis products. The percentage of each constituent of rice husks, reported by Kawabata et. al., was 24–39% cellulose, 20–34% lignin, and 17–26% hemicellulose [18], while that of Todo-fir, reported by Migita et. al., was 31.7–41.0% α-cellulose, 21.8–33.0% lignin, and 10-20% hemicellulose

[19]. Thus differences were not necessarily remarkable for the basic components. The measured ash content of rice husks (15.7%) was much higher than that of Todo-fir (0.1%) and cellulose (0.0%).

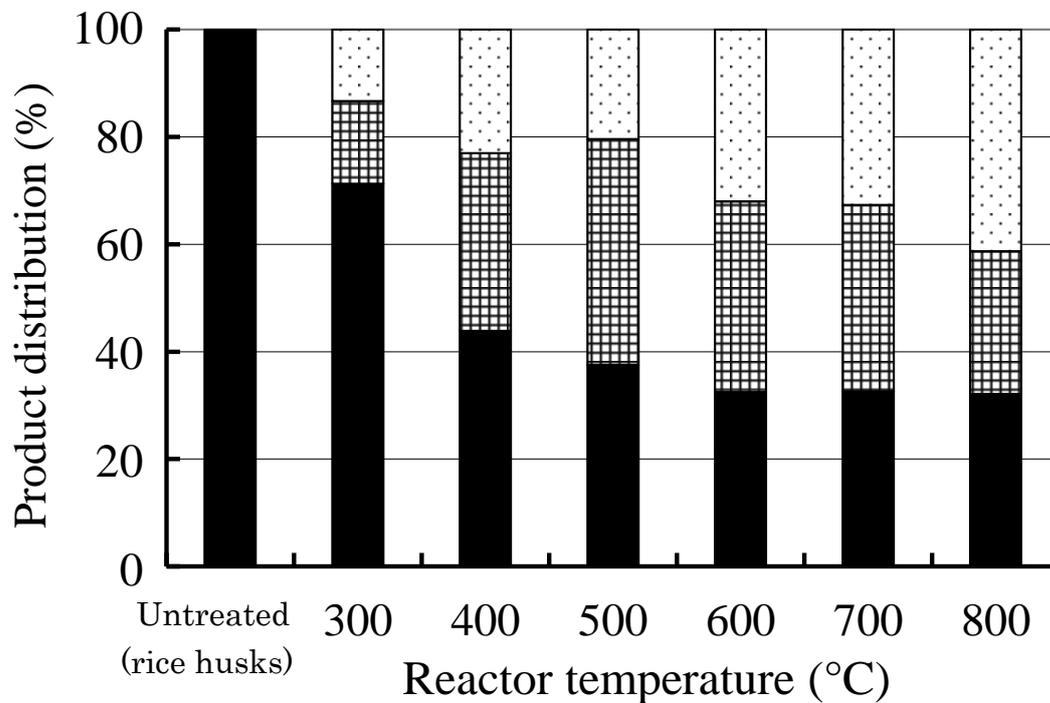


Fig. 4.1 Product distribution at various reactor temperatures for rice husks  
 Legend: : Gas, : Pyrolysis oil, : Char

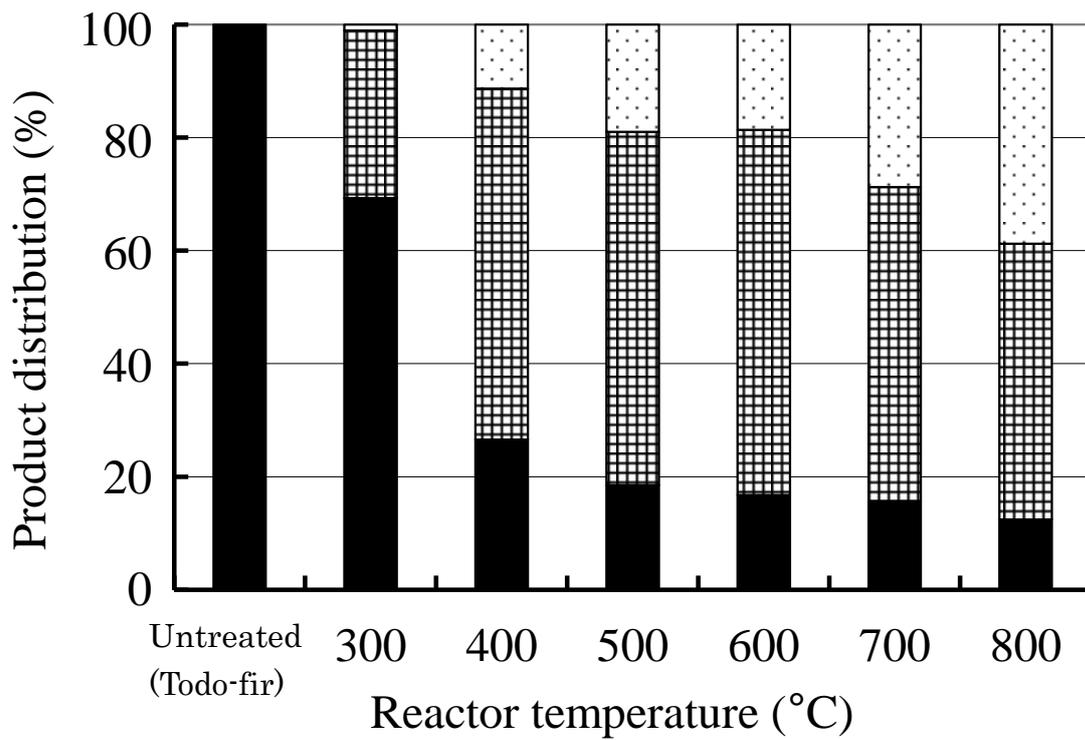


Fig. 4.2 Product distribution at various reactor temperatures for Todo-fir  
 Legend: : Gas, : Pyrolysis oil, : Char

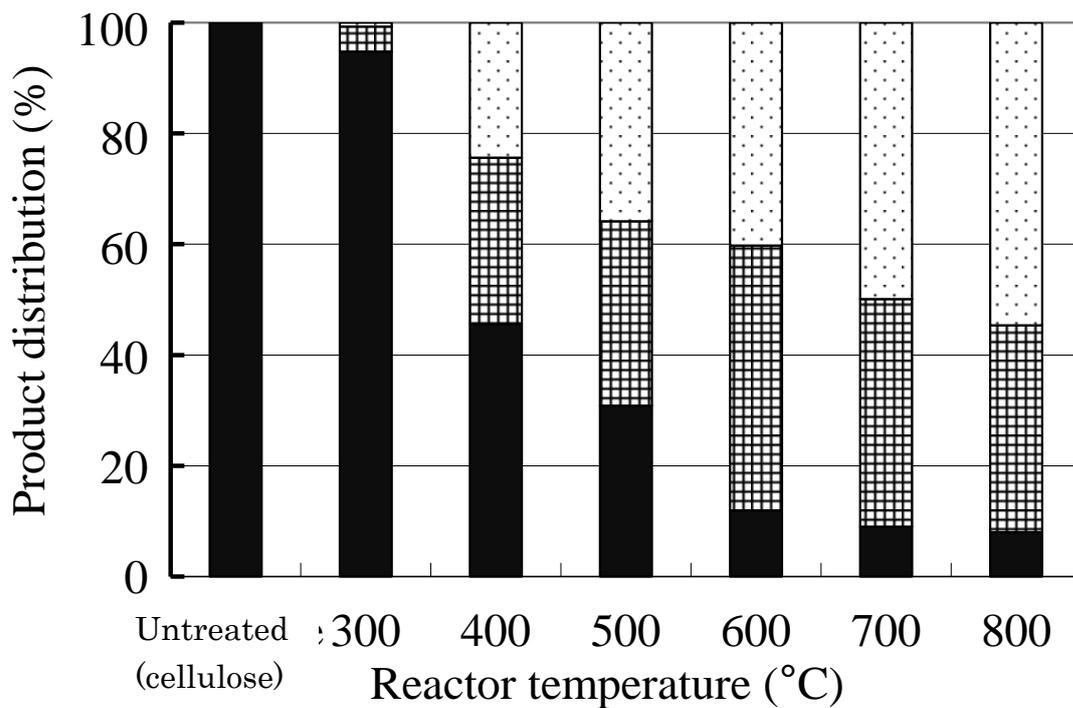


Fig. 4.3 Product distribution at various reactor temperatures for cellulose  
 Legend: : Gas, : Pyrolysis oil, : Char

A similar trend was observed for the yield of pyrolysis oil obtained by pulse current heating, where the maximum yield was reported at 500 °C by previous papers [13, 20-27] related to the distribution of products obtained by the fast-pyrolysis of rice husks with fixed bed or fluidized bed reactors. The yield of pyrolysis oil obtained from rice husks increased at 300 and 400 °C, and reached the maximum at 500 °C; subsequently, it decreased at 600 and 700 °C, and reached about 28% at 800 °C. The char yield decreased notably at 300 and 400 °C, while it decreased gradually, with increasing pyrolysis temperature at 500–800 °C, and became about 32% at 800 °C. The char yield of rice husks was 2 to 3 times higher than that of Todo-fir and cellulose at 500–800 °C. Raveendran et al. [11] reported that the removal of ash contributed to the increase in the yield of pyrolysis oil obtained from rice husks. Hence, the yield of pyrolysis oil obtained from rice husks was lower than that from Todo-fir and cellulose. At 800 °C, the char content, which increased because of the influence of the ash content of raw materials, was about 32%, 12%, and 8% for rice husks, Todo-fir, and cellulose, respectively.

The yield of pyrolysis oil obtained from Todo-fir increased remarkably at 300 and 400 °C and reached the maximum at 500-600 °C, and was higher than that from rice husks and cellulose in the 500–800 °C range; it gradually decreased with increasing pyrolysis temperature in the 700–800 °C range. The char yield notably decreased in the 300–400 °C range, while it decreased gradually, with increasing pyrolysis temperature, in the 500–800 °C range, and became about 12% at 800 °C. The trend of the distribution of pyrolysis oil, gas, and char products in the 400–800 °C range was similar to that

reported for Japanese cedar in Chapter 1. The yield of pyrolysis oil obtained from cellulose increased greatly from 400 °C to 600 °C, and it fell gradually at 700–800 °C. The yield of char decreased remarkably at 400–500 °C and became about 8% at 800 °C. The yields of both pyrolysis oil and char were similar to those expected based on the reports on Japanese cedar in Chapter 1. The maximum yield of pyrolysis oil, which was about 42%, 65%, and 48%, for rice husks, Todo-fir, and cellulose, respectively, was generally obtained in the 500–600 °C range. At 400–700 °C, the yield of pyrolysis oil for rice husks and cellulose became 33–42% and 30–48%, respectively, which was slightly lower than that reported in the fast pyrolysis using fixed bed or fluidized bed reactors [21-24]. In the same temperature range, the yield of pyrolysis oil obtained from Todo-fir became 56–65%, which was relatively high. The yield of char obtained by the pyrolysis of rice husks and Todo-fir was 32–44% and 16–27% at 400–700 °C, respectively.

#### ***4.3.2. Elemental composition***

The effect of pyrolysis temperature, using pulse current heating, on the elemental composition of pyrolysis char from Todo-fir showed a trend similar to that observed for Japanese cedar (Chapter 1). Carbonization progressed by thermal decomposition reactions, such as dehydration, decarbonylation, and dehydrogenation, in fast pyrolysis as well as in conventional pyrolysis. At the same pyrolysis temperature, the carbonization of rice husks was slightly slower than that of Todo-fir.

Table 4.1 Elemental analysis of char obtained from rice husks pyrolyzed in the temperature range of 300 - 800 °C

	Untreated (rice husks)	Reactor temperature (°C)					
		300	400	500	600	700	800
H (%)	6.0	5.9	4.8	4.2	3.6	3.3	3.0
C (%)	47.8	54.7	67.2	71.8	76.4	78.5	82.9
N (%)	0.4	0.5	0.8	0.8	0.8	1.1	0.9
O <sup>a</sup> (%)	45.8	38.9	27.2	23.2	19.1	17.0	13.3

a: by difference

Table 4.2 Elemental analysis of char obtained from Todo-fir pyrolyzed in the temperature range of 300 - 800 °C

	Untreated (Todo-fir)	Reactor temperature (°C)					
		300	400	500	600	700	800
H (%)	6.2	5.7	4.3	3.4	3.1	2.9	1.9
C (%)	49.4	55.4	73.2	77.2	82.5	85.6	89.6
N (%)	0.1	0.2	0.3	0.2	0.2	0.2	0.5
O <sup>a</sup> (%)	44.3	38.7	22.3	19.2	14.1	11.4	8.0

a: by difference

Table 4.3 Elemental analysis of char obtained from cellulose pyrolyzed in the temperature range of 300 - 800 °C

	Untreated (Cellulose)	Reactor temperature (°C)					
		300	400	500	600	700	800
H (%)	6.1	6.1	4.9	4.4	5.0	5.0	4.3
C (%)	43.7	44.0	59.9	66.7	62.1	60.6	68.7
N (%)	0.0	0.1	0.1	0.1	0.1	0.1	0.2
O <sup>a</sup> (%)	50.3	49.7	35.1	28.8	32.7	34.2	26.8

a: by difference

During pyrolysis, the hydrogen content decreased while the carbon content increased on increasing the pyrolysis temperature, as shown Tables 4.1 and 4.2, wherein the elemental compositions of the char obtained from rice husks and Todo-fir at 300–800 °C are listed. The carbon content of Todo-fir was about 80% and 90% at 500 and 800 °C, respectively, and it showed a trend of higher carbon content at higher temperature, similarly to the pyrolysis of Japanese cedar in Chapter 1. The carbon content in rice husks was about 80% and hydrogen content was about 3%, which were similar to those of the char from Todo-fir at 600 °C. Gasification progressed relatively fast, while carbonization slowly, which was judged from the fact that a notable amount of residue, about 32 wt%, including mineral components was obtained at 800 °C, wherein most of the raw materials were gasified and liquefied. At 800 °C, the char from cellulose, which was obtained with a yield of about 8%, had a carbon content of about 70%, and the carbonization progressed relatively slowly (Table 4.3).

In Figs. 4.4-4.6, the atomic ratio of O/C was plotted against the ratio of H/C for chars obtained from rice husks, Todo-fir, and cellulose, respectively by pulse current heating. When the relationship between the reactor temperature and both atomic ratios was compared with that obtained conventional pyrolysis, the followings are found: The carbon content of the char from Todo-fir with pulse-current heating (Fig. 4.5) was lower and the change of atomic ratios was slower than those of the char from Japanese cedar [28], Todo-fir (as shown in Chapter 2) obtained with conventional pyrolysis at the same processing temperature.

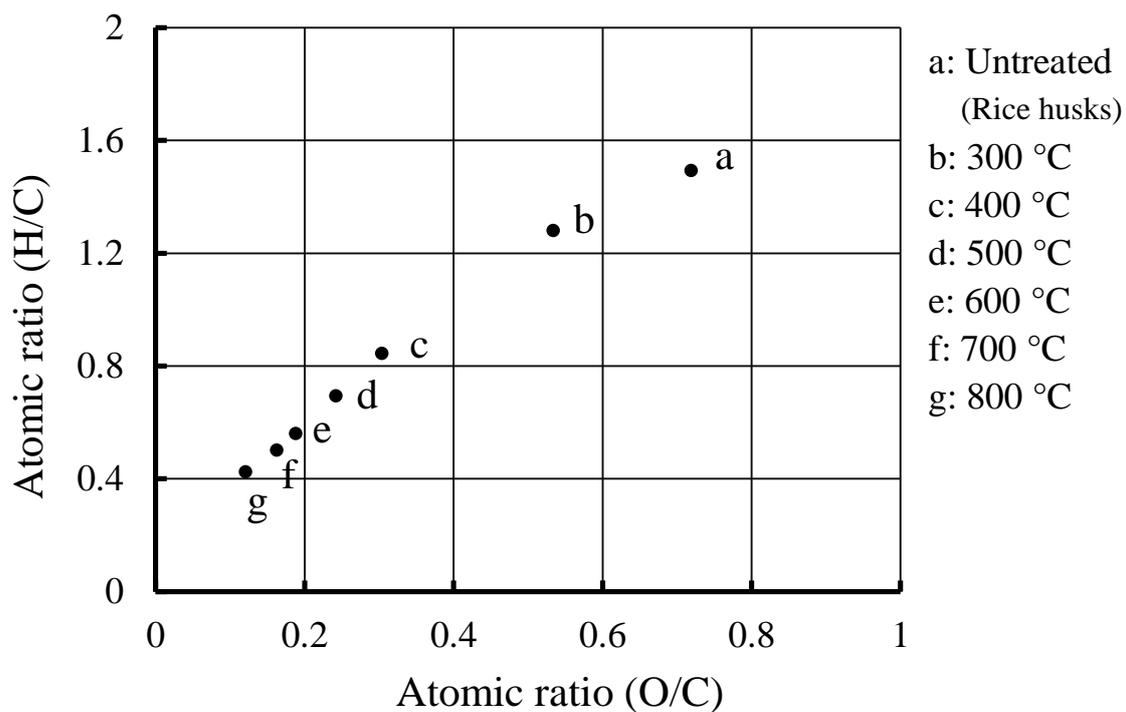


Fig. 4.4 Van Krevelen plot for chars obtained from rice husks pyrolyzed in the temperature range of 300 - 800 °C

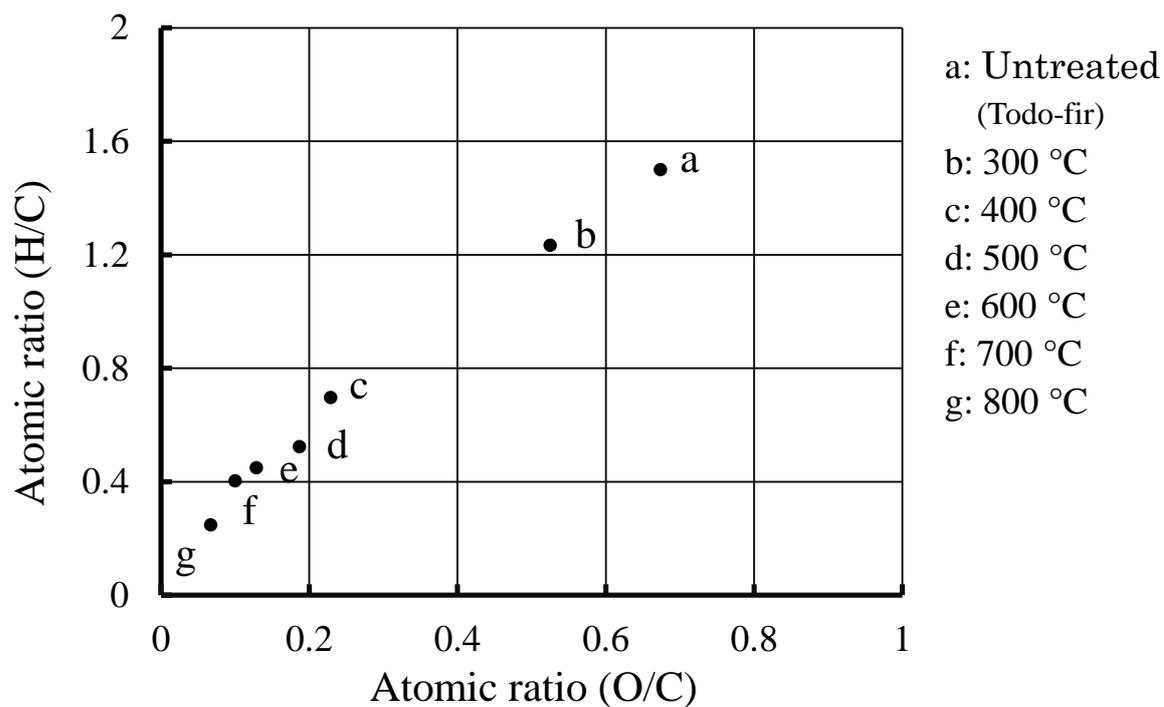


Fig. 4.5 Van Krevelen plot for chars obtained from Todo-fir pyrolyzed in the temperature range of 300 - 800 °C

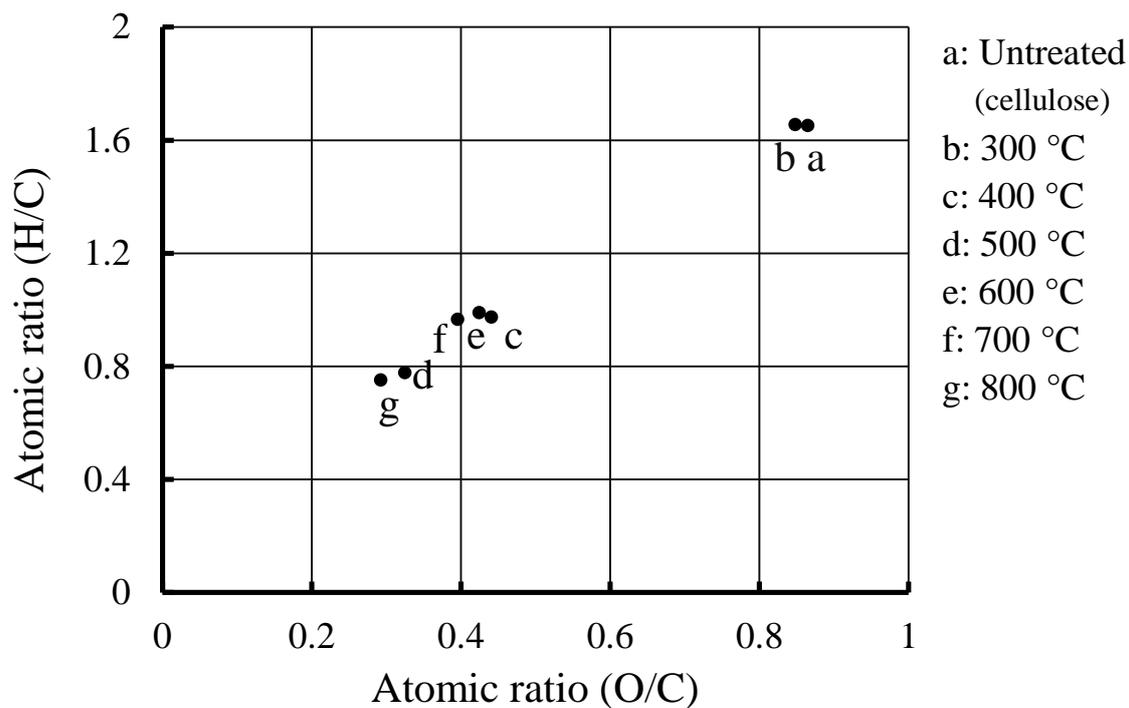


Fig. 4.6 Van Krevelen plot for chars obtained from cellulose pyrolyzed in the temperature range of 300 - 800 °C

The difference of the above-mentioned pyrolysis conditions was due to the pyrolysis reaction affected by processing temperature and the elemental composition, H/C and O/C ratios of char. Since the pyrolysis conditions under the pulse current heating was operated at much higher heating rate and much shorter resident time compared to conventional pyrolysis.

In the conventional carbonization of Japanese cedar, Kuriyama suggested that dehydration, decarbonylation, demethanization, and aromatization occurred at 310–400 °C; elimination of functional groups and hydrogen, and polycyclic aromatization occurred at 400–500 °C; dehydrogenation mainly occurred above 500 °C, forming planes of the hexagonal network because of the rapid condensation of polycyclic aromatics

[28]. The relationship between the pyrolysis temperature and elemental composition, i.e. H/C and O/C, of char for Todo-fir (Fig. 4.5) was similar to that for Japan cedar (Chapter 1). In the sample of Todo-fir, with pulse current heating, dehydration and decarbonylation were suggested to occur at 500–600 °C, while the elimination of functional group or hydrogen, and condensation occurred at 700–800 °C.

On elemental compositional analysis, an H/C value of 0.042 and 0.036 was obtained at 700 and 800 °C, respectively for the pyrolysis of rice husks. Inorganic constituents, which were about 32wt% of the char from rice husks at 800 °C, had little effect on the pyrolysis.

The relationship between processing temperature, the elemental composition of cellulose char, and H/C and O/C ratios was different from those obtained for Japanese cedar, Todo-fir, and rice husks. Tang et al.[29] reported that the occurrence of dehydration, decarbonylation, aromatization, and carbonation was observed in the conventional pyrolysis of cellulose, while such a trend was not observed in the pyrolysis of cellulose using pulse current heating; the change in the compositions was small at 600–800 °C (Fig. 4.6). The main part of the char was suggested to originate from the tar fraction, since heating rate of pyrolysis in this research was much higher than that of conventional pyrolysis, and then, liquefaction and gasification quickly occurred during pyrolysis at 600–800 °C.

#### ***4.3.3. Compositions of pyrolysis oil***

At low temperatures, more aromatic hydrocarbons were observed in the

pyrolysis oil obtained from rice husks than those from Todo-fir and cellulose, although the yield of pyrolysis oil was lower than that of Todo-fir and cellulose (Table 4.4). Toluene as well as phenolic compounds, such as phenol, *o*-cresol, and *p*-cresol, were detected in the oil obtained by the pyrolysis of rice husks

Table 4.4 Pyrolysis oil components for rice husks, Todo-fir, and cellulose pyrolyzed at 500 °C

Retention time (min.)	Pyrolysis oil	Pyrolysis oil	Pyrolysis oil
	rice husks	todo fir	cellulose
	area/I. S. area	area/I. S. area	area/I. S. area
6.21 Benzene	-	-	-
8.85 Toluene	0.04	-	-
10.14 Furfural	0.15	0.13	0.27
10.97 Ethynylbenzene	-	-	-
11.25 Styrene	-	-	-
12.48 Phenol	0.07	0.12	-
13.62 <i>o</i> -Cresol	-	-	-
13.74 1-Propynylbenzene	-	-	-
13.90 <i>p</i> -Cresol	-	0.09	-
14.19 Guaiacol	0.20	-	-
15.40 Catechol	0.10	0.19	-
15.57 <i>m</i> -Cresol	0.18	0.17	-
15.77 Naphthalene	-	-	-
17.07 Methyl-naphthalene	-	-	-
17.45 Eugenol	-	-	-
17.95 Biphenyl	-	-	-
18.00 Vanillin	-	-	-
18.49 Isoeugenol	-	0.23	-
18.89 Acenaphthylene	-	-	-
18.97 Levoglucosan	0.45	0.96	4.06
20.22 <i>o</i> -Biphenylenemethane	-	-	-
21.84 Phenanthrene	-	-	-
21.91 Anthracene	-	-	-
24.05 Pyrene	-	-	-
25.00 Internal standard (Tetracosane)	1.00	1.00	1.00

Table 4.5 Pyrolysis oil components for rice husks, Todo-fir, and cellulose pyrolyzed at 800 °C

Retention time (min.)		Pyrolysis oil	Pyrolysis oil	Pyrolysis oil
		rice husks	todo fir	cellulose
		area/I. S. area	area/I. S. area	area/I. S. area
6.21	Benzene	0.47	2.62	1.02
8.85	Toluene	0.21	1.86	0.46
10.14	Furfural	-	0.61	0.89
10.97	Ethynylbenzene	0.20	0.48	-
11.25	Styrene	0.42	1.48	0.51
12.48	Phenol	0.47	1.73	0.60
13.62	<i>o</i> -Cresol	0.11	0.78	-
13.74	1-Propynylbenzene	0.84	2.14	-
13.90	<i>p</i> -Cresol	0.19	1.07	-
14.19	Guaiacol	-	-	-
15.40	Catechol	-	1.78	-
15.57	<i>m</i> -Cresol	-	-	-
15.77	Naphthalene	1.92	3.17	0.63
17.07	Methylnaphthalene	0.16	-	-
17.45	Eugenol	-	-	-
17.95	Biphenyl	0.10	-	-
18.00	Vanillin	-	-	-
18.49	Isoeugenol	-	-	-
18.89	Acenaphthylene	0.58	1.05	-
18.97	Levoglucosan	-	1.39	29.77
20.22	<i>o</i> -Biphenylenemethane	0.17	0.40	-
21.84	Phenanthrene	0.37	0.61	-
21.91	Anthracene	0.12	-	-
24.05	Pyrene	0.23	0.37	-
25.00	Internal standard (Tetracosane)	1.00	1.00	1.00

at 500 °C (Table 4.4). Aromatic hydrocarbons, such as benzene and styrene as well as polycyclic aromatic hydrocarbons, such as naphthalene, phenanthrene, anthracene, and pyrene, were detected at 600–800 °C (Table 4.5, Fig. 4.7). At 500 °C, a small amount of levoglucosan was obtained in the pyrolysis oil of rice husks because of the catalytic effect of ash, as reported by Bakar et al.

[27]. These results show a trend similar to that of previous studies, wherein low molecular weight aromatics, such as phenol or toluene, were obtained by the fast pyrolysis of rice husks near 500 °C, using a fixed bed or a fluidized bed reactor [21-24]. Phenol and alcohol were the main components, while other aromatic hydrocarbons were not detected in the pyrolysis oil of Todo-fir obtained at 500 °C (Fig. 4.8). At 800 °C, more phenols than poly aromatic hydrocarbons were detected (Table 4.5, Fig. 4.8) in the pyrolysis oil of Todo-fir.

A peak with a relatively large area, attributed to levoglucosan, was detected in the GC-MS analysis of the pyrolysis oil obtained from Todo-fir at 400–800 °C. Scott et al. reported that the levoglucosan content in pyrolysis oil notably increased as a result of the deionization process on poplar wood carried out during fast-pyrolysis [30]. In addition, Richards et al. reported that the levoglucosan content in the pyrolysis oil of cottonwood and cellulose were remarkably influenced by the presence of metal ions and metal salts [31]. Takahashi et al. reported the ash composition after combustion, which is related to the amount of inorganic constituents, of Todo-fir [32]. The contents of SiO<sub>2</sub>, CaO, and K<sub>2</sub>O were 31%, 26%, and 19%, respectively, while MgO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>O, SO<sub>3</sub>, Cl, TiO<sub>2</sub> were also detected [32]. The influence of ash on the pyrolysis of levoglucosan was very limited, because the amount of ash of Todo-fir was only 0.1%, which was extremely small amount compared to that of rice husks.

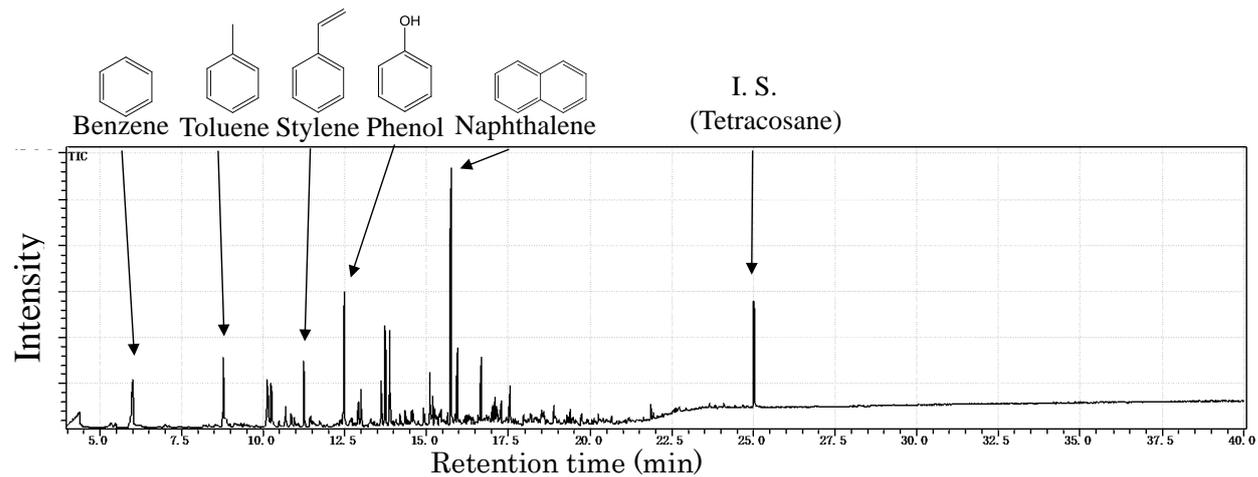
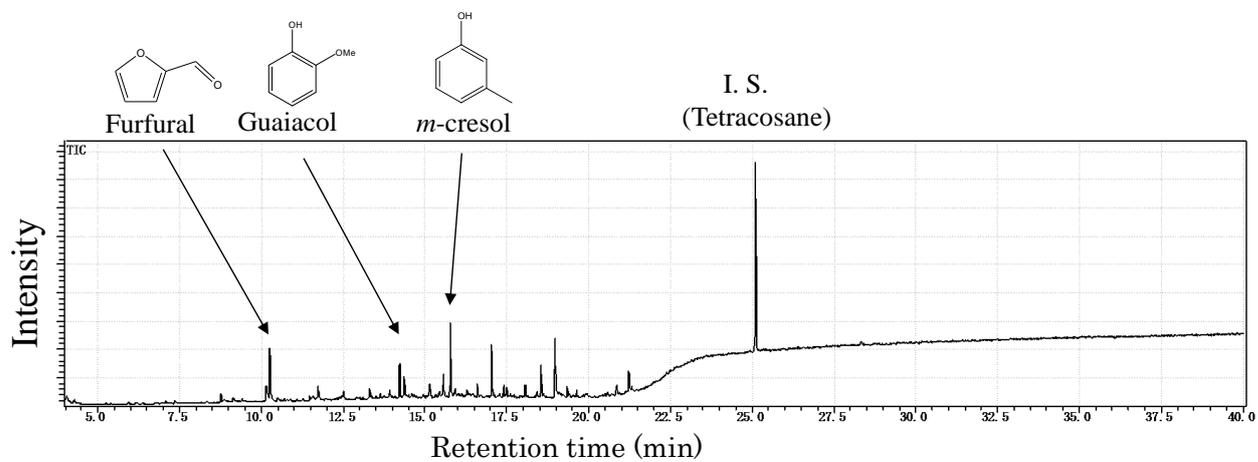


Fig. 4.7 TIC for oil fraction derived from rice husks pyrolyzed at 500 °C (upper) and 800 °C (lower)

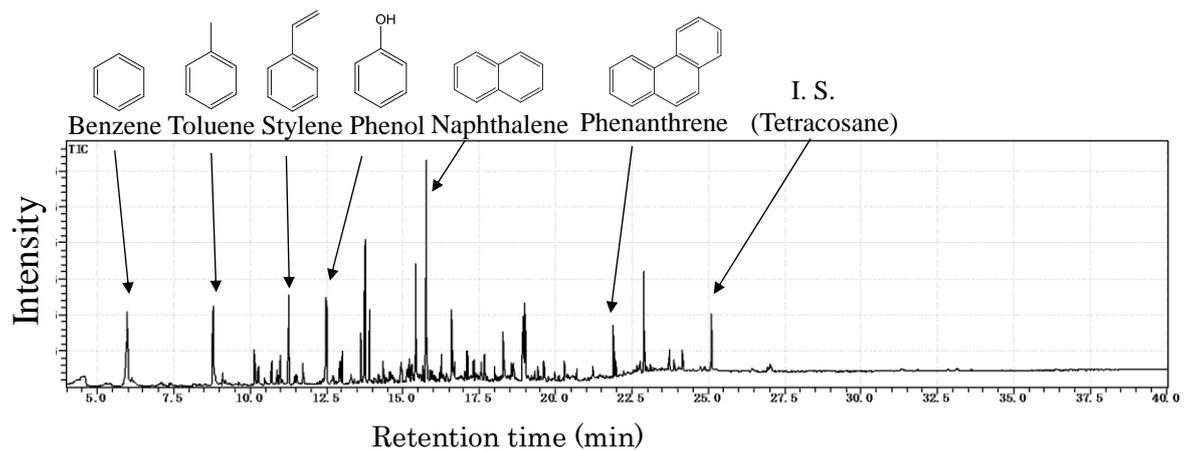
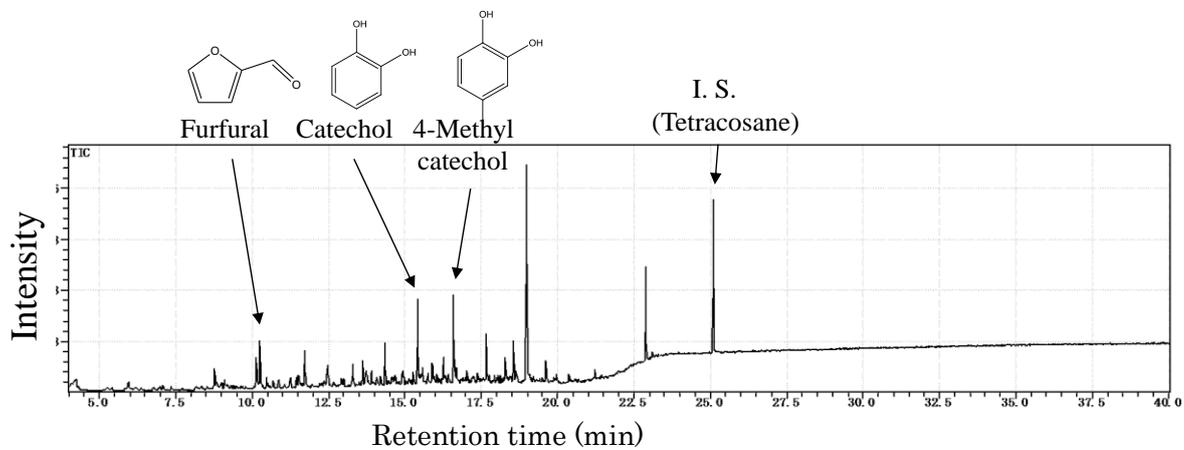


Fig. 4.8 TIC for oil fraction derived from Todo-fir wood meal pyrolyzed at 500 °C (upper) and 800 °C (lower)

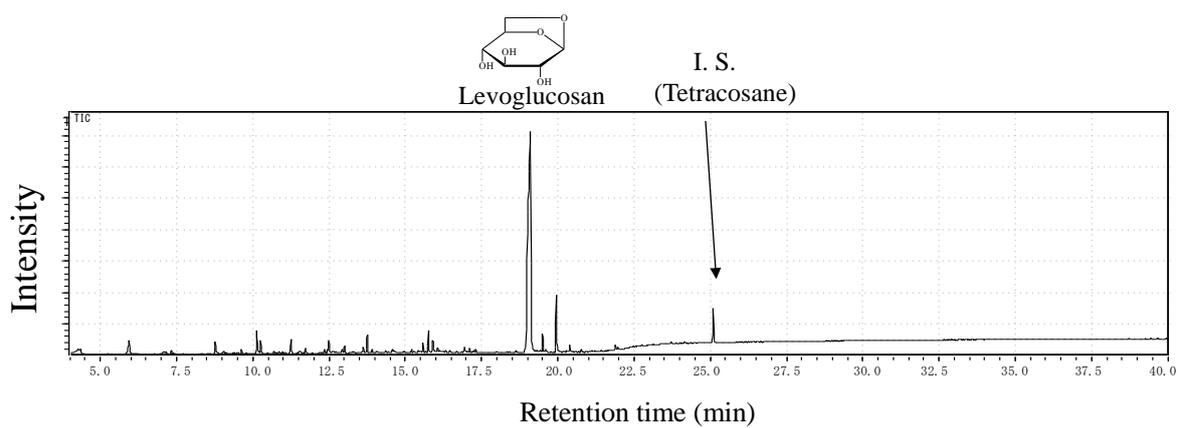
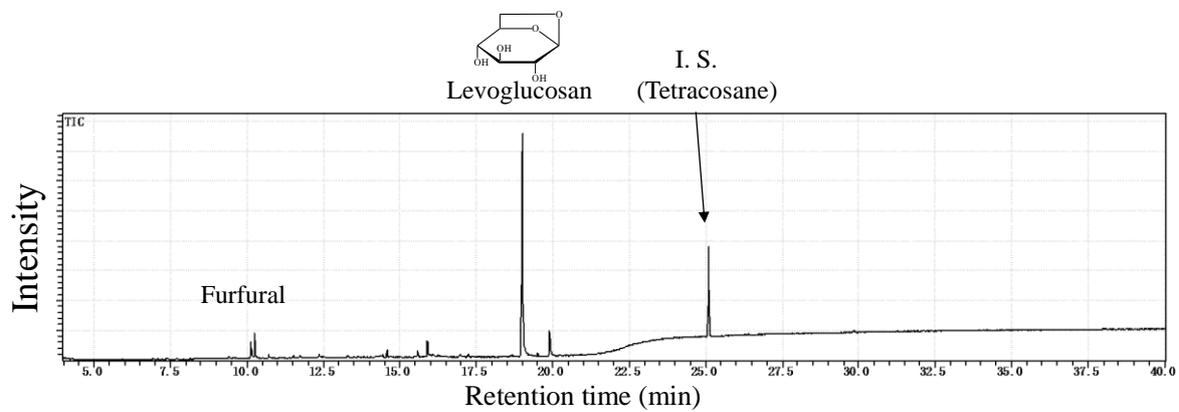


Fig. 4.9 TIC for oil fraction derived from cellulose pyrolyzed at 500 °C (upper) and 800 °C (lower)

The pyrolytic mechanism of cellulose without catalysts and other ingredients at 500–800 °C, using pulse current heating, in term of the production of levoglucosan was explained as follows: in the pyrolysis of cellulose without mineral salts, formic acid or glycolaldehyde were not formed during pulse current heating process. In the pyrolysis oil of cellulose, a peak with a large area, attributed to levoglucosan, and a peak of furfural were detected in the 500–800 °C range (Fig. 4.9). Many minor peaks attributed to aromatic compounds were detected in the 700–800 °C range. Patwardhan et al. reported a remarkable decrease in the amount of levoglucosan and an increase in the amount of formic acid upon the increase of pyrolysis temperature [12] in the pyrolysis oil during the fast pyrolysis of cellulose. They also reported a decrease in the amount of levoglucosan upon addition of a small amount of alkaline and alkaline-earth metals, although both amounts of formic acid and glycolaldehyde were increased [12].

#### **4.4 Summary**

The pyrolysis of rice husks, Todo-fir, and cellulose by pulse current heating was examined to elucidate the influences of reaction temperature on their product distributions and chemical properties of the resulting oil and char fractions for utilization of pyrolysis products obtained from biomass. Some common characteristics were found for each product distribution: The maximum yield of pyrolysis oil obtained from each material was observed at 500–600 °C. In contrast, the following characteristic properties of pyrolysis products obtained from each material were observed: High ash content and

char yields at each processing temperature were found in the rice husk pyrolysis products. Aromatic hydrocarbons were detected in the pyrolysis oil obtained from rice husks at lower temperature pyrolysis. The yield of pyrolysis oil obtained from rice husks was lower than that from Todo-fir, and the yield of pyrolysis oil obtained from Todo-fir tended to be higher than those from rice husks and cellulose at all temperatures. Plenty of levoglucosan was detected in the pyrolysis oil obtained from cellulose at 500–800 °C, although the yield of the pyrolysis oil was not so high. In the pyrolysis oil obtained from rice husks, such aromatic hydrocarbons as benzene and styrene, as well as polycyclic aromatic hydrocarbons like naphthalene, phenanthrene, anthracene, and pyrene, were detected at 600–800 °C.

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## Conclusions

This research was carried out for the purpose of utilizing both pyrolysis oil and char that were obtained from woody biomass, and for selectively producing functional carbon composite materials and pyrolysis oil containing useful compounds. The pyrolysis products were characterized, and the effects of the pyrolysis conditions on product distribution, pyrolysis oil composition, and carbon composite material composition were investigated.

In Chapter 1, the effects of pyrolysis using the pulse current heating method on product distribution, pyrolysis oil composition, and the characteristics of char obtained from wood biomass (Japanese cedar) were investigated to evaluate the applicability of the aforesaid method in the synthesis of useful chemical components. The conditions for obtaining char with useful oxygen functionalities and pyrolysis oil composed of useful aromatic/hydrocarbon compounds were examined. The relationship between pyrolysis oil composition and reactor temperature was determined. Numerous aromatic hydrocarbon compounds were observed in the pyrolysis oil that was obtained at 800 °C, while aromatic compounds with a high degree of oxygen functional groups were observed in the pyrolysis oil that was obtained at 500 °C. Thus, useful pyrolysis oil and char materials can be selectively obtained at given reactor temperatures by pyrolysis using the pulse current heating method. The wood meal was considered to be pyrolyzed using radiant heat transmitted through a quartz tube placed in a graphite die and heat conduction efficiently for above process. Further studies on practical production methods that involve improving the yield by controlling the

pyrolysis conditions (heating rate, temperature, and atmosphere) are described. Furthermore, studies on the expansion of the range of biomass species that can be used as starting materials are necessary for the efficient application of this technology.

Information relating to the changes in chemical structure with increasing reactor temperature was obtained, in addition to the maximum ammonia adsorption capacities for the char that was obtained at 500 °C. The functionality of the residual char as an ammonia adsorbent and the co-production of aromatic chemicals can be highlighted as a new process designed for efficient usage of woody biomass with using pulse current heating. Further development of this technology with the use of appropriate catalysts systems would allow much better control over the pyrolysis oil composition as well as the functionalization of char or char composites; this in turn would aid in devising highly efficient chemical manufacturing processes. .

In Chapter 2, the relationship between adsorption ability and pyrolysis conditions for Todo-fir char was investigated. Pyrolysis under an air atmosphere was effective in generating acidic functional groups such as carboxylic acid groups, and it improved the properties of the Todo-fir char. A pyrolysis temperature of 300 °C was found to be most effective, and the change in the chemical structure of cellulose was reflected in the formation of acidic functional groups by the pyrolysis of Todo-fir in air. From these results, it was concluded that pyrolysis under an air atmosphere was effective in generating acidic functional groups such as the carboxyl group, which

improved the ability of the product to adsorb basic substances like ammonia.

In Chapter 3, the effects of the catalyst conditions employed for the pyrolysis of woody biomass on product distribution are discussed. In addition, the characterization of pyrolysis oil and the composition of the char obtained simultaneously are described. The composition of some aromatic compounds changed noticeably when using metal oxides as the catalyst. Furthermore, the phenomenon of coexistence or dissolution at the interface of the carbon and oxides was more remarkable in the case of  $\text{Fe}_3\text{O}_4$  than in the case of  $\text{TiO}_2$ . A micro-graphite layer was observed to form in the char pyrolyzed in the presence of  $\text{Fe}_2\text{O}_3$  as the catalyst. Partial graphitization was expected to contribute to the physical characteristics and functionality (such as conductivity) of the char obtained by catalytic pyrolysis with pulse current heating at 800 °C. The pyrolysis oil composition ratio changed remarkably when using a catalyst, as opposed to that in the case of char obtained by wood meal pyrolysis without any catalyst. The composition ratio of PAHs such as naphthalene in the pyrolysis oil tended to increase in the catalytic pyrolysis with pulse current heating at 800 °C. In this chapter, iron oxides were demonstrated to be interesting catalysts that afforded the desired pyrolysis oil composition and properties of the char in the pyrolysis of wood biomass by the pulse current heating method. When iron oxides and  $\text{TiO}_2$  were used as catalysts, the composition ratio of aromatic hydrocarbon compounds such as naphthalene tended to increase, even at a processing temperature of 500 °C. Since similar yields of pyrolysis oil were obtained in both catalytic and non-catalyzed pyrolysis, the pyrolysis of biomass using pulse current heating with

an adequate amount of catalyst is expected to yield specific aromatic compounds at lower temperatures.

In Chapter 4, rice husks, Todo-fir meal, and cellulose were used to investigate the effect of pyrolysis temperature on the composition of pyrolysis products prepared with pulse current heating is described. The amount of pyrolysis oil obtained from rice husk was the lowest, and the inorganic constituents were considered to have some effect on the production of pyrolysis oil, carbonization, and gasification. Comparison of the pyrolysis oil obtained from rice husks, Todo-fir meal, and cellulose by pyrolysis with pulse current heating revealed that the processing factors of pyrolysis temperature, raw material components, and inorganic constituents affected the composition of the polycyclic aromatic hydrocarbons and the levoglucosan content. The choice of pyrolysis conditions and catalyst type, as well as the inorganic constituents in the raw materials, is important to selectively convert plant biomass into useful products.

Characteristic features regarding the composition of the pyrolysis oil were found for each set of pyrolysis conditions by investigating the relationship between the properties of the obtained pyrolysis oil and the catalytic effects of the metal oxides, and the pyrolysis conditions in the pulse current heating method. Aromatic hydrocarbons were considered to be produced at lower processing temperatures by the catalytic effect of the metal oxides. A technology for the selective production of useful materials can be established by controlling the pyrolysis conditions and confirming the properties and composition of the aromatic compounds included in the

pyrolysis oil.

The chemical structure and microscopic structure of the carbon composite materials obtained at each pyrolysis temperature were shown by investigating the relationship between the pyrolysis conditions and the catalytic effect of the metal oxide. Since suitable pyrolysis conditions for producing ammonia adsorbent and the characteristics of the metal oxide carbon composite material were shown, char obtained as a pyrolysis residue was considered to contribute to the production of a useful material in addition to pyrolysis oil. Moreover, this method was applied for the production of silica carbon composite material along with the pyrolysis oil, by using rice husk, a previously unutilized biomass, as the raw material. Accordingly, the results of this research are expected to contribute to the effective use of unused resources for producing pyrolysis oil containing useful compounds and functional carbon composite materials.

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