

Selective Pyrolysis of Japanese Cedar to C₁-Chemistry Materials. I. Particle Size, Part of Wood, Temperature and Time Dependence of Weight Loss and of Conversion Ratio to CO

Tetsuo NAKAGAWA*, Kazuya MINATO**
and Yukio KATAYAMA**

Received July 14, 1994

In order to obtain the basic information about the method of utilizing wood for raw materials of C₁-chemistry, the valid condition of pyrolysis of Japanese cedar (*Cryptomeria japonica* D. Don) powder has been investigated varying particle size, part of wood (*i.e.* difference between sapwood and heartwood), pyrolysis time and temperature in views of the weight loss and the conversion ratio to CO. This decomposition reaction has been carried out using pyrolyzer equipped with gas chromatograph. The quantities of the products such as CO, CO₂, and CH₄ have been measured from the respective peak areas of pyrogram spectra. The negative peak of H₂ has also been found in higher temperature region. In general, the higher pyrolysis temperature is, the more significant the weight loss of wood and the conversion ratio to CO are, which are almost irrespective of both particle size and part of wood.

Key Words: C₁-chemistry/ Pyrolysis/ Gas chromatograph/ Weight loss/ Sapwood/
Heartwood/ Conversion ratio

1. INTRODUCTION

C₁-chemistry is one of the most effective tools of producing chemically various useful compounds such as methanol¹⁻³⁾ from mainly carbon monoxide (CO) and hydrogen (H₂).⁴⁾ However, there remains still a significant problem what is used for the raw materials. The materials must be both abundant and C-rich. Wood is mainly composed of C (50wt%), H (6wt%), and O (44wt%),⁵⁾ and it is said that the main gaseous products of pyrolyzing wood are H₂, CO, methane (CH₄), and carbon dioxide (CO₂),⁶⁾ and therefore wood is worth noticing from the viewpoint of C₁-chemistry. In particular, if the commercially valueless wood is used for the materials, that is significant for considering the conservation of limited natural resources.

By the way, pyrolysis gas chromatography (PY-GC) has been used for the analyses of various polymer compounds, but this tool has not been much applied to wood science extensively.^{7,8)} Many studies on wood pyrolysis are mainly on the change of weight loss.⁹⁻¹¹⁾ Hence it is interesting to try to use this PY-GC procedure for wood decomposition analysis.

In this paper, in order to obtain the basic information about the method of utilizing wood for

* 中川徹夫 : Laboratory of Interface Science I, Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu, 611.

** 湊 和也, 片山幸士 : Department of Wood Science and Technology, Faculty of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-01.

raw materials of C₁-chemistry, we have investigated the dependence of the pyrolysis of Japanese cedar (*Cryptomeria japonica* D. Don) powder on particle size, part of wood (sapwood or heartwood), reaction temperature, and time using gravimetric and the PY-GC procedure, and have searched for the more useful condition of high yield of CO.

2. EXPERIMENTAL

2.1. Sample

The powder (60~80, 80~100, and 100~120 mesh) of sapwood and heartwood of Japanese cedar (*Cryptomeria japonica* D. Don) was used without further pre-treatment. No catalyses were used.

2.2. Pyrolysis

The pyrolyses have been carried out using a Simadzu pyrolyzer PYR-1A equipped with a Simadzu gas chromatograph GC-7AG. The experimental geometry is shown as Fig. 1. The helium (He) gas was used as a carrier of decomposed compounds.

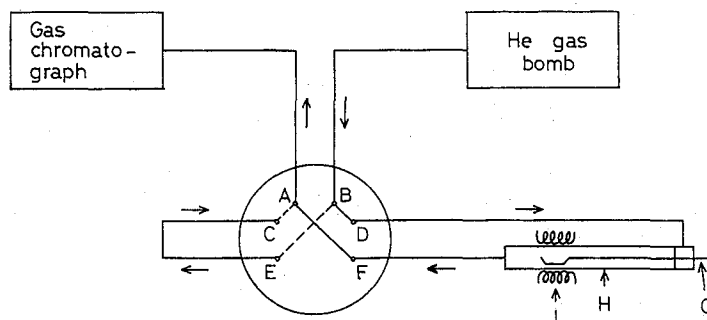


Fig. 1. Experimental geometry for pyrolysis gas chromatography (PY-GC).

The about 10-mg sample was weighted correctly with the platinum (Pt) plate, taken in the tube (H) with the bar (G) in front of the heater (I). The gas route was switched from B→E→C→A to B→D→F→A, and the tube was completely filled with the carrier gas, and the sample was taken to the heater and heated there. The pyrolyses were conducted from 200 to 700°C, and from 0.5 to 40 minutes.

2.3. Gas chromatography

The identification of produced gaseous compounds was carried out by the use of a Simadzu gas chromatograph GC-7AG equipped with a thermal conductivity detector (TCD). At first, we tried to use the nitrogen (N₂) gas as a atmosphere of pyrolyses and a carrier, but the spectra of CO and CO₂ were splitted. This is why the concentration dependence of thermal conductivities for the N₂-CO and N₂-CO₂ systems is changed complicatedly.¹²⁾ Hence instead of the N₂ gas, we used the He gas. For the H₂-He system, the same phenomena appeared as for the N₂-CO and N₂-CO₂ ones, and therefore we gave up the quantitative analysis of the H₂ gas. Active carbon (60~80 mesh) was used for the column packing reagent. The temperature of the column was 70°C. The speed of the He carrier gas was 50 ml/min. The retention times of standard gases are shown in Table 1. There is a linear relationship between the volume and the

Table 1. Retention times of standard gases.

Standard gas	Retention time/min.
H ₂	0.8
Air	1.7
CO	2.0
CH ₄	3.6
CO ₂	8.5

Table 2. Regression equations for calibrating the volumes of standard gases.

Standard gas	Calibration curve
Air	$V=1.27 \times 10^{-4}A-0.0045$
CO	$V=1.11 \times 10^{-4}A-0.0070$
CH ₄	$V=1.25 \times 10^{-4}A-0.0274$
CO ₂	$V=9.71 \times 10^{-5}A-0.0184$

peak areas of pyrogram for the whole standard gases, and the first order regression equations for calibrating the volumes of the respective gases can be obtained (see Table 2).

3. RESULTS AND DISCUSSION

3.1. Weight loss

Temperature dependence

Figure 2 shows the relationship between pyrolysis temperature and weight loss of Japanese cedar powder for 10 minutes. Where W_i is the initial weight of wood, and W is the final one. For both sapwood and heartwood, the weight loss occurs significantly in the 200~300°C range, irrespective of the particle size and part of wood. These findings indicate that these decomposition reaction occurs effectively more than 300°C temperature range. We also try to perform the pyrolyses for 5 or 20 minutes, and obtain the similar results to that for 10 minutes.

Time dependence

Figure 3 shows the relationship between pyrolysis time and weight loss of Japanese cedar

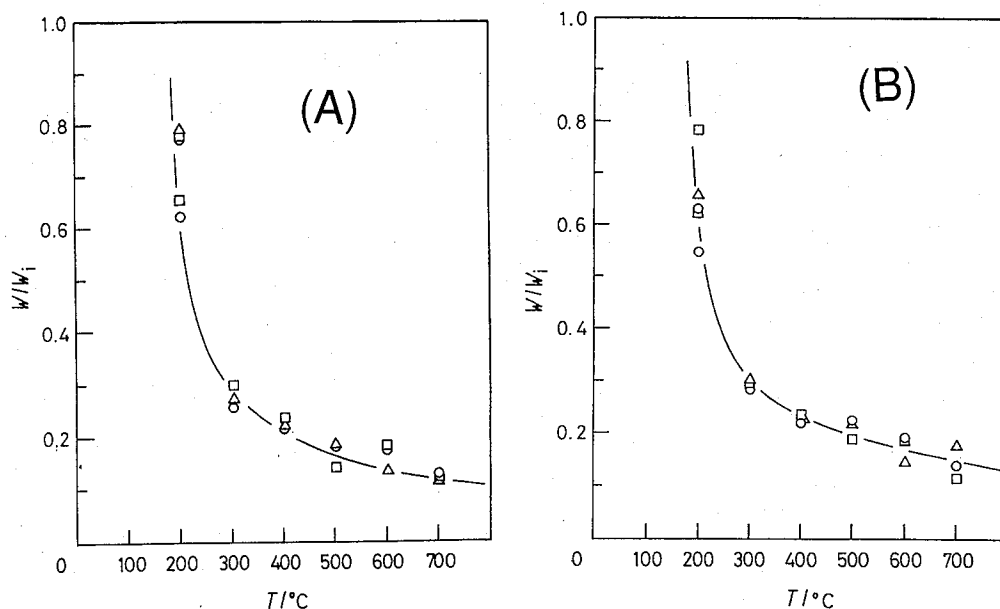


Fig. 2. Relationship between pyrolysis temperature (T) and weight loss of Japanese cedar powder (W/W_i). (A) and (B) represent sapwood and heartwood, respectively. Pyrolysis period is 10 minutes. $\circ$, $\triangle$, and $\square$ are for 60~80, 80~100, and 100~150 mesh, respectively.

Pyrolysis of Japanese Cedar

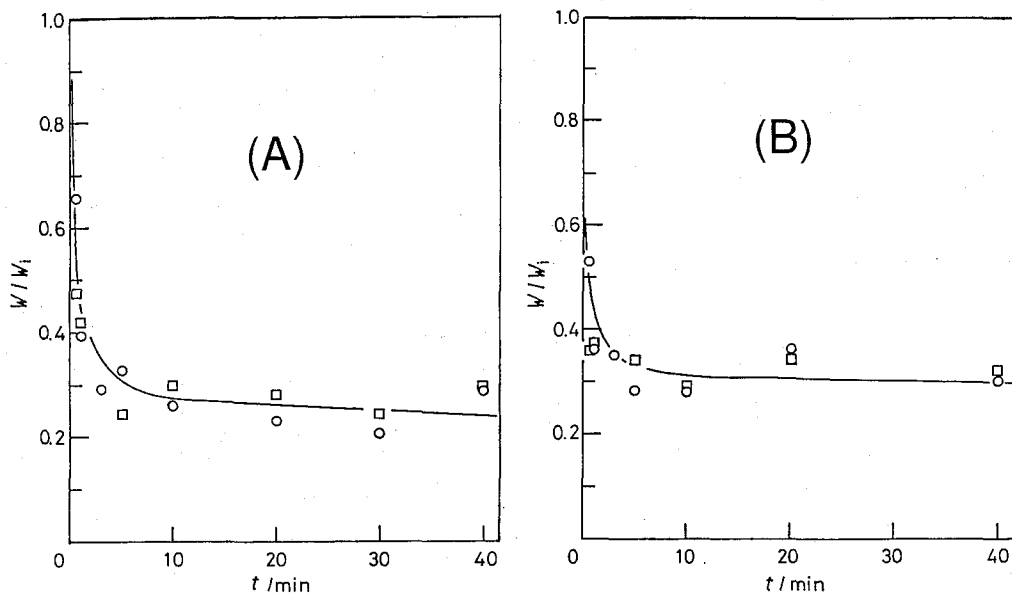


Fig. 3. Relationship between pyrolysis time (t) and weight loss of Japanese cedar powder (W/W_i). Pyrolysis temperature is 300°C. Legends are the same as in Fig. 2.

powder at 300°C. Seeing this figure, we find that it is necessary to decompose these samples enough for more than 10 minutes at 300°C. We also try to perform the pyrolyses for 200, 400, and 500°C. For 200°C, the curve of weight loss decreases slowly with reaction time. For 400°C and 500°C, we know that it is necessary to decompose enough for more than 5 minutes and 1 minute, respectively.

3.2. Conversion to CO

Pyrogram (Gas chromatogram)

Figure 4 shows the temperature dependence of pyrogram (gas chromatogram) of the pyrolysis gaseous C_1 -products of Japanese cedar powder (sapwood, 60~80 mesh). We can easily recognize that the areas of respective C_1 -compound peaks are increasing as the reaction temperature rises. For the H_2 gas, we cannot discuss quantitatively because of the above-mentioned reason. However, we can admit the negative peak due to this H_2 gas at 700°C. These facts suggest qualitatively that the amount of the raw materials of C_1 -chemistry such as H_2 and CO are more increasing as the reaction temperature raises.

Temperature dependence

In order to discuss the results obtained quantitatively, we evaluate the conversion ratio to CO using the following functions:

$$X = 100w/W_i \quad (1)$$

$$Y = 100w/(W_i - W) \quad (2)$$

where W_i is the initial weight, W is the final one, w is the weight of every produced gas (CO , CO_2 , and CH_4). The function X indicates the conversion ratio to CO in the initial wood, and Y does that in the decomposed products. We postulate that all the decomposition products are

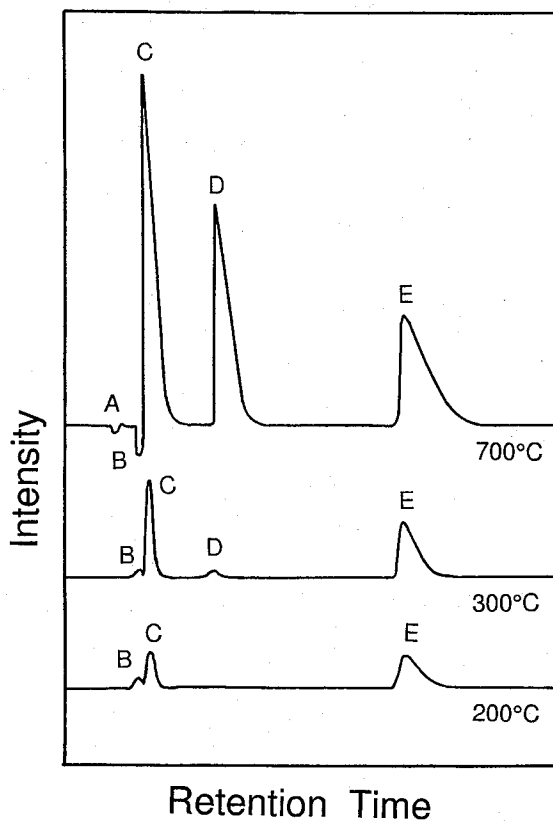


Fig. 4. Temperature dependence of gas chromatogram of the pyrolysis gaseous products of Japanese cedar powder. A, B, C, D, and E are for H_2 , air, CO, CH_4 , and CO_2 , respectively.

ideal gases and residuals, and we estimate the w values using the following equation :

$$w = PVM/RT \quad (3)$$

where P is the pressure ($P=1$ atm), V is the volume, M is the molar mass, R is the gas constant, and T is the absolute temperature ($T=20^\circ C$). We use the V values in Table 2, and convert V to w using Eq. (3).

Figures 5 and 6 are the relationship between pyrolysis temperature and the conversion ratio to CO, and the weight ratio of CO to the pyrolysis products, respectively. Below $300^\circ C$ region, both X and Y functions of heartwood are larger than those of sapwood irrespective of particle size. Above this temperature, however, vice versa. Both X and Y increase tremendously as the pyrolysis temperature is higher, and moreover the rate of increasing of these function on temperature also increase. We can safely say that the high yield of CO is obtained as the reaction temperature is higher.

Figures 7 and 8 are the same meaning as Figs. 5 and 6 for CO_2 , and Figs. 9 and 10 are for CH_4 . For the CO_2 gas, both X and Y increase more as the temperature is higher, irrespective of particle size and part of wood, but the rate of increasing of these functions decrease. For the CH_4 gas, however, that of these function increase. This fact suggest that the generated H radicals

act violently as reduced reagents for CO or CO₂ in the higher temperature range. We must consider the useful condition of the conversion of wood to CO with the CO₂ and CH₄ gases decreasing because both gases are chemically inert and invalid for the raw materials of

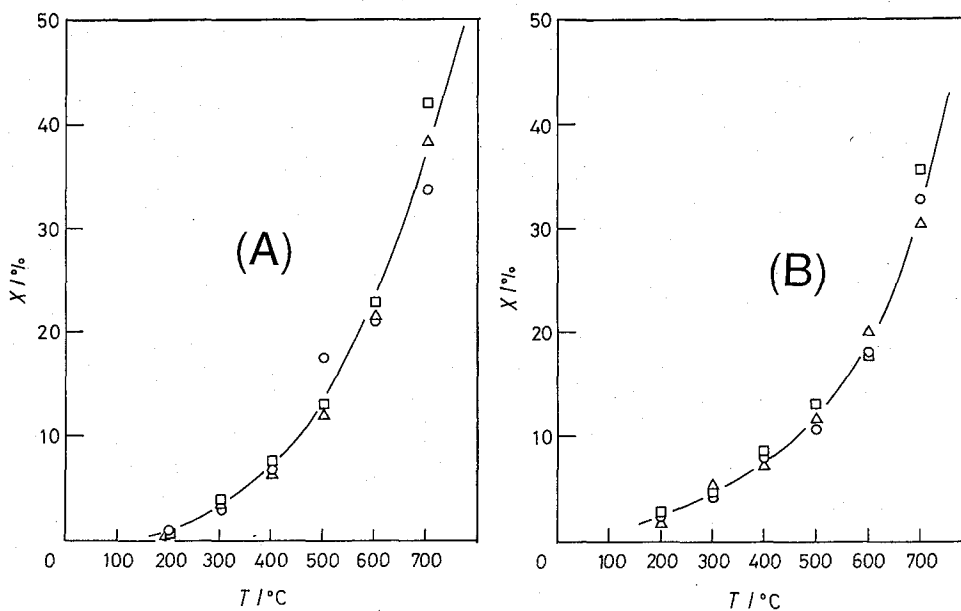


Fig. 5 Relationship between pyrolysis temperature (T) and conversion ratio of Japanese cedar powder to CO (X). Pyrolysis period is 10 minutes. Legends are the same as in Fig. 2.

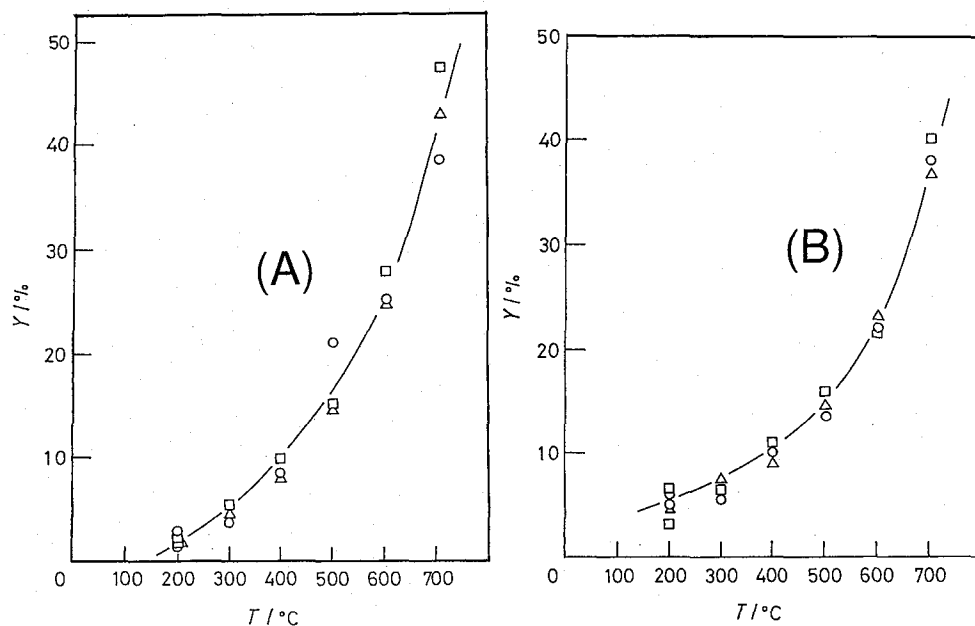


Fig. 6. Relationship between pyrolysis temperature (T) and weight ratio of CO to the pyrolysis products (Y). Pyrolysis period is 10 minutes. Legends are the same as in Fig. 2.

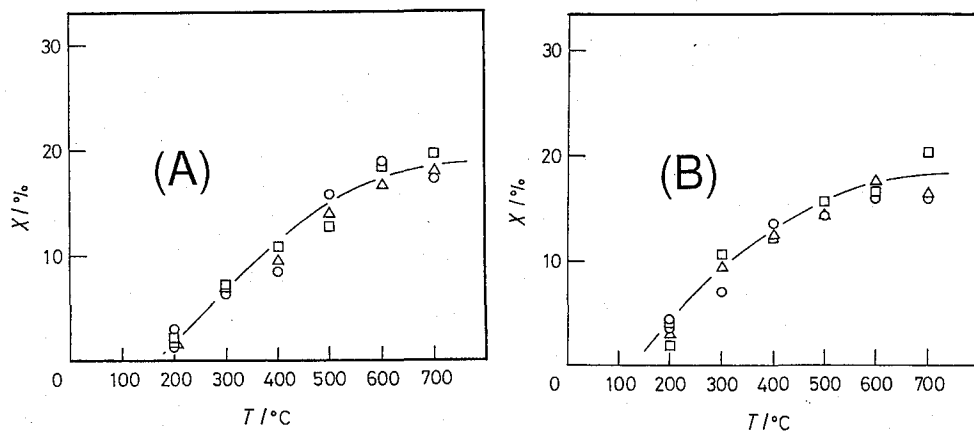


Fig. 7. Relationship between pyrolysis temperature (T) and conversion ratio of Japanese cedar powder to CO_2 (X). Pyrolysis period is 10 minutes. Legends are the same as in Fig. 2.

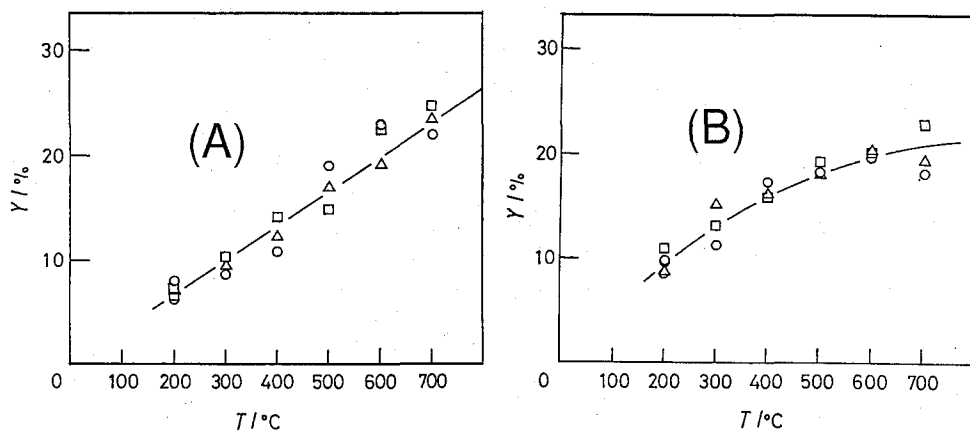


Fig. 8. Relationship between pyrolysis temperature (T) and weight ratio of CO_2 to the pyrolysis products (Y). Pyrolysis period is 10 minutes. Legends are the same as in Fig. 2.

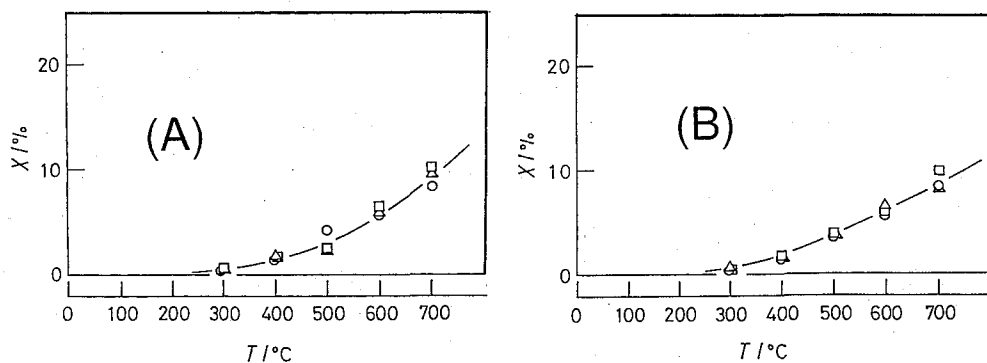


Fig. 9. Relationship between pyrolysis temperature (T) and conversion ratio of Japanese cedar powder to CH_4 (X). Pyrolysis period is 10 minutes. Legends are the same as in Fig. 2.

Pyrolysis of Japanese Cedar

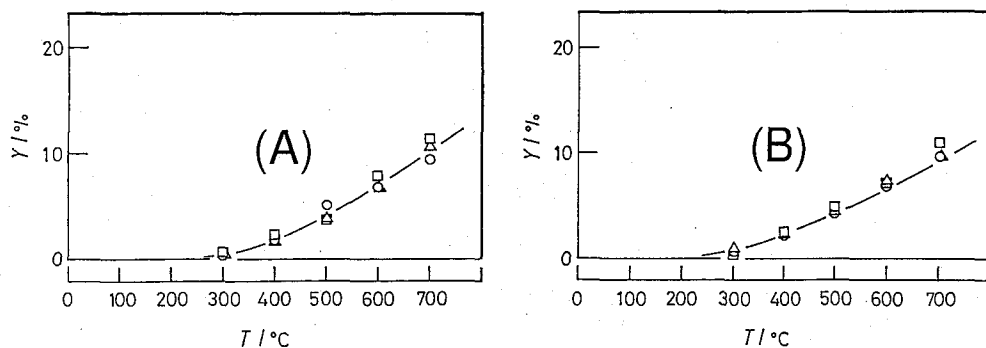


Fig. 10. Relationship between pyrolysis temperature (T) and weight ratio of CH_4 to the pyrolysis products (Y). Pyrolysis period is 10 minutes. Legends are the same as in Fig. 2.

Table 3. Relationship between pyrolysis time and conversion to CO for sapwood at 300 $^{\circ}\text{C}$.

t/min	1	5	10	20
$x/\%$ 60~80 mesh	3.3	4.3	2.8	5.9
100~150 mesh	3.3	3.9	3.8	5.2
$y/\%$ 60~80 mesh	5.5	6.4	3.8	7.7
100~150 mesh	5.2	5.2	5.5	7.3

Table 4. Relationship between pyrolysis time and conversion to CO for sapwood at 700 $^{\circ}\text{C}$.

t/min	1	5	10	20
$x/\%$ 60~80 mesh	34.2	—	37.2	33.8
100~150 mesh	40.3	40.0	40.5	42.2
$y/\%$ 60~80 mesh	38.4	—	44.7	38.7
100~150 mesh	47.7	41.7	42.9	47.8

C_1 -chemistry.

Summarized the above-mentioned findings, we conclude that the higher temperature is necessary for occurring the effective pyrolysis.

Time dependence

Tables 3 and 4 show the relationship between pyrolysis time and conversion to CO at 300 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$, respectively. Obviously, we can hardly admit the the time dependence of conversion to CO, and about 10 minutes are sufficient for obtaining high yield of CO.

4. CONCLUDING REMARKS

The valid condition of pyrolysis of Japanese cedar powder has been investigated varying particle size, part of wood (*i.e.* difference between sapwood and heartwood), pyrolysis time, and temperature in views of the weight loss and the conversion ratio to CO. The higher pyrolysis temperature is, the more significant the weight loss of wood and the conversion ratio to CO are, which are almost irrespective of both particle size and part of wood. In the lower temperature region (*e.g.* 200 $^{\circ}\text{C}$), the longer pyrolysis period is more effective, but the higher one, there is hardly the period dependence of weight loss and conversion ratio to CO. The dependence of the portion of CO in produced gases on temperature and time, and the kinetics for this system will be discussed in Part II.

ACKNOWLEDGMENT

We thank Professor Soichi Hayashi, Dr. Junzo Umemura, and Dr. Noriyuki Kimura,

Institute for Chemical Research, Kyoto University, for giving encouraged to us and for giving their valuable suggestions and discussion to us.

REFERENCES

- (1) R.G. Herman, K. Klier, G.W. Simmons, B.P. Finn, J.B. Vulko, T.P. Lobyliniski, *J. Catal.*, **56**, 407 (1979).
- (2) R.M. Agny and C.G. Takoudis, *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 50 (1985).
- (3) P. Villa. P. Forzatti, G. Buzzi-Feraris, G. Garone and I. Pasquon, *Ind. Eng. Chem. Process Des. Dev.*, **24**, 12 (1985).
- (4) See for example, S. Tanaka, *Kagaku Sohsetsu*, **36**, 51 (1982); E. Kikuchi, "Yukishigen no Kagaku", Kagaku Zoukan, No.90, Kagaku Dojin, Kyoto, p.65 (1981).
- (5) J. Nakano, "Mokuzai Kagaku", Yuni Syuppan, Tokyo, p.5 (1983).
- (6) G. Simmons and M. Sanchez, *J. Anal. Appl. Pyrolysis*, **3**, 161 (1981).
- (7) K. Kuroda, *Mokuzai Kogyo*, **48**, 460 (1993).
- (8) T.P. Wampler, *J. Anal. Appl. Pyrolysis*, **16**, 291 (1989).
- (9) D.F. Arseneau, *Can. J. Chem.*, **39**, 1915 (1961).
- (10) R.M. Knudsen and R.B. Williamson, *Wood Sci. Technol.*, **5**, 176 (1971).
- (11) H.A. Becher, A.M. Phillips, and J. Keller, *Combust. Flame*, **58**, 163 (1984).
- (12) L.S. Schmauch and R.A. Dinerstein, *Anal. Chem.*, **32**, 343 (1960).