林試研報 Bull. Gov. For. Exp. Sta. No. 263, 1974

Effects of Inorganic Salts on Pyrolyses of Wood and Cellulose, Measured with Thermogravimetric and Differential Thermal Analysis Techniques. I

Kinetics of the pyrolyses of untreated wood and cellulose *in vacuo*

By

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Summary : Pyrolyses of wood and cellulose, and effects of diammonium phosphate, ammonium bromide and sodium tetraborate decahydrate as effective flame-retardants, and sodium chloride as an ineffective salt on the pyrolyses of these materials were studied by means of thermogravimetry and differential thermal analysis techniques *in vacuo* as the basis for flame retardation of wood. Kinetics of the pyrolyses of untreated wood and cellulose is described in this paper.

Pyrolysis of cellulose seems to be controlled by two reactions, whose kinetic parameters were determined through the mechanism presented by CHATTERJEE and CONRAD, and their calculating method modified in order to be applied to the results of the dynamic thermogravimetry. The kinetic parameters of the pyrolyses of lignin and hemicellulose in a limited range of temperatures were derived from the thermogravimetry of wood, based on the assumed threshold temperature of pyrolyses and contents of cellulose, lignin and hemicellulose in wood.

1. Introduction

It is usually accepted that the thermal decomposition of wood prior to its burning occurs with heating, and then the decomposed products bring about the burning of wood. Many attempts to obtain fire-retardative wood have been carried out changing the course of this thermal decomposition preceding the combustion of wood.

There is a considerable number of papers which reported on the researches on the thermal decompositions of wood and its components by means of thermal analysis techniques; such as, thermogravimetry (TG) to measure the weight change and differential thermal analysis (DTA) to measure the heat content change as change of the physical quantity of them in heating. These do not seem, however, to be satisfactory means for the quantitative determination of effects of fire-retardants on the thermal decomposition of wood and its components. Perhaps, this is due to not only the complicated course of decomposition of the materials, but also to the contention that the thermal analysis, a physical technique in association with another chemical one should become a more valid mean for the investigation of this subject.

Received August 31, 1973

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In dynamic thermogravimetry of wood and its components treated with chemicals, the threshold temperature and the apparent activation energy of the thermal decomposition would be lowered, the residual char would be increased, and the volatile products would be decreased in comparison with those of the untreated materials. The thermal decomposition of wood is considered to be expressed as a composite of the behavior of each component[1][4], but the active decomposition of wood which is considered to cause its ignition seems to be mostly borne by cellulose. Therefore, in the research on the effects of fire-retardants upon the thermal decomposition of wood, cellulose which plays the most important role among its components in the combustion of wood shall be the main material to be investigated.

In this study, wood and cellulose as materials were adopted for the clarification of the mechanism of cellulose pyrolysis and of effects of flame-retardants on cellulose pyrolysis, and of the thermal decomposition of wood treated with flame-retardants based on the simpler decomposition of cellulose than of wood.

Diammonium phosphate, ammonium bromide, sodium tetraborate, and sodium chloride were used for the treatment of the materials, and they have been recognized as good flame-retardants for wood except the last one. The mechanisms of their effects are thought to be different from one another. Since sodium chloride is ineffective for flame retardation of wood, it was chosen for comparison with other effective flame-retardants. Three levels of the content of these salts in the treated samples for the TG and the DTA were applied for the investigation on mechanisms of their effects.

In this paper, kinetics of the pyrolyses of untreated wood and cellulose derived from the results of the TG is reported. The results of the dynamic TG of cellulose are well interpreted through the mechanism proposed by CHATTERJEE and CONRAD[5] and their equations so modified that they are able to be applied to the dynamic TG. The kinetic parameters of the pyrolyses of lignin and hemicellulose in limited ranges of temperatures are derived from the results of the TG of wood.

The pyrolyses of treated wood and cellulose will be reported in part II.

2. Theory of pyrolysis of cellulose

2. 1 Fitness of cellulose pyrolysis for first-order kinetics

Pyrolysis reaction of cellulose has been assumed to follow first-order kinetics[1][2][4]. Thus,

$$-\frac{dw}{dt}=kw \quad \cdots\cdots (1)$$

where, k is the rate constant to follow the ARRHENIUS equation;

$$k=Ze^{-\frac{E}{RT}} \quad \cdots\cdots (2)$$

w is the decomposable weight of sample present at the time t, E the activation energy of the pyrolysis reaction, R the gas constant, T the absolute temperature of sample, and Z the pre-exponential factor. Then, when $T=T_0+\phi t$, where T_0 is the initial temperature and ϕ the constant rate of temperature rise,

$$-\frac{dw}{dT}=\frac{Z}{\phi}e^{-\frac{E}{RT}}w \quad \cdots\cdots (3)$$

$$ln\left(-\frac{d\,ln\,w}{dT}\right)=ln\frac{Z}{\phi}-\frac{E}{RT} \quad \cdots\cdots (4)$$

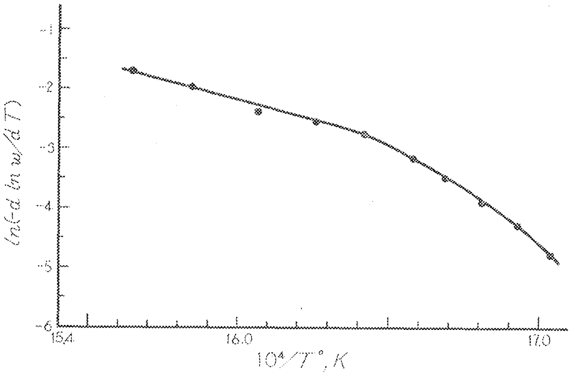
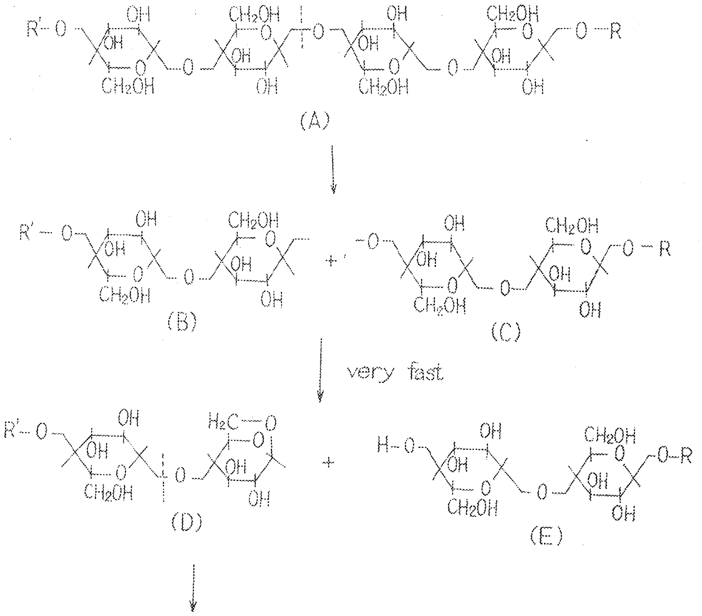


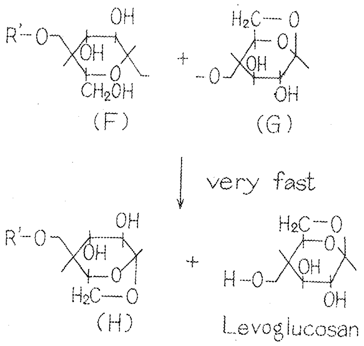
Fig. 1 Plots based on first-order kinetics for determination Arrhenius activation energy of pyrolysis of cellulose.

Therefore, the plots of the values of the left-hand side of eq. (4) obtained from a TG curve vs. the reciprocals of absolute temperature shall bear a straight line whose slope and intercept give the activation energy and the pre-exponential factor, respectively. The preliminary plots of them shown in Fig. 1, however, actually produce a curve which has a straight segment in the high temperature range. Hence, the pyrolysis in the high temperature range seems to follow first-order kinetics. Then, the mechanism and the rate equation to explain the plots in Fig. 1 need to be developed.

2. 2 Mechanism of cellulose pyrolysis

By CHATTERJEE and CONRAD[5], the weight loss in pyrolysis of cellulose was assumed to be caused by the splitting levoglucosan as a monomer from cellulose molecules as follows :





The fragment (C) which occurs with the break of the glucosidic bond in the cellulose molecule becomes temporally stable in the fragment (E), obtaining a proton from the fragment (B) which is turned into the fragment (D). Then, by the further break of the glucosidic bond, the fragment (D) produces levoglucosan which causes weight loss by the volatilization *in vacuo* and high temperature.

Golova and Kryilova[8)] showed in the measurements of the degree of polymerization and of the amount of levoglucosan yielded during the pyrolysis of cellulose in the isothermal heatings that since the average degree of the polymerization which was lowered with the progress of the pyrolysis had reached a certain value, other cellulose molecules with lower degree of the polymerization were not observed, and the yield of levoglucosan increased suddenly.

On the basis of these reports, if it is assumed that the cellulose molecules with the degree of polymerization under a certain value in the above fragment (D), which is attained with the break of glucosidic bond, are consumed by the faster depolymerization reaction alone to form levoglucosan, the rate equations for the initiation reaction to break glucosidic bond and for the propagation reaction to give levoglucosan are derived after the manner of Chatterjee and Conrad[5)] as follows.

2. 3 **Derivation of theoretical equations**

2. 3. 1 Equations for propagation reaction

An original cellulose molecule A is cut into fragments with an end anhydroglucose unit B, and with an end hydroxyl group A', by the break of glucosidic bond. Thus,

$$A \xrightarrow{k_i} B + A'$$

where, k_i is the rate constant of the initiation reaction. The rate of the formation of the fragment B depends upon the initial number A_0 of cellulose molecules as follows :

$$\frac{d[B]}{dt} = k_i A_0 \cdots\cdots (5)$$

Then,

$$\frac{d[B]}{dT} = \frac{Z_i}{\phi} e^{-\frac{E_i}{RT}} A_0 \cdots\cdots (6)$$

where the subscript i denotes the initiation reaction. Further, the fragment A' with the break of glucosidic bond,

$$A' \xrightarrow{k_i} B' + A''$$

and if it is supposed that the molecule in the form B is rapidly lost to produce levoglucosan by depolymerization, although it has the chances to be decomposed with the initiation reaction, then,

$$\begin{array}{ll} B_1 \xrightarrow{\quad k_p \quad} & B_2 + L\uparrow \\ B_2 \xrightarrow{\quad k_p \quad} & B_3 + L\uparrow \\ \vdots & \vdots \quad \vdots \end{array}$$

where, k_p is the rate constant of the propagation reaction, and L denotes levoglucosan. Therefore, for the propagation reaction to produce levoglucosan,

$$\frac{d[L]}{dt} = k_p \sum B_j \quad \cdots\cdots (7)$$

$$-\frac{d\sum B_j}{dT} = \frac{d[L]}{dT} = \frac{Z_p}{\phi} e^{-\frac{E_p}{RT}} \sum B_j \quad \cdots\cdots (8)$$

The subscript p designates the propagation reaction. According to the result by GOLOVA and KRYILOVA[8], if it is assumed that in the later stage of the pyrolysis, there are only the cellulose molecules of a constant degree of polymerization attained with the initiation reaction and the chain reaction of the propagation alone is involved, then the weight loss in this stage may be shown as the function of the number of the molecule,

$$-\frac{dw}{dT} = -\frac{d\sum B_j M_j}{dT} = \frac{Z_p}{\phi} e^{-\frac{E_p}{RT}} \sum B_j M_j = \frac{Z_p}{\phi} e^{-\frac{E_p}{RT}} w \quad \cdots\cdots (9)$$

where, M_j is the molecular weight of the B_j (also M_j may be constant). Hence,

$$ln\left(-\frac{d\,ln\,w}{dT}\right) = ln\frac{Z_p}{\phi} - \frac{E_p}{RT} \quad \cdots\cdots (10)$$

Thus, the plot of the values of the left-hand side of eq. (10) in the later stage of the pyrolysis, which the high temperature range of the TG is assumed to correspond to, vs. the reciprocals of temperature shall bear a straight line whose slope and intercept give the activation energy and the pre-exponential factor, respectively.

2. 3. 2 Equations for initiation reaction

In the first stage involving the initiation reaction, the number of the molecule produced obeying the rate equation (5) or (6) has to be taken into consideration. From eq. (6),

$$\sum B_j = \int_0^{\Sigma B_j} d[B] = \int \frac{Z_i}{\phi} e^{-\frac{E_i}{RT}} A_0 \, dT \quad \cdots\cdots (11)$$

If the number of the molecule A, which bears the molecule B, is constant during the first stage and equal to its initial number A_0, then

$$\sum B_j = \frac{Z_i A_0}{\phi} \int e^{-\frac{E_i}{RT}} dT \quad \cdots\cdots (12)$$

By making a partial integration and assuming initial conditions that $\sum B_j = 0$, at $T=0$, the right-hand side may be described as the following asymptotic series :

$$\sum B_j = \frac{Z_i A_0}{\phi} e^{-\frac{E_i}{RT}} \frac{R}{E_i} T^2 \left[1 - \frac{2RT}{E_i} + 6\left(\frac{RT}{E_i}\right)^2 - 24\left(\frac{RT}{E_i}\right)^3 + \cdots\cdots\right] \quad \cdots\cdots (13)$$

Although the series does not converge sharply except for $RT/E_i \ll 1$, the error resulting from the leaving out of account the series after the second term is negligible for the accuracy needed in this study, since, for instance, the sum of the values of the terms omitted from the series amounts to about -0.0604 at the conditions that $T=600°K$ and $E_i=36$ kcal/mole, by the calculation with aid of the given numerical tables[6)7)17)] cited by Kanbe[9)]. Therefore, it is readily shown that the parenthesized series of eq. (13) may be regarded as constant for the narrow range of the temperatures involving the initiation reaction. Then,

$$\sum B_j \approx \frac{Z_i A_0 R}{\phi E_i} T^2 e^{-\frac{E_i}{RT}} \quad \cdots\cdots(14)$$

Furthermore, on the basis of the observation by Golova and Kryilova[8)], if it is assumed that nearly all the molecule B formed with the initiation reaction have the constant molecular weight $\bar{M}$ in the temperature range where the relatively great weight loss occurs, eq. (14) may be substituted for $\sum B_j$ in eq. (9) in which $M_j=\bar{M}=$constant, thus,

$$-\frac{dw}{dT}=\frac{Z_i Z_p A_0 R \bar{M}}{E_i \phi^2} e^{-\frac{E_i+E_p}{RT}} T^2 \quad \cdots\cdots(15)$$

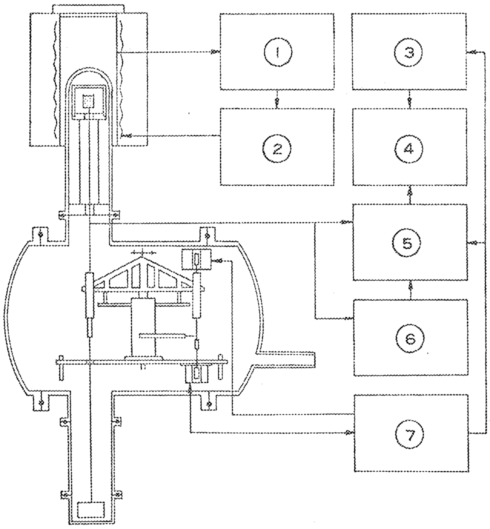
$$ln\left(-\frac{dw}{dT}\right)-2\,ln\,T=ln\left(\frac{Z_i Z_p A_0 R \bar{M}}{E_i \phi^2}\right)-\frac{E_i+E_p}{R}\left(\frac{1}{T}\right) \quad \cdots\cdots(16)$$

Hence, a straight line of a slope to give E_i shall be obtained by the plotting $[ln(-dw/dT)-2\,ln\,T]$ vs. $(1/T)$.

3. Experimental

3. 1 Apparatus for thermogravimetry and differential thermal analysis

The apparatus, Differential Thermal Balance TGD-1500M (made by Sinku Riko Co., Yokohama, Japan), by means of which the TG and the DTA could be carried out simultaneously, was used for this study. Its block diagram is shown in Fig. 2. The weight of reactant in the platinic cell which was mounted on a balance in null method system was automatically recorded on the ordinate with one of the two pens of an X-Y recorder through a differential transformer and an amplifier.



1. Circuit for temperature program, 2. PID-SCR temperature controller, 3. Differentiation circuit, 4. Recorder, 5. Circuit for range shift of recorder, 6. DC amplifier for DTA, 7. Thermogravimetry circuit.

Fig. 2 Block diagram of apparatus for thermogravimetry and differential thermal analysis.

The sample temperatures and the temperatures differences between the sample and the standard cell also were recorded on the ordinate and the abscissa of the above recorder in electromotive forces of a platinum-platinum phodium thermocouple which had the conections close to and under the cells, respectively. Two recording pens of the recorder are placed at the distance of 2 mm in the abscissa direction. By the way, a very fine wire which composes the thermocouple permits measurement of these temperatures without affecting weight change, being helically wound before the connection with the amplifier. The ambient atmosphere can be made vacuum.

About 40 mg of either wood or cellulose sample, and the constant volume of the standard sample of α-aluminium oxide as much as the reactant sample in the cylindrical cell were set in the sample holder, and after being sealed, the sample cabin was very gently evacuated through a very small opening in a glass stopcock with a rotary pump so that abrupt discharge of air accompanied with flying about of the fine granular sample was prevented. After the sample weight was free from the influence of current and buoyancy change of the atmosphere, and reached a constant value, the samples were heated at the rate of 5°C/min from room temperature to 500°C. Vacuum conditions between 10^{-1} and 10^{-2} mmHg were used in the experiments.

3. 2 Studied materials

The wood samples used in this study were Japanese cedar sapwood which was powdered in a Wiley mill, was passed through a 60 mesh and trapped in a 120 mesh screen, and then was sufficiently extracted with acetone.

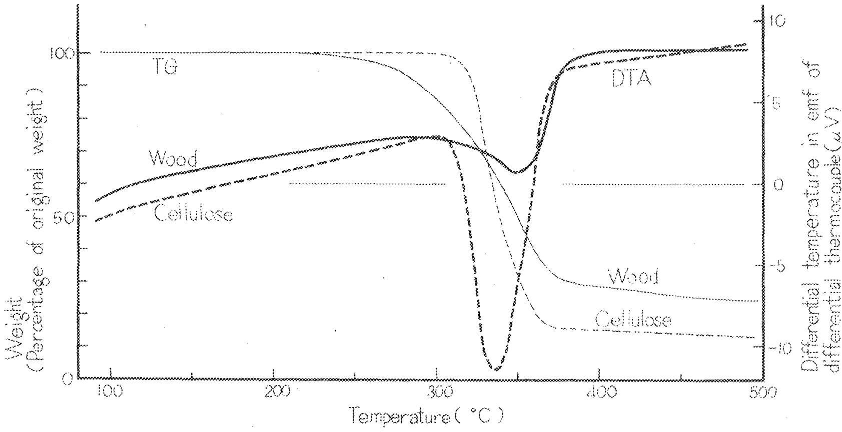
The cellulose samples were Whatmam cellulose powder (grade standard, Batch No. 103660).

4. Results and discussions

4. 1 Observations on the DTA curves

The TG and the DTA curves of the cellulose and the wood are shown in Fig. 3. The maximum rate of the weight loss for both cellulose and wood correspond with each DTA peak in agreement with the result obtained theoretically by Akita and Kase[2)].

The DTA curves show nearly linear slopes from the endothermic toward the exothermic side with the rise of temperature except the temperature ranges involving weight loss. This shift of base lines might be due to the discrepancy of the thermal diffusivity between the reactant and the standard sample. When the sample cells can be regarded as an infinite cylinder, and the effects of temperature and material consumption upon the thermal diffusivity are negligible, the temperature changes in these cells are expressed as follow, respectively[2)18)].



Fine and thick lines correspond to TG and DTA, respectively. —— wood, and …… cellulose.

Fig. 3 Thermogravimetric and differential thermal analysis curves for both untreated cellulose and wood (Japanese ceder).

$$\frac{\partial T_1}{\partial t}=\kappa_1\left(\frac{\partial^2 T_1}{\partial r^2}+\frac{1}{r}\frac{\partial T_1}{\partial r}\right) \quad\cdots\cdots(17)$$

$$\frac{\partial T_2}{\partial t}=\kappa\left(\frac{\partial^2 T_2}{\partial r^2}+\frac{1}{r}\frac{\partial T_2}{\partial r}\right)+\frac{q}{c_2 w_2}\left(\frac{dw}{dt}\right) \quad\cdots\cdots(18)$$

where, the subscript 1 and 2 designate the standard and the sample cells, respectively, and r is the radial coordinate, κ the thermal diffusivity of material, q the heat of reaction, c the specific heat, and (dw/dt) the pyrolysis rate. Hence, it is seen that a DTA curve depends on the thermal diffusivities and the temperature gradients in both the standard and reactant sample as well as pyrolysis of sample. The presence of the differences of density, specific heat, and thermal conductivity between two samples most likely brought about such shift of the DTA base lines.

4. 2 **Kinetics of pyrolysis of cellulose**

In order to determine the kinetic parameters for two reactions of the propagation and of the initiation, the calculations were plotted in Fig. 4. The plots of the values of the left-hand side eq. (10) vs. the reciprocals of temperature form a curve with a segment of a straight line in the high temperature region. The activation energy and the pre-exponential factor for the propagation reaction which were derived from the slope and the intercept of the

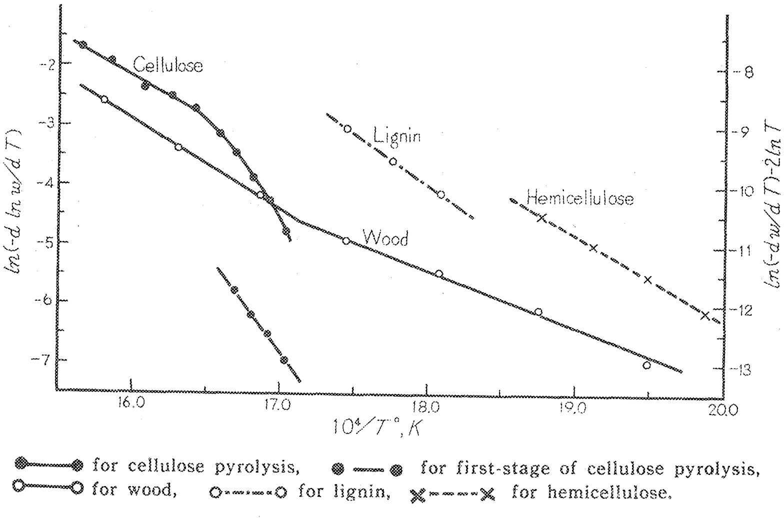


Fig. 4 Plots of $ln(-d\,ln\,w/dT)$ or $[ln(-dw/dT)-2\,ln\,T]$ vs. $1/T$ for determination of activation energy of pyrolysis.

Table 1. Kinetic parameter for pyrolysis of cellulose and wood based on first-order kinetics

Materials	Activation energy (kcal/mole)	Pre-exponential factor (min^{-1})
Cellulose		
Initiation reaction	39.5	$1.35\times10^{9)}$
Propagation reaction	26.8	
Lignin	34.8$^{a)}$ (in 280 to 300°C)	$4.34\times10^{12)a)}$
Hemicellulose	28.5$^{a)}$ (in 220 to 280°C)	$2.88\times10^{10)a)}$

a) Calculated from the result of the wood pyrolysis.

segment of the straight line are given in Table 1.

The plots for the initiation reaction based on eq. (16) make a straight line as shown in Fig. 4. As stated above, the value of the slope of the obtained straight line is $(E_i+E_p)/R$. The activation energy for the initiation, E_i is also given in Table 1.

4. 3 Kinetics of pyrolysis of wood

The plots of $ln(-d\,ln\,w/dT)$ vs. $1/T$ based on eq. (4) assuming the reaction order to be unity, in the same manner as for the above cellulose, bring about the solid line in Fig. 4 composed of two segments which cross each other at about 315°C. Since the point of this intersection is close to the threshold temperature of the weight loss of the above cellulose, it is supposed that the cellulose in the wood began to lose its weight with pyrolysis, though it is reasonably considered that the component, cellulose of this wood somewhat differed from the above cellulose.

It may be asserted that weight loss of wood during pyrolysis is expressed as a sum of corresponding weight loss of each component of it[1]. It is now thought that in the temperature higher than 315°C, both decompositions of cellulose and lignin existed together in one of the wood and under 315°C both the lignin and hemicellulose dominated the pyrolysis of the wood. In TG, hemicellulose is thermally less stable than lignin and the greater part of lignin is considered to remain in solid phase after the completion of active pyrolysis of hemicellulose[3][10][14]. Then, assuming that in the lower temperature range over 220°C the pyrolysis of hemicellulose predominated and in the range 280 to 300°C the weight loss of wood, which was little affected by hemicellulose, mostly owed to the degradation of lignin[*1], the similar plottings for each component were tried as shown in Fig. 4. Incidentally the amounts of cellulose, lignin, and hemicellulose and others in the wood of this species, and of the char residue after the completion of active pyrolysis of each component, which were used in the calculations for these plots, were derived from literature or the results of this experiment and are listed in Table 2.

The kinetic parameters thus determined by the plots of $ln(d\,ln\,w/dT)$ vs. $1/T$ are given together with those of cellulose in Table 1. These plots evidently make straight lines as shown in Fig. 4, though their significance is restricted by the above assumptions.

Table 2. Amounts of components in wood and of their char residues

Component	Content (%)	Char[a] (%)	Contribution from component to char of wood (%)
Cellulose	52.8[b]	17.0[d]	9.0
Lignin	31.4[b]		10.3[f]
Hemicellulose and others	15.8[c]	30.0[e]	4.7
Wood	100.0	24.0	24.0

a) Percentage of the initial weight.
b) A mean of values derived from the reference (12).
c) Calculated as the difference of the content between wood and cellulose plus lignin.
d) Derived from the present experiment.
e) Derived from the reference (16).
f) Calculated as the difference between the char of wood and the contribution of cellulose plus of hemicellulose.

[*1] The temperatures, 280° and 300°C were adopted as the temperature at the completion of active pyrolysis of hemicellulose[8][10][14][15] and as that before the outset of active pyrolysis of cellulose[4][10][14][20][21] in TG, respectively, although they are variable depending on the heating rate.

4. 4 Discussions on obtained activation energies

Since CHATTERJEE and CONRAD[5)] presented the mechanism of cellulose pyrolysis that consisted of the initiation reaction to break a glucosidic bond and the further propagation reaction to produce levoglucosan, and derived kinetic parameters for the reactions from their static TG curves, the result which seems to support their theory has been given by RAMIAH[14)]. From their theory, it results that these reactions shall be reflected on plots for the determination of kinetic parameters by means of dynamic TG technique in which temperature is a function of time. By RAMIAH[14)], the activation energies for pyrolysis of Avicel cellulose based on first-order kinetics were 60±2 kcal/mole in the first stage of low temperature, and 39±1 kcal/mole in the second stage of high temperature. By CHATTERJEE and CONRAD[5)], the activation energies for the initiation reaction and for the propagation reaction of pyrolysis were 54.3 kcal/mole and 33.0 kcal/mole for cotton, and 75.0 kcal/mole and 37.1 kcal/mole for amorphous cellulose, respectively. These values, including ours, seem proper when differences among the materials as well as the methods of their determination are taken into consideration. In all of them, the higher activation energies in the first stage than in the second stage agree with the mechanism of cellulose pyrolysis by CHATTERJEE and CONRAD in which the process of the propagation reaction is faster than the initiation.

The result from a dynamic TG by TANG[21)], however, showed the lower activation energy, 23 kcal/mole in the low temperature range than 54 kcal/mole in the high temperature range and was inconsistent with CHATTERJEE and CONRAD's.

In addition to these, pyrolysis of cellulose was shown to be controlled by more than one mechanism[1)10)11)13)20)]. In the isothermal condition[1)], the higher activation energy based on first-order in the low temperature range than in the high temperature range may be interpreted as evidencing that in the high temperature range, the rate of weight loss was mostly dependent on the propagation reaction, so as to be consistent with CHATTERJEE and CONRAD's theory. Furthermore, zero-order as well as first-order kinetics was reported on cellulose pyrolyses[11)13)20)]. The kinetic parameters for cellulose pyrolysis seemed to be differently determined depending on calculating processes, pyrolysis procedures and origins or structures of material. It is hard to explain systematically the discrepancies among those parameters.

The overall reaction order for wood pyrolysis was reported to be unity[19)], but AKITA[1)] has shown the rate of wood pyrolysis as the summation of the rate of the first-order for pyrolysis of individual wood components as follows :

$$-\frac{dw}{dt}=\sum_{j} k_j w_j \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (19)$$

where the subscript j denotes a wood component j. On the other hand, since in dynamic TG wood components would begin to be pyrolyzed in the order, hemicellulose → lignin → cellulose[1)4)10)14)21)], though the range of the active pyrolysis of lignin partially overlapped that of hemicellulose and extended beyond that of cellulose, the kinetic parameters for the pyrolyses of lignin and hemicellulose in the limited range with the assumption of threshold temperature of each pyrolysis were derived from the TG curve of wood as stated above. The activation energy, 28.5 kcal/mole for hemicellulose and 34.8 kcal/mole for lignin are somewhat higher than the value for hemicellulose derived from the data of wood pyrolysis by AKITA[1)] and the values for the isolated hemicelluloses[3)10)14)15)], and for the isolated lignins[1)3)10)14)15)21)]. But, they do not agree with one another in each group.

The present kinetic parameters for the pyrolyses of hemicellulose and lignin will be of much interest, when they come to be related to the type of pyrolysis, such as elimination of side groups from structural units, random scission, or depolymerization of chains in thermal degradation of polymers.

5. Conclusions

1) The kinetics of pyrolysis of cellulose in the dynamic TG is expressed by means of CHATTERJEE and CONRAD's method5) so modified as to apply to a dynamic TG, based on the mechanism proposed by them and the result by GOLOVA and KRYILOVA8). It supports their theory that the obtained activation energy is higher for the initiation reaction to break the glucosidic bond of cellulose than for the propagation reaction to form levoglucosan, and both values are in suitable region (see Table 1).

2) The kinetic parameters for pyrolyses of lignin and hemicellulose in the limited ranges of temperature of the dynamic TG were obtained based on first-order reaction from the TG curve of wood, and with the assumption of the amounts of cellulose, lignin, and hemicellulose in wood and of the threshold temperature of their pyrolysis in the TG which were derived from the present experiment or the references3)4)10)12)14)15)20)21) (Table 1 and 2). The obtained activation energies are somewhat higher than the values previously reported by others1)8)10), 14)16)19)21). These values shall be explained with mechanisms of pyrolyses in the limited ranges.

Acknowledgement

The authors wish to express their appreciation and thanks to Mr. K. NAITO, Government Forest Experiment Station, Tokyo, Japan, for the preparation of the samples.

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熱重量および示差熱分析法で求められた木材および セルロースの熱分解におよぼす無機塩の効果

(第1報)

無処理木材およびセルロースの熱分解の速度論

平田利美[1]

(概要)

1. 緒言

木材の燃焼に先立ち，木材の熱分解が発生し，その生成物が分解して燃焼がひき起こされることは一般に認められている。この燃焼に先行する熱分解の過程を，材料の化学的処理によって変え，木材の防火を達成しようというこころみが，いろいろと行なわれてきた。

木材の熱分解において，各成分の挙動をみると，まず，ヘミセルロースが200°C以下で熱分解を開始し，リグニンがこれに続く。ヘミセルロースは300°C以下で主要な熱分解を終える。リグニンはゆっくりと分解し，600°C以上でもかなりの量が固相に残っている。これに対し，セルロースは300°Cあたりから急激に分解し，大量のタールと気体を生成し，可燃性ガスを形成して木材の着火の原因となると考えられる。木材の着火をひき起こす急激な熱分解は，主としてセルロースの熱分解によって構成されていると思われるので，木材の熱分解におよぼす薬剤の効果を研究する上で，セルロースは重要な役割を演ずる成分である。

この研究では，試料として木材およびセルロースをとりあげ，木材の熱分解におけるセルロースの役割をより明確にするとともに，より単純なセルロースの熱分解の解明によって，複雑な木材の熱分解にアタックしようとするものである。

処理に用いた薬剤は，りん酸二アンモニウム，臭化アンモニウム，四ほう酸ナトリウム10水塩（ほうしゃ）および塩化ナトリウム（食塩）で，りん酸アンモニウムはりん系統の，臭化アンモニウムはハロゲン系統の，ほうしゃはほう素系統の各木材防火薬剤の典型であり，食塩は安定で効果のない薬剤の代表で，有効な防火薬剤とその効果を比較するために選ばれた。熱重量および示差熱分析された処理試料の薬剤含有量には3水準あり，薬剤含有量の変化によってその作用の機構の追跡をこころみた。

この研究の第1報では，無処理木材およびセルロースの熱分解の動力学を，動的熱重量分析の結果から求めて報告している。

第2報では，処理された木材およびセルロースの熱分解を報告する予定である。

1973年8月31日受理

(1) 木材部

2. セルロースの熱分解の理論

2. 1 セルロースの熱分解反応の1次反応速度に対する適合性

セルロースの熱分解は1次反応速度に従うとみなされてきた[1)2)4)]。1次反応を仮定して得られる次式

$$ln\left(-\frac{d\,lnw}{dT}\right)=ln\frac{Z}{\phi}-\frac{E}{RT}\cdots\cdots(4)$$

に従って，Fig. 1 にプロットしてみたところ，カーブになり，全体が1次反応に従うことがないと推定された。ここに，w は時間 t において存在している分解可能な試料の重量，T は絶対温度で，$T=T_0+\phi t$ に従って変化する試料温度である。T_0 は加熱の初期温度，ϕ は一定の昇温速度である。Z は前置係数，E は活性化エネルギー，R は気体定数である。そこで，Fig. 1 に示されたカーブを解釈するための理論を展開する必要がある。

2. 2 セルロースの熱分解機構と速度式

Chatterjee および Conrad[5)] によれば，セルロースの熱分解における重量減少は，セルロース分子のグルコシド結合の切断によって形成された，無水グルコース単位を末端に有するセルロースフラッグメントが解重合され，モノマーとしてレボグルコサンが放出され，それが気化することによって起こされる。

Golova および Kryilova[8)] は等温加熱によるセルロースの熱分解における重合度変化と，レボグルコサンの生成量を測定し，熱分解の進行につれて低下した重合度がある値に達すると，それより小さい重合度のセルロース分子があらわれず，その時点からレボグルコサンの生成量が急激に増加したことを報告した。

これらの報告をもとにして，セルロースの熱分解の後期には，解重合の連鎖反応によってレボグルコサンを生成する生長反応のみ存在するとして，重量減少について次の速度式を導いた。

$$-\frac{dw}{dT}=\frac{Z_p}{\phi}e^{-\frac{E_p}{RT}}w\cdots\cdots(9)$$

ここに脚付 p は生長反応を示す。これから，

$$ln\left(-\frac{d\,lnw}{dT}\right)=ln\frac{Z_p}{\phi}-\frac{E_p}{RT}\cdots\cdots(10)$$

そこで，TG カーブの高温領域から (10) 式の左辺を求め，$1/T$ に対してプロットすれば，E_p/R を勾配とする直線が得られ，その縦軸の切片から前置係数が求まる。

一方，熱分解の前期では，グルコシド結合切断の開始反応も存在して，重量減少に関係しているのでそれを考慮して次式が導かれた。

$$-\frac{dw}{dT}=\frac{Z_pZ_iA_0R\overline{M}}{E_i\phi^2}e^{-\frac{E_i+E_p}{RT}}T^2\cdots\cdots(15)$$

ここに脚付 i は開始反応を意味する。A_0 ははじめのセルロース分子の数，$\overline{M}$ はセルロース分子のフラッグメントの分子量で，重量減少を示す熱分解の段階では一定とみなした。これから，

$$ln\left(-\frac{dw}{dT}\right)-2\,ln\,T=ln\left(\frac{Z_pZ_iA_0R\overline{M}}{E_i\phi^2}\right)-\frac{E_i+E_p}{R}\left(\frac{1}{T}\right)\cdots\cdots(16)$$

したがって，〔$ln(-dw/dT)-2\,ln\,T$) 対 ($1/T$) を X－Y グラフにプロットすることにより，E_i を求めることができる。

3. 実験方法

3. 1　熱重量分析および示差熱分析装置

使用された装置は真空理工社製の示差熱天秤 TGD-1500 M で，TG と DTA を同時に行なうことができる。そのブロックダイヤグラムを Fig. 2 にのせている。試料の量は約 40 mg で，標準試料は α 酸化アルミニウムである。昇温速度 5°C/min で，10^{-1}～10^{-2} mmHg の真空度の範囲で実験された。

3. 2　試　料

木材試料はスギ辺材の粉末でアセトン抽出されたものである。セルロースは Whatman のセルロース粉である。

4. 結果および検討

4. 1　セルロースの熱分解

セルロースの TG および DTA カーブを Fig. 3 にのせている。この TG カーブから (10) 式の左辺の値を求め，$1/T$ に対してプロットしてみると，Fig. 4 に示されている高温領域で直線線分を有するカーブが得られた。この直線部分の勾配と切片から，連鎖的にレボグルコサンを生成する生長反応の活性化エネルギーと前置係数を算出し，Table 1 にのせている。

同じ TG カーブの低温領域（熱分解による重量減少を示す温度範囲の中で）から，(16) 式の左辺の値を求め，$1/T$ に対してプロットしたところ，Fig. 4 に示しているように，直線が得られた。この直線の勾配は E_i+E_p/R に相当し，これから，グルコシド結合切断の開始反応の活性化エネルギー，E_i を計算し，同じく Table 1 にのせている。

4. 2　木材の熱分解

木材の TG および DTA カーブもまた Fig. 3 に描かれている。木材の熱分解に対して1次反応を仮定して，(4) 式にもとづいて，$ln(-d\,ln\,w/dT)$ 対 $1/T$ をグラフにプロットしてみると，Fig. 4 に示されているような結果になった。そのプロットは 315°C で交点を有する2本の直線を示している。この温度は，前のセルロース試料の熱分解による重量減少の開始温度に一致しているので，この木材中のセルロースと，使用されたセルロース粉末とは異なるとはいえ，多分，この木材中のセルロースの熱分解も 315°C で開始したものと考えられる。

熱分解中の木材の重量減少は，その各成分の対応する重量減少の合計で表わされる[1]。そこで，この TG の 315°C 以上では，木材の熱分解がリグニンとセルロースの熱分解によるものとし，さらに 220 から 280°C の温度範囲では主としてヘミセルロースが木材の熱分解を支配し[3)10)14)15)]，280 から 300°C の温度範囲ではリグニンの熱分解が支配するものと仮定し[4)10)14)20)21)]，Table 2 に示されている条件を用いて (4) 式に基づく計算を行ない，グラフにプロットしたのが Fig. 4 に示されている。この2つのプロットは，ともに直線を示す。その直線の勾配と切片から求めた活性化エネルギーと前置係数は Table 1 にまとめられている。

4. 3　検　討

Chatterjee および Conrad[5] がグルコッド結合切断の開始反応と，レボグルコサンを連鎖的に生成する生長反応からなる，セルロースの熱分解機構を提案して以来，われわれより以前に，Ramiah[14] が2段階

からなるセルロールの熱分解を示す動力学パラメターを提出した。Ramiah によれば，動的TGにおいて，低温領域で高い活性化エネルギーを有する熱分解反応が存在することになり，Chatterjee および Conrad に一致する。また，秋田1) は等温加熱の条件によるセルロースの熱分解は，高温と低温とで異なることを示した。かれによれば，低温領域における熱分解の活性化エネルギーは，高温領域のそれより大きい。熱エネルギーの豊富な高温領域では，熱分解による重量減少が主としてレボグルコサン生成の生長反応に支配されていると解釈すれば，Chatterjee および Conrad の理論に一致する。

しかしながら，同じ2段階に分かれた熱分解を示した Tang の報告21) では，低温段階の活性化エネルギーが小さく，上述されたことと矛盾している。さらにまた，0次反応を含む熱分解段階の存在を示した報告もあり11)13)20)，これらの間のくいちがいを統一的に説明することは，ほとんど不可能といってよい。

木材の熱分解のデータから，その構成分の分解の動力学パラメターを算出した報告1) はすでに存在している。この研究で得られた，ヘミセルロースおよびリグニン熱分解の活性化エネルギーは，すでに報告された値より1)3)10)14)15)21) 多少高い。この研究における値は，限られた温度範囲における熱分解に関するものであり，多くの仮定を経て得られた。動力学パラメターは，その対応する反応機構と結びつけられる必要がある。