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

Pyrolyses of treated woods and celluloses *in vacuo*

By

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Summary : Pyrolyses of wood and cellulose, and effects of ammonium phosphate, ammonium bromide, sodium borate, and sodium chloride 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. The pyrolyses of the samples treated with the above salts are reported in this paper.

Some peaks were observed on the DTA curves of the treated samples. The reactions to which the peaks correspond are proposed based on the changes of the peaks with the salt content. The peak temperature changes with the salt content permitted the effects of the salts to be deduced. It was available for the supposition of the mechanisms of the increase in the char residue with the action of the salts that the peak areas for the original cellulose fractions directly relate to the char yield. The increase in the char residue of the wood with the treatments seems to be much contributed from cellulose, but the contribution from other components to the increase somewhat increased with the higher salt content.

1. Introduction

In the previous paper[4], the pyrolyses of the untreated wood and cellulose was reported. The pyrolyses of wood and cellulose treated with diammonium phosphate, ammonium bromide, sodium tetraborate and sodium chloride are described in this paper.

In the pyrolyses of chemically treated wood and its components, the outset temperature and the apparent activation energy of the pyrolysis would be lowered, the residual char would be increased, and the volatile products would be decreased in comparison with those of untreated materials. AKITA and KASE[1] simultaneously performed the thermogravimetry (TG) and the differential thermal analysis (DTA) of cellulose treated with ammonium dihydrogen phosphate, and determined the kinetic parameters for the decomposition of three of four ingredients observed in the course of the pyrolysis with changing the heating rate and by means of the agreement between a DTA peak and a maximum rate of weight loss which was theoretically derived. Furthermore, they identified the ingredients by the change of the DTA peak area with the salt content. In this paper, the data are analyzed utilizing suggestions from their methods.

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2. Experimental

The TG and DTA apparatus, and wood and cellulose which were already described in the previous paper4), were used in the experiment.

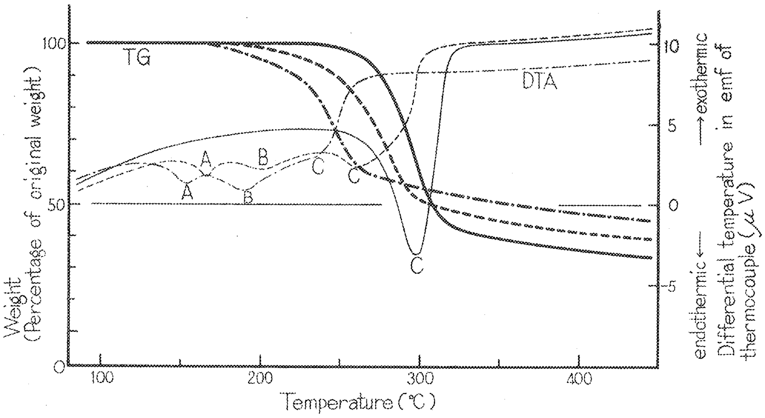
Each CP grade of diammonium hydrogen phosphate, ammonium bromide, sodium tetraborate decahydrate, and sodium chloride was used for the treatment of the materials.

The cellulose and the wood samples were immersed in each aqueous solution of the salts which had concentration appropriate to a required content in a sample, and these samples were then dried on a water bath at 90°C. Subsequently, these were dried at 60°C and then were kept on silica gel in desiccators, just before the experiment. There were three levels of 1, 5, and 10% in the content of each salt.

3. Results and discussions

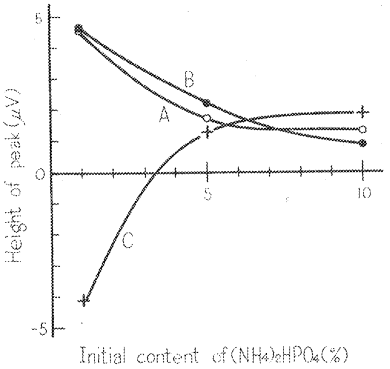
3. 1 Samples treated with diammonium phosphate

The TG and the DTA curves of cellulose treated with diammonium phosphate are shown in Fig. 1. The more salt the sample contained, the more the threshold temperature of active weight loss lowered and the char residue increased, as seen in the figure. Three endothermic peaks are found on the DTA curve. By Akita and Kase1), four peaks on the DTA curve of cellulose containing dihydrogen ammonium phosphate corresponded to the decomposition of the salt itself, to the pyrolyses of modified cellulose with the salt and of residual cellulose, and to the secondary reaction of products generated from the pyrolysis of modified cellulose, in the order of the occurence, respectively. Similar results were obtained in the present experiment. In Fig. 2, where the depth of each peak is given as a function of the content of the salt in the cellulose, it is found that the depths of two peaks (A and B in Fig. 1) in the region of low temperature increased, and the peak C at the high temperature shallowed with the increase in the salt content in agreement with Akita and Kase1). Therefore, it is assumed that these endotherms indicate the pyrolyses of the salt, of modified cellulose and of residual one, respectively. The fourth peak which was observed at the highest temperature



Thick and fine lines correspond to TG and DTA, respectively.
——— 1%, ------ 5%, and —·—·— 10%, of salt content.

Fig. 1 TG and DTA curves of cellulose treated with diammonium phosphate.

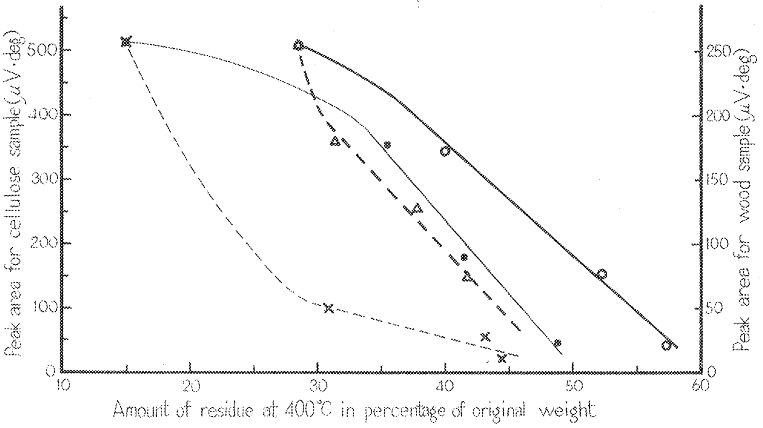


The curves, A, B, and C correspond to the peaks shown in Fig. 1.

Fig. 2 Changes of height of DTA peaks for cellulose sample with amount of diammonium phosphate.

by Akita and Kase, however, was not confirmed in the present experiment, but as seen in Fig. 1, the levelling off at 290 to 330°C on the DTA curve of the sample with the highest content, may correspond to it. This endotherm could not be utilized in the determination of kinetic parameters from lack of the sharpness in their study.

Since the depth of the DTA peak corresponding to pyrolysis of the residual cellulose decreased with the increase in one for the modified cellulose as seen in Fig. 2, it seems that the volatized fraction was decreased and the char residue was increased with the modification in cellulose on heating. It is found in Fig. 3 that the DTA peak area for the residual cellulose, which is assumed to indicate the amount of this fraction, decreased with the increase in the amount of the char residue. Then it is thought that the residual cellulose gave more volatized fraction and less char residue, and the modified cellulose produced less volatized fraction and more char residue. This supposition does not conflict with the mechanism of flame retarding of phosphoric acid cited by Browne[2].



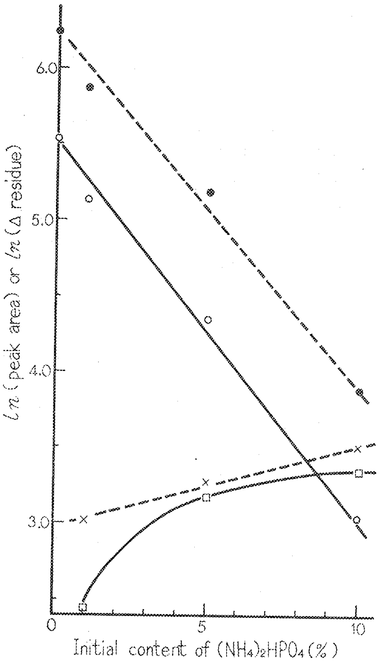
○——○ Wood treated with $(NH_4)_2HPO_4$, ●······● Cellulose treated with $(NH_4)_2HPO_4$,

△- - -△ Wood treated with NH_4Br, ×- - -× Cellulose treated with NH_4Br,

⊗ and ⊠ Untreated wood and cellulose, respectively.

Fig. 3 Correlations between amount of residue and DTA peak area[*1] corresponding to pyrolysis of original cellulose.

[*1] The amounts of the char residue were corrected for the contained salts, assuming ammonium phosphate to be changed into metaphosphoric acid[6] and ammonium bromide to be removed from the residue up to 400°C. The peak areas in this figure and others were always corrected for the initial content of the salt.



●------● Area of peak C for cellulose sample, ○——○ Area of peak C′ for wood sample, ×------× Residue increment of cellulose sample, □——□ Residue increment of wood sample.

Fig. 4 Plots of logarithms of residue increment (between 0% and another level of salt content) or of area of DTA peak vs. amount of diammonium phosphate.

The DTA peak area for the residual cellulose decreased with the increase in the salt content in the tendency of an exponential function. It seems that there is a linear relation between the logarithms of the peak area and the salt content as seen in Fig. 4, though the number of the plots is not plenty. If the linear relation between these two quantities is true, the following explanation may be possible.

When the total amount of cellulose c at time t is expressed with the modified cellulose fraction c_m and the residual cellulose fraction c_r, and if the residual cellulose was consumed by the modification alone during it,

$$c=c_m+c_r \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

and then, with the condition of $dT/dt=\phi$ which is constant,

$$-\frac{dc_r}{dT}=\frac{dc_m}{dT}=\frac{Z}{\phi}e^{-\frac{E}{RT}}c_r[P] \quad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where, $[P]$ is the concentration of the salt or a product of the salt and is assumed to be in proportion to the initial content of the salt, T the temperature, Z the pre-exponential factor, E the activation energy, R the gas constant. Assuming that $[P]$ was constant during the term when the modified cellulose was borne by the salt and the residual cellulose, and initial conditions are $c_r=c$ and $c_m=0$ at $T=T_1$, the integration of eq. (2) for T gives

$$\Big[-ln\,c_r\Big]_c^{c_r}=ln\,c_m=\frac{Z}{\phi}[P]\int_{T_1}^{T_2}e^{-\frac{E}{RT}}dT \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

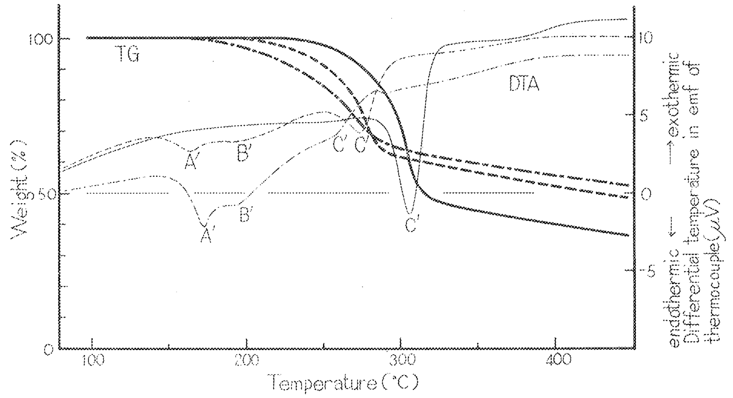
where, T_2 is the termination temperature of the formation reaction of the modified cellulose. After the manner of the derivation of eq. (14) in the previous paper[4],

$$ln\,c_m=ln(c-c_r)\approx\frac{Z}{\phi}[P]\,\varDelta T^2 e^{-\frac{E}{R\varDelta T}}=K[P] \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (4)$$

is derived, where $\varDelta T=T_2-T_1$, and K is regarded as constant. Eq. (4) shows that the logarithms of the modified cellulose fraction is in proportion to the amount of the salt. From eq. (4),

$$ln\,c_r=-K[P] \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (5)$$

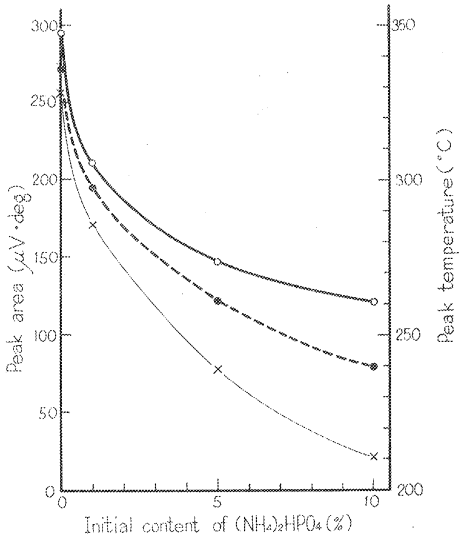
is readily derived and it corresponds to the above result in Fig. 4, assuming that the peak area for the residual cellulose is directly proportional to its amount. Development of a mechanism to form the modified cellulose in which $[P]$ is independent of the time of the reaction is needed. The modification of cellulose molecules with a product of the salt and the liberation of the product from the modified cellulose by pyrolysis might occur in the way of a chain reaction.



Thick and fine lines correspond to TG and DTA, respectively.
——— 1%, ------ 5%, and —·—·— 10% of salt content.

Fig. 5 TG and DTA curves of wood treated with diammonium phosphate.

The TG and the DTA curves of the treated wood resemble those of the cellulose as shown in Fig. 5. The endotherm A′ in the lowest temperature is thought to represent the pyrolysis of the salt, as compared with the case of the cellulose. The peak C′, for example, at 305°C for the 1% sample, probably indicates the pyrolysis of the residual cellulose in the wood, for its peak area decreased with the increase in the salt content as shown in Fig. 6 and the tendency of this decrease is analogus to that of the cellulose as seen in Fig. 4. It is considered that effect of the salt on the pyrolysis of cellulose alone is identical with that in wood in principle.

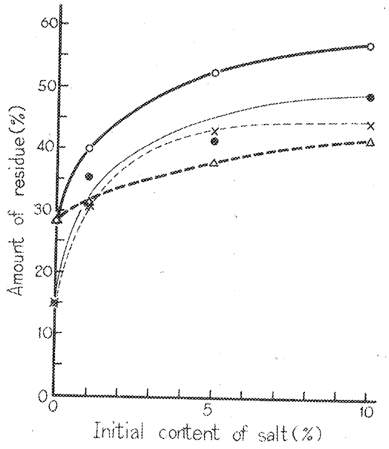


○——○ Temperature of peak C′ for wood sample, ●----● Temperature of peak C for cellulose sample, ×——× Area of peak C′ for wood sample.

Fig. 6 Changes in DTA peaks (C in Fig. 1 and C′ in Fig. 5) with amount of diammonium phosphate.

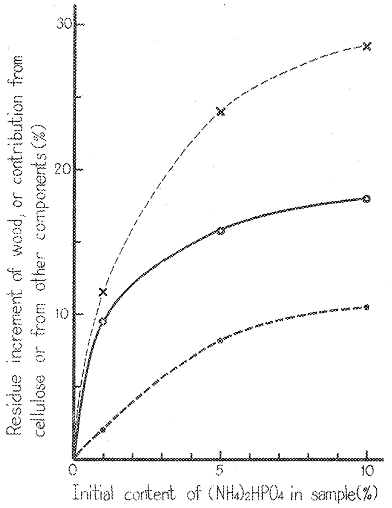
In Fig. 6 the temperatures of the DTA peaks for the residual cellulose are compared between the cellulose and the wood. Both peaks shifted toward the low temperature side with the increase in the salt content. It is found in the figure that the residual cellulose in the wood sample was thermally more stable than in the cellulose sample. The dependence of the pyrolysis temperature of the residual cellulose on the salt content suggests that its pyrolysis was accelerated by the salt.

The yield of the char residue increased with the increase in the salt in a similar manner between the wood and the cellulose as seen in Fig. 7. The increase in the char residue yielded from the wood appears to be much dependent on cellulose. Then, as given in Fig. 8, the increase in the char yield from the treated wood was divided into two parts contributed from cellulose and from other components. Fig. 8 shows that in the lesser content of the



○——○ Residue of wood treated with $(NH_4)_2HPO_4$,
●——● Residue of cellulose treated with $(NH_4)_2HPO_4$,
△----△ Residue of wood treated with NH_4Br,
×----× Residue of cellulose treated with NH_4Br.

Fig. 7 Effects of salt contents on amount of residue at 400°C.



○——○ Contribution from cellulose to increment in residue,
●----● Contribution from other components,
×----× Increment in residue of wood between 0% and another level of content of $(NH_4)_2HPO_4$.

Fig. 8 Increase in residue of wood with treatment of diammonium phosphate and contributions[*1] from cellulose and other components to its increment.

salt, cellulose played a more important role in the increase in the char residue of the wood. By the way, since the weight content of cellulose in wood is approximately equal to the sum of the amounts of other components, each contribution is proportional to the value per unit weight of them. It is reasonable to assume that the amounts of the components in the wood derived from the reference[5], which were used in the determination of the contributions in Fig. 8, somewhat differ from the actual values. This, however, will not change the tendency of each component in Fig. 8 in principle.

The plots of the initial contents of the salt vs. the logarithms of the residue increments in the cellulose and in the wood samples are given in Fig. 4, in which it is seen that the residue increments in the cellulose samples with the increase in the salt content may be expressed as,

$$ln\ \varDelta R_c = a[P] + b \quad \cdots\cdots\cdots (6)$$

where, a is the slope of the corresponding straight line, b the intercept of the ordinate which is free from the change of the initial salt content $[P]$, and $\varDelta R_c$ the residue increment. Since the char residue of the cellulose increased with the decrease in the DTA peak area for the residual cellulose as already seen in Fig. 3 and is an exponential function of the salt content as shown in Fig. 4, the char residue is likely to be increased through the modification of cellulose with the salt as stated above. The mechanism seems to involve a process in which

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[*1] The contribution from cellulose was determined as the product of the char yield from the cellulose in Fig. 7 and the mean content of cellulose in the wood of this species[5], and that from others was determined as the difference between the one from cellulose and the char yield from the wood. The contributions in Fig. 13 and so on were determined in the same way.

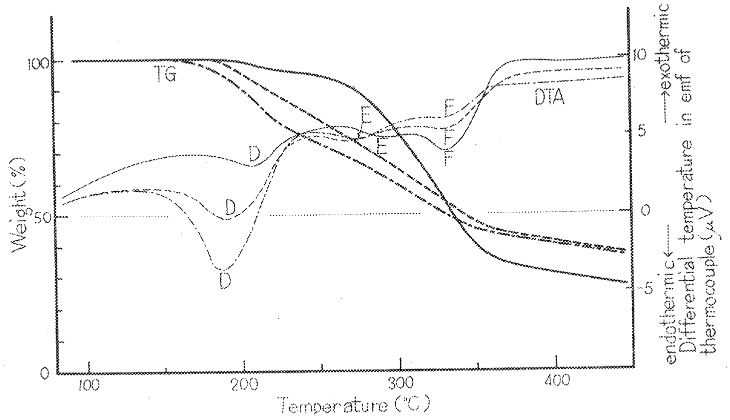
the cellulose was spent and the salt content [P] was retained constant, though the plotted number was but few. Such mechanism, however, does not account for the char increment b in eq. (6) independent of the salt content [P].

The relation between the salt content and the char yield from the wood is more complicated than for the cellulose, as seen in Fig. 4. It will be unable to explain the relation except the account of effects of the salt on others than cellulose.

3. 2 **Samples treated with ammonium bromide**

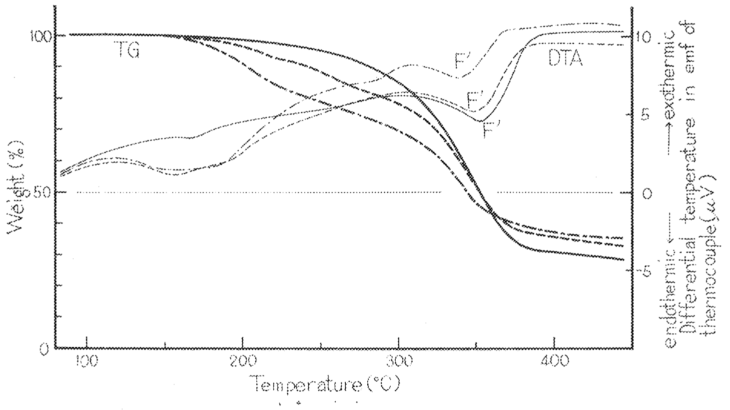
As seen in Fig. 9 and 10, both threshold temperatures of the wood and the cellulose pyrolysis were lowered, the yields of the char residues increased and the over-all rate of the weight loss decreased with treatment of ammonium bromide. Three or four endotherms are observed on the DTA curves.

The depths of the DTA peaks for the cellulose sample are given as a function of the content of the salt in Fig. 11. The firstly occurred endotherm D probably represents the decomposition or the sublimation of ammonium bromide, for its depth was increased with



Thick and fine lines correspond to TG and DTA, respectively.
——— 1%, -------5%, and —·—·— 10% of salt content.

Fig. 9 TG and DTA curves of cellulose treated with ammonium bromide.



Thick and fine lines correspond to TG and DTA, respectively.
——— 1%, -------5%, and —·—·— 10% of salt content.

Fig. 10 TG and DTA curves of wood treated with ammonium bromide.

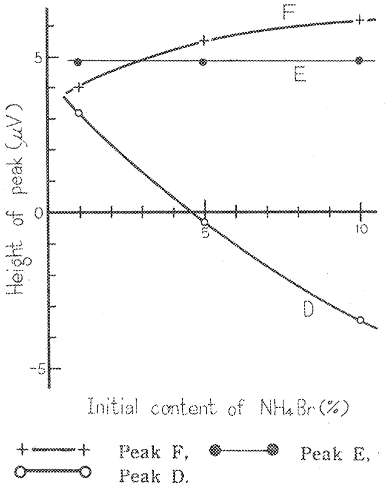


Fig. 11 Changes in heights of DTA peaks (in Fig. 9) with amount of ammonium bromide.

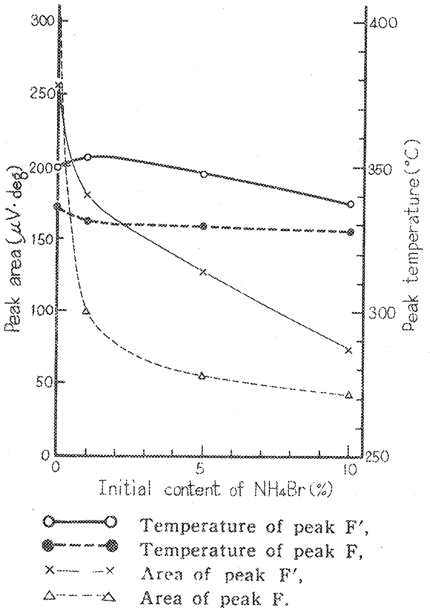


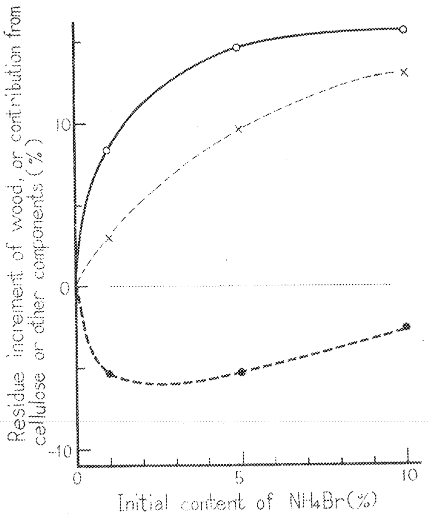
Fig. 12 Changes in DTA peaks (F in Fig. 9 and F′ in Fig. 10) with amount of ammonium bromide.

the increase in the salt content. The second peak E in the temperature range 260 to 290°C is independent of the change of the salt content. The third peak F at the highest temperature which was shallowed with the increase in the salt content, probably corresponds to the pyrolysis of original cellulose which is assumed to be essentially identical with the pyrolysis of untreated cellulose.

The temperature and the area of the DTA peak F, which are assumed to indicate the thermal stability and the amount of the original cellulose respectively, behaved under the content change of the salt as shown in Fig. 12. The thermal stability of this fraction was little changed with the salt as seen in the figure. This might be due to the salt thoroughly consumed up to 300°C, and permits the conjecture that the amount of the fraction was decreased with the increase in the salt content, because the peak area was decreased with the increase in the salt content.

In Fig. 7, the increase in the char residue yielded from the treated cellulose stands out more than from the wood. The char yield from the wood was not increased so much as was expected from the increase in the cellulose sample. In Fig. 13 where two contributions from cellulose and from other components to the increase in the char yield from the wood are shown, this salt appears to promote the pyrolysis and to hinder the char formation of components other than cellulose in the wood. Since ammonium bromide decomposes in relatively low temperature and is considered to form very active products, thermally decomposable components and groups other than cellulose in the temperature range in which active products of the salt were present in the wood, might be the source of the decrease in the char yield from the components other than cellulose. It is thought that cellulose was thermally stable in such temperature range and the mechanism of effect of the salt on cellulose pyrolysis was different from those on other components.

Nothing of certainty can be proposed as to the mechanism of the char increase. It is seen in Fig. 3 that the char residue was increased with the decrease in the DTA peak area for the original cellulose. This tendency is more pronounced in the wood than in the cellulose sample. Since the treated wood owed the residue increase to cellulose as seen in Fig. 13, it is reasonable to assume that the last peak F' at the highest temperature in the wood sample corresponds to the pyrolysis of the original cellulose.



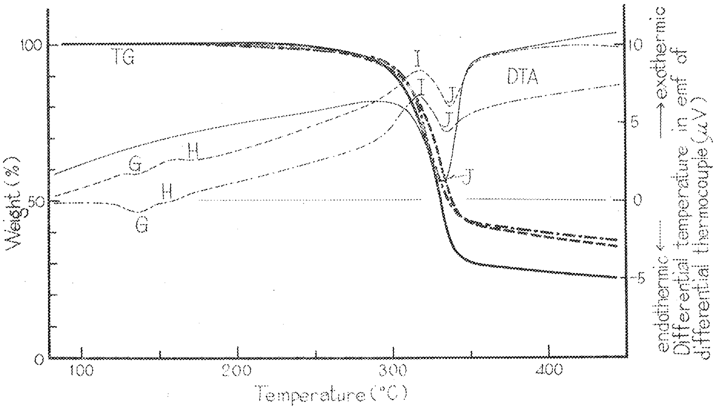
○——○ Contribution from cellulose, ●---● Contribution from other components, ×----× Increment in residue of wood between 0% and another level of content of NH_4Br.

Fig. 13 Increase in residue of wood with treatment of ammonium bromide, and contributions from wood components to the increment.

3. 3 Samples treated with sodium tetraborate decahydrate

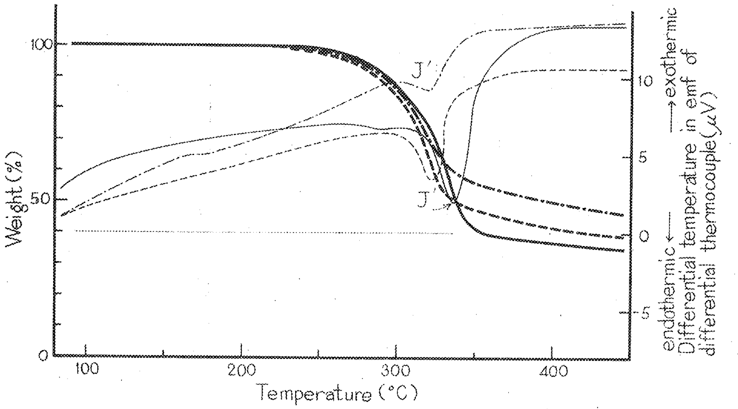
The cellulose and the wood treated with sodium borate in the TG are characteristic in that the temperature of the maximum rate and of the threshold temperature of the weight loss were little changed with the salt content, as shown in Fig. 14 and 15. Similar results were previously reported for cellulose treated with boric acid[8].

In Fig. 14, it seems that there are an exothermic (I) and three endothermic peaks G, H, and J on the DTA curves of the treated cellulose. Probably, two endotherms G and H in the low temperature range were caused by changes of the salt itself. The peak H of them at the higer temperature which accompanied weight loss as seen in the TG curve may correspond to the dehydration from the salt. If the apparent exothermic peak I at 320°C represents a true exothermic reaction, it may be assumed that the exotherm I corresponds to the heat of a reaction to form a more stable



Thick and fine lines correspond to TG and DTA, respectively.
——— 1%, ------ 5%, and —·—·— 10% of salt content.

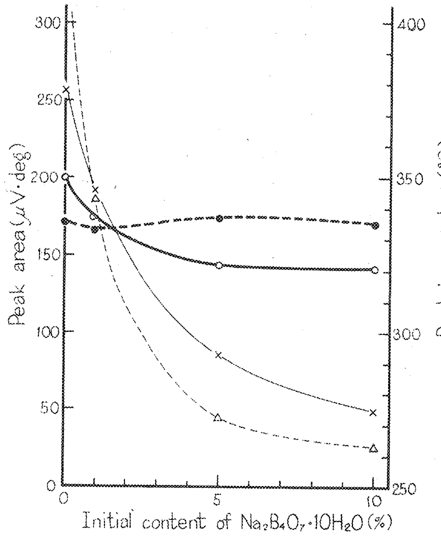
Fig. 14 TG and DTA curves of cellulose treated with sodium tetraborate decahydrate.



Thick and fine lines correspond to TG and DTA, respectively.
——— 1%, - - - - - -5%, and —·—·—10% of salt content.

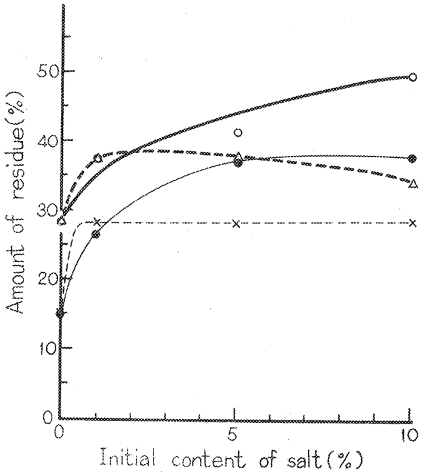
Fig. 15 TG and DTA curves of wood treated with sodium tetraborate decahydrate.

product. Moreover, it is possible to give the interpretation that the more the salt content increased, though the extent of risen temperature was small, the more the threshold temperature of active pyrolysis rose, because of the more stable modified cellulose formed in the exothermic reaction, and the weight loss rate was greater in the sample with 10% than with 5% of the salt content, by reason of the encouraged pyrolysis of the cellulose with the prece-



○——○ Temperature of peak J′,
●- - -● Temperature of peak J,
×——× Area of peak J′,
△- - - -△ Area of peak J.

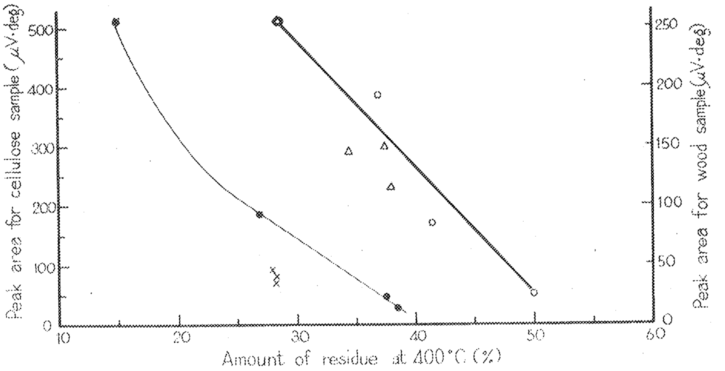
Fig. 16 Changes in DTA peaks (J in Fig. 14 and Fig. 15) with amount of sodium tetraborate decahydrate.



○——○ Residue of wood treated with $Na_2B_4O_7 \cdot 10H_2O$,
●——● Residue of cellulose treated with $Na_2B_4O_7 \cdot 10H_2O$,
△- - -△ Residue of wood treated with NaCl,
×- - -× Residue of cellulose treated with NaCl.

Fig. 17 Effect of salt contents on amount of residue[*1] at 400°C.

[*1] The amounts of the residues were corrected for the contained salts, assuming sodium tetraborate decahydrate to lose its water of crystalization and the original amount of sodium chloride to be kept up to 400°C.

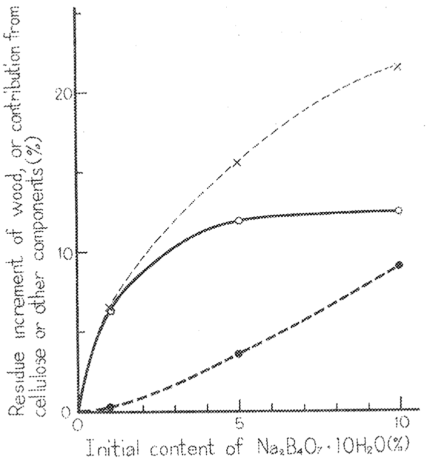


○——○ Wood treated with $Na_2B_4O_7 \cdot 10H_2O$, ●——● Cellulose treated with $Na_2B_4O_7 \cdot 10H_2O$, △ Wood treated with NaCl, × Cellulose treated with NaCl, ⊙ and ⊗ Untreated wood and cellulose, respectively.

Fig. 18 Correlations between amount of residue and DTA peak area[*1] corresponding to pyrolysis of original cellulose.

dently generated reaction heat.

The last endotherm J in the highest temperature is thought to correspond to the pyrolysis of the above original cellulose, for the peak area was decreased with the increase in the salt content as shown in Fig. 16. The temperature of the peak J in the cellulose sample was little changed with the salt content as seen in the same figure. This apparently shows that the salt did not have any chemical effect on the pyrolysis of the original cellulose. On other hand, this endothermic peak in the wood sample moved somewhat toward the low temperature side with the increase in the salt content.



○——○ Contribution from cellulose, ●----● Contribution from other components, ×----× Increment in residue of wood between 0% and another level of content of $Na_2B_4O_7 \cdot 10H_2O$.

Fig. 19 Increase in residue of wood with treatment of sodium tetraborate decahydrate and contributions from wood components to its increment.

The tendency of the char yield to be increased with the increase in the salt content is shown in Fig. 17, though the char yield from the cellulose sample with 5% of the salt content is almost equal to that with 10% of the content. A similar situation is observed for the peak area in Fig. 16. Then, the expected close relation between the char yield and the area of the peak (J) for the original cellulose is shown in Fig. 18. It seems that the char yield was increased with the decrease in the amount of the original cellulose. But the salt is obviously limited in its effect to decrease the original cellulose in the cellulose sample and therefore to increase the char yield.

As for the wood sample in the studied range of the salt content, however, the char yield does not seem to attain such a limiting value as seen in Fig. 17. The contributions from cellulose and other components to the increase in the char

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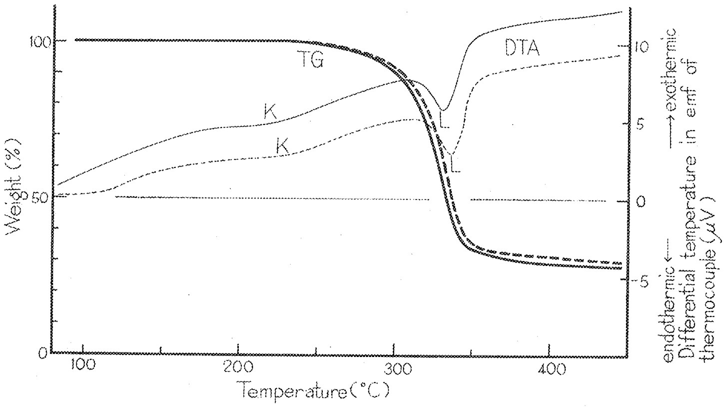
[*1] The values of the peak area were corrected for the initial contents of the salts. The same values were used in Fig. 16 and so on.

yield from the wood sample which are given in Fig. 19, show that the increase in the char residue of the wood sample depended much on not only cellulose but also other components in the salt contents of more than 5%. It may be regarded that after reactivity of cellulose to the salt or its products was first saturated, then other components reacted to the salt or its products to increase the char residue.

3. 4 **Samples treated with sodium chloride**

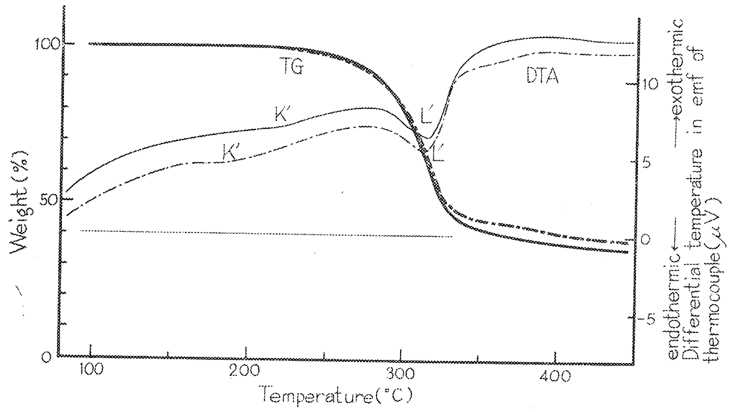
The TG and the DTA curves of both cellulose and wood treated with sodium chloride were little changed with the salt content, as can be seen in Fig. 20 and 21. There are two endotherms on the DTA curves of both cellulose and wood samples. In the cellulose, the peak area of the endotherm L in the high temperature which probably corresponds to the pyrolysis of the above-mentioned original cellulose was steeply decreased with the increase in the salt content 0 to 1% and little decreased with the further increase in it, as shown in Fig. 22.

A situation similar to this is observed in Fig. 17 showing the char yield changed with



Thick and fine lines correspond to TG and DTA, respectively.
——— 1% and ------ 5% of salt content.

Fig. 20 TG and DTA curves of cellulose treated with sodium chloride.



Thick and fine lines correspond to TG and DTA, respectively.
——— 1% and —·—·— 10% of salt content.

Fig. 21 TG and DTA curves of wood treated with sodium chloride.

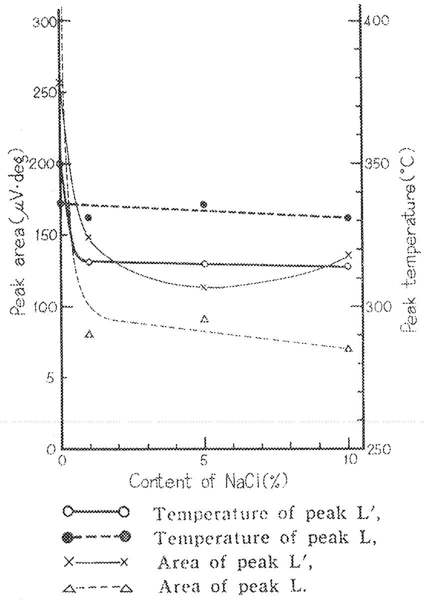


Fig. 22 Changes in DTA peaks (L in Fig. 20 and L′ in Fig. 21) with amount of sodium chloride.

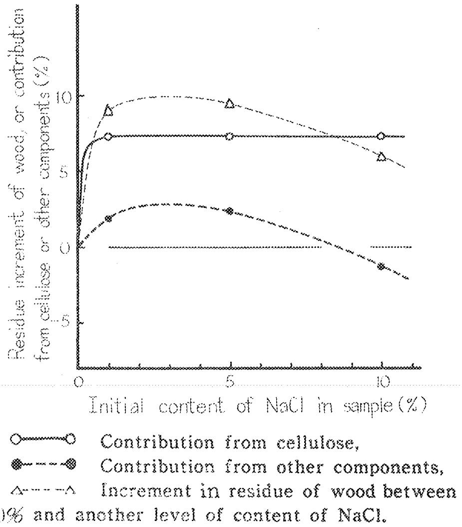


Fig. 23 Increase in residue of wood with treatment of sodium chloride and contributions from wood components to its increment.

the salt content. The char yield from the cellulose sample which was increased with the increase from 0 to 1% in the salt content was constant in spite of the further increase in it. This constant increment in the char yield seems to be achieved in the presence of an amount of salt less than 1% and to be free from the change in the salt content.

It would seem that the broad DTA peak K at the low temperature accompanied with some weight loss prior to another one in Fig. 20, occurred in compensation for the decrease in the peak area of the latter. Then it is suggested that a certain part of cellulose reacted to sodium chloride in its pyrolysis, and the reaction was independent of the change in the salt content, resembling catalysis and made the constant increment in the char residue.

Since the DTA peak (L) temperature for the original cellulose in the cellulose sample was almost constant in spite of the change in the salt content as seen in Fig. 22, this stable fraction of the cellulose might be decomposed without the influence of the salt. In Fig. 18, the plots of the char yield vs. the peak area for the original cellulose in the cellulose samples show the tendency to be concentrated into a point, for the char yield as well as the peak area was almost constant despite the change in the salt content.

It is to be noted that the behaviors of the DTA peak (L′) area for the original cellulose and of the char yield in the wood samples with the change in the salt content somewhat differed from those in the cellulose sample. The observations in Fig. 22 that the peak area for the original cellulose reached the minimum at 5% and then increased with the increase in the salt content from 5 to 10% seem to correspond to the decrease in the char yield with the increase in the salt content from 5 to 10% in Fig. 17.

The gradual decrease in the char yield in the wood sample with the increase in the salt content from 1 to 10% as shown in Fig. 17 might be due to thermally less stable ingredients in the wood which accepted the action of the salt. The contributions from cellulose and from other components to the char yield in Fig. 23, illustrate this.

4. Conclusions

1) Three or four endotherms were observed on the DTA curves of the samples treated with diammonium phosphate. In the treated cellulose, it is considered that the first peak at the lowest temperature, the second peak, and the third peak at the highest temperature correspond to the pyrolyses of the salt, of the modified cellulose, and of the residual cellulose, respectively. In the wood, the first peak at the lowest and the last one at the highest temperature are considered to represent the pyrolyses of the salt and of the residual cellulose, respectively.

The effect of the salt to decrease inflammable volatile products seems to be caused through the modification of cellulose with the salt. The DTA peak area for the residual cellulose and the increment in the char yield with the treatment may be expressed as exponential functions of the salt content. The increase in the char yield from the treated wood was most contributed from cellulose.

It seems that pyrolysis of the residual cellulose in the wood as well as in the cellulose sample was affected by the salt.

2) In the samples treated with ammonium bromide, three endotherms were observed on the DTA curves. It is thought that the first peak at the lowest temperature and the last one at the highest temperature were caused by the change of the salt alone and the pyrolysis of original cellulose. It seems that the pyrolysis of the original cellulose was little affected by the salt.

It is considered that the treated wood was indebted to cellulose for the increase in the char yield, and the char yield from other components in the wood was conversely decreased with the treatment.

3) The threshold temperatures of the weight loss of the samples treated with sodium tetraborate decahydrate were almost independent of the content change in the salt in the TG. An exotherm and two or three endotherms were observed on the DTA curves. The endotherms in the region of low temperature and the endotherm at the highest temperature seem to represent the change of the salt and the pyrolysis of the original cellulose, respectively.

The more the salt content in the wood increased, the more the contribution from components other than cellulose to the increase in the char yield from the wood sample increased, but the contribution from cellulose to it was always larger than from others. It is considered that the decrease of the original cellulose fraction with the treatment permitted an increase in the char yield and a decrease in the inflammable volatile fraction in the pyrolysis, on the basis of the relation between the char yield and the peak area.

4) The TG and the DTA curves of the samples treated with sodium chloride showed little difference among the salt contents. Two endotherms were observed on the DTA curve. One in the high temperature region is thought to correspond to the pyrolysis of the original cellulose.

In the cellulose sample, the DTA peak area for the original cellulose and the char yield are about constant. The action of the salt on the cellulose pyrolysis seems to be similar to catalysis. It could be said that the decrease in the char yield from the wood sample after the maximum with the increase in the salt content was due to the effect of the salt on the pyrolysis of unstable groups and components other than cellulose.

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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2報）

処理された木材およびセルロースの熱分解

平田利美(1)・阿部寛(2)

（概要）

1. 緒言

この研究の第1報では4)，無処理の木材およびセルロースの熱分解について，熱重量分析（TG）および示差熱分析（DTA）のデータにもとづき，その反応の動力学を述べた。

この報告では，化学的に処理された木材およびセルロースの熱分解を述べる。化学的に処理された木材およびその成分の熱分解においては，熱分解の開始温度およびそのみかけの全体的な活性化エネルギーが低下し，炭残渣が増加し，反対に揮化生成物の量が減少する。Akita and Kase1) はりん酸アンモニウムで処理されたセルロースの TG と DTA を行ない，その熱分解過程で観測された3成分の熱分解反応の速度論的パラメターを，理論的に誘導した DTA ピークと反応の極大速度の一致性を用いて算出した。さらに，かれらは観測された4成分を，塩含量による DTA ピークの変化等から同定した。この報告におけるデータの分析はかれらの研究から示唆を受けて行なわれた。

2. 実験方法

第1報で報告した木材とセルロースを試料に使った。

処理に使用した薬剤は1級試薬の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（ほう砂）および食塩で，これらの水溶液にセルロースあるいは木材を浸漬し，水分を蒸発させて所定の塩含量を得た。塩含量には，1，5，10%の3水準がある。

3. 結果

3.1 りん酸二アンモニウム処理試料

りん酸二アンモニウムで処理された試料の DTA 曲線には3ないし4個の吸熱がみられる（Fig. 1 および 5）。処理されたセルロースの場合，塩含量によるそのピークの変化から考えて（Fig. 2），最も低い温度で現われた最初のピークは塩それ自身の熱分解，2番目のピークは変性セルロース，3番目のピークは未変性セルロースの熱分解にそれぞれ対応していると考えられる。

炭収量が未変性セルロースに対する DTA のピーク面積が減少するにつれて増加しているので（Fig. 3），この塩の可燃性の揮化生成物を減少する効果は，この塩によるセルロースの変性によって起こされたようである。未変性セルロースに対する DTA のピーク面積および炭収量の増加量は塩含量の指数関数と

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(1)(2) 木材部

して表わし得る（Fig. 4）。処理によって木材の炭残渣が増加したのは，主としてセルロースの対応する炭が増加したためで，塩含量が多くなるとセルロース以外の他の成分も，木材の炭の増加にかなり寄与してくるが，セルロースにはおよばない（Fig. 8）。

セルロース試料においても，木材試料においても，未変性セルロースの熱分解は塩によって促進されているようである。

3. 2　臭化アンモニウム処理試料

臭化アンモニウムで処理された試料には，DTA カーブに3個の吸熱が観測された。塩含量による DTA ピークの変化から（Fig. 11），最も低い温度におけるピークおよび最高温度における最後のピークは，塩自体の変化およびフリーなセルロースの熱分解によって，それぞれひき起こされたものと思われる。木材およびセルロース試料ともに，フリーなセルロースに対する DTA のピーク温度が塩含量に独立であるから（Fig. 12），このフラクションの熱分解は薬剤の影響を受けていないように思われる。

塩含量の増加による炭収量の増加は，木材におけるよりセルロースにおいて著しい（Fig. 7）。したがって，処理された木材の炭残渣の収量増加はセルロースのおかげであり，セルロース以外の他の成分からの炭収量は，逆に処理によって減ったのではないかと思われる（Fig. 13）。

3. 3　ホウ酸ナトリウム処理試料

TG におけるホウ酸ナトリウム処理試料の重量減少の開始温度は，塩含量の変化にほとんど無関係である（Fig. 14 および 15）。処理されたセルロースの DTA カーブには1個の発熱および2個あるいは3個の発熱ピークが観測された。低温領域におけるふたつの吸熱は多分塩自体の変化によるもので，高温における吸熱はフリーなセルロースの熱分解によるものであろう。

セルロース試料からの炭収量は塩含量の増加にしたがって増加する傾向を示しているとはいえ，その炭収量の増加は限定されているようである。他方，木材試料の場合，研究された塩含量の範囲ではこのような限界値があるように思われない（Fig. 17）。木材中の塩含量が増加すればするほど，炭残渣の増加に対するセルロース以外の成分からの寄与が増加したが，セルロースからの寄与はいつもこれを上まわっていた（Fig. 19）。

セルロース試料中のフリーなセルロースに対するピーク面積と炭収量の間には密接な関係がある（Fig. 18）。フリーなセルロースフラクションが処理によって減少し，炭収量が増加し，可燃性フラクションが減少したと考えられる。

3. 4　食塩処理試料

食塩で処理された試料の TG および DTA カーブは，塩含量がちがってもほとんど異なっていない（Fig. 20 および 21）。

セルロース試料では，処理による炭の増加およびフリーなセルロースに対する DTA ピーク面積はほとんど一定で，塩含量の変化に関係ない。セルロースの熱分解におよぼす塩の作用は触媒反応に類似している。

木材試料の場合，塩含量の増加とともに炭収量が極大点を過ぎて減少していくのは，セルロース以外の不安定な基や成分が，この塩の作用によって熱分解が促進されるためと思われる（Fig. 17）。

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