# Pyrolysis and Combustion of Cellulose in the Presence of Inorganic Salts

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(Received March 2, 1951)

## Introduction

Some chemicals which when applied to cellulose inhibit flaming of gases or combustion charcoal are called fire-resisting compounds, and several of them are, for example, ammonium sulphate and phosphate, aluminium sulphate and zinc chloride. Many investigations have been made on the action of the compounds since olden times.(1)~(6)

The present author has studied on the process of carbonization of cellulose in the previous paper(7) and reached the following conclusion. Generally speaking, by the carbonization of cellulose, charcoal is not produced by the continued collapse of cellulose structure, but the high molecules of cellulose are first depolymerised to low molecules by heat, a part of which evaporates increasingly as the rate of heat increases and the other part, being dehydrated, polymerizes to yield a high polymer, direct origin of charcoal. This polymer is degassed by heat, being cut its weak bindings and proceeding aromatization side by side in the structure. Such gases as carbon dioxide, carbon monoxide, methane or hydrogen are evolved from it, consequently producing the "molecular roughness" or "Ultraporosität" in it. By further heating the gas evolution and the aromatization proceed and the "molecular roughness" increases till about 800°. However, it begins, in turn, to be eliminated by gradual breaking down of the skeleton of the polymer structure over 1000°, and by the severe treatment of heat the graphitization proceeds.

In the presence of some chemicals the process of carbonization of cellulosse being affected, the change in flammability of cellulose in this case is possibly attributed to that in carbonization process.

In this paper, the carbonization and combustibility of cellulose in the presence of various salts are reported to consider the action of fire-resisting compounds.

## Experimental

**Effect of Inorganic Salts on the Pyrolysis of Cellulose:**—The sample(8) was treated in the 0.1 mol. solutions of various salts. About 0.5 g. of dry sample was put in the bottom of the quartz tube which was closed at one end. The tube was connected to a gas burette. After evacuating the air from the tube and the burette, the sample was thermally decomposed by inserting the bottom of the tube perpendicularly in an electric heater, the temperature of which was 480°. The gas evolved by the decomposition of the sample was conducted to the gas burette and after being heated for an hour, the gas was

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(1) Gay Lussac, *Ann. chim. phys.*, **18**, 211 (1821).

(2) S. Tamaru, Y. Imai and T. Momma, *J. Chem. Soc. Japan*, **55**, 30 (1934).

(3) N. A. Richardson, *Chem. and Ind.*, **56**, 202 T (1937).

(4) R. W. Little, *American Chemical Society Monograph* No. 104 (1947).

(5) K. Tamaru, *J. Chem. Soc. Japan*, **69**, 20 (1948).

(6) American Chemical Society Symposium on "Flame Retarding of Textiles," *Ind. Eng. Chem.*, March, 1950.

(7) K. Tamaru, *J. Chem. Soc. Japan*, **69**, 21 (1948).

(8) Toyo Filter Paper No. 41, which contains no inorganic salt, was used as the sample.

Table 1

| Salt | Total gas volume, cc./g. | $CO_2$, % | CO, % | $CH_4$, % | $H_2$, % | Others, % | $R_1$, % | $R_2$, % | $V$, % |
|---|---|---|---|---|---|---|---|---|---|
| Without salt | 144 | 48 | 34 | 17 | 0 | 1 | 6 | 31 | 24 |
| $H_3BO_3$ | 120 | 44 | 43 | 11 | 2 | 1 | 13 | 20 | 33 |
| $NH_4Cl$ | 101 | 44 | 31 | 15 | 8 | 2 | 29 | 2 | 51 |
| $(NH_4)_2SO_4$ | 132 | 45 | 35 | 19 | 0 | 0 | 33 | 0 | 66 |
| $(NH_4)_2HPO_4$ | 89 | 42 | 43 | 9 | 2 | 4 | 39 | 0 | 79 |
| $NH_4$-molibdate | 148 | 51 | 29 | 14 | 6 | 0 | 34 | 4 | 57 |
| $(NH_4)_2PtCl_6$ | 149 | 42 | 24 | 18 | 17 | 0 | — | 9 | 45 |
| LiCl | 151 | 49 | 29 | 18 | 0 | 5 | 25 | 13 | 61 |
| KCl | 178 | 45 | 32 | 21 | 0 | 2 | 29 | 11 | 60 |
| KBr | 128 | 53 | 26 | 16 | 1 | 3 | 24 | 17 | 57 |
| KI | 109 | 53 | 23 | 15 | 7 | 3 | 28 | 18 | 56 |
| $KClO_3$ | 155 | 48 | 35 | 13 | 3 | 1 | 17 | 22 | 62 |
| $K_2SO_4$ | 192 | 44 | 29 | 25 | 0 | 2 | 19 | 19 | 50 |
| $KNO_3$ | 239 | 45 | 29 | 16 | 11 | 0 | 29 | 5 | 71 |
| $KH_2PO_4$ | 123 | 46 | 39 | 15 | 0 | 0 | 31 | 10 | 58 |
| $K_2CO_3$ | 242 | 42 | 23 | 26 | 6 | 3 | 31 | 1 | 75 |
| KCN | 234 | 42 | 33 | 25 | 0 | 0 | 35 | 0 | 76 |
| KCNS | 237 | 43 | 29 | 21 | 6 | 2 | 30 | 0 | 73 |
| $K_4Fe(CN)_6$ | 266 | 38 | 23 | 15 | 24 | 0 | 55 | 1 | 71 |
| $K_3Fe(CN)_6$ | 276 | 40 | 20 | 14 | 25 | 0 | 47 | 0 | 69 |
| $K_2SiO_3$ | 234 | 43 | 30 | 22 | 4 | 2 | 35 | 0 | 78 |
| $K_2Cr_2O_7$ | 240 | 49 | 16 | 23 | 10 | 3 | 39 | 0 | 55 |
| NaOH | 223 | 46 | 34 | 20 | 0 | 0 | 28 | 1 | 79 |
| NaCl | 165 | 50 | 28 | 20 | 0 | 2 | 20 | 12 | 56 |
| $Na_2SO_4$ | 177 | 46 | 34 | 18 | 0 | 1 | 18 | 17 | 45 |
| $Na_2S_2O_3$ | 219 | 51 | 32 | 17 | 0 | 0 | 31 | 0 | 84 |
| $Na_2CO_3$ | 210 | 45 | 36 | 19 | 0 | 1 | 29 | 1 | 82 |
| $Na_2B_4O_7$ | 132 | 51 | 32 | 16 | 1 | 1 | 43 | 3 | 73 |
| $MgCl_2$ | 124 | 50 | 32 | 16 | 0 | 1 | 28 | 2 | 59 |
| $CaCl_2$ | 143 | 54 | 22 | 21 | 2 | 3 | 42 | 2 | 62 |
| $BaCl_2$ | 128 | 51 | 31 | 17 | 0 | 1 | 20 | 15 | 49 |
| $AlCl_3$ | 129 | 43 | 40 | 17 | 0 | 1 | 22 | 14 | 41 |
| $Al_2(SO_4)_3$ | 140 | 46 | 43 | 8 | 2 | 1 | 39 | 1 | 76 |
| Rb-alum | 146 | 51 | 33 | 14 | 1 | 1 | 21 | 13 | 47 |
| $CrCl_3$ | 146 | 45 | 29 | 16 | 9 | 2 | 29 | 9 | 57 |
| $MnCl_2$ | 124 | 49 | 32 | 15 | 3 | 2 | 32 | 7 | 47 |
| $MnSO_4$ | 164 | 49 | 31 | 15 | 5 | 1 | 21 | 18 | 34 |
| $FeCl_2$ | 90 | 48 | 32 | 12 | 6 | 2 | 18 | 23 | 53 |
| $FeSO_4$ | 146 | 52 | 26 | 15 | 6 | 2 | 27 | 9 | 52 |
| $FeCl_3$ | 118 | 46 | 28 | 13 | 11 | 3 | 33 | 5 | 69 |
| $CoCl_2$ | 120 | 29 | 37 | 15 | 15 | 4 | 45 | 2 | 65 |
| $NiCl_2$ | 161 | 33 | 32 | 16 | 16 | 4 | 29 | 12 | 49 |
| $CuCl_2$ | 118 | 42 | 32 | 13 | 12 | 2 | 20 | 17 | 54 |
| $CuSO_4$ | 158 | 45 | 35 | 13 | 7 | 0 | 26 | 10 | 66 |
| $AgNO_3$ | 179 | 47 | 28 | 11 | 13 | 1 | 16 | 23 | 48 |
| $ZnSO_4$ | 146 | 43 | 37 | 7 | 12 | 1 | 25 | 6 | 51 |
| $CdCl_2$ | 143 | 43 | 16 | 15 | 20 | 6 | 31 | 8 | 56 |
| HgCl | 70 | 49 | 37 | 10 | 4 | 1 | 17 | 21 | 46 |
| $HgCl_2$ | 92 | 46 | 35 | 13 | 4 | 2 | 14 | 31 | 39 |
| $HgI_2$ | 46 | 49 | 36 | 10 | 5 | 1 | 14 | 46 | 48 |
| $SnCl_2$ | 151 | 41 | 21 | 11 | 24 | 2 | 41 | ·2 | 55 |
| Pb-acetate | 214 | 46 | 25 | 21 | 8 | 1 | 34 | 1 | 41 |
| $PdCl_2$ | 218 | 25 | 46 | 15 | 13 | 1 | 16 | 24 | 78 |
| $CuSO_4$* | 131 | 52 | 35 | 8 | 3 | 2 | — | — | 62 |
| $CuSO_4$** | 154 | 45 | 35 | 14 | 6 | 1 | 35 | 2 | — |

* The experiment was carried out at 430°.

** The experiment was carried out under the pressure of one atmosphere of carbon dioxide.

Table 2

The Effect of Inorganic Salts on the Combustion of Cellulose (1)

| Salt | $t$, sec*. | Height of flame, cm. |
|---|---|---|
| Without Salt | 35.0 | 3.2 |
| $H_3BO_3$ | 31.6 | 2.6 |
| $NH_4Cl$** | 35.0 | 2.7 |
| $(NH_4)_2HPO_4$** | 35.8 | 2.2 |
| $(NH_4)_2SO_4$** | 40.3 | 1.8 |
| LiCl | 33.7 | 2.8 |
| KCl | 28.8 | 3.4 |
| KBr | 26.4 | 4.2 |
| KI | 24.7 | 5.0 |
| $KClO_3$ | 20.2 | 4.8 |
| $K_2SO_4$ | 38.7 | 2.6 |
| $KNO_3$ | 29.8 | 2.4 |
| $KH_2PO_4$** | 47.3 | 1.3 |
| KCNS | 38.0 | 2.1 |
| $Na_2SO_4$ | 38.1 | 2.4 |
| $NaHSO_4$ | 25.1 | 4.2 |
| $Ca(OH)_2$ | 37.7 | 2.8 |
| $BaCl_2$ | 29.3 | 3.4 |
| $MnSO_4$ | 25.1 | 3.3 |
| $FeSO_4$ | 28.3 | 2.6 |
| $CuCl_2$ | 31.2 | 4.2 |
| $CuSO_4$ | 35.3 | 2.1 |
| $ZnSO_4$** | 26.3 | 3.3 |
| $CdCl_2$** | 28.5 | 3.0 |
| $HgCl_2$ | 30.7 | 3.3 |
| Pb-acetate | 37.7 | 2.4 |

* The time taken to spread the flame in the middle 12 cm. length of the sample.

** The sample remained as charcoal as it was after the flame had passed over.

pumped out and then analysed. Carbon dioxide, carbon monoxide and heavy hydrocarbons were determined by absorbing with potassium hydroxide solution, cuprous chloride solution and fuming sulphuric acid, respectively and after the removal of the above gases, hydrogen and methane were estimated by the explosion method.

The results are shown in Table 1. $R_1$ in the table denotes the charcoal yield and $V_1$ the approximate percentage of the gas evolved in the first three minutes and it shows the rough decomposition velocity. Organic vapour produced by the decomposition was condensed at the upper part of the tube out of the heater, then the liquid produced went down along the tube and carbonized at the entrance of the heater. The amount of chars thus produced is designated by $R_2$ in the table.

**Effect of Inorganic Salts on the Combustion of Cellulose:**—The effect of inorganic salts on the combustion of cellulose was measured by burning the filter paper which was treated by 0.1 mol solution of various salts. The sample was supported its both sides by the folded sheets of glass plates respectively and was placed in such a way that the glass plates were parallel with the width of 1.5 cm.(9) and its gradient was 1/7 to horizon. The sample was ignited at its lower end and the time taken to spread the flame 12 cm. length in the middle was measured. The height of the flame was also measured using a perpendicular graduated mirror. Every experiment was carried out under the same condition as possible and the results were obtained by taking an average of the repeated experiments.

The results are shown in Table 2. The samples treated by such salts as potassium carbonate, silicate, bichromate and ferrocyanide, borax, $Na_2S_2O_3$ and alminium sulphate were non-flammable and when the sample was horizontally placed those of ammonium sulphate and phosphate were also incombustible.

## Consideration

We will see in Table 1 that by the presence of inorganic salts, $R_1$ was increased, $R_2$ decreased, while the velocity of decomposition became faster.

The volume of the gas produced was much affected by the inorganic salts. For example, in the experiment of mercuric iodide it was 46 cc. / (g. cellulose) and of potassium ferricyanide 276 cc. / (g. cellulose). The former was approximately one third of that of the untreated cellulose and the latter, about two times of it. The volume of the gas was increased by palladium and alkaline salts and decreased by mercuric or mercurous salts. The alkaline salts increased the volume of the gas in the following order: lithium, sodium, potassium and rubidium salts. The difference of valency showed a different effect as shown in the case of Fe salts. As for the anions, the volume of the gas was increased by carbonate, hydroxide, cyanide, ferri- and ferrocyanides and nitrate. Moreover, among sulphate, chloride, bromide and iodide, the relation that, if the cation present is the same, the volume of the gas became smaller in the order described above was found out.

As to the composition of the gas, it did not show so much effect of the compounds, that is, about 45 to 50% was carbon dioxide and ts 30% was carbon monoxide and the major part of the remainder was methane. But most salts of the transition metals showed an increased content of hydrogen relative to oxygen in the gas.

When the pyrolysis was carried out in the atmosphere of carbon dioxide, the result was approximately the same, except the increased

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(9) If a larger width was taken the flame became higher and the velocity of combustion larger.

value of $R_1$ and decreased $R_2$. This showed that the evaporation of the organic vapour was suppressed by the presence of carbon dioxide and that the gaseous products by the carbonization of the organic vapour and those of the cellulose were not so different in this case.

At the lower decomposition temperature, the volume of the gas was decreased and its composition became richer in oxygen, showing that oxygen was more easily decomposed than hydrogen by the carbonization.

As to the results of the combustion experiment, it will be seen in Table 2 that higher the flame, faster the combustion velocity, and the velocities in the order of decreasing rates were: iodide, bromide, chloride and sulphate.

Oxidizing agents, such as potassium nitrate and chlorate, showed a faster velocity of combustion. The effect of the hydrated water on the salts was not directly observed.

T. Tatibana(10) studied on the effect of the inorganic compounds on the ignition temperature of cellulose. He measured the lowest temperature enough to set cellulose, which was treated by inorganic salts, on fire, when the sample was put in the furnace. The "ignition temperature," which he so called, corresponds to the temperature at which the sample begins to ignite without flame, and the "flaming temperature," to fire with flame.

H. Akamatu and H. Hamada(11) measured the effect of the various inorganic salts on the ignition temperature of carbon black(12), which contanied 5% salts in it using a simple thermobalance. The results are shown in Table 3.

Table 3

The Effect of Inorganic Salts on the Ignition Temperature of Carbon Black

| Salt | Ignition temp., °C. | Salt | Ignition temp., °C. |
|---|---|---|---|
| Without salt | 491 | Rochelle salt | 359 |
| $LiCl$ | 394 | $KAl(SO_4)_2$ | 469 |
| $Li_2CO_3$ | 413 | $CuCl_2$ | 318 |
| $NaOH$ | 330 | $CuSO_4$ | 370 |
| $NaCl$ | 414 | $AgNO_3$ | 413 |
| $NaNO_3$ | 349 | $MgCl_2$ | 457 |
| $Na_2SO_4$ | 445 | $MgSO_4$ | 480 |
| $Na_2CO_3$ | 355 | $CaCl_2$ | 400 |
| $KOH$ | 296 | $SrCl_2$ | 416 |
| $KCl$ | 408 | $BaCl_2$ | 424 |
| $KBr$ | 428 | $ZnSO_4$ | 451 |
| $KI$ | 388 | $CdSO_4$ | 452 |
| $KCN$ | 339 | $AlCl_3$ | 483 |
| $KCNS$ | 419 | $Al_2(SO_4)_3$ | 466 |
| $KNO_3$ | 346 | $SnCl_2$ | 451 |
| $KClO_3$ | 397 | Pb-acetate | 333 |
| $K_2SO_4$ | 443 | $CrCl_3$ | 412 |
| $K_2CO_3$ | 323 | $MnSO_4$ | 450 |
| $K_2Cr_2O_7$ | 344 | $FeCl_3$ | 401 |
| $K_4Fe(CN)_6$ | 336 | $CoCl_2$ | 390 |
| $K_3Fe(CN)_6$ | 350 | $NiCl_2$ | 420 |

Now we come to consider the action of fire-proofing compouuds, referring to the above-mentioned data. Some investigators suggested(2) that the action of fire-roofing compounds is possibly to let the valume of the combustible gas evolved by the pyrolysis to decrease and render cellulose noninflammable. However, though potassium carbonate, for instance, showed a large increase in the amount of combustible gas and, more over, the velocity of pyrolysis was large, it is practically one of the fire-resisting compounds. On the other hand, mercuric chloride showed only a small amount of combustible gas and had a slow decomposition velocity and, nevertheless, it is'not a fire-resisting compound.

This contrast shows that the fire-resisting action is not mainly responsible to the amount of the conbustible gas, but suggests that the organic vapour, which was carbonized to produce $R_2$, plays an impotant rôle in the combustion, as potassium carbonate produced no $R_2$, while mercuric chloride produced an appreciable amount of it, and, furthermore, the fire-retarding compounds generally produced no or little $R_2$ and those which yielded a considerable amount of $R_2$ are not to be fire-resisting compounds as we see in the table. Thus the organic vapour might be considered, so to say, as a kindling material, when cellulose burns(5).

The general process of combustion of cellulose is thought to its preceding thermal decomposition and successive ignition of the combustible materials, such as chars, combustible gases and vapours, and of these materials organic vapour is thought to be the most easily combustible.

Thus the inorganic salts are generally classified according to their effects on the combustion of cellulose as follows:

(I) Those that produce no or little organic vapour by the pyrolysis.

- (A) Those that do not lower the ignition temperature of chars appreciably.
  $Al_2(SO_4)_3$, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, $ZnCl_2$, etc. (fire-resisting compounds)
- (B) Those that appreciably lower the ignition temperature of chars.
  $NaOH$, $K_2CO_3$, $K_2Cr_2O_7$, etc.

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(10) Tatibana, *J. Chem. Soc., Japan*, **63**, 924 (1942).

(11) H. Akamatu and H. Hamada, *J. Chem. Soc. Japan*, **66**, 8 (1942).

(12) This sample was made by the Mitsubishi Kasei Co. Ltd.

(II) Those that produce a considerable amount of organic vapour by the pyrolysis.

- (A) Those that produce a large quantity of organic vapour.
  $H_3BO_3$, without salt.
- (B) Others.
  KCl, $HgCl_2$, $BaCl_2$, etc.

The salts in the first group, which produce no or little organic vapour, do not or hardly make cellulose to set flames under normal condition and potassium carbonate, silicate and ferrocyanide, sodium thiosulphate and alminium sulphate and so on belong to this group.

But some salts in the group which lower considerably the ignition temperature of chars, as shown in Table 3, set cellulose on fire without flame, setting the produced chars on fire. Consequently the salts in the first group and those which do not lower the ignition temperature of chars appreciably, such as alminium sulphate, ammonium sulphate and phosphate are to become the fire-retarding salts. And it is to be noted that no or little organic vapour associates to much charcoal yield and thus small quantity of heat evolved at the flames.

In the results of Tatibana(10) alminium sulphate, ammonium sulphate and phosphate have no "ignition temperature," suggesting that the charcoal yielded is not to be set on fire without the aid of the organic vapour, while such salts as potassium carbonate and sodium hydroxide show a lower temperature of ignition probably due to their lowering action of ignition temperature of chars.

In the case of the salts that produce a considerable amount of organic vapours by pyrolysis, cellulose burns in various ways according to the amounts and combustibilities of chars, gases and vapours. But when the organic vapours are so much as in the case of boric acid and untreated cellulose, the kindling material being so much, cellulose is not to be set on fire without flame and thus have no "ignition temperature" as shown by Tachibana(10).

The action of such salts as zinc sulphate, cadmium chloride, ammonium sulphate and phosphate by which cellulose remained as charcoal after the flame had passed over, is to be explained by their comparatively small amount of organic vapour and less lowering action of ignition temperature of chars.

Thus we see that the actions of various inorganic salts are explained from two major factors: the yield of the tarry product and the catalytic action in the combustion of charcoal. Of course, other factors such as the formation of glaze, evolution of inert gas, and absorption of heat by the salts also play a part but only to a minor extent compared with the two major factors.

The chief effect of the fire-resisting compounds upon the above-mentioned carbonization process of cellulose is possibly considered that they promote the polymerization rate by catalysis or ready dehydration from cellulose, consequently, producing little organic vapour.

## Summary

(1) The effects of the various inorganic salts on the thermal decomposition of cellulose were investigated.

(2) The combustion of cellulose in the presence of various inorganic salts was measured.

(3) It was suggested that the organic vapour produced by the pyrolysis plays an important rôle in the combustion of cellulose and that the major action of the fire-resisting compounds is to prohibit the yield of this vapour.

(4) The effect of the inorganic salts on the combustion of cellulose were classified and were explained from the two major factors: the yield of organic vapour and the lowering action of ignition temperature of the charcoal.

The author expresses his sincere thanks to Dr. J. Sameshima and Dr. H. Akamatu for their kind guidance and encouragement throughout this work.

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