Free Radicals in Charcoal and the Combustion of Compositions Containing Charcoal

Freie Radikale in Holzkohle und die Verbrennung von Holzkohle enthaltenden Verbindungen

Radicaux libres au charbon de bois et la combustion de compositions qui contiennent du charbon de bois

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Summary:

Thermal decomposition of cellulose furnishes charcoal containing free radicals detected by ESR technique. The maximum concentration of free electrons was found at the temperature of carbonization of c. 475 ° C. The curve: free radical concentration against temperature of carbonization of cellulose is of the same shape as the curve: rate of burning against temperature of carbonization of charcoal in the "Ammonpulver" the latter having maximum of the rate of burning near 500°. This supports the view that burning of mixtures containing charcoal is strongly influenced by the presence of free radicals in charchoal.

Zusammenfassung:

Die thermische Zersetzung von Zellulose liefert Holzkohle, die freie Radikale enthält, welche durch ESR-Verfahren ermittelt wurden. Die maximale Konzentration freier Elektronen wurde bei der Verkohlungstemperatur von 475 ° C festgestellt. Die Kurve: freie Radikal-Konzentration gegen Verkohlungstemperatur von Zellulose ist von der gleichen Form wie die Kurve: Verbrennungsgeschwindigkeit gegen Verkohlungstemperatur von Holzkohle im „Ammonpulver", wobei das Maximum an Verbrennungsgeschwindigkeit des letzteren bei ca. 500 ° C liegt. Dies stützt die Ansicht, daß das Verbrennen von Gemischen, die Holzkohle enthalten, stark von der Anwesenheit freier Radikale in Holzkohle beeinflußt wird.

Résumé:

La décomposition thermique de cellulose fournit un charbon de bois qui contient des radicaux libres découverts par la technique ESR. Le maximum de concentration d'électrons libres fut trouvé à la température de carbonisation d'environ 475 ° C. La courbe: concentration de radicaux libres contre température de carbonisation de cellulose est de la même forme comme la courbe: vitesse de combustion contre température de carbonisation de charbon de bois dans la „poudre d'ammonium", dont le maximum de la vitesse de combustion se trouve à environ 500 ° C. Ceci appuie l'opinion que la combustion de mélanges qui contiennent du charbon de bois est fort influencée par la présence de radicaux libres dans le charbon de bois.

Introduction

The recent publication of Milsch, Windsch and Heinzelmann [1] prompts us to report our own research on formation of free radicals when cellulose was subjected to thermal decomposition at temperatures from 245 ° to 600 °. This was a continuation of our former experiments on infra-red spectra of thermally decomposed cellulose [2] and also was connected with the problem why charcoal possesses remarkable property of facilitating burning mixtures of the type of black powder and similar pyrotechnic compositions. One of the authors of the present paper advanced a suggestion [3] that this is due to the presence of free radicals in charcoal which he found by means of ESR apparatus [4].

In view of this, our technique differed from that of the said authors: our samples were charred in a stream of nitrogen free of oxygen, but after cooling the samples were exposed to the air. This was due to our desire to investigate stable radicals, which are permanently found in charcoal, irrespective of the condition of their storage.

Experimental

Cotton linters (nitration grade) were purified by extracting with chloroform (18 hours), ethanol (18 hours), washed at room temperature with aqueous 18 % solution of sodium hydroxide (to free cellulose from β- and γ-cellulose), followed by washing with cold water to the neutral reaction to litmus, washed with acetone, ethanol and ether. The content of α-cellulose was practically 100 %.

Nitrogen was purified in a standard way over copper wool heated to 700 ° and by passing through a number of absorption tubes [5].

Cotton cellulose (4.0 g) was placed in a quartz tube 26 mm diameter heated in an electric oven at a constant temperature. Nitrogen was drawn through the tube at the rate of 0.75 dcm^3/min. and the outlet was connected with a water pump (working at a slow stream of water) to achieve a quicker removal of the gaseous products of the decomposition of cellulose.

After the decomposition was terminated, the heating was stopped and the samples were cooled in the stream of nitrogen. They were withdrawn, weighted, subjected to elementar analysis and examined in ESR apparatus.

It has been found that $3^1/_2$ hours of heating are sufficient to complete the reaction of the decomposition: the weight of the samples and the intensity of the RSR signal remained unchanged if the reaction was prolonged.

The ESR measurements were made at the room temperature on an X-band spectrometer having 100 kHz magnetic field modulation. For calibration the stable radical diphenylpicrylhydrazyl (DPPH) was used.

Results and Discussion

The loss of weight and elementar analysis were in full areement with our previous findings [2].

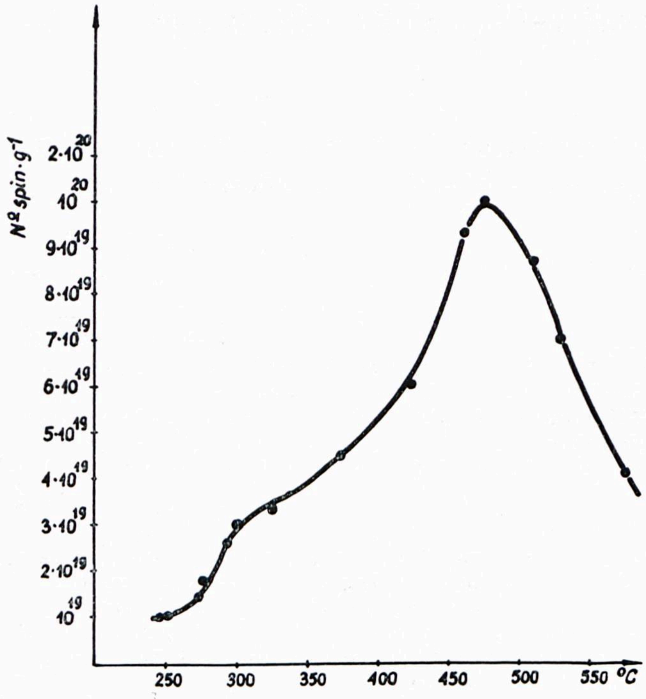

Fig. 1
Spin concentration in dependance on the temperature of carbonization of cellulose

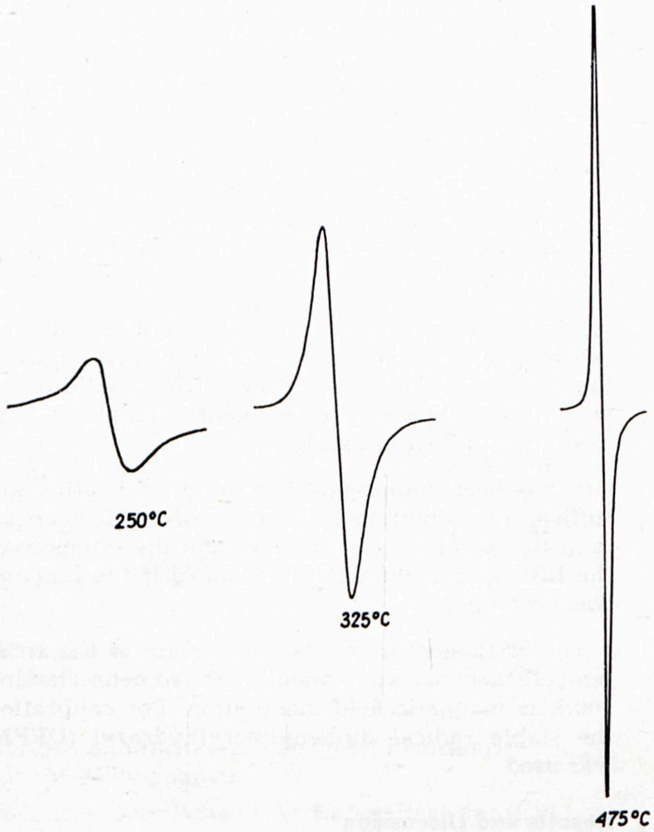

Fig. 2
ESR signals for the range of temperatures of carbonization 250—475 °

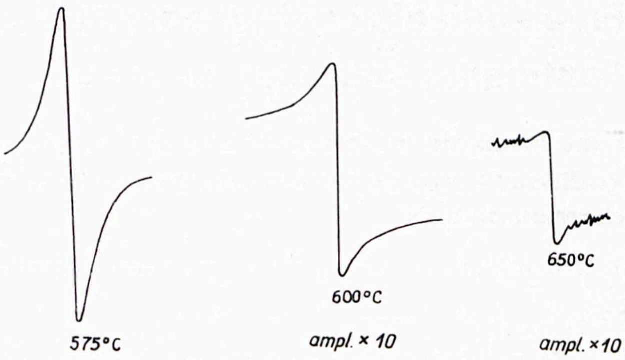

Fig. 3
ESR signals for the range of temperatures of carbonization 575—650 °. The signals for 600 ° and 650 ° are tenfold amplified

The formation of free radicals was first observed at carbonization temperature of 245 °. The concentration of free radicals increased with the increase of the carbonization temperatures and reached its maximum at 475 °. Further increase of the temperature produced the fall of the free radical concentrations (Table 1 and Fig. 1).

In the range 245—475 ° the shape of ESR signals was typical for stable free radical state which appears in many coal samples of different origin. The increase of the carbonization temperature is here accompanied by the decrease of the signal width from c. 6 G to 0.8 G (Figs. 2 and 3).

This considerable narrowing of the absorption lines indicates a strong spin-spin exchange interaction. The broadening of signals of the samples heated at the lower temperatures (250—325 °) seems to be caused by unresolved hyperfine structure of the signals due to the presence of hydrogen atoms in not fully carbonized molecules of cellulose. Similarly, with an increase of the temperature the g-factor changed from 2.0068 to 2.0027, close to the free spin values (Fig. 4).

Above 475 ° the width of the lines increased with temperature. The beginning of the curve did not coincide with the end, (magnetic field sweep △ H ~ 100 G); this deviation increased with the temperature.

Grinding of charcoal

If the charcoal was ground, the number of free radicals increased. This was in agreement with the previous finding [4]. A brief grinding in an agate mortar produced an increase of the number of free electrons by c. 10 %.

Rate of burning of blackpowder and similar mixtures

It is well known that the ignition temperature of blackpowder to great extend depends on the temperature of carbonization of wood [6]. Also the rate of burning depends on this temperature [7] — the fact well known to the manufactures of blackpowder [8]. The problem was investigated by Urbański and Tęsiorowski [8], Blackwood and Bowden [9].

Urbański and Tęsiorowski examined the rate of burning of “Ammonpulver” — a mixture composed of 85 % ammonium nitrate and 15 % charcoal-using charcoal obtained by carbonization of wood at temperatures ranging from 300 ° to 900 °.

The rate of burning was determined in a manometric bomb of Sarrau-Vieille-Burlot [10] at the density of 0.1 and expressed as $\frac{dp}{dt}$ max [11]. The plot of the rates of burning against the temperature of carbonization gave the curve (Fig. 5) with a maximum near 500 °. The similarity of both curves — Fig. 1 and Fig. 5 seems to substanciate the view expressed by the author of the present paper that the burning of blackpowder and similar mixtures is mainly a free radical reaction and the rate of burning is considerably influenced by the number of unpaired electrons in charcoal [3].

Table 1

No	Temperature	Number of spins in the sample	Number of spins per 1 gram	g_{max}
1.	245 ° C	$1{,}09 \times 10^{17}$	$1{,}076 \times 10^{19}$	2.0068
2.	250 ° C	$2{,}01 \times 10^{17}$	$1{,}084 \times 10^{19}$	2.0055
3.	265 ° C	$1{,}41 \times 10^{17}$	$1{,}410 \times 10^{19}$	2.0041
4.	270 ° C	$1{,}82 \times 10^{17}$	$1{,}791 \times 10^{19}$	2.0040
5.	285 ° C	$2{,}83 \times 10^{17}$	$2{,}551 \times 10^{19}$	2.0037
6.	300 ° C	$3{,}00 \times 10^{17}$	$3{,}00 \times 10^{19}$	2.0036
7.	325 ° C	$3{,}51 \times 10^{17}$	$3{,}321 \times 10^{19}$	2.0035
8.	375 ° C	$5{,}71 \times 10^{17}$	$4{,}450 \times 10^{19}$	2.0033
9.	425 ° C	$1{,}031 \times 10^{18}$	$6{,}151 \times 10^{19}$	2.0032
10.	460 ° C	$1{,}49 \times 10^{18}$	$9{,}252 \times 10^{19}$	2.0031
11.	475 ° C	$1{,}65 \times 10^{18}$	$1{,}012 \times 10^{20}$	2.0030
12.	510 ° C	$1{,}42 \times 10^{18}$	$8{,}751 \times 10^{19}$	2.0029
13.	530 ° C	$1{,}18 \times 10^{18}$	$7{,}050 \times 10^{19}$	2.0029
14.	575 ° C	$6{,}51 \times 10^{17}$	$4{,}110 \times 10^{19}$	2.0027

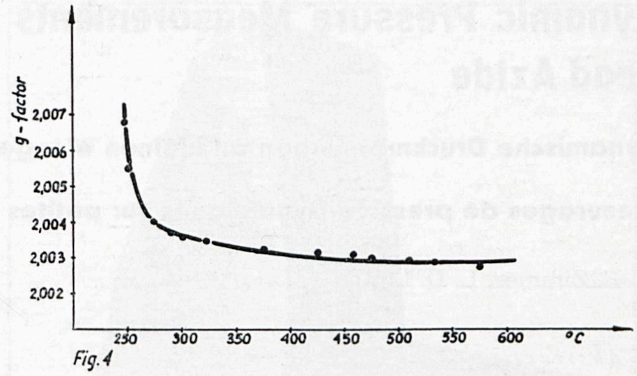

Fig. 4
g-Factor dependence on the temperature of carbonization

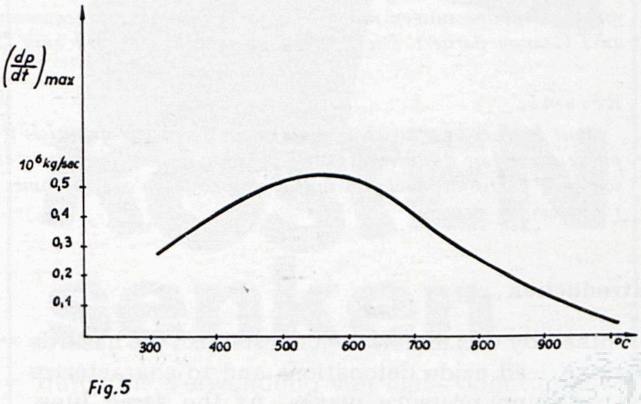

Fig. 5
Rate of burning of Ammonpulver in dependence on the temperature of carbonization

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