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COMPARISON OF THE RESULTS OF THERMAL ANALYSIS AND STEPWISE PYROLYSIS GAS CHROMATOGRAPHY BY INVESTIGATING THERMAL DESTRUCTION OF SOME CELLULOSE DERIVATIVES

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ABSTRACT

This paper compares pyrolysis gas chromatographic and thermal analysis data and shows the importance of pyrolysis product analysis in supplementing the latter.

INTRODUCTION

Thermal analysis techniques are the most widely used method for investigating the thermal destruction of high-molecular compounds. However, it should be pointed out that only data on performance characteristics of material can be obtained. Conclusions about the structure of a substance or the chemism of destruction remain still constructive. Information on thermal analysis somewhat increases by investigating the composition of thermal degradation products of polymer at different stages of degradation.

We use pyrolysis gas chromatography (PGC) to study the dependence of the composition of thermal destruction products of cellulose on the type and amount of various modifiers.

MEASURING METHODS

A quantitative method - stepwise pyrolysis gas chromatography (SPGC) - has been developed to elucidate the temperature dependence of the yields of individual thermal degradation products of polymers. Our method consists in that 1-10 g samples weighed in quartz tubes were heated in a microreator (Fig.1) at 100-500°C, elevating the temperature in the pyrolyzer by 10-25°C. After each heating (15 sec) the quantitative composition of the major pyrolysis products were analyzed by gas chromatography.

RESULTS AND DISCUSSION

The SPGC data were compared with those on thermal analysis. The latter were in good agreement with data on the rate of evolution of H_2O, CO and CO_2 on cellulose pyrolysis, i.e. the temperatures of the

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maximum rate of dehydration, decarboxylation and decarbonylation occur in the region of those of the maximum weight loss of cellulose samples.

Very interesting results were obtained by investigating the thermal degradation of cellulose copolymer with polyacrylonitrile (PAN). The thermogram shown in Fig.2 provides little information on the processes taking place by the copolymer thermal degradation. Only data on the quantitative composition and temperature dependence of the yields of CO, CO_2, H_2O, NH_3 and HCN (see Table 1) made it possible to suggest the mechanism of copolymer thermal decomposition.

Table 1

Dependence of the yields of pyrolysis products of cellulose copolymers with PAN on copolymer composition

PAN/cellulose ratio by weight	Total pyrolysis product yield				
	H_2O	CO_2	CO	NH_3 mg/g PAN	HCN ΔS/g PAN
	mg/g	cellulose			
1. 0 / 100	122	69	39,2	-	-
2. 13,3 / 86,7	125	80	29,6	9,8	traces
3. 22,5 / 77,5	130	91	37,2	9,3	"
4. 29,6 / 70,4	151	100	35,2	9,0	"
5. 37,0 / 63,0	161	109	37,2	4,0	"
6. 50,0 / 50,0	152	111	38,0	44,6	1699

This mechanism consists in saponification of nitrile groups of PAN at 300-400°C with pyrolysis water separated by the cellulose thermal degradation.

$$H_2O + R\text{-}CN \xrightarrow{t^o} NH_3 + R\text{-}COOH$$

On the basis of our work the optimum composition of copolymer with lowest HCN yield by pyrolysis for producing carbon was determined.

By investigating the thermal destruction of phosphorus - containing cellulose fibres a quantitative relationship between parameters of dehydration reaction and combustibility was established /3/. The study of the pyrolysis of boron-containing cellulose fibres gave evidence of a completely different mechanism of combustibility of these fibres compared with phosphorus-containing antipyrenes.

The data in Table 2 show that the role of dehydration reaction in cellulose combustibility with boron-containing compounds is insignificant, although the rate of dehydration increases in the presence of nitrogen synergists and halogens. The main importance is attributed to increasing thermal stability of cellulose.

Table 2

Effect of antipyrenes on pyrolysis product yield

(% of their yield on initial cellulose pyrolysis)

Sample	H_2O %		CO_2 %		CO %		Carbon residue,%	Oxygen index,%
	yield	T°C	yield	T°C	yield	T°C		
Cotton+B+N	+20	+6	+2,7	+4,8	+112	+14	+101	+ 80
Cotton+B	+ 6	-3,6	-6	+3	+ 53	+ 3	+ 34	+ 50
Cotton+B+N+Br	+51	-40	-36	-29	-83	± 0	+ 87	+102
Cotton+B+N+Cl	+47	+7	+20	+14	+179	+10	+184	+132

The above examples demonstrate how information on thermal analysis can be increased by analyzing the composition of pyrolysis products.

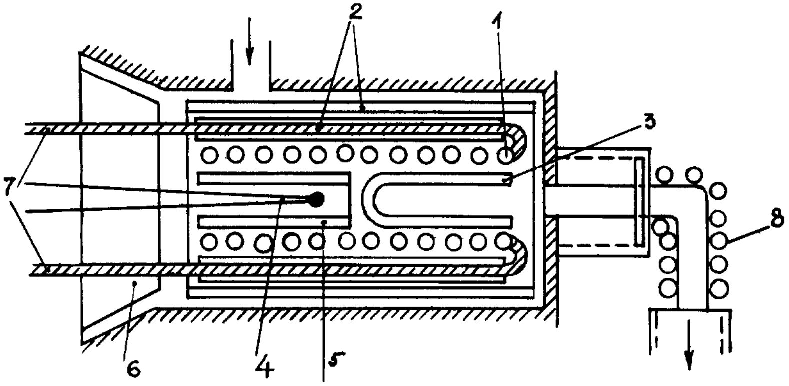

Fig.1. Schematic diagram of pyrolyser.

1 - platinum spiral,
2,3,5 - quartz tubes,
4 - thermocouple,
6 - Teflon lid,
7 - copper wire,
8 - heating.

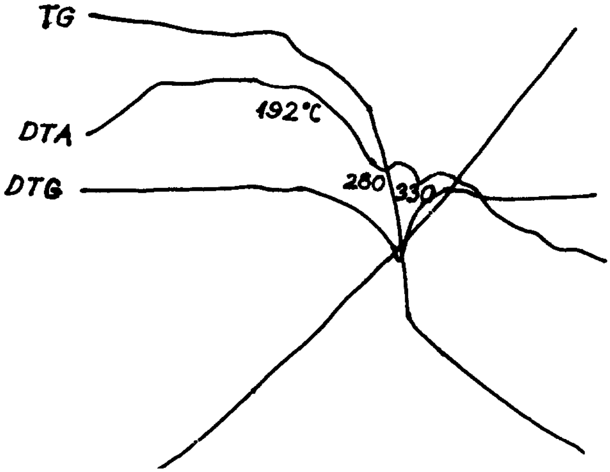

Fig.2. Thermal analysis data of cellulose copolymer with PAN.

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