Thermal degradation of corncobs and straw

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The composition of the pyrolyzate of untreated and H_3PO_4-impregnated corncobs and straw was studied by g.l.c.—mass spectrometry. The major products of thermal degradation were 2-furaldehyde, acetic acid, levoglucosenone, and the other significant compounds were identified as 3-hydroxy-2-penteno-1,5-lactone, levulinic acid, guaiacol, acrylaldehyde, and 4-hydroxy-3-methoxy-1-vinylbenzene. The treatment of corncobs and straw with acid catalyst before the pyrolysis showed expressive changes of amount and distribution of pyrolytic products. Substantial departures between the composition of the pyrolyzate of corncobs and straw were not found. The results of dynamic thermal analysis (TG, DTG, DTA) are also reported.

Был изучен состав пиролизата необработанных и H_3PO_4-обработанных кукурузных кочерыжек и соломы путем газо-жидкостной хроматографии и масс-спектрометрии. Главными продуктами термического разложения являлись 2-фуральдегид, уксусная кислота, левоглюкозенон и остальные значительные соединения были идентифицированы как 3-гидрокси-2-пентено-1,5-лактон, левулиновая кислота, гваякол, акрилальдегид и 4-гидрокси-3-метокси-1-винилбензол. Обработка кукурузных кочерыжек и соломы каталитическим количеством фосфорной кислоты влекла за собой значительные изменения в количестве и составе продуктов пиролиза. Коренные изменения в составе пиролизата кукурузных кочерыжек и соломы не были определены. Тоже указаны результаты динамического термического анализа (ТГ, ДТГ, ДТА).

Pyrolytic reactions have special significance in relation to problem of fire, solid-waste disposal, pollution, and in other areas. In the centre of attention was and still is especially thermal degradation of cellulosic materials [1—6], lignin and xylans [7—10]. Recently, furthermore, renewed interest in the conversion of the enormous amounts of biomass residues into feedstuff as well as useful and also

necessary chemicals has promoted research into the application or pyrolytic methods.

Only little attention was paid to the thermal degradation of corncobs and straw relating to the qualitative composition of pyrolyzate [11—14]. Till now presented papers deal mainly with physicochemical and technical problems of the pyrolytic process — as *e.g.* measurement of mass loss, variations in the material structure due to heating, total carbonization, facility of transformation to oil, gasification, *etc.* [15—19].

Corncobs and straw contain partly hexosic units, partly pentoglycans and lignin, from which may be deduced a variety of composition of the pyrolyzate which considerably depends on composition of the substrate. Further, it may be expected from the comparison of numerical data about the composition of corncobs and straw [20, 21] that distribution of the products of pyrolysis from both materials will be similar. These facts were experimentally confirmed in our work.

Experimental

Materials

The samples for pyrolysis were obtained by grinding (grain size was about 1 mm) of raw material (wheat straw and corncobs one year after gleaning) and drying in vacuum desiccator over $CaCl_2$ over five days. Impregnated samples were prepared by treatment of ground material with 3 % of phosphoric acid (calculated on mass of raw material) and drying *in vacuo* at temperature below 50 °C. Authentic samples of the products *14b*, *15*, and *18* were prepared according to known procedures [3, 6, 8]. The other samples of the preparates were commercial (Merck, Darmstadt).

Thermal analysis

The TG, DTG, and DTA data were obtained with a Mettler Thermoanalyzer 2, using 7 mg samples in platinum pans. Platinum and rhodium-platinum thermocouples employing aluminium oxide as the reference were used for DTA. The samples were heated at the rate of 10 °C min^{-1} in a flow of inert gas (nitrogen, 116 cm^3 s^{-1}).

Pyrolysis — g.l.c.

Samples (9.6 mg) were pyrolyzed in a Pyroprobe 150 pyrolysis unit (Chemical Data System) preheated to 400 °C and connected directly to the carrier-gas stream (nitrogen) of temperature-programmed (100—230 °C; 10 °C min^{-1}) Chrom 4-gas chromatograph equipped with a column (3.7 m × 3.1 mm) of 15 % of 20 M Carbowax on Chromosorb WAW.

Compounds were identified by comparison of their retention times with those of the standard samples.

Direct pyrolysis—g.l.c. — mass spectrometry

The mass spectra (12 eV) were recorded with a JMS-D 100 mass spectrometer equipped with Jeol pyrolyzer, Model PL-723 and gas chromatograph JGC-2OK, using a column (3.0 m × 3.1 mm) of 3 % of 20M Carbowax on Chromosorb WAW (80/100 mesh) with a temperature program 90—120 °C at the rate of heating of 10 °C min^{-1}. The samples (7 mg) were introduced into pyrolyzer preheated to 400 °C and the time of pyrolysis was 30 s. All the pyrolyses were carried out in a nitrøgen atmosphere.

Preparative pyrolysis

Acid-impregnated resp. untreated material was pyrolyzed in 25 g batches in 250 ml round-bottomed Pyrex flask preheated to 320 °C in a metal bath. Each pyrolysis, carried out in the atmosphere of nitrogen, was complete within ~30 min. The volatile products were collected in a trap cooled to −78 °C. The crude pyrolyzate from ten pyrolyses was separated into organic and aqueous layer. From the latter, levoglucosan was obtained by crystallization using acetone (according to Ref. [22]), and from the organic layer a mixture of 2,4-dinitrophenylhydrazones of carbonyl compounds was obtained (according to Ref. [23, 24]), which was separated on t.l.c. plates Silufol UV-254 (Kavalier, Votice) using carbon tetrachloride—ethyl acetate (volume ratio 9:1) as mobile phase. Levoglucosenone was obtained from the organic layer by extraction into a methanol—water mixture (volume ratio 4:1) and by following distillation under diminished pressure [25].

Results and discussion

We identified twenty compounds of thermal degradation of corncobs and straw using direct connection of the pyrolysis with gas-liquid chromatography and recording of the mass spectrum. Levoglucosan, as a twenty-first component, was obtained from the aqueous layer of the pyrolyzate (see preparative pyrolysis). The records from the gas-liquid chromatography are shown in Figs. 1—4 and the corresponding description of compounds as well as the methods of identification are shown in Table 1.

From Figs. 1—4 is evident that between the products of pyrolysis of corncobs and straw are not great differences, while significant differences were found in the distribution of products from the pyrolysis of untreated and acid-impregnated (3 % of phosphoric acid on mass of substrate) materials. Impregnated samples produced by the pyrolysis 2-furaldehyde, acetic acid, acrylaldehyde, and levoglucosenone

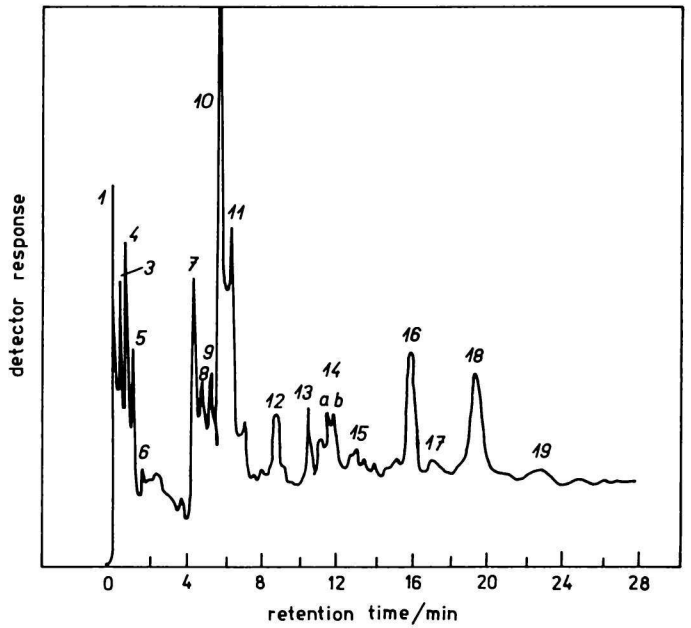

Fig. 1. Chromatogram from direct pyrolysis—g.l.c. of corncobs.

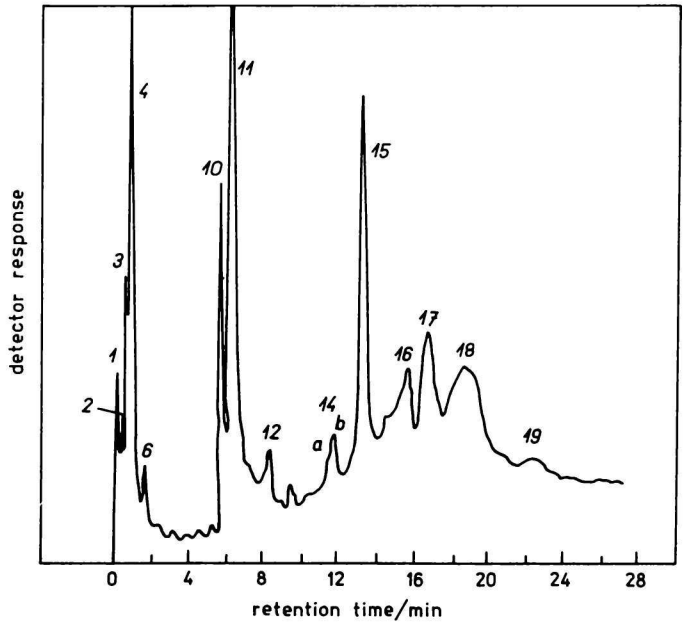

Fig. 2. Chromatogram from direct pyrolysis—g.l.c. of corncobs in the presence of phosphoric acid.

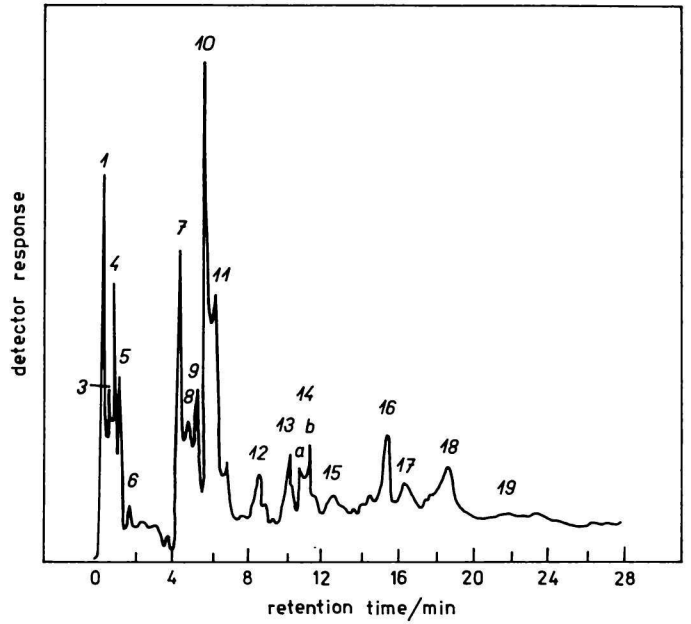

Fig. 3. Chromatogram from direct pyrolysis—g.l.c. of straw.

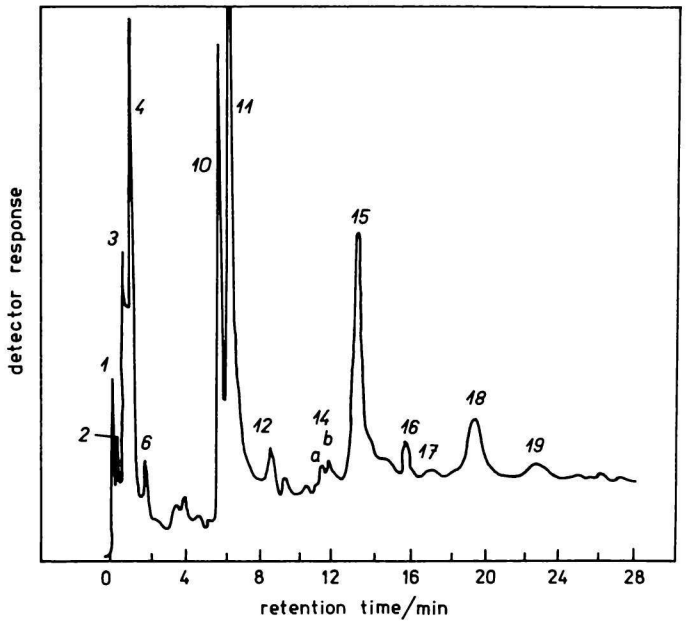

Fig. 4. Chromatogram from direct pyrolysis—g.l.c. of straw in the presence of phosphoric acid.

Table I

Pyrolysis products of corncobs and straw

G.l.c. peak	Compound	M_r	Mass-spectral data *m/z*	Identification methods
1	Acetaldehyde	44	44, 43, 29	*a*, *b*, *c*
2	Furan	68	68, 40,39,38,29	*a*
3	Acetone	58	58, 43, 42	*a*, *b*, *c*
4	Acrylaldehyde	56	56, 55, 28, 27, 26	*a*, *b*, *c*
5	Methanol	32	32, 31, 29, 28	*a*
6	2,3-Butanedione	86	86, 69, 68, 43, 41	*a*, *b*, *c*
7	Pyruvaldehyde	72	43, 29, 18	*a*, *b*, *c*
8	1-Hydroxy-2-propanone	74	74, 43, 31	*a*, *b*, *c*
9	Glyoxal	58	29, 18	*a*, *b*, *c*
10	Acetic acid	60	60, 45, 43, 29	*a*
11	2-Furaldehyde	96	96, 95, 51,42,40, 39	*a*, *b*, *c*
12	5-Methyl-2-furaldehyde	110	110, 109, 81, 53, 51, 50, 43, 39	*a*, *b*, *c*
13	β-Angelicalactone	98	98, 83, 69, 55, 54, 43, 39, 28, 27	*a*
14a	Guaiacol	124	124, 109, 81, 53	*a*
14b	3-Hydroxy-2-penteno-1,5-lactone	114	114, 85, 58, 57, 55, 43, 42, 41, 39, 29	*a*
15	Levoglucosenone	126	98, 96, 68, 53, 42, 41, 39, 29, 27, 26	*a*, *b*, *c*
16	Levulinic acid	116	116, 101, 99, 73, 71, 56, 43	*a*
17	4-Hydroxy-3-methoxy-1-vinylbenzene	150	150, 135, 107, 89, 79, 77, 63, 51	*a*
18	1,4:3,6-Dianhydro-α-D-glucopyranose	144	144, 99, 98, 86, 85, 73, 71, 70, 69, 60	*a*, *d*
19	5-Hydroxymethyl-2-furaldehyde	126	126, 97, 69, 53, 51, 41, 39	*a*, *b*, *c*

a) Comparison of the retention time and of mass-spectral data with those of standard sample.
b) Comparison of R_f data of 2,4-dinitrophenylhydrazones from t.l.c.
c) Comparison of m.p. of 2,4-dinitrophenylhydrazones.
d) Comparison of m.p. of the acetyl derivatives.

(1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranose-2-ulose) as main products, while untreated samples gave only very small portions of levoglucosenone, lower yield of 2-furaldehyde, and higher amount of acetic acid, pyruvaldehyde, and acrylaldehyde. The lignin component of corncobs and straw is responsible for the pyrolytic formation of guaiacol and 4-hydroxy-3-methoxy-1-vinylbenzene [26, 27], while 3-hydroxy-2-penteno-1,5-lactone originates from the xylan component [7—10, 28].

The physical and chemical transformations which take place on heating of corncobs and straw (for comparison also cellulose and levoglucosan) from 25 to 600 °C at constant rate of heating of 10 °C min^{-1} were investigated by dynamic thermal analysis. The results of thermal analyses are shown in Figs. 5—7 and are summarized in Table 2.

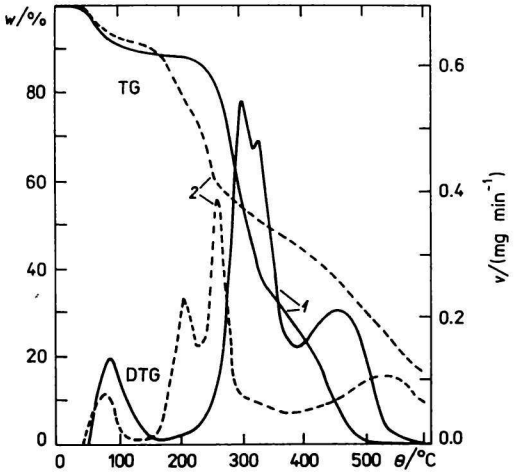

Fig. 5. Thermal analysis of corncobs.
1. Untreated sample; *2.* acid-impregnated sample.

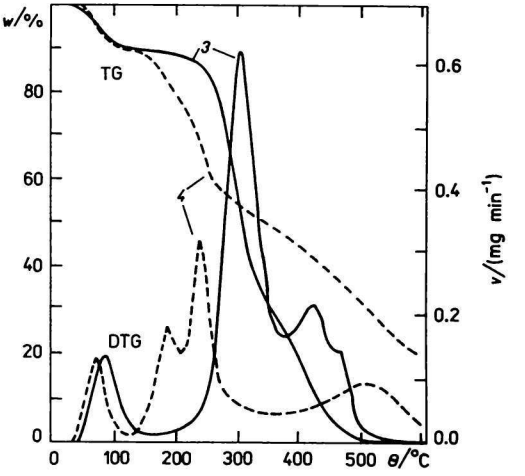

Fig. 6. Thermal analysis of straw.
3. Untreated sample; *4.* acid-impregnated sample.

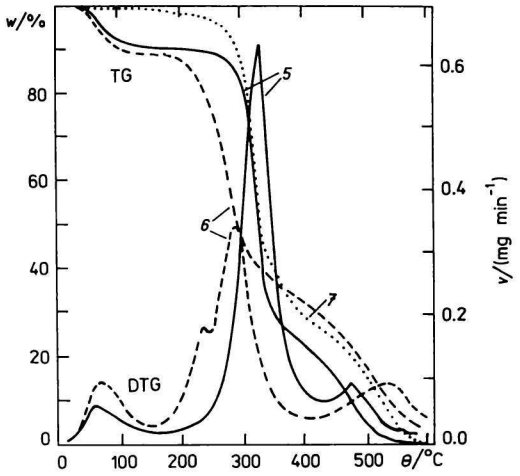

Fig. 7. Thermal analysis of cellulose and levoglucosan.
5. Untreated cellulose; *6.* acid-impregnated cellulose; *7.* untreated levoglucosan.

Thermal decomposition of corncobs and straw starts at about 70 °C by removing of free water, the content of which is about 9 %. Further course is considerably dependent on the fact whether untreated material is pyrolyzed or the decomposition is catalyzed by an acidic impregnating agent. Untreated samples showed maximum rate of decomposition at higher temperature — about 290 °C. In this case, the sample starts to decompose at lower temperature, thermal degradation proceeds more rapidly and at higher temperatures lower content of resistant residue results as in the case of acid-impregnated samples. These latter showed maximum rate of decomposition at the temperature about 240 °C.

Xylan component of corncobs and straw starts to decompose at about 200 °C but the decomposition proceeds over a wider temperature range than that of cellulose. Thermal decomposition of lignin component takes place also over a wider temperature range but the pyrolysis leaves a larger carbonaceous residue. Impregnated sample of cellulose (Fig. 7) thermally decomposes in two kinetic steps. The first step — within the temperature range 200—250 °C and the second step within the range 250—350 °C. Untreated sample decomposes within the range 250—370 °C. Levoglucosan is thermally stable up to the temperature 250 °C, then decomposes at such temperatures as an untreated sample of cellulose; maximum rate of decomposition is at 330 °C.

Up to the present time, the mechanism involving the action of an acidic impregnating agent in the pyrolysis process, is not unambiguously explained. Theoretically, it may be considered that the catalytic effect of phosphoric acid is produced through repeated esterification of the glucose units in the cellulose molecule and regeneration of the phosphorylating agent after preferential decomposition of the esterified units. The esterified units readily dehydrate and the effect

Table 2

Thermal analysis features of the samples

Number[a]	Sample	DTA peaks θ/°C	DTG peaks θ/°C	Maximum rate v/(mg min^{-1})	Residue at 500 °C w/%
1	U Corncobs	70[b], 321, 439	70, 283, 310, 440	0.55	0.2
2	AI Corncobs	78[b], 310, 510	75, 196, 248, 525	0.39	30.8
3	U Straw	76[b], 232[b], 320, 413	76, 290, 413, 460	0.62	0.3
4	AI Straw	75[b], 316, 490	70, 184, 235, 508	0.32	32.2
5	U Cellulose	63[b], 203, 285[b], 345, 419[b], 475	63, 330, 473	0.64	4.4
6	AI Cellulose	73[b], 87[b], 315, 435[b], 502	72, 285, 505	0.34	17.6
7	U Levoglucosan	125[b], 185[b], 300[b], 360, 518	300, 523	0.60	15.2

AI — acid-impregnated sample, U — untreated sample.

a) Number of sample at curves in Figs. 5—7; *b*) endothermic.

of phosphoric acid would be in retardation of combustion of volatiles in the gas phase. The mentioned dehydration is acid-catalyzed and the distribution of the volatile pyrolysis products indicates that extensive dehydration and decarboxylation reactions are occurring rather than fragmentation reactions. In agreement with this, most of the pyrolysis products, including levoglucosenone, furan derivatives, levulinic acid, and β-angelicalactone are usually considered acid-catalyzed dehydration products of carbohydrates.

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