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GAS CHROMATOGRAPHY OF THE PRODUCTS FORMED BY THERMAL DECOMPOSITION OF "PYROLYSIS RESIN"

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SUMMARY

The subject of this study was to determine the amount and composition of the pyrolysis products formed by pyrolysis of so called "Pyrolysis Resin", which is a waste material formed during the cracking of light hydrocarbons to propylene. In the first part of this paper the pyrolysis products obtained at temperatures from 500° to 1000° in a molten metal bath were determined by direct chromatography. The products of thermal degradation consisted mostly of aromatic hydrocarbons. Benzene, toluene, xylene, indene and 2-methylindene were present in the amounts of about 1-2%. Substantially larger amounts of naphthalene (about 20-25%) were found at degradation temperatures of 900-1000°. The total weight of the pyrolysis procedure was determined over the same temperature range.

"Pyrolysis Resin" investigated here is a high molecular weight organic residue that is usually removed as an unidentified material after pyrolysis of light hydrocarbons to propylene.

INTRODUCTION

Many methods have already been described for carrying out pyrolysis-gas chromatography. Among these the most commonly used is the degradation of the substance by applying it to an electrically-heated spiral wire¹⁻⁵. This method cannot be used for solid samples without special precautions. A number of devices have been designed for this purpose⁶⁻¹⁰. Most of them suffer from the unsatisfactory heat transfer to the sample and some from the necessity of interrupting the carrier gas flow before each experiment.

KARR *et al.*¹¹ used this technique to compare the chemical natures of the resinous fractions isolated from the low temperature tar formed by brown coals, caking and non-caking coals, and electrode pitch. GRILING¹² has studied the degradation products formed when different coals were heated in such a manner as to produce a steady rate of temperature rise. BRICTEUX¹³ compared the pyrograms of exinite and vitrinite while HOLDEN AND ROBB¹⁴ have heated coal samples directly in the ionisation chamber of a mass spectrometer.

DIRECT DETERMINATION OF PYROLYSIS PRODUCTS

The thermal decomposition of "Pyrolysis Resin" was carried out in a quartz pyrolyser that contained a molten tin bath. Pyrolysis was accomplished by dropping a small sample into a bath of molten tin kept at a constant temperature by an external electric heater. 2 mg of sample were carefully weighed beforehand into a hollow tin cylinder which was then closed by a small plug of the same metal. The cylinder had a height and diameter of 5 mm, the plug had a diameter of 4 mm and a height of 2 mm. Because of the high heat capacity of the bath and the rapid rate of heat transfer the sample container melted almost instantaneously.

The samples after insertion in the cylinders were fed to the pyrolyser by means of an automatic magazine which operated at certain preset times. The magazine was made from a block of polymethylmethacrylate (1, 2) with holes drilled in it as shown in Fig. 1. The samples in the cylinders were piled one above the other in the hollow tube (13) which was closed with a metal screw and packing (10). The carrier gas entered at (12) and purged the magazine containing the samples of the resin. The lowest sample cylinder in the pile sits in the hole (14) of the feeder rod (4) and was moved by the solenoid (3) to a position over the opening of tube (7), through which it fell into the metal bath of the pyrolyser. The rod can be adjusted with a screw (6). The next sample then moved into the hole (14) upon the return of the feeder rod which was actuated by spring (5). The magazine was connected to the pyrolyser by a piece of vacuum rubber tubing. Tube (7) was fastened to the feeder with a gland nut (8) and PVC seal (9).

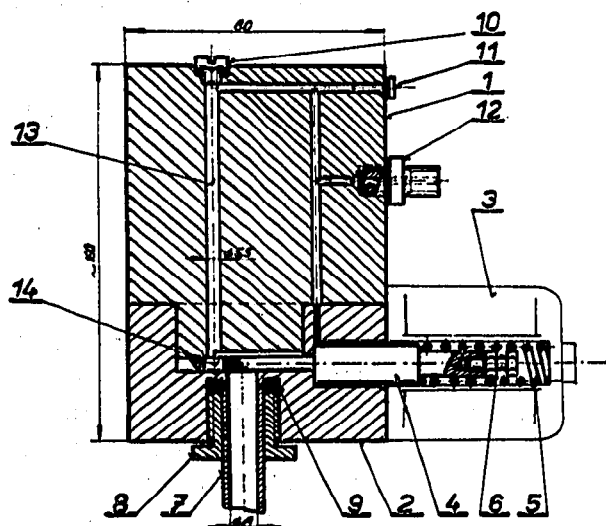


Fig. 1. Automatic magazine. 1, 2 = body made from polymethylmethacrylate; 3 = solenoid; 4 = iron core; 5 = spring; 6 = adjusting screw; 7 = sample outlet tube for connection to pyrolyser; 8 = gland nut; 9 = PVC seal; 10 = metal screw with packing; 11 = blanked-off opening; 12 = carrier gas inlet; 13 = hollow tube for holding sample cylinders; 14 = hole in feeder rod.

The pyrolyser (Fig. 2) was made of quartz. The samples fell from the sample magazine down tube (4) into the bath of molten tin (6), the temperature of which was measured by a thermocouple situated outside the wall of the pyrolyser (8). The pyrol-

ysis products were removed by the carrier gas from the pyrolyser through a capillary (7). The pyrolyser was heated externally by an electric heater and could be set to the desired temperature of the metal bath.

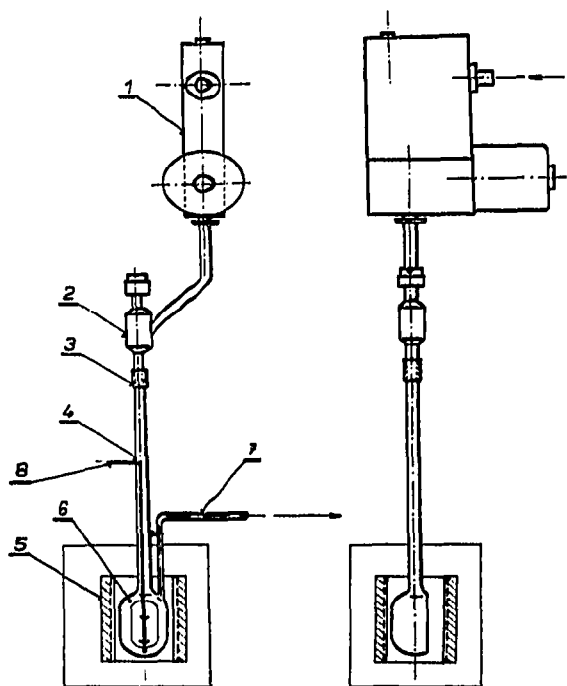


Fig. 2. Pyrolyser with automatic magazine attached. 1 = automatic magazine; 2 = union; 3 = rubber tubing; 4 = sample inlet; 5 = electric furnace; 6 = molten tin bath; 7 = carrier gas outlet; 8 = thermocouple.

The products of the thermal decomposition were analysed by a gas chromatograph Chrom II. The column was 4 m long, with a diameter of 6 mm, and packed with Celite 545 coated with 20 % of Apiezon L. The flow of carrier gas was maintained at its optimum value of 50 ml/min for nitrogen, 40 ml/min for hydrogen and 400 ml/min for air. The working temperature of the column was 168°. The temperatures of the tin bath were for individual runs 620, 700, 800, 850, 900, 950 and 1000°.

Qualitative evaluation of the results was carried out on the basis of comparing the elution times of the pyrolysis products with the elution times of various pure hydrocarbons. This was done by adsorbing the vapours of these pure hydrocarbons on the surface of a resin sample. A sample would then be kept for a definite time in a stoppered weighing bottle under the vapours of the hydrocarbon suspected of producing the particular peak of interest. On pyrolysis of the sample prepared in this way the adsorbed hydrocarbon caused a marked increase in the height of the peak in question if identical with the standard, the elution time being the same.

Celite 545 coated with 20 % of tricresylphosphate at 120° instead of Apiezon L was used for determination of the elution times for some important compounds.

The quantitative evaluation of the chromatographic peaks was carried out on the basis of calibration curves, which were obtained by dosing 1 % solutions of pure compounds in a solvent which did not interfere with the compounds used. The results are shown in Table I and Figs. 3 and 4. Only compounds with low boiling point (from

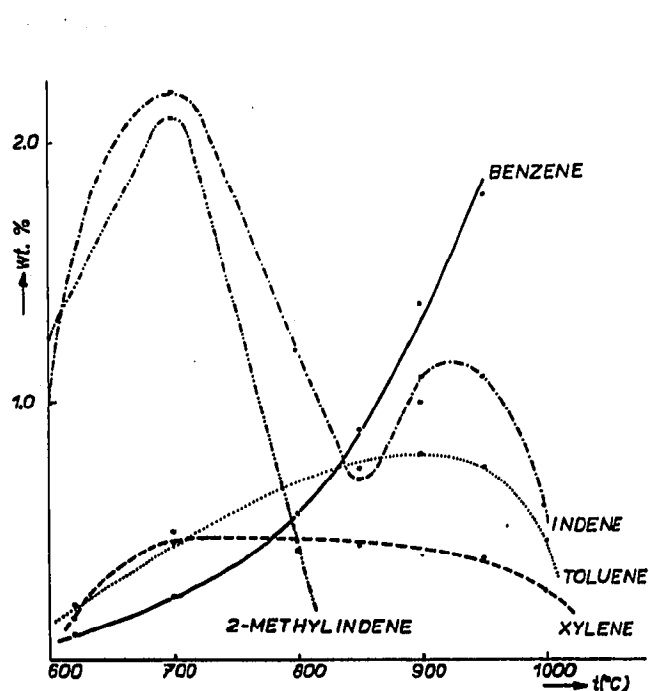


Fig. 3. Content of light aromatic hydrocarbons in pyrolysis gas.

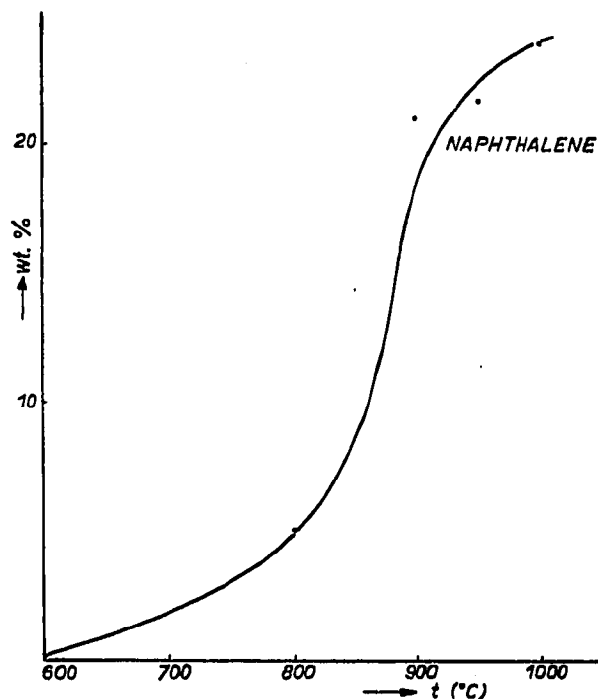


Fig. 4. Content of naphthalene in pyrolysis gas.

benzene up to naphthalene) were determined by this method. The content of light aromatic hydrocarbons in the pyrolysis gas (Fig. 3) is relatively low and ranges from 1 to 2%. A considerably higher concentration was found in the case of naphthalene (Fig. 4). The amount of naphthalene produced in the pyrolysis range of 900–1000° was about 25% (with respect to the total weight of the resin).

TABLE I

DEPENDENCE OF THE YIELD OF PYROLYSIS PRODUCTS ON THE TEMPERATURE

Temperature of pyrolysis	% benzene per g of resin	% toluene per g of resin	% xylene per g of resin	% indene per g of resin	% 2-methylindene per g of resin	% naphthalene per g of resin
620	0.1	0.22	0.33	1	1.25	1
700	0.26	0.46	0.55	2.2	2.1	2.2
800	0.38	0.56	0.45	1.2	0.43	5.2
850	0.78	0.74	0.45	0.7	—	8.5
900	1.38	0.8	0.4	1	—	21
950	1.8	0.75	0.4	1.1	—	21.6
1000	2.6	0.47	0.27	0.6	—	24.1

DETERMINATION OF THE TOTAL CONTENT OF THE SOLID, LIQUID AND GASEOUS PRODUCTS OBTAINED BY THE DECOMPOSITION OF PYROLYSIS RESIN AT DIFFERENT TEMPERATURES

The pyrolysis apparatus (Fig. 5) consisted of an electrically heated feeder (1), which was equipped with a capillary jet (7) on the lower, narrower end. The pyrolyser,

which was connected with the feeder by a joint, was equipped with an inlet tube for the carrier gas, a thermocouple well, and an outlet tube for the pyrolysis products. In order to increase the heat capacity, the reaction vessel was filled up to 1/3 of its height with small pieces of crashed quartz.

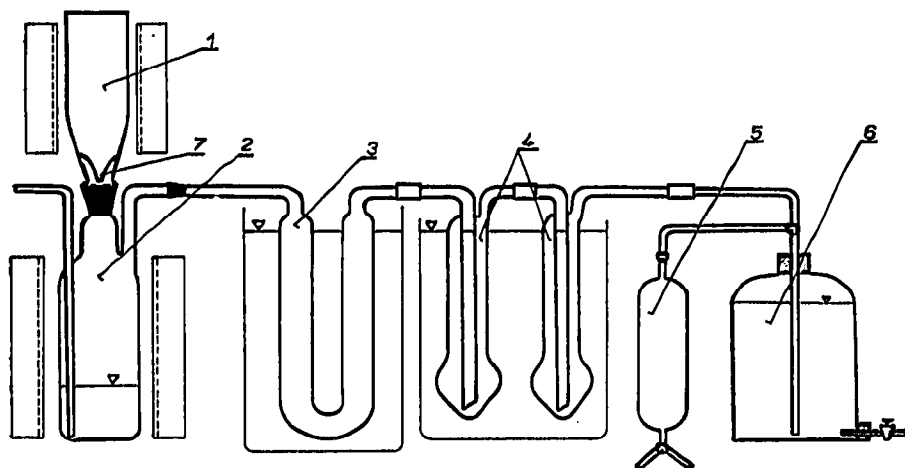


Fig. 5. Pyrolysis apparatus. 1 = Electrically heated feeder; 2 = pyrolyser; 3,4 = condensation vessels; 5 = gas sample vessel; 6 = store bottle; 7 = capillary jet; 8 = electric furnace; 9 = inlet of carrier gas; 10 = outlet of pyrolysis products.

The condensation vessels, the pyrolyser, and the feeder that contained the resin were weighed before the measurement. The apparatus was then set up according to Fig. 5, and purged with pure nitrogen. After removal of air from the pyrolyser and the condensation vessels, the flow of nitrogen was stopped and the tube sealed off. The condensation vessel (3) was cooled with ordinary water, vessels (4) were cooled in a bath of dry ice in methanol. The pyrolyser was heated to the desired decomposition temperature. After the temperature in the pyrolyser became steady, the vent on the side outlet of the store bottle (6) was opened, and the feeder was heated at the same time. The molten resin dropped into the pyrolyser at a rate of 1 drop per 2–3 sec.

The pyrolysis products formed condensed mostly in vessel (3); only a small amount of the light portions condensed in vessel (4). The amount of pyrolysis gas was equal to the amount of water that flowed out of the store bottle. A sample of the gas was taken into the vessel (5). The analysis was carried out on a gas chromatograph of the JANÁK type. Some of the pyrolysis products condensed on the cooler outlet tube of the pyrolyser during the decomposition. In order to remove these products, the inlet of carrier gas was opened and the store bottle was disconnected. The flow of the carrier gas was adjusted to 100 ml/min. The condensed products were transferred to the condensation vessels by this operation at the temperature used for 1 h. The individual parts of the apparatus were weighed after the run was over and total balance calculated. The results are presented in Table II and Fig. 6. The largest proportion of liquid products was obtained at temperatures of 500–600°; with higher temperatures than these the yield of the liquid products fell to 19% at a temperature of 1000°. Simultaneously with the decrease of the amount of the liquid portion, the amount of the solid portion increased. The solid portion consisted of coke and soot. The formation of soot became observable at a temperature of 800° and formed a sub-

stantial part of the solid residue (about one half) at a temperature of 1000°. Similarly, the total amount of pyrolysis gas increased with increasing temperature and, consequently, the composition of the gas changed as well.

TABLE II

WHOLE-WEIGHT BALANCE OF PYROLYSIS RESIN

Temperature of pyrolysis	Residue of pyrolysis (wt. %)	Liquids (wt. %)	Amount of gas (ml/g of resin)	Composition of gas		
				H ₂ (%)	CH ₄ (%)	Higher hydrocarbons (%)
500	27	71	33	19.4	60	20.6
600	29	69.8	62	27	60	13
650	29.8	69	75	31.4	59	9.6
700	31	67.5	120	37	56	7
750	32.1	63.9	200	40	53.1	6.9
800	35	59.5	340	49.5	44.5	6
850	36	50.5	460	53	42	5
900	40	40	550	60	35.4	4.6
1000	63.7	19.1	1130	67.8	29.0	3.2

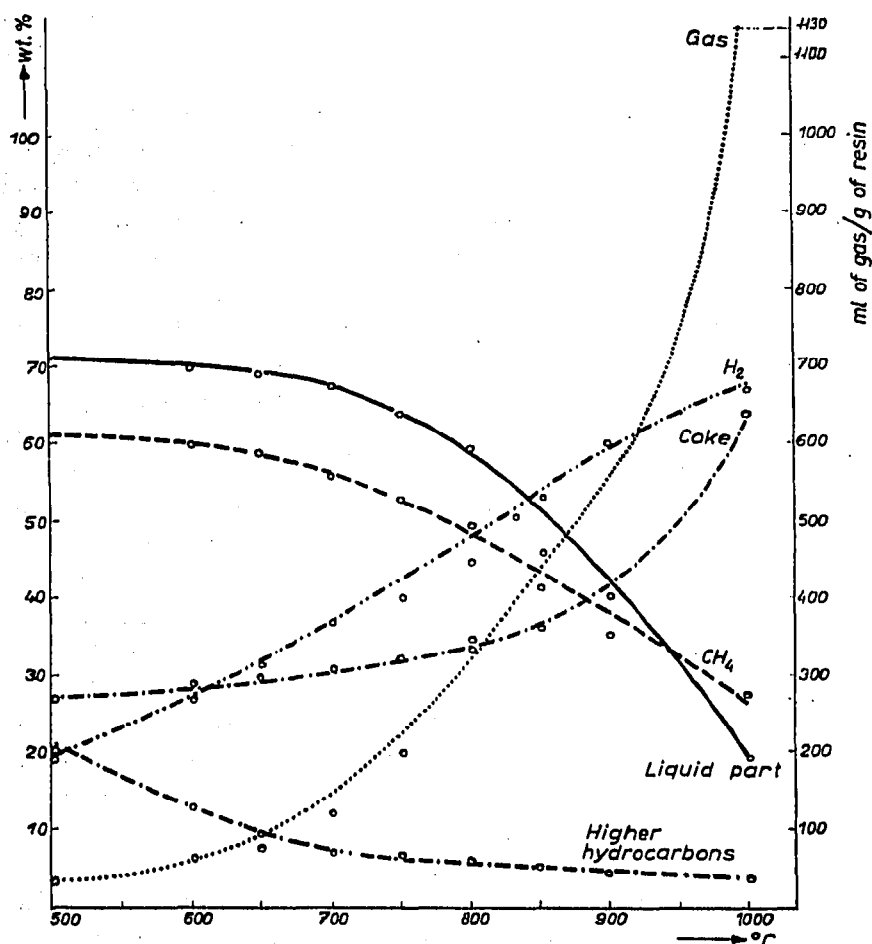


Fig. 6. Total yield of pyrolysis products.

In the range of temperatures 500–650°, the content of methane in the gas was about 60 %, only 27 % of methane was found at a temperature of 1000°. On the other hand, the concentration of hydrogen increased almost linearly with increasing temperature in the range of temperatures of 500° (about 20 % of hydrogen) to 1000° (about 68% of hydrogen). Concentrations of both methane and hydrogen were roughly equal (about 47 % of each component) at temperatures close to 800°. The content of higher hydrocarbons decreased from 20.5 % at 500° to 3 % at 1000°.

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