FOREWORD

This work was conducted by the National Carbon Company, a Division of Union Carbide Corporation, under USAF Contract AF 33(616)-6915. This contract was initiated under Project No. 7350 "Refractory Inorganic Non-Metallic Materials," Task No. 735002 "Refractory Inorganic Non-Metallic Materials: Graphitic"; Project No. 7381 "Materials Application," Task No. 738102 "Materials Process"; and Project No. 7-817 "Process Development for Graphite Materials." The work was administrated under the direction of the Air Force Materials Laboratory, Research and Technology Division with Captain R. H. Wilson, L. J. Conlon and W. P. Conrardy acting as Project Engineers.

The work covered in this report was performed between November 1960 and March 31, 1963, primarily by the Armour Research Foundation of the Illinois Institute of Technology, Chicago, Illinois, under Subcontract No. 1960-R2 from National Carbon Company. Some materials and direction of the program were supplied by the Research Laboratory of National Carbon Company, Parma 30, Ohio.

Other reports issued under USAF Contract AF 33(616)-6915 have included:

WADD Technical Notes 61-18 and 61-18, Part II, progress reports covering work from the start of the contract on May 1, 1960, to October 15, 1961, and the following volumes of WADD Technical Report 61-72 covering various subject phases of the work:

Volume I	Observations by Electron Microscopy of Dislocations in Graphite, by R. Sprague.
Volume II	Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence.
Volume III	Decoration of Dislocations and Low Angle Grain Boundaries in Graphite Single Crystals, by R. Bacon and R. Sprague.
Volume IV	Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch.
Volume V	Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper.
Volume VI	Creep of Carbons and Graphites in Flexure at High Temperatures, by E. J. Seldin.
Volume VII	High Density Recrystallized Graphite by Hot Forming, by E. A. Neel, A. A. Kellar, and K. J. Zeitsch.

ABSTRACT

The work described in this report presents the concluding part of a program concerned with the bonding and pyrolysis characteristics of two synthetic binders. The binders, alumina-condensed furfuryl alcohol resin and acenaphthylene pitch, were evaluated both by themselves and in conjunction with selected fillers to determine binder-filler interactions during pyrolysis and to develop a more complete understanding of the carbon bonding process.

In the discussion, the data accumulated from a number of techniques are presented and interpreted. Pyrolysis and physical property data for specimens molded with both the resin and pitch binders are also presented.

It has been found that some fillers are essentially unbondable by carbon, while others can materially alter binder pyrolysis.

This report has been reviewed and is approved.

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1. INTRODUCTION

This report represents the conclusion of a fundamental study on the formation of the carbon bond. Because of the complexity of such a study, the work was restricted to two relatively simple synthetic binders. These were used in conjunction with several fillers chosen for their specific physical and chemical properties.

The objectives of the research have been:

1. To achieve a detailed understanding of the chemical and physical properties of the binders, by themselves and in combination with both inert and active fillers.

2. To determine the molding and rheological properties of the two binders.

3. To determine the sequence of thermal degradation of the binders, both by themselves and in combination with filler materials.

4. To determine the species of products evolved during thermal degradation.

5. To determine whether binder pyrolysis is materially affected by interaction with filler materials, and the extent of the interaction.

6. To establish whether a true chemical bond is achieved, or whether the bonding is one of physical cementation aided by the mechanical interlocking and interpacking of filler materials.

The binders used in the program were a highly converted liquid resin prepared by the catalytic condensation of furfuryl alcohol employing activated alumina as the condensation catalyst, (Ref. 1) and a synthetic pitch prepared by the thermal transformation and condensation of acenaphthylene.

The binders were chosen because of their high degree of conversion, high coking residues, ease of preparation, and reproducibility. Both were considered to be relatively simple from a compositional standpoint inasmuch as each was prepared from a single compound of known structure. Furthermore, the furfuryl alcohol resin binder was representative of the thermosetting class of "hard" binders while the acenaphthylene pitch was representative of the thermoplastic class of "soft" binders.

The selection of filler materials for use with the above binders was based on the objectives to be attained. First, a narrow particle size range was desired to limit the degree of particle interpacking and to eliminate any possible effect of extreme fines. Second, the particle shape factor had to be taken into account and its effect delineated. Third, non-carbon fillers were included to determine the effects of filler composition on binder pyrolysis or bonding characteristics.

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The techniques available for characterization of binders, with and without fillers, are many and varied. The ones chosen for the study are those that through past experience have proved particularly useful in the carbon and graphite field. These included:

a. Differential thermal analysis (DTA) to monitor thermosetting reactions and major structural rearrangements during pyrolysis.

b. Thermogravimetric analysis (TGA) to determine the shape of the weight-loss curve during coking.

c. Elastic modulus measurements to observe binder softening during coking.

d. X-ray diffraction to observe changes in degree of graphitization.

e. Mercury porosimetry to determine pore size distribution.

f. Metallographic techniques for visual observation of microstructure.

g. Optical methods to observe and measure binder shrinkage during pyrolysis.

h. Fractional distillation and synthesis of standards for identification comparisons.

i. Infrared and ultraviolet absorption, gas phase chromatography, and mass spectrometry to identify binder components and pyrolysis products.

These techniques are reported in detail in this and in a previous report. (Ref. 2).

2. CONCLUSIONS

1. The chemical compositions of the two synthetic binders, alumina-condensed furfuryl alcohol resin and acenaphthylene pitch are not nearly as simple as their parent compounds. The resin consists chiefly of various esters with substantial amounts of difurfuryl ether. Structures of typical components are illustrated below.
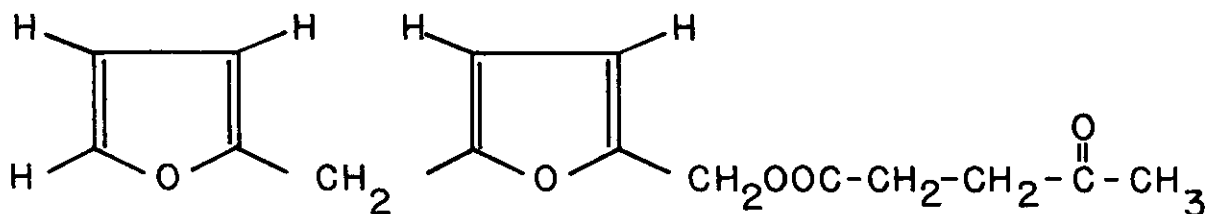
(5-Furfurylfurfuryl Ester of Levulinic Acid)

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Contrails
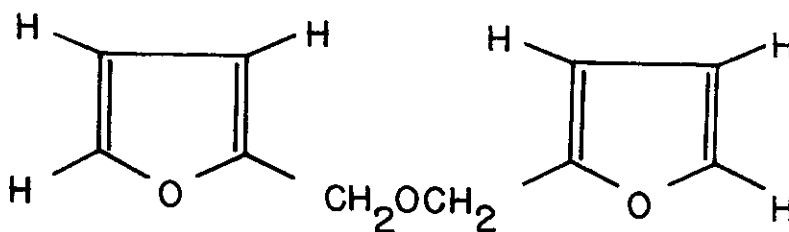
(Difurfuryl Ether)

The surprising feature of the resin composition is the near-absence of terminal OH groups, a finding which was completely unexpected.

Acenaphthylene pitches are composed of a complex mixture of poly-nuclear aromatic compounds. Substantial amounts of acenaphthene, the hydrogenated derivative of acenaphthylene, are present and perform the important function of regulating the softening point. (Ref. 3). The sequence of reactions leading to pitch is discussed in detail in Volume XXVII of this series. (Ref. 4).

2. The comparatively low viscosity (8150 cps) resin binder does not permit fillers to flow and distribute themselves as evenly as does the pitch binder. It is believed that an optimum viscosity for filler mobility is reached during softening of the pitch in the forming process. Therefore, it is much more important to use care in loading the mold when using low viscosity binders than when using the pitch.

3. The shape of the filler particles has a definite effect on the properties of a molded body. In general, bodies containing irregularly shaped particles have significantly higher strengths in both the green and the coked states than those containing spherical particles. However, the effect of particle shape is not nearly as great as the effect of composition. Fillers capable of developing a chemical bond with the binder clearly show higher strengths in spite of the shape factor. This behavior is particularly evident after coking.

4. On pyrolysis, the major components evolved by the resin are water, carbon dioxide, carbon monoxide, methane, ethane, and hydrogen. They are evolved essentially in the order listed, although there is considerable overlap in the evolution sequence.

5. The major component evolved during coking of the pitch is ace-naphthene. Small amounts of naphthalene, methyl naphthalene, hydrogen, methane, ethane, propane,and ethylene are also evolved along with sub-stantial amounts (approximately 20%) of high-boiling components that have not been fully identified.

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6. In general, it appears that coke fillers have little, if any, effect on the pyrolysis characteristics of either the resin or the pitch binder. Alumina fillers, however, exert a marked catalytic effect on the pyrolysis of the resin. Alumina also has an influence on the pitch binder but to a lesser extent. The net effect of the catalysis is to shift the evolution of some of the normal pyrolysis products to a lower temperature range.

7. A good carbon bond can be established with certain fillers, such as coke and magnesia (MgO), that is believed to be chemical in nature. With other fillers, such as silicon carbide (SiC), the bond mechanism appears to be one of physical cementation of interlocking angular particles with, perhaps, some degree of chemical bonding. Fillers of a third class are essentially unbondable by carbon. This last class includes alumina (Al_2O_3), silica (SiO_2), and doubtless others. At the present time, it is not possible to predict into which of the classes specific fillers will fall.

3. RESULTS AND DISCUSSION

3.1. Materials

3.1.1. Alumina-Condensed Resin

The resin used for the molding experiments was a highly converted material of medium viscosity (8150 cps) from which 15.2% water of condensation had been separated and collected. It contained no residual monomeric furfuryl alcohol and virtually no terminal OH groups because of esterification of the polyalcohols by way of reaction with internally generated levulinic and homologous acids.

The catalyst used in thermosetting the resin consisted of 50 weight per cent of para-toluenesulfonic acid dissolved in absolute methyl alcohol. Five per cent of the solution by weight of the resin was mixed with the resin prior to mixing with the aggregate.

3.1.2. Acenaphthylene Pitch

The acenaphthylene pitch, which had a softening point of 120°C, was prepared by National Carbon Company for inclusion in this work and was designated by the code number 13-40-80. Because it was supplied in lump form, it was ground to a powder in a Wiley mill prior to experimentation.

3.1.3. Aggregates

At the inception of the program, it was decided that the two binders should be studied in conjunction not only with the usual carbon fillers but with less conventional fillers as well. The carbon fillers were considered as active aggregates in that they either might influence binder pyrolysis or might have some degree of surface reaction with the binder. In contrast, the non-carbon fillers were considered to be inert at least as far as pyrolysis was concerned. It was reasoned that comparison of data from

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specimens made with the different aggregates would contribute to an understanding of the bonding mechanism.

Petroleum coke was the obvious choice for the carbon fillers. The inert fillers selected were silicon carbide and glass microspheres. The carbide was selected because the crushed particles would approximate the shape and packing characteristics of the coke; the glass spheres were selected because they would eliminate both the shape factor and mechanical interlocking of the grains. As the work proceeded, it was found that the glass beads constituted an unworkable filler system, and that any comparison with the silicon carbide filler could not be justified. At this time, alumina spheres prepared by an arc plasma spraying process became commercially available. Consequently the originally selected aggregates were abandoned in favor of angular and spherical alumina.

3.2. Sample Preparation

It was decided that a maximum amount of information concerning bonding per se could be generated by limiting the filler particle size distribution to a very narrow range (44-74 microns). This was done to minimize variations caused by particle interpacking and interlocking, and also to eliminate any effects from extreme fines.

It also was decided that a binder-saturated system would eliminate extraneous effects of void volume, particularly when aggregate densities were different.

The void volume of each filler was measured by displacement in absolute methyl alcohol. This volume was checked by combining the indicated amount of resin with the filler and pressing at 1000 psi to determine whether or not the calculated volume was correct. In practice, it was usually found that a slight correction was required. The binder level was then adjusted until a very small quantity of resin was squeezed out during pressing. This procedure allowed saturated bars to be pressed with a binder level error of less than 1 part in 25.

In preparing bars bonded with acenaphthylene pitch, the powdered binder (-100 mesh) was physically mixed with the aggregate at room temperature. This was done to avoid loss of the very volatile acenaphthene; hot mixing or solvent mixing followed by solvent extraction would unquestionably have raised the softening point of the pitch. It was determined that a residence time of 15 minutes in a hot mold (125° C) was necessary to thoroughly soften the pitch and wet the filler particles. Holding time in excess of 15 minutes did not measurably change the properties of the molded bars.

The required amounts of pitch binder and the different aggregates were placed in two-quart jars and mixed on jar mill rolls. This was entirely satisfactory for the angular grains and the needle coke but some

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segregation was noted in mixes made with spherical grains. This segregation became evident as black streaks when the latter mixes were poured back and forth on paper. Under the microscope it could be seen that the segregated particles were, for the most part, the larger pitch particles. This was not considered to be serious because it was expected that the pitch would soften and that both the pitch and the spheres would be mobile under pressure thus giving a uniform distribution.

The die cavity used in pressing was 4 3/8 inches in length by 1 1/8 inches in width. Both the mold and plunger were heated to 125°C by means of internal resistors. A 1/8 inch thick steel plate was placed in the bottom of the cavity prior to filling; the charge was capped with a second plate to facilitate sample removal in case of sticking. In charging, a weighed amount of mix sufficient to yield a bar somewhat greater than 1/4 inch in thickness was placed in the mold and leveled with a scraper.

A pressure of 1000 psi was applied for a period of 15 minutes. This pressure was selected to avoid excessive spring-back in pitch-bonded samples and to avoid laminar cracking in resin-bonded samples. Both of these phenomena are related to the high binder levels used. After molding, the samples were ejected from the die and cooled to room temperature before the steel plates were removed. The plates have a tendency to free themselves from the specimen because of difference in thermal expansion; however, with the pitch binder and with non-coke fillers, the samples occasionally broke either in cooling or in plate removal.

In preparing specimens with the resin binder, the liquid was first mixed with the para-toluenesulfonic acid catalyst and then with the aggregate. Much of the mixing of small batches could be done with a bowl and spoon, but final uniformity could be accomplished only by hand kneading. The resulting mix was weighed into the desired amounts and hand rolled into cylinders which were placed on the steel die inserts. These were placed in a refrigerator to retard the action of the catalyst until they could be pressed. The preformed cylinders were also pressed at 125°C for 15 minutes which is just sufficient to thermoset the resin. After forming, the bars were placed in an oven at 180°C overnight to insure complete curing.

When molding of both binder systems was completed, the bars were measured as to length, width, depth, and weight; the ones to be coked were packed in petroleum coke in a stainless steel covered box. This box was placed inside a second sealed container which was fitted with a gas inlet and outlet through which helium was circulated during thermal treatment. The boxes and bars were all heated in a Globar furnace automatically controlled to give a temperature rise of about 15°C per hour. When 1000°C was reached, the furnace was held for 2 hours, turned off and cooled to room temperature.

One difficulty constantly experienced with the pitch binder, was the "bread loafing" or bloating encountered on release of the die pressure. This phenomenon, which is related to the narrow filler size range and

also to the high-binder level, was probably caused by gas pressure generated by the volatile acenaphthene present in the pitch. Other difficulties were sticking of the samples to the hot mold walls and excessive drag against the walls during ejection. None of the various mold release agents tried, including extrusion oil, overcame these difficulties. The result was that the pitch bonded samples were all slightly bloated, and had poor side surfaces. After removal from the mold, shrinkage on cooling against the top and bottom separator plates frequently caused spontaneous transverse rupture of the bars. This was particularly true of specimens made with the spherical alumina.

In pressing the resin bonded alumina samples, the bars made with the angular particles had some tendency to develop laminations after release of the pressure following thermosetting; approximately half of the bars showed some type of horizontal flaw. However, the bars containing spherical alumina all displayed more or less severe laminar cracks. The spherical grain simply does not have sufficient mechanical interlocking to resist even low gas pressures. Samples made with the calcined coke filler displayed no cracking or other forming flaws.

With the dry powdery mixtures of pitch and filler, no observations as to relative mobility of the materials could be made other than that there were little or no differences in density developed along the length of the bars. Viscosity changes in the pitch as it is heated under pressure apparently are such that good flow properties within the mix are attained at some point between room temperature and 125°C. This movement seems to be independent of the type of filler.

With the liquid resin binder, however, it could be readily observed that the spherical alumina grain had unlimited flow characteristics, while the angular grain had only limited flow properties. The middle sections of the bars made with the angular grain were more tightly packed than the ends. No differences in packing could be discerned within the resin-coke bars. The coke apparently had better flow characteristics, perhaps because of its lower density and higher binder demand. It may be presumed that the coke would not migrate as readily as the spherical particles, but there is no satisfactory method of determining this at such high binder levels.

Intuitively, it is felt that the optimum binder viscosity for the best flow of filler materials is achieved at some unspecified temperature during the softening of the pitch, and that this viscosity is higher than the initial viscosity of the resin. If this is indeed the case, it is evident that much more care must be exercised in loading the die when using a comparatively low viscosity resin binder than when using a binder that will develop optimum viscosity at some point in the forming process. The limited flow characteristic of the resin containing bodies may also be aggravated by the decreasing viscosity of the resin during heating and prior to achievement of the thermoset stage.

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3.3 Physical Properties of Molded Samples

Table 1 lists the physical properties obtained with the binders and fillers discussed above. It is notable that the surface area of the spherical alumina grain is nearly three times that of the irregularly shaped angular grain, and that the helium density is greater for the angular than for the spherical grain. This apparent anomaly is explained on examination of the aluminas at high magnifications. Many of the individual spherical particles, made by plasma spraying of angular grain, have internal voids, some of which are closed and some of which are open or accessible to area measurements. The closed voids therefore contribute to a low apparent density, while the open voids contribute to the high surface area.

Although both the resin and pitch binders have practically identical densities (1.3 g/cc), in the case of the angular alumina grain, the pitch bonded green samples show slightly higher densities than the resin bonded samples in spite of a small amount of bloating during molding. This is attributed to the poorer flow characteristics of the resin binder, and the consequent lower densities at the ends of the bars. In comparing the green densities of samples made with the highly mobile spherical alumina, the resin bonded samples show higher densities because of the tendency of the pitch to bloat the specimens; in this case, the density along the lengths of the resin bonded bars is quite uniform. The same mechanism is suggested as an explanation for the higher density of the resin bonded coke samples as compared to the pitch bonded samples.

In comparing flexural strengths of the green bars, it is quite obvious that the resin bonded samples are intrinsically stronger than comparable pitch bonded samples. Judgment made on green strength, however, is unreasonable, since the binder must be coked and graphitized to yield meaningful data.

The relatively small decrease in coked density of the resin bonded coke filled bars is due to the strong shrinkage mechanism operative throughout the temperature range of 250°-1000°C. This is related to the fact that the binder retains its solid state during pyrolysis. The pitch, on the other hand, loses the great majority of its weight while still in the liquid phase, and thus has little tendency to shrink; instead, it has a positive and natural tendency to bloat.

No comparison of coked density and weight loss on coking could be made for the pitch bonded alumina filled samples because of adherence of the protective packing coke and because of the fragility and friability of the coked bars. The agglomerated, partially cemented packing mixture was actually stronger than the bars to which it clung and there was no way to remove it without also losing the edges and surfaces of the sample.

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Table 1. Physical Properties of Molded Samples

| Type | Aggregate (100 pts) (-200 +325 mesh) | | Binder (pts) | | Green Samples | | Coked Samples (1000°C) | | | |
	Surface Area Sq.M/g	Helium Density g/cc	Alumina Condensed Resin	Acenaphthylene Pitch	Density g/cc	Flexural Strength (psi)	Weight Loss %	Dimensional Change %	Density g/cc	Flexural Strength (psi)
Al_2O_3 (angular)	0.28	3.907	24		2.45	2944	8.96	-0.71	1.83	182
Al_2O_3 (angular)				24	2.51	839	*	+0.71	*	45
Al_2O_3 (spherical)	0.82	3.472	24		2.37	1998	8.71	+0.71	1.90	37
Al_2O_3 (spherical)				24	2.02	390	*	+2.16	*	10
Petroleum Coke (cal-cined)	2.90	2.087	67		1.66	8600	17.94	-4.97	1.56	3400
Petroleum Coke (cal-cined)				67	1.44	1105	23.12	-0.71	1.15	1320
SiC (angular)	-	-	34		2.22	6313	9.5	-0.65	1.99	1023

* Determinations not possible.

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With the coke filler, the weight loss on coking was considerably higher for the pitch bonded samples than for the resin bonded specimens. Conversion of the values to coke residues shows a coking value for the pitch of only 42.5 per cent, and for the resin, 55 per cent. This residue is normal for the resin but is abnormally low for the pitch binder considering that bulk-coked pitch samples were found to have residues of 60 per cent or more. The most probable explanation of this behavior is that some of the thermosoftening pitch exuded from the samples and was absorbed by the packing coke during pyrolysis. This exudation may be attributable to the high binder level.

With the alumina fillers, both binders show such drastic decreases in strength that the grains may be considered to be essentially unbonded. That the resin binder shows slightly higher coked strengths than the pitch binder is insignificant when compared to the strength loss encountered on coking.

The comparative strengths of the coke-filled bars after carbonization show the resin-coke bonded samples to be significantly stronger. However, when it is considered that the pitch bonded samples had lost some of the binder by exudation during coking and had lower densities both green and coked, no conclusions regarding comparative strengths can be drawn.

The data in Table 1 on the abandoned silicon carbide filler system is included only for general interest as a filler which develops a strength intermediate between that of the alumina and coke filled bodies. While much of this strength must be attributed to the physical cementation of particles whose shapes are amenable to mechanical interlocking, some of the strength may be attributed to a partial chemical bond whose existence has not been proved.

In a series of somewhat parallel studies for an industrial sponsor, dense sea water periclase (MgO) was used as a filler with the resin. On coking, the bars actually doubled in flexural strength. Here is an instance in which the binder carbon establishes a strong bond with the oxide even though the grains are dense, rounded and quite hard. In Gilmore's study of pitch bonded anthracite coal fines, (Ref. 5) he molded compacts with rounded silica sand grains as the filler. After coking, the compacts were too weak to test.

It would seem to be indicated that carbon bonding runs the full gamut from that which is essentially chemical, through bonding that may be partially chemical and partially physical cementation, to some materials with which bonding cannot be accomplished by either mechanism.

From the observations made to date, there appears to be no way of predicting the character of the bond that will be established with a specific filler material. At present, trial and error is the only approach to the selection of fillers that are amenable to carbon bonding.

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3.4. Pyrolysis Studies by Gas Chromatography

To understand the evolution of the carbon bond from forming through binder cracking to the ultimate bond, knowledge of the identity and sequence of pyrolysis products and of the mechanisms of binder degradation and transformation to carbon is required. To gain this information, the pyrolysis products have been periodically sampled during the coking stage and the different species quantitatively monitored by gas chromatography.

The data on the acenaphthylene pitch are reported here for the first time but, for comparison purposes, some of the data on the alumina condensed furfuryl alcohol resin that have been previously reported (Ref. 2) are included.

3.4.1. Pyrolysis Studies of Furfuryl Alcohol Resins by Gas Chromatography

Data obtained by gas analyses at 50° C temperature intervals are presented in Table 2. However, to present the data in a more illustrative manner, the results have been calculated on a molar basis and plotted against temperature. The actual units are moles of gas per milligram of base polymer per degree centigrade. Plots of these data are shown in Figures 1, 2, and 3. The distribution of the minor components from the same three polymers are plotted on an expanded scale, Figure 4.

These profiles clearly illustrate the relative rate and temperature at which the various pyrolysis products are obtained. For example, in the base furfuryl alcohol polymer (Figure 1), the only component released in appreciable amount below 200° C is water. Some carbon dioxide is released at about 160° C and continues to rise in quantity until it is a major component at 325° C at which temperature water is evolved in approximately the same quantity.

Water continues to increase in quantity toward another maximum but at 425° C carbon monoxide is the predominant peak; some carbon dioxide, methane, and a little ethane are also present. At 475° C, methane becomes the major component with water still present in considerable quantity; ethane, although at its peak, is a minor component--about one-third the quantity of methane. Hydrogen is present but only to the extent of a few per cent.

Methane continues to be the major component to about 550° C. At 600° C, almost equal quantities of water, hydrogen, and methane, with small quantities of other gases are evolved. After 650° C, hydrogen becomes the major constituent showing a rapid increase up to 725° C. Between 725° and 825° C a small dip in the curve appears, after which the amount of hydrogen continues to increase rapidly. Water and methane continue to fall to low values after 700° C.

Two furfuryl alcohol resin-filler samples were investigated using the procedures employed for the study of the base polymer; one of these con-

Table 2. Gaseous Products from the Thermal Decomposition of Furfuryl Alcohol Polymer

10^{-8} moles of product/temperature interval

COMPONENT	POLYMER SAMPLE*	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	TOTAL
HYDROGEN	1								TRACE	0.095	0.294	0.703	0.626	2.22	2.96	2.38	3.58	12.86
	2								TRACE	0.075	0.312	0.657	1.22	1.67	2.74	2.43	2.18	11.28
	3								TRACE	0.122	0.330	0.695	1.43	1.84	3.21	2.74	2.95	13.32
CARBON MONOXIDE	1						TRACE	0.356	1.33	0.905	0.685	0.385	0.278	TRACE				3.94
	2							0.427	1.45	1.34	0.683	0.440	0.346	0.210				4.90
	3							0.137	1.01	0.548	0.283	0.133	0.109					2.22
CARBON DIOXIDE	1			0.009	0.136	0.437	0.543	1.02	0.345	0.373	0.068	0.060	0.030	-0.027				3.05
	2		TRACE	TRACE	0.022	0.198	0.434	0.384	0.324	0.230	0.108	0.067	0.034	0.023	0.014			1.84
	3			0.014	0.152	0.523	0.695	0.590	0.458	0.320	0.192	0.052	0.070	0.060	0.030			3.16
METHANE	1							0.105	0.638	1.40	1.70	1.04	0.669	0.260	0.143			5.96
	2							TRACE	0.672	1.05	1.30	0.777	0.495	0.330	0.185	0.052		4.86
	3							TRACE	0.547	1.40	1.40	1.04	0.482	0.181	0.205		0.108	5.36
ETHANE	1							0.032	0.226	0.476	0.068							0.802
	2							TRACE	0.069	0.246	0.111	0.022						0.448
	3							0.014	0.140	0.360	0.189	0.073						0.776
ETHYLENE	1																	TRACE
	2								0.038	0.098	0.060	0.015						0.211
	3									0.023	0.018							0.041
PROPANE	1							TRACE	0.038	0.179								0.217
	2								0.016	0.023	0.016							0.055
	3								0.035	0.082	0.012							0.129
PROPYLENE	1									TRACE								TRACE
	2								0.015	0.060	0.038							0.113
	3								0.006	0.018								0.024
FURAN	1					TRACE	0.004	0.012	0.050	0.029	TRACE	0.004						0.095
	2					0.008	0.019	0.031	0.069	0.048	0.022							0.201
	3					0.004	0.011	0.015	0.038	0.034	0.009							0.111
METHANOL	1			TRACE	0.029	0.049	0.034	0.029	0.021	0.007								0.169
	2		0.015	0.021	0.045	0.136	0.116	0.092	0.072	0.030	0.017							0.544
	3		0.012	0.041	0.068	0.062	0.058	0.042	0.031	0.007								0.321
ETHANOL	1								0.015									0.015
	2																	
	3																	
PROPANOL	1							0.006	0.017	0.009								0.032
	2																	
	3																	
WATER	1	0.149	0.309	0.434	0.614	0.683	0.625	0.718	0.924	0.970	0.867	0.920	1.036	1.09	0.524	0.056		9.86
	2	0.008	0.148	0.206	0.433	0.683	0.683	0.455	0.740	1.32	1.86	1.10	0.570	0.445	0.165			8.87
	3	0.096	0.186	0.348	0.387	0.532	0.608	0.865	0.955	0.880	1.09	1.03	0.970	1.21	0.536	0.504		10.20

*POLYMER SAMPLES   1 = BASE FURFURYL ALCOHOL POLYMER.   2 = ALUMINA-FILLED RESIN.   3 = COKE FILLED RESIN.

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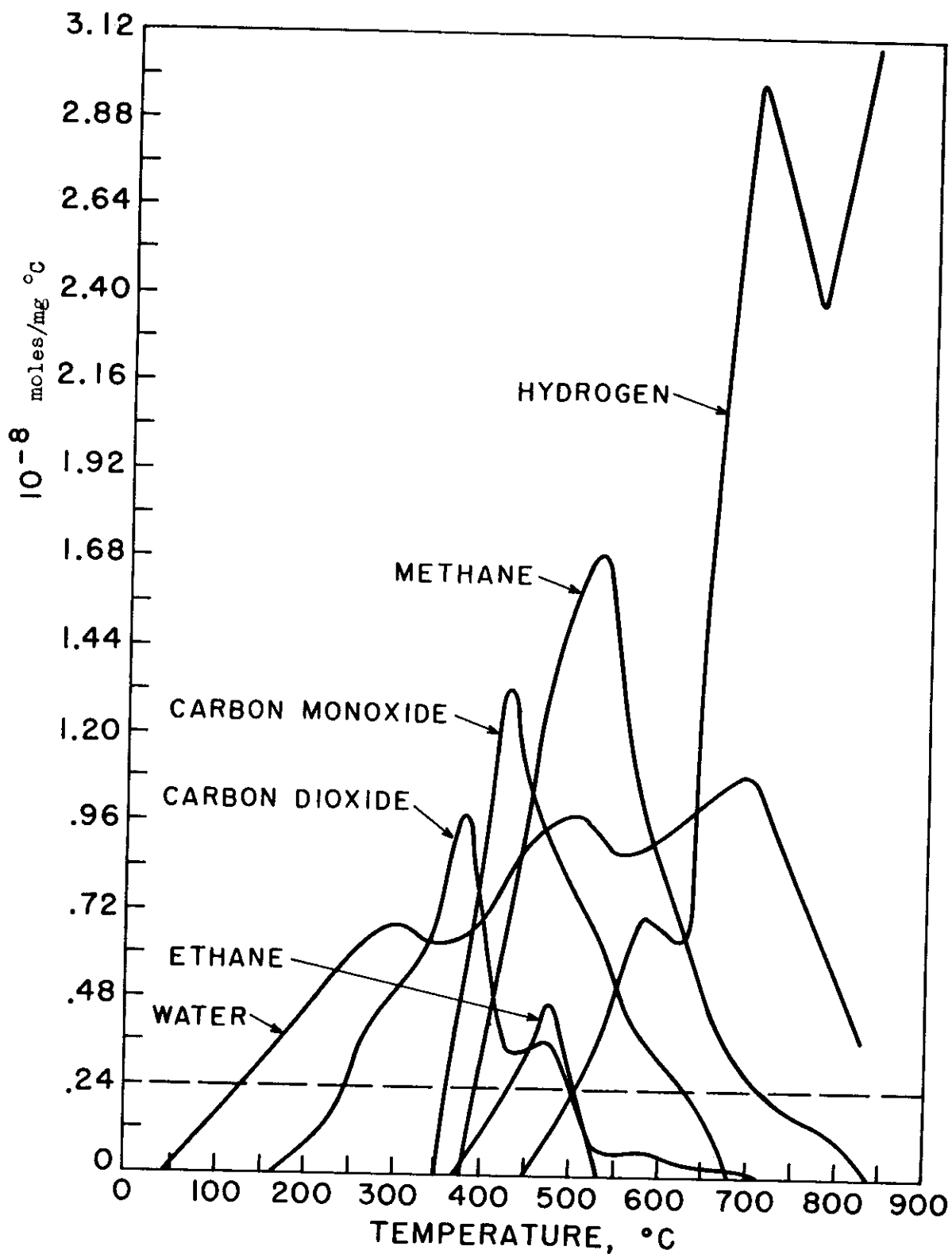
FIG. 1 - ELUTION PROFILES OF PYROLYSIS PRODUCTS FROM ALUMINA CONDENSED RESIN

13

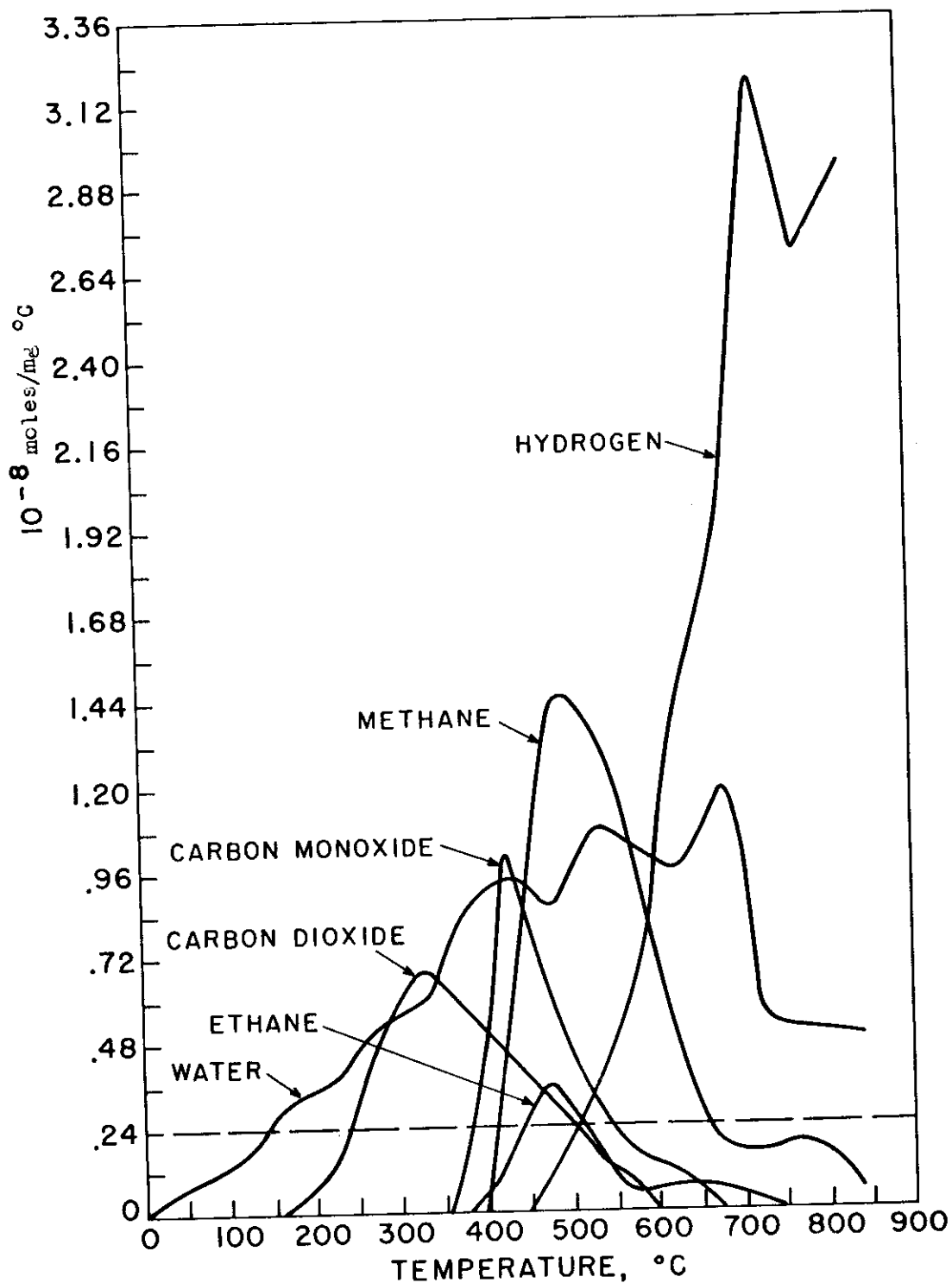FIG. 2 - ELUTION PROFILES OF PYROLYSIS PRODUCTS FROM ALUMINA CONDENSED RESIN CONTAINING 60% PETROLEUM COKE FILLER
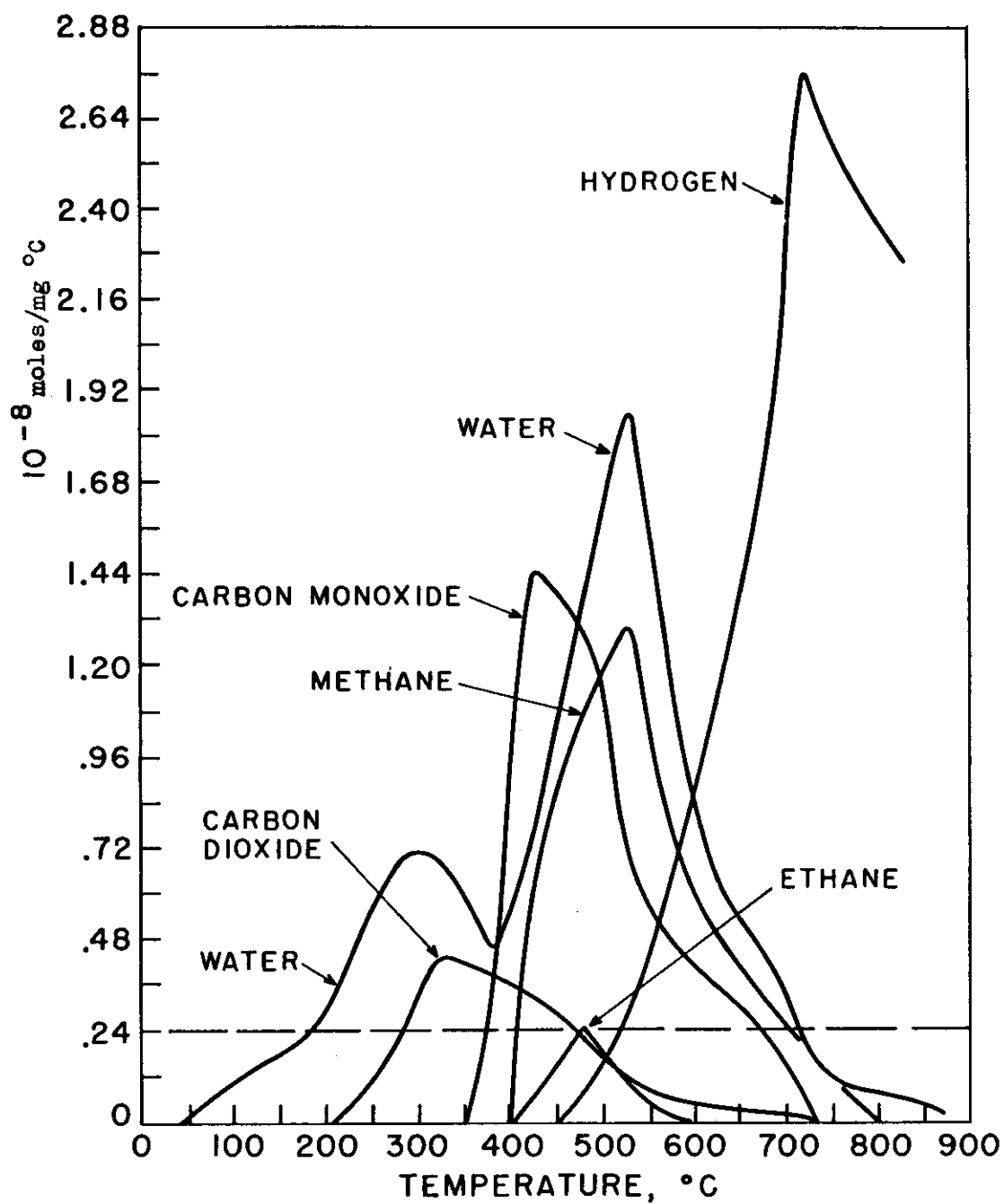
14

FIG. 3 - ELUTION PROFILES OF PYROLYSIS PRODUCTS FROM
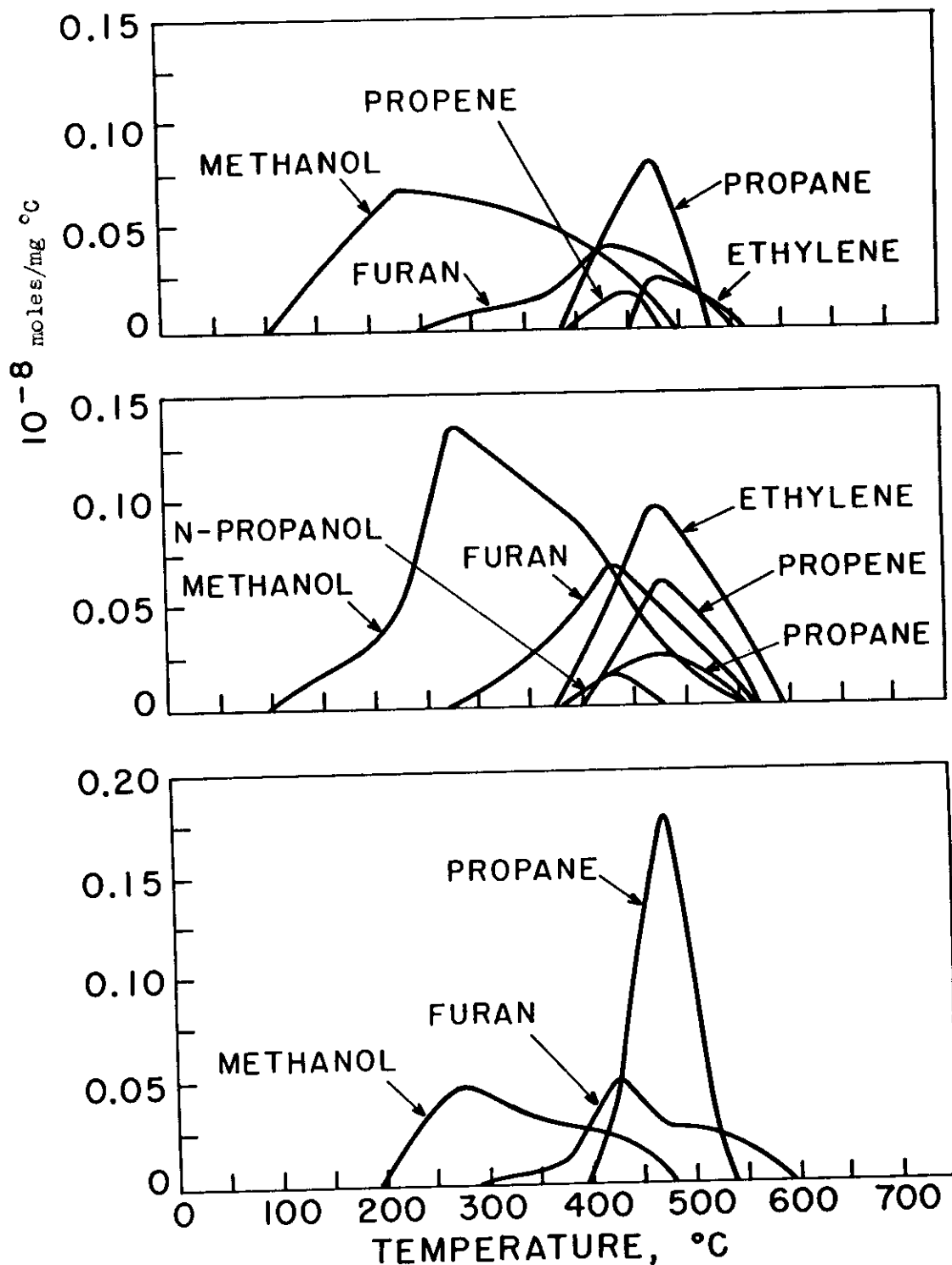ALUMINA CONDENSED RESINS CONTAINING 80.7%
ALUMINA FILLER

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FIG. 4 - COMPOSITE OF ELUTION PROFILES OF PYROLYSIS PRODUCTS FROM RESIN 1 (BOTTOM), 2 (MIDDLE), AND 3 (TOP) EXHIBITING LESS THAN 0.24 x 10⁻⁸ MOL OF PRODUCT PER DEGREE

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tained a coke filler while the other contained an aluminum oxide filler. For this work, gas chromatography analyses were performed on portions of the specimens, and the results were calculated on the basis of the binder content or moles of gas per milligram of actual resin.

The results obtained for the resin-coke specimen exhibited much similarity in the over-all elution profiles to those for the base polymer, indicating that the coke filler exerted little, if any, gross catalytic effect during pyrolysis. Rather, the coke behaved more as a diluent or, at best, a surface site for moderating the degradative processes, as suggested by the more moderate curves obtained for carbon dioxide and methane (Figure 2). In spite of these minor differences, all three of the components, carbon dioxide, methane and water are evolved in almost identical quantities.

In contrast to the coke-filled resin, the aluminum oxide-filled sample showed a completely different distribution for the same off-gases. This difference, which is attributed to a catalytic effect introduced by the alumina filler, is most pronounced for the major components, i.e., water, carbon monoxide, and methane. Of particular interest is the lack of a water maximum at 700°C and the variation in the hydrogen evolution at about 775°C. There is also a marked change in the percentages of certain gases compared to those of the base polymer. Carbon dioxide, ethane, and propane show decreases of 39.5, 44, and 77 per cent, respectively, while furan, carbon monoxide, and methanol show increases of 53, 20 and 69 per cent, respectively. Also, low levels of substituted furans, such as 2-methyl furan and 2,5-dimethyl furan, were detected solely from the alumina-filled resin.

The last two components were identified qualitatively from mass-spectrometry analysis and were not part of the off-gas analysis by gas chromatography. The mass-spectrometry procedure involves subjecting a separate sample of the base polymer to the entire temperature range and collecting all the gases as a single sample. The temperature in this case was not raised above 650°C because all the hydrocarbons show up before this temperature is reached, and continued heating to 850°C would dilute the sample with hydrogen.

Results of the mass-spectrometry analysis, which was performed solely to check the qualitative identification of the various components of the base binder and the aluminum oxide-filled resins, are presented in Table 3. In view of the differences in the heating and sampling techniques between the gas-chromatography and the mass-spectrometry procedures, the values cannot be directly correlated.

A summary of the total weight percentage of the identifiable degradation products for each polymer is presented in Table 4 along with the weight per cent loss per weight of base polymer in each sample.

Information from a series of controlled pyrolyses can be useful not only for the identification of the individual components of the pyrolysates

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Table 3. Results of Analysis of Furfuryl Alcohol Resin and Aluminum Oxide Resin Mixture by Mass Spectrometry

Component	Base Resin, mol %	Aluminum Oxide-Resin, mol %
Hydrogen	8.2	10.1
Carbon monoxide	27.1	35.7
Carbon dioxide	19.3	13.8
Methane	32.2	24.7
Ethane	4.5	2.8
Propane	6.6	4.0
Propene		0.9
Furan		0.6
2-Methyl furan		2.8
2,5-Dimethyl furan		1.4
Methanol	0.8	1.1
Residual gases	1.3	2.1

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Table 4. Distribution of Pyrolysis Products
Based on Weight Per Cent of Total
Weight Loss of Each Polymer

Component	Furfuryl Alcohol Polymer		
	Base	Alumina Filler	Coke Filler
Hydrogen	3.100	2.380	3.214
Carbon monoxide	13.300	14.340	7.107
Carbon dioxide	16.100	8.602	16.409
Methane	11.830	8.381	9.998
Ethane	2.900	1.354	2.730
Ethylene		0.623	0.143
Propane	1.150	0.266	0.658
Propene	Trace	0.504	0.105
Furan	0.788	1.498	0.852
Methanol	0.658	2.092	1.273
Ethanol	0.053	0.071	Trace
n-propanol	Trace	0.226	
Water	21.200	17.054	22.120
Total	71.17*	57.39*	64.1*
Total wt % loss per wt of base polymer (mg/mg)	41%	43%	47%

*Represents weight % of identified pyrolysis products per total
weight loss of base polymer of each sample.

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but also to give some insight as to the general types of reactions and temperatures involved in their formation. It may also aid in interpreting differential thermal analyses performed on the same resin mixtures.

Profile tracings of the off-gas compositions as presented in Figures 1-3 indicate three basic steps to the pyrolysis mechanism. The first step, starting at temperatures as low as 150° C and continuing up through approximately 350° C, involves dehydration and decarboxylation reactions.

The second, or intermediate, step involves carbon-carbon scission with the formation of free radicals which produce by disproportionation a series of low molecular weight hydrocarbons as typified by the relatively large volume of methane. This phase occurs in all the resin mixtures in the temperature range of 375° to 600° C with a sharp maximum at 500° C. The third step involves dehydrogenation of the resin mixture and has an abrupt increase after 600° C.

Regardless of these characteristic reproducible evolution patterns, the mechanism involved in the pyrolysis of furfuryl alcohol resins is neither simple nor straightforward. Adding to the difficulty of a mechanistic interpretation is the fact that there are degradation products such as formaldehyde which are capable of being reabsorbed by the base polymer to act as crosslinking agents. In addition, the resins can further polymerize not only during thermal degradation but also through nuclear double bonds and can undergo major nuclear rearrangements. The presence of these factors, plus the fact that there can be considerable overlapping between the three general steps, are indicative of the uncertainty associated with designating the origin of each component.

In spite of this ambiguity, the profile curves exhibit definite variations or shifts for certain components which can be directly attributed to the particular filler used with the binder. In comparing the two fillers, aluminum oxide gave the greatest variation. For instance, in the base polymer, water peaks were observed at 300°, 500°, and 700° C, while the alumina-filled resin had peaks only at 300° and 525° C. However, the total water removed (2.06×10^{-8} mol) during the latter two maxima in the base polymer was almost equal to the total quantity of water removed at the 525° C maximum from the alumina-resin (1.86×10^{-8} mol). Undoubtedly, alumina effectively catalyzes the final stages of pyrolysis (ring opening) by dehydration of the resin at a temperature nearly 200° C below that of the base binder alone.

Another variation noted in the alumina-resin mixture as opposed to both the base and the coke-filled resin is an increase in the amount of unsaturated hydrocarbons over that of the saturated homologues. For instance, with the alumina filler ethylene was increased fivefold over the coke-filled resin, while ethane was correspondingly reduced by almost 50 per cent. Only trace quantities of ethylene could be detected in the base binder. The same was true for propylene which was also increased fivefold in the alumina-resin mix with a corresponding decrease in propane

of approximately 50 and 75 per cent for the coke-filler and base polymer, respectively. Increases in furan and methanol were also noted. However, since the latter component was added exogenously as a diluent for the p-toluenesulfonic acid catalyst in the curing procedure, its presence must be qualified even though traces of other alcohols, such as ethanol and propanol, were detected.

It is apparent that certain filler materials used with furfuryl alcohol resins can exhibit an appreciable effect on the thermal degradation of the base binder and the effect can be demonstrated by this pyrolysis procedure. It is unlikely that an analysis of the total off-gas products collected as a single specimen could exhibit such a variation.

3.4.2. Pyrolysis Studies of Acenaphthylene Pitch by Gas Chromatography

Analysis of the pyrolysis products evolved by the acenaphthylene pitch presented problems not previously encountered with the resin analyses. In the case of the resin the products were principally light gases which could be handled by ordinary gas chromatography techniques. Such gases were only minor products of the pitch pyrolysis and were handled by the same methods used for the resin. However, a second group of compounds was evolved consisting of high boiling point liquids and solids that tended to condense at critical points in the apparatus and thus precluded all possibility of attaining quantitative results.

Because temperatures in the order of 500° C would be required to maintain the "high boilers" in a gaseous state, it became necessary to develop major procedural and apparatus changes. The techniques finally used are described in detail in the Appendix.

3.4.2.1. Light Gas Fractions

Table 5 and Figures 5, 6, and 7 show data for the various light gases given off from the pitch. The largest volume as well as weight of gas evolved is hydrogen. Most of this is evolved at high temperature where the hydrogen is being stripped from the nucleus of the molecules in the coking process. However, there is almost as much weight of methane given off as there is of hydrogen. The ethane evolved is somewhat less than either of the above while ethylene and propane are almost negligible. The three gases, hydrogen, methane, and ethane, make up 90-95 per cent of the off-gas in all cases. Table 6 shows the weights of the gases evolved and their per cent of the total weight loss through 850° C. It can be seen that the light gases account for only a small per cent of the total volatilized materials--from 5 to 6.6 per cent, with not much variation between the different samples. With no filler, about one-third of the gas was evolved through 300° C and the other two-thirds was evolved from 300° to 850° C. With both fillers, about half of the gas was given off through 300° C and the rest from 300° to 850° C.

Table 5.   Total Light Gas Fractions*
from Acenaphthylene Pitch
Samples

Compound	No Filler	Alumina Filler	Coke Filler
Hydrogen	675.	576.	676.
Methane	65.7	56.7	57.5
Ethane	14.4	11.5	8.8
Ethylene	2.35	4.35	3.1
Propane	3.55	2.25	1.7
CO_2	Trace	Trace	Trace

* 10^{-8} moles/milligram of pitch

Table 6.   Light Gas Products Expressed as Weight Per Cent
of Volatilized Material

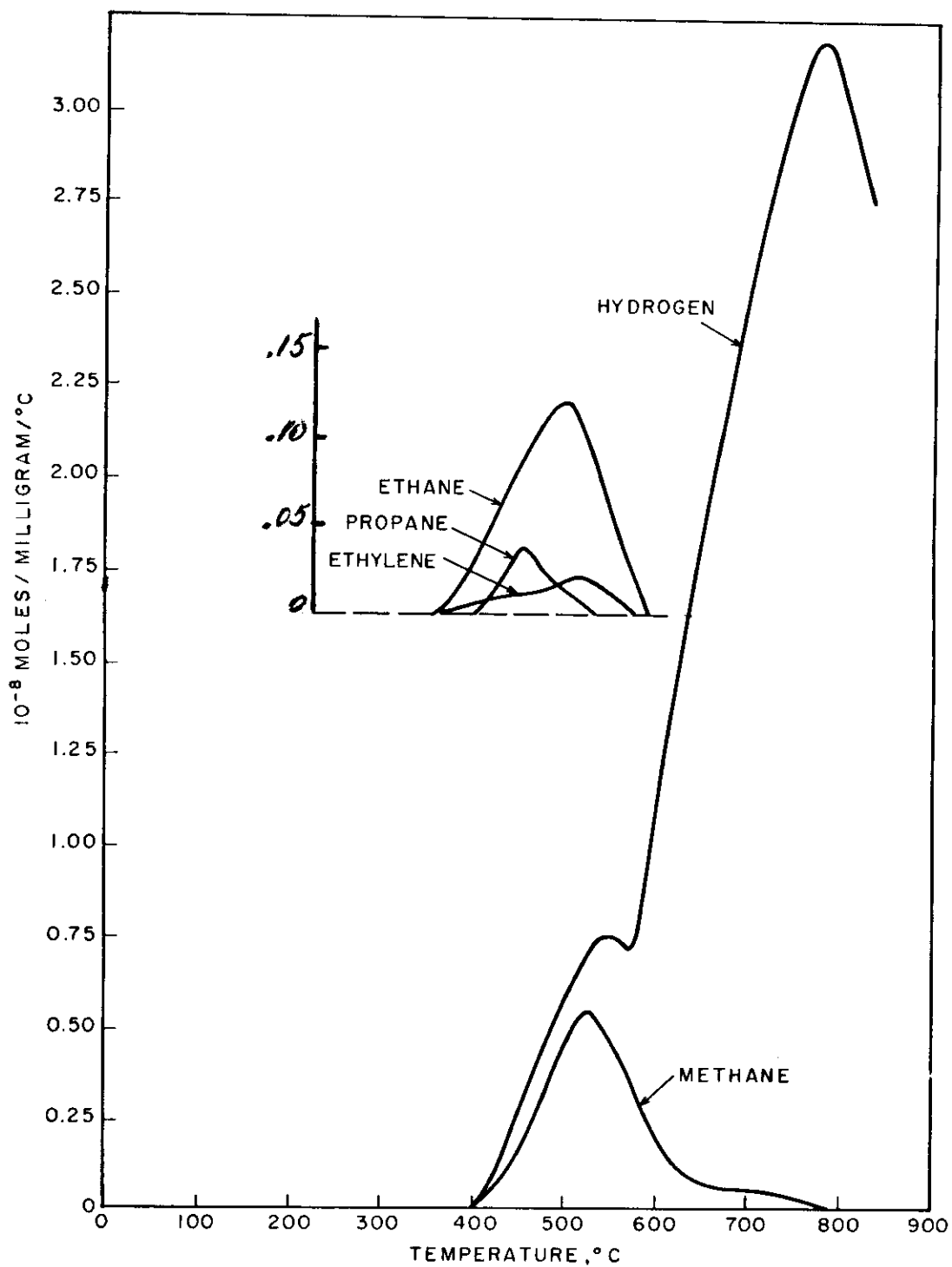| Compound	No Filler		Alumina Filler		Coke Filler	
	mg	%	mg	%	mg	%
Hydrogen	.01350	2.95	.01150	2.19	.01352	2.90
Methane	.01023	2.24	.00909	1.73	.00920	1.98
Ethane	.00431	0.94	.00346	0.66	.00264	0.57
Ethylene	.00066	0.14	.00123	0.23	.00087	0.19
Propane	.00156	0.34	.00101	0.19	.00075	0.16
Total Weight	.03026		.02629		.02687	
Total %		6.6		5.0		5.8
Pitch Weight Loss to 850°C		45.8		52.6		46.6

FIG. 5 - ELUTION PROFILES OF PYROLYSIS PRODUCTS FROM
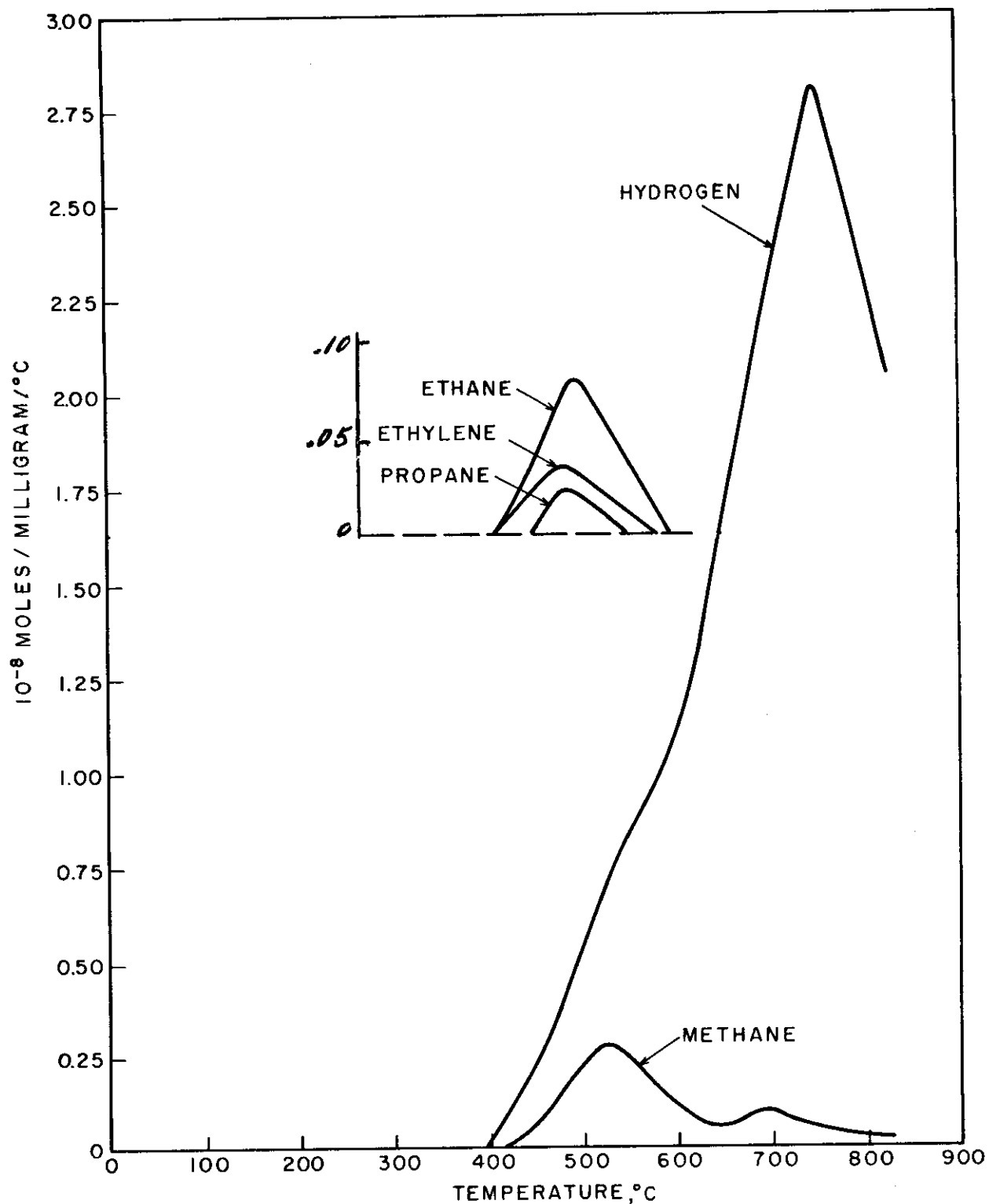ACENAPHTHYLENE PITCH

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FIG. 6 - ELUTION PROFILES OF PYROLYSIS PRODUCTS FROM
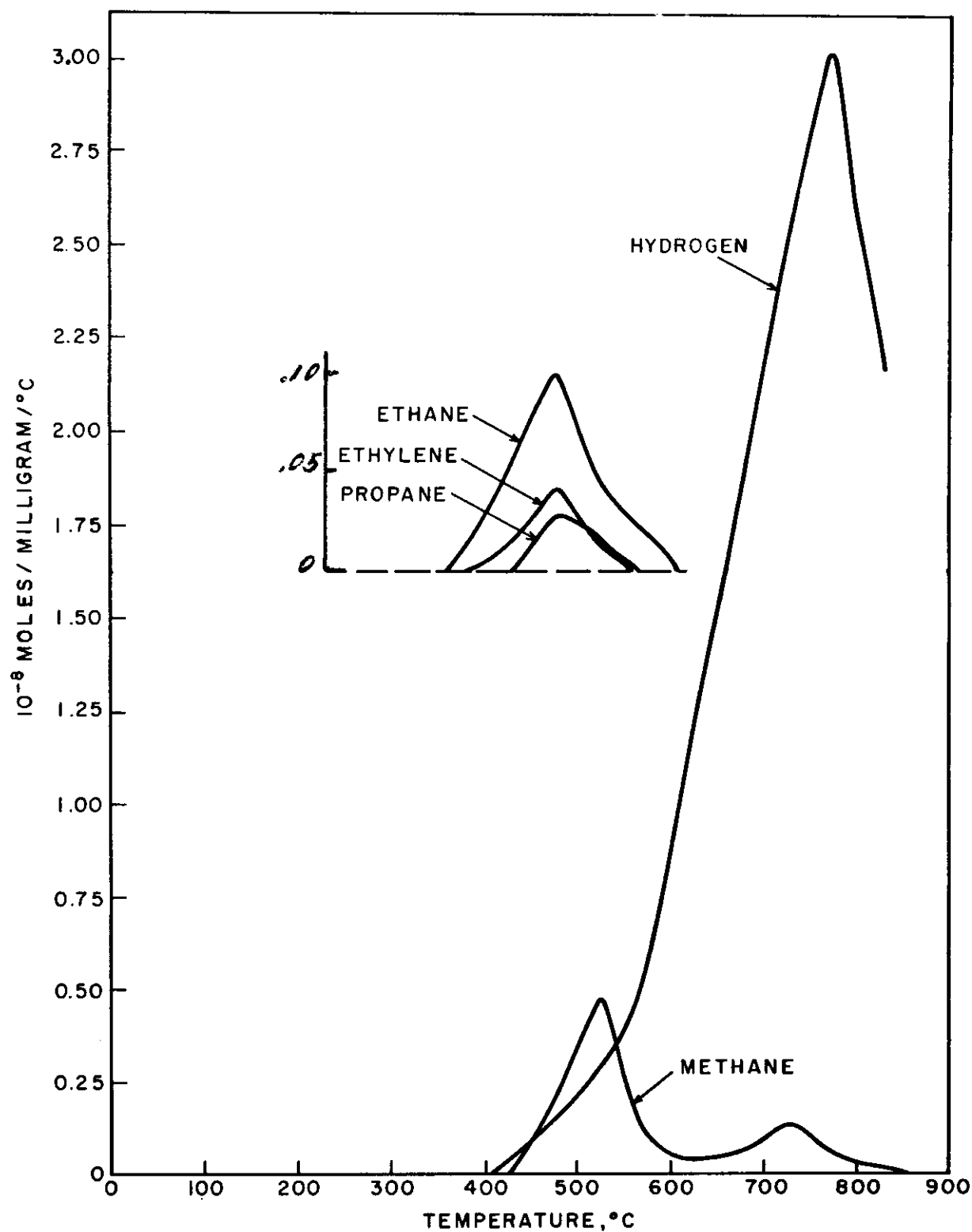ACENAPHTHYLENE PITCH WITH 60% PETROLEUM
COKE FILLER

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FIG. 7 - ELUTION PROFILES OF PYROLYSIS PRODUCTS FROM
ACENAPHTHYLENE PITCH WITH 80.7% ALUMINA FILLER

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3.4.2.2. High Boiling Point Fractions

In the case of the liquid products (Table 7), several attempts were made to fabricate different types of furnaces and arrange lines with heated tapes to prevent condensation of the products. However, the combination of high melting point materials along with the subliming characteristics of the materials proved too formidable for the time limitations of the project. It was necessary to abandon the method of injecting the pyrolysis fraction directly onto the gas chromatograph column because of frequent plugging of lines and back streaming from the pyrolysis chamber.

The relatively high boiling range of the pyrolysis products explains to a large extent the problem of condensation in sample delivery lines. Those materials with a boiling point of about 500°C probably have a melting point of 200°C or over and are very difficult to quantitatively transfer from one point to another in the apparatus in a vapor state. On the other hand, many of these problems are elimated when such materials are placed in a solvent. It was decided therefore to collect the pyrolysis fractions successively in traps. Each trap could then be washed with chloroform, the washings concentrated in a water bath and the sample in chloroform hypodermically injected onto the gas chromatograph column. The gas chromatography separations were performed on two different columns. One of these, a 6 foot x 1/4 inch column packed with 10 per cent Apiezon on 60-80 mesh Chromosorb W, was used to separate the lighter gases and acenaphthene. The column was operated at 200°C and the flash heater at about 325°C. Gage pressure of the argon was 25 lb. Under these conditions, acenaphthene was eluted in 11 minutes. Naphthalene and 1-methyl naphthalene were readily separated at 3.5 and 5.5 minutes. Another peak was distinguished in the 450°-550°C fraction between methyl naphthalene and acenaphthene that is believed to be 1,8-dimethylnaphthalene but, because no pure material was available, this has not been verified.

A second column was used to study the fractions when it was realized after several runs that high boilers were present that were not being eluted from the Apiezon column. The second column, also 6 feet long by 1/4 inch diam, was packed with 3 per cent Se 30 on 60-80 mesh Gas Pack F. The flash heater was set to about 350°C and the column operated at 250°C. At a gage pressure of 25 lb., acenaphthene was eluted very easily--a little less than 0.5 minute after the solvent. A known sample of pyrene (BP 385C) was eluted in 1.8 minutes and chrysene (BP 448°C) in 3.5 minutes. The high boiling materials were found to elute between 6 and 15 minutes. The most prominent peak and a small following peak were isolated on still another gas chromatograph with the same SE 30 packing by making repeated runs and using a sample collector. The ultraviolet spectra of these two fractions are shown in Figure 8. The UV shows the most prominent fraction to be almost identical with that of acenaphthene; it is reasoned that its structure retains most of the features of the acenaphthene structure with very little fragmenting of the 2-methylene carbons bridging the 1,8 positions. It is readily observed that the successive fractions are quite different in UV character. The closest resembling UV spectrum that could be found in available reference material was that of tetraphenyl ethylene in Friedel

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Table 7. Distribution of Liquid Pyrolysis Fractions in Weight Per Cent

Temp. Range, °C	No Filler			Alumina Filler			Coke Filler		
	50-450	450-550	550-650	50-450	450-550	550-650	50-450	450-550	550-650
Low boilers[1]	<0.5	4-5	<0.5	<0.5	2.5	<0.5	<0.5	4-5	<0.5
Acenaphthene[2]	75-90	65-80	70-85	75-90	67-82	70-85	75-90	65-80	70-85
High boilers[3]	10-25	15-30	15-30	10-25	15-30	15-30	10-25	15-30	15-30

1. Mostly naphthalene, methyl naphthalene and probably 1, 8-dimethylnaphthalene
2. A small quantity of acenaphthylene is included; generally not over 2 per cent of the total
3. Mostly dimers boiling about 500° C and over

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and Orchin (Ref. 6). It does not seem reasonable that a molecule of this nature exists in this material. However, the phenyl groups could be alternately represented by naphthyl groups without seriously altering the symmetry of the molecule and still be consistent with the type of product expected.

From Table 5, one can calculate the gas given off as methane, ethane, and propane to arrive at some idea of the fragmentation that occurs in the 350° to 650°C region. If it is assumed that a mole of acenaphthylene in undergoing thermal stress releases about 1 per cent by weight of methane, then about 10 mole per cent of the acenaphthylene is fragmenting to a methyl naphthalene and a methyl radical. This mechanism also assumes that none of the gaseous methylene (CH_2) or methyl (CH_3) groups recombine with other radicals. The propane is most likely produced from some combination of C_2H_4 or C_2H_5 groups with CH_2 or CH_3 groups. Although acenaphthene is the main product, methyl-naphthalene is a prominent product of the minor components in the liquid portion of the 350° to 650°C pyrolysis fractions. Therefore, it is reasonable to assume that methyl-naphthalene radicals could have recombined to form structures of the following possible configurations, viz:
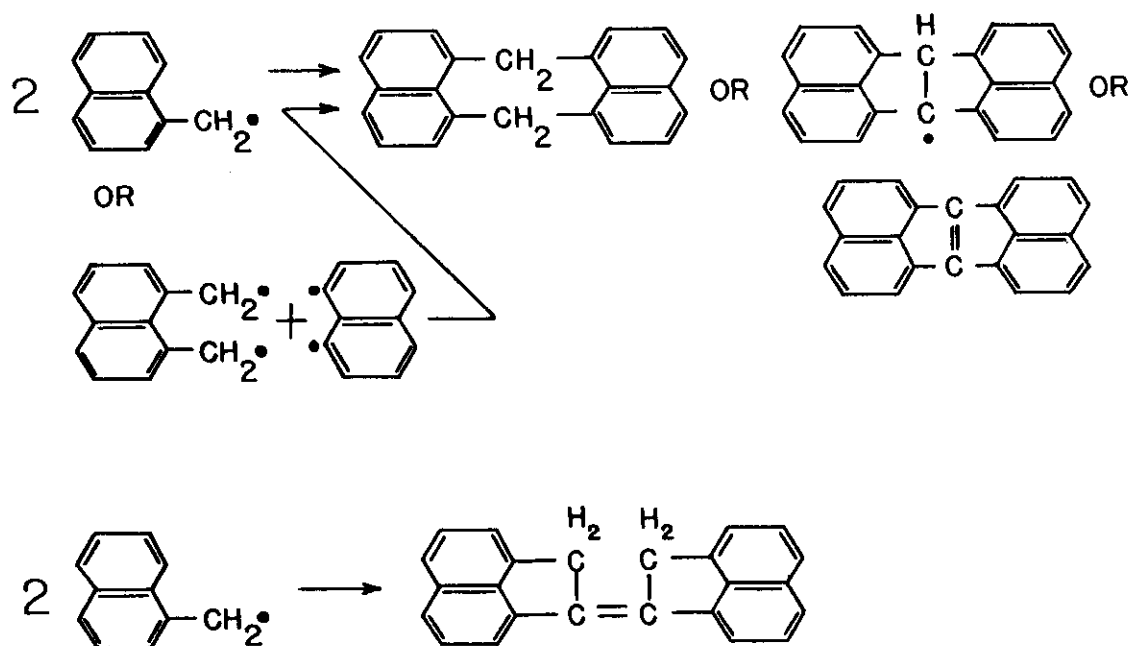
These are only some of the possible combinations of the methyl-naphthalene radicals and if the UV spectra can be matched with those of known pure compounds, the present ambiguity can be resolved.

However, the gas chromatograph data show that one of the high boiling constituents predominates in the 350° to 650°C pyrolysis fractions; its UV spectrum is shown in the upper curve of Figure 8.

As mentioned above, one can estimate from the yield of ethylene and ethane that the quantity of naphthalene radical formed is about one-fourth that of the 1-methyl naphthalene radical. This estimation disregards the possibility of the combination of two methyl radicals to form ethane or two methylene radicals to form ethylene. Thus, 2-naphthalene radicals could combine to form a dinaphthyl. Although there could be other combinations of the various radicals and reactive compounds, the gas chromatography data indicate that the number is limited. The elution curves (Figure 9) of three pyrolysis fractions from 350° to 650°C show the presence of five peaks. The curves suggest a minimum of five different compounds; if incomplete resolution and if doubling of peaks has occurred, there may be more. The presence of many of the radicals in random recombinations account for the higher boiling components and as temperatures are increased, a number of variations should appear along with degradation products from skeleton breakdown.

The data in Table 7 reflect the best estimates that can be made of the liquid pyrolysis fraction distribution because of the lack of calibration standards for checking the UV extinction coefficients as well as the response factors of the argon ionization detector. The high boilers had to be eluted rapidly on the gas chromatograph or they would not record at all. Under these conditions the acenaphthene was eluted too rapidly for the recorder to follow so that quantitative results are questionable. Temperature programming would be the solution to such a wide boiling range from naphthalene to over 500°C but time and budget did not permit determination of the column parameters for doing this in a single run.

3.5. Differential Thermal Analysis

The apparatus used for this work was a three-cup system in which the temperature difference between the sample and an opposed reference standard is measured while heating at a uniformly constant rate. In the present program the rate was 10°C per minute to a maximum temperature of 1000°C.

Although some DTA was performed on binder-aggregate composites, this was discontinued when it was found that the aggregate obscured the peaks and valleys developed by binder reactions. On the other hand, when the resin alone was used, good results could be obtained through most of the thermosetting stage but the exotherm generated late in the stage caused frothing and overflowing of the cups.
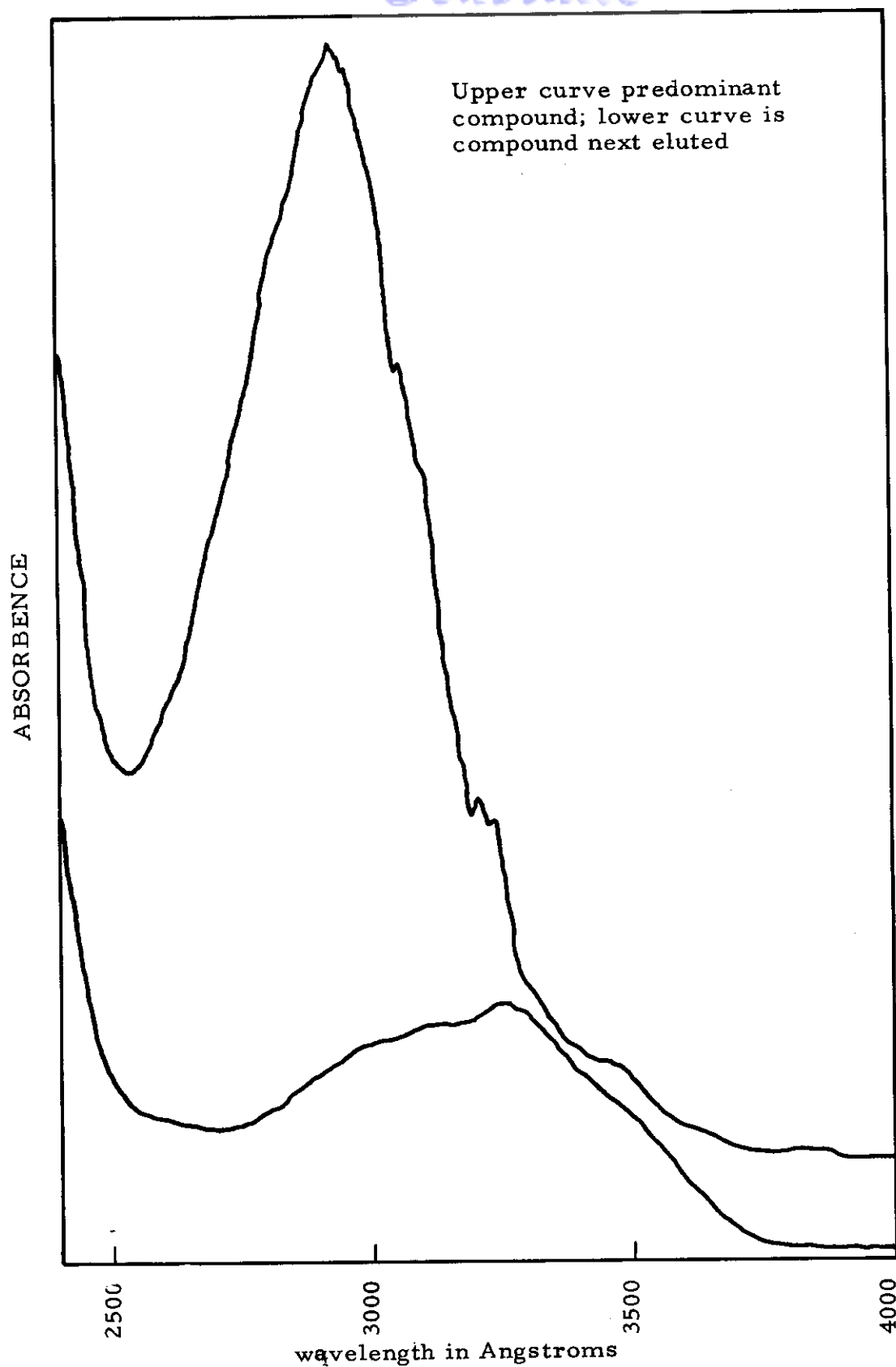
29

Upper curve predominant
compound; lower curve is
compound next eluted

ABSORBENCE

2500   3000   3500   4000

wavelength in Angstroms

FIG. 8 - ULTRAVIOLET ABSORPTION SPECTRA OF MOST PREDOMINANT
HIGH BOILING COMPOUND AND COMPOUND NEXT ELUTED ON
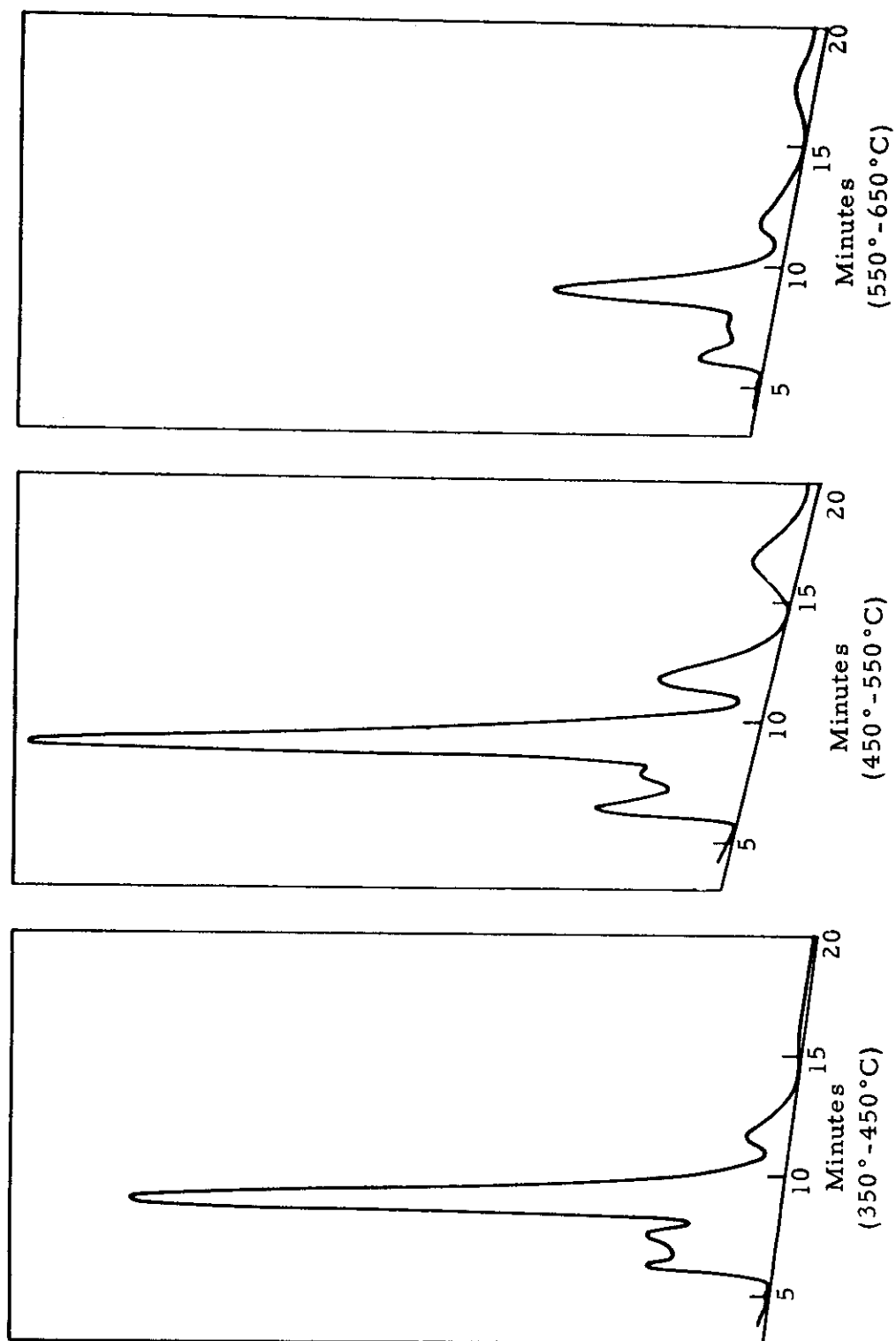GAS CHROMATOGRAPH

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FIG. 9 - ELUTION PROFILES OF HIGH BOILING COMPONENTS THROUGH INCREASING TEMPERATURE RANGES FROM GAS CHROMATOGRAPHY. THESE COMPOUNDS ARE ALL ELUTED AFTER THE MAJOR COMPONENT, ACENAPHTHENE.

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It was finally found that if two cups were filled with catalyzed resin, one of which was immediately analyzed while the second was aged at 40° C for 24 hours and then cured at 150° C for two hours prior to analysis, two curves, one of the thermosetting stage and one of pyrolysis, could be obtained. These could then be joined to give a single continuous curve.

The pitch samples required no special pre-treatment, and were analyzed directly.

Figures 10 and 11 illustrate the DTA traces for both the alumina condensed resin and the acenaphthylene pitch. The trace for the resin has previously been reported (Ref. 2) and correlated with the evolution of pyrolysis products. The trace for the pitch samples shows a general endothermic drift between room temperature and 115° C; this is probably related to the loss of volatiles. The slight dip above 115° C is interpreted as the beginning of melting. Above 200° C, an exotherm is developed, followed by a period of general exothermic activity. This period of activity extends to a temperature slightly above 500° C where two small peaks are recorded. The peaks may be associated with methane and/or ethane evolution. The last peak, at about 900° C, is no doubt associated with hydrogen evolution. This curve must be qualified, however, because it does not check too well with two previous curves which showed poor resolution. The absence of sharply defined peaks is not surprising in view of the gradual sublimation of the major pyrolysis product, acenaphthene, and the competing (and possibly nulling) reactions of the other pyrolysis components.

3.6. Thermogravimetric Analysis

As an aid to understanding pyrolysis, samples of each binder were analyzed by thermogravimetric methods. Two techniques were used. In one, the sample was suspended from a quartz helix and vertical displacement due to weight loss was measured optically. The sample was heated at a rate of 3° C per minute to a maximum temperature of 827° C.

In the other method, the sample was suspended from the core of a linear variable differential transformer which in turn was suspended from a quartz helix. Displacement caused by weight change was indicated by a change in voltage. In this work, the sample was heated to 1000° C at a rate of 3° C per minute.

Weight-loss curves for both the alumina condensed resin and the acenaphthylene pitch are shown in Figure 12. The shape of the resin curve, a rather smooth "S", shows that the pyrolysis products are released over a broad temperature range (200°-1000° C). The pitch, on the other hand, loses weight rapidly in the 100°-500° C temperature range, and then at a very slow rate from 500° to 1000° C. The slight hump in the pitch curve between 250° and 475° C is interpreted as the range through which the major pyrolysis product, acenaphthene, is distilled off. At the very steep section between 475° and 500° C, the pitch loses almost 10 per cent of its weight and changes from a liquid to a solid state. This condensation reaction is fairly violent, and causes the sample cup to bounce noticeably.
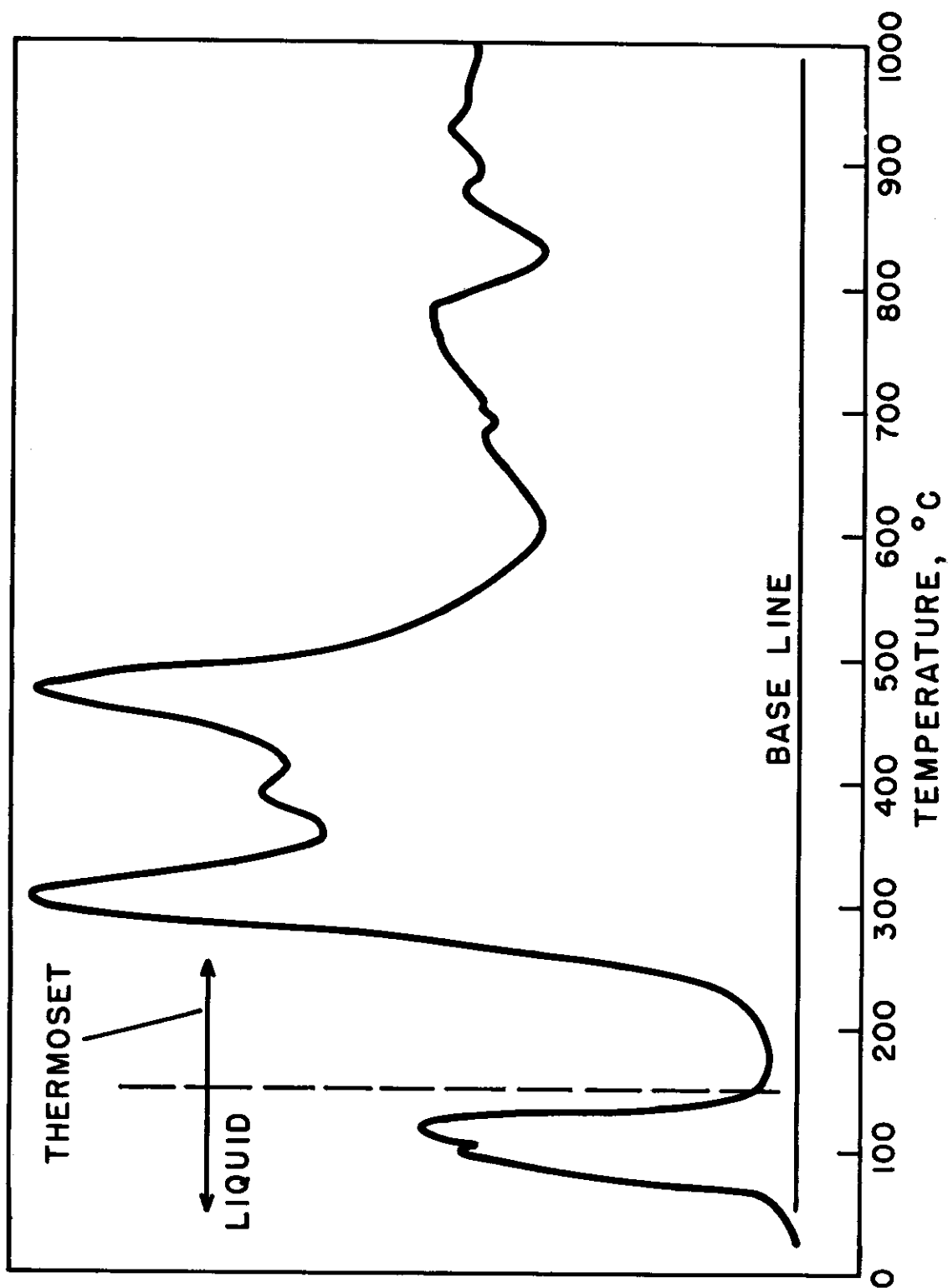
32

FIG. 10 - DTA TRACE OF ALUMINA CONDENSED FA POLYMER
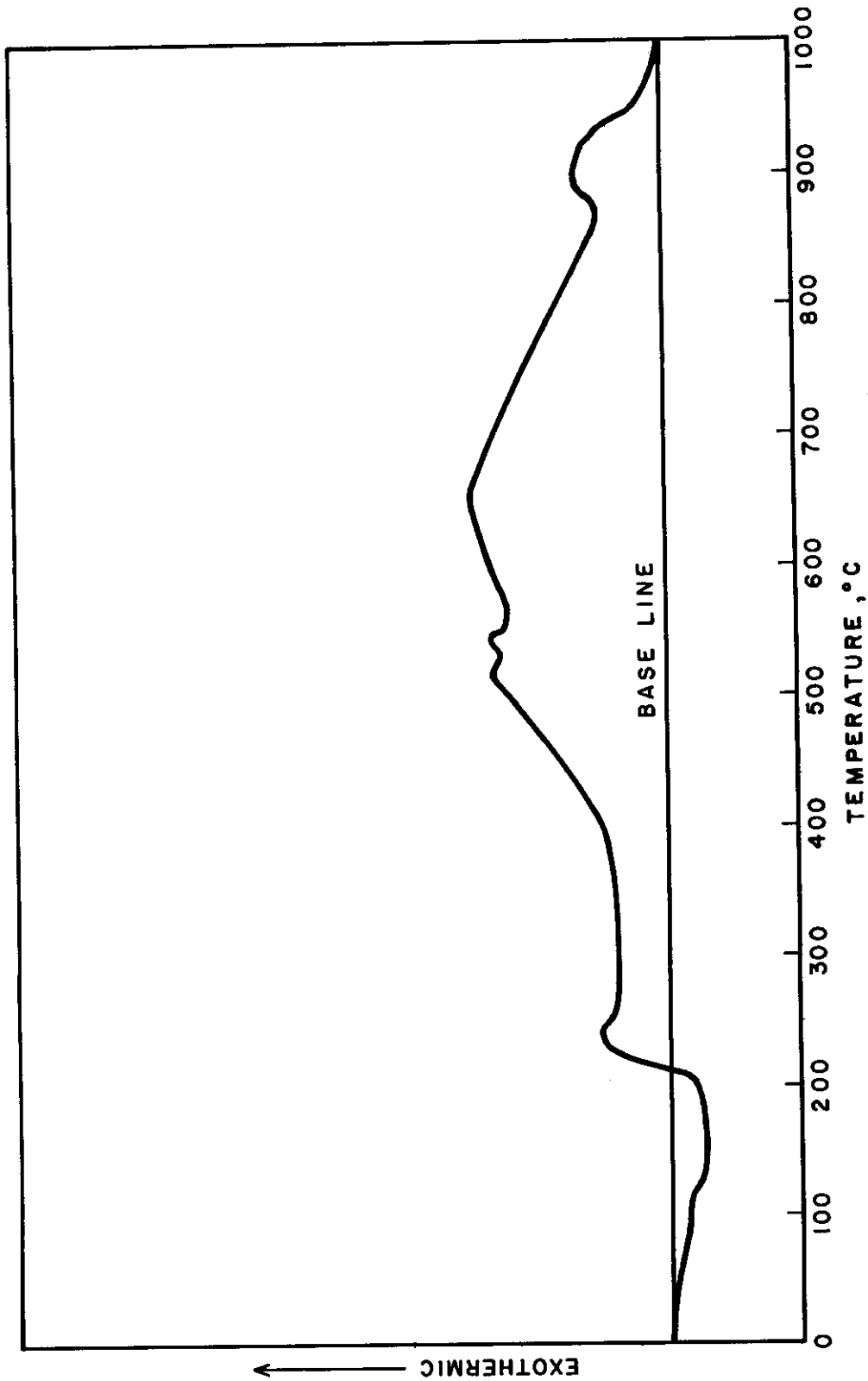8150 CPS, 15.2% H_2O REMOVED

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FIG. 11.- DTA TRACE OF ACENAPHTHYLENE PITCH,
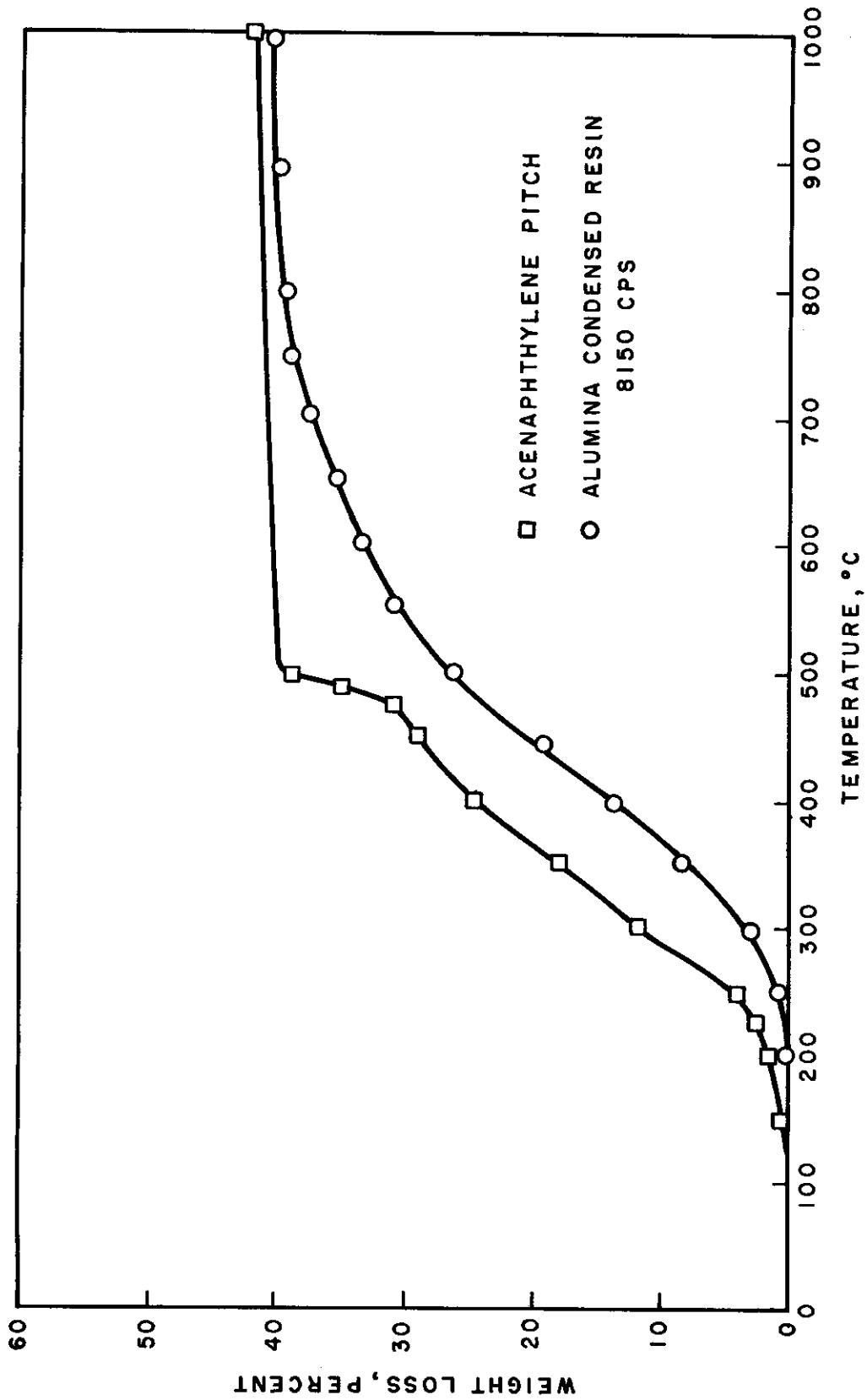CODE 13-40-80

34

FIG. 12 - THERMOGRAVIMETRIC ANALYSIS OF ALUMINA CONDENSED RESIN AND ACE-
NAPHTHYLENE PITCH

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The acenaphthene distilled off during early pyrolysis was found to deposit as acicular yellow crystals on the nearest cool surface; this must be taken into consideration in apparatus design to avoid plugging of gas lines, vents and the like.   The coking residues of both of the synthetic binders were found to be approximately 60 per cent.

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4. REFERENCES

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2. WADD Technical Report TR 61-72, Vol. XV, "Alumina-Condensed Furfuryl Alcohol Resins," C. W. Boquist, E. R. Nielsen, H. J. O'Neil, and R. E. Putcher.

3. WADD Technical Report TR 61-72, Vol. XXXII, "Studies of Binder Systems for Graphite," T. Edstrom, I. C. Lewis, R. L. Racicot, and C. F. Stout.

4. WADD Technical Report TR 61-72, Vol. XXVII, "Carbonization Studies of Polynuclear Aromatic Hydrocarbons," I. Lewis and T. Edstrom.

5. D. W. Gilmore, "Some Factors Influencing the Strength of the Carbonized Bond Between Anthrafines and Bituminous Materials," Doctoral Thesis, 1954, The Pennsylvania State University.

6. R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," J. Wiley and Sons, 1951.

5. APPENDIX

5.1. Techniques Used in Pitch Pyrolysis Studies by Gas Chromatography

Details of the gas chromatography pyrolysis studies are included here for readers who might desire to employ the technique. Presumably, similar studies would shed light on the pyrolysis mechanisms of natural pitch binders, and be capable of detecting interactions or modifications of combination binders such as resin-pitch mixtures.

5.1.2. Pitch Pyrolysis

Pyrolysis studies, similar to those for furfuryl alcohol resins, have been carried out on acenaphthylene pitch both with and without coke and alumina fillers to establish whether or not there are differences in pyrolysis characteristics over the temperature range from ambient to about 850°C.

The procedure used in this pyrolysis study was similar, but not identical to that used for the resin. Need for apparatus modification was apparent after the initial attempts to apply the earlier procedure. The products released during the heating cycle of the acenaphthylene pitches were found to sublime from the combustion tube and immediately deposit on the nearest cold surface. This necessitated the construction of a completely heated reaction system.

Because deposition of the sublimates invariably plugged the exit lines leading from the furnace, two analytical methods were used. The first method was concerned with the identification of the light gases produced through the indicated temperature range. To eliminate the problem of sublimation, a representative sample of the pitch and pitch-filler mixtures was placed in a standard muffle furnace where it was heated to 300°C and flushed continually with dry nitrogen to remove major portions of the acenaphthene. The weight loss of each sample was determined under identical conditions. The stripped samples were then placed in a newly designed pyrolysis chamber (Figure 13), and analyzed by the technique described for the resin studies.

The second method was used for the identification of the liquid or higher boiling constituents where the samples obviously could not be pretreated in the same fashion as the samples just described for the gas analyses. In this method, the higher boiling or condensable materials were analyzed by direct pyrolysis of the whole pitch. The samples (100-200 mg) were placed in the furnace assembly and heated at a rate of 10°-14°C/min. The exit line from the furnace contained a toggle gas valve and approximately 10 inches of narrow bore tubing, all of which was maintained at 300°C by means of heating tape and a variable transformer. The end of the exit line was connected via silicone seals to a U-shaped Pyrex trap which contained a small plug of glass wool and was maintained at room temperature. At the end of each 100°C heating interval, pyrolysis products were swept from the chamber with helium at a

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TOP VIEW

SILICONE
SEAL

THERMO-COUPLE
LOCATIONS

SAMPLE DISH
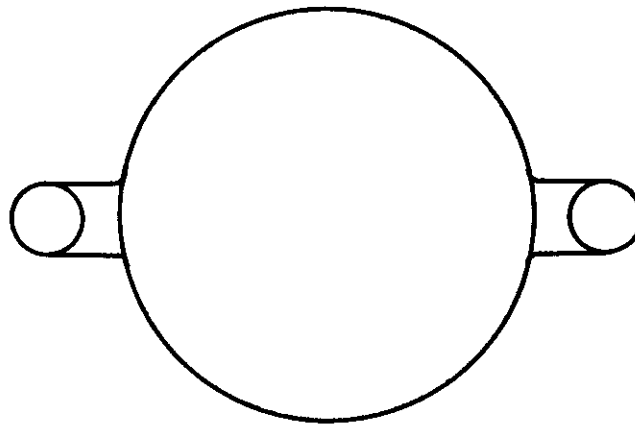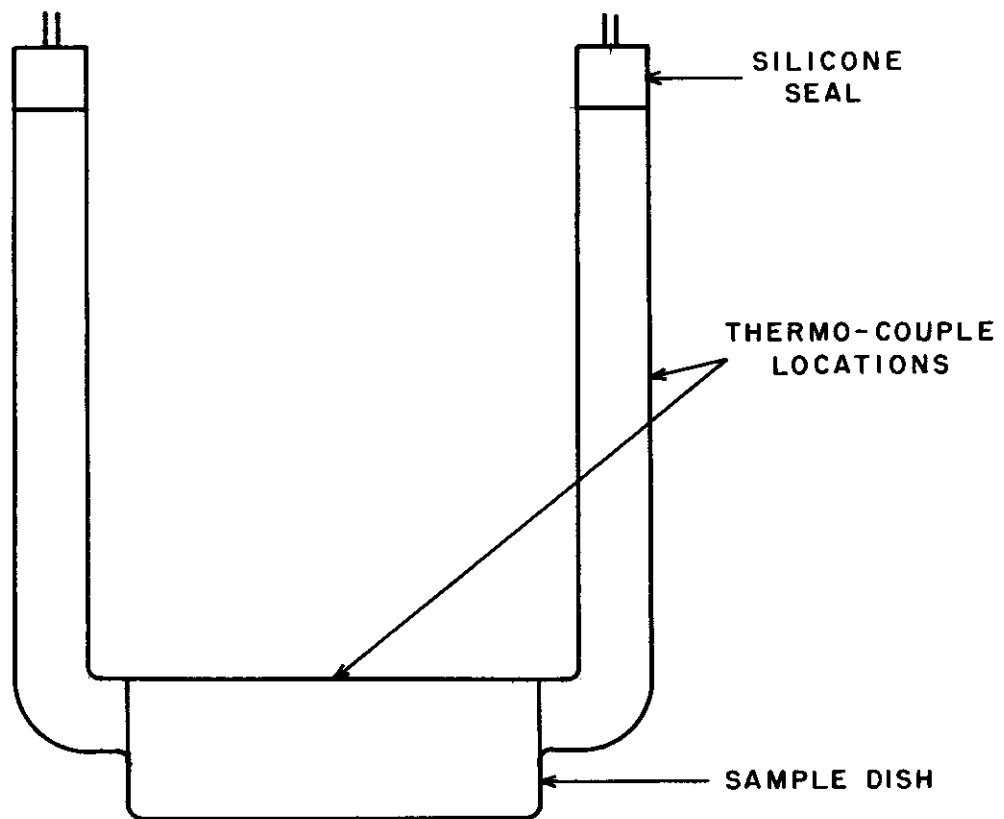
SIDE VIEW

FIG. 13 - DIAGRAM OF PYROLYSIS CHAMBER USED FOR ACE-
NAPHTHYLENE PITCH SAMPLES

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flow rate of about 140 ml/min. and trapped on the wool plug of the pre-weighed collection tube. For each run, a total of six samples, one for each 100°C interval, was taken in the range of 50M to 650°C. The weigh-ed material, dissolved in 95 per cent ethyl alcohol, was quantitatively transferred to a 25 ml volumetric flask for ultraviolet studies (Cary model 14 ultraviolet spectrometer). The UV absorption spectra of the total pyrolysis sampling through selected temperature ranges, all show acenaphthene to be the major component (Figures 14, 15, and 16).

For the gas chromatograph work, the trapped pyrolysates were sol-vented with chloroform for direct injection to the columns. These analyses also showed acenaphthene to be the major product. The amounts were calculated from the UV data in conjunction with the gas chromatography data.

The lighter of the high boiling components--naphthalene, 1-methyl naphthalene, acenaphthene, and residual acenaphthylene--were analyzed by gas chromatography on a 6 foot x 1/4 inch U-shaped glass column containing 10 weight per cent Apiezon N on 60-80 Chromosorb. The analyses were performed using a Barber-Colman model 10 gas chroma-tograph under the following conditions: column temperature, 200°C; cell voltage, 1000 volts; flash heater, 275°C; detector, 260°C.

Analyses of the components with boiling points higher than acenaph-thene were made on the same instrument, with the exception that the U-shaped column contained 3 weight per cent SE-30 on 60-80 mesh Gas Pack F at a column temperature of 250°C.
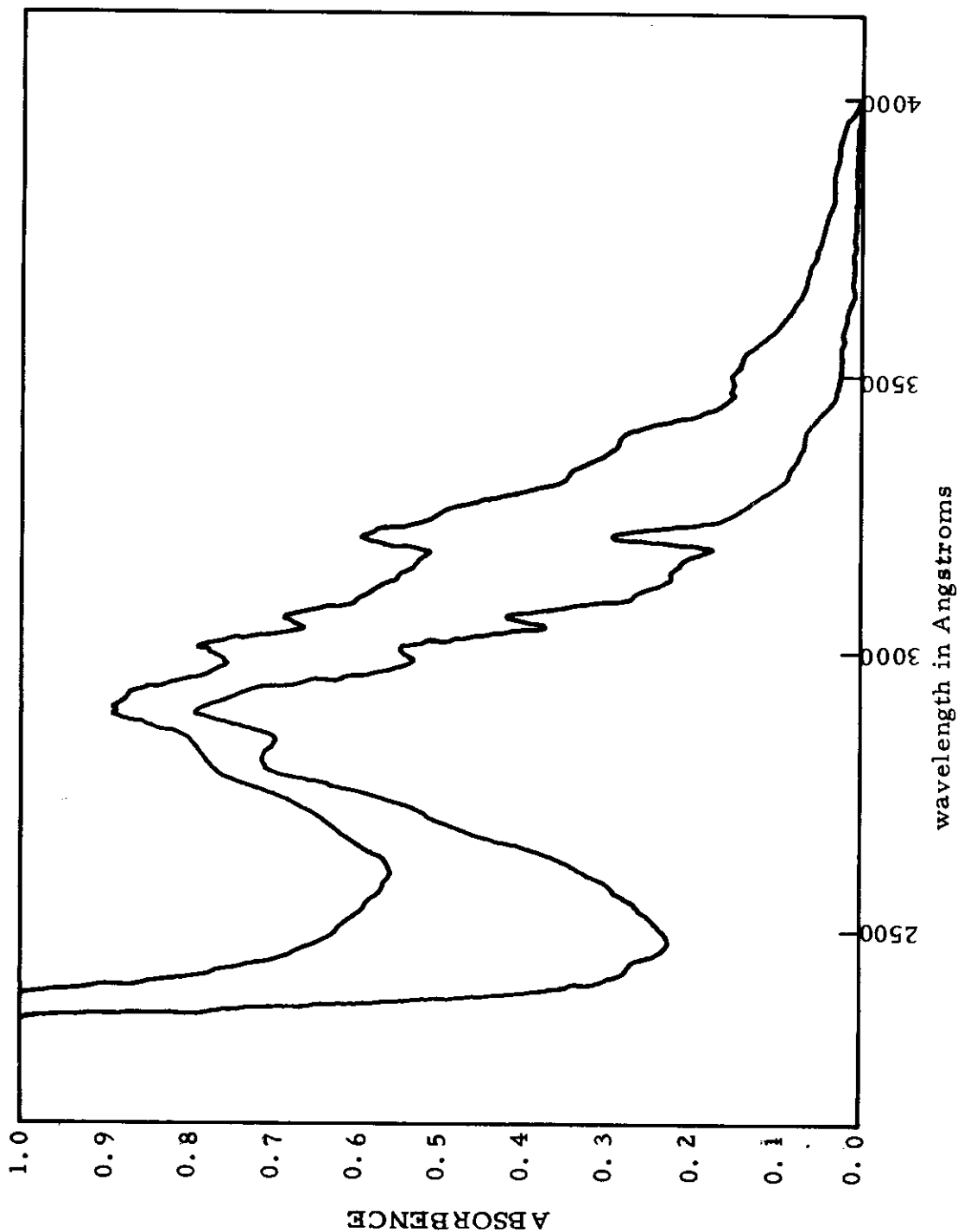
FIG. 14 - ULTRAVIOLET ABSORPTION SPECTRA OF TOTAL PYROLYSIS PRODUCT
COLLECTED IN THE 450°-550°C RANGE (LOWER CURVE) AND 550°-650°C
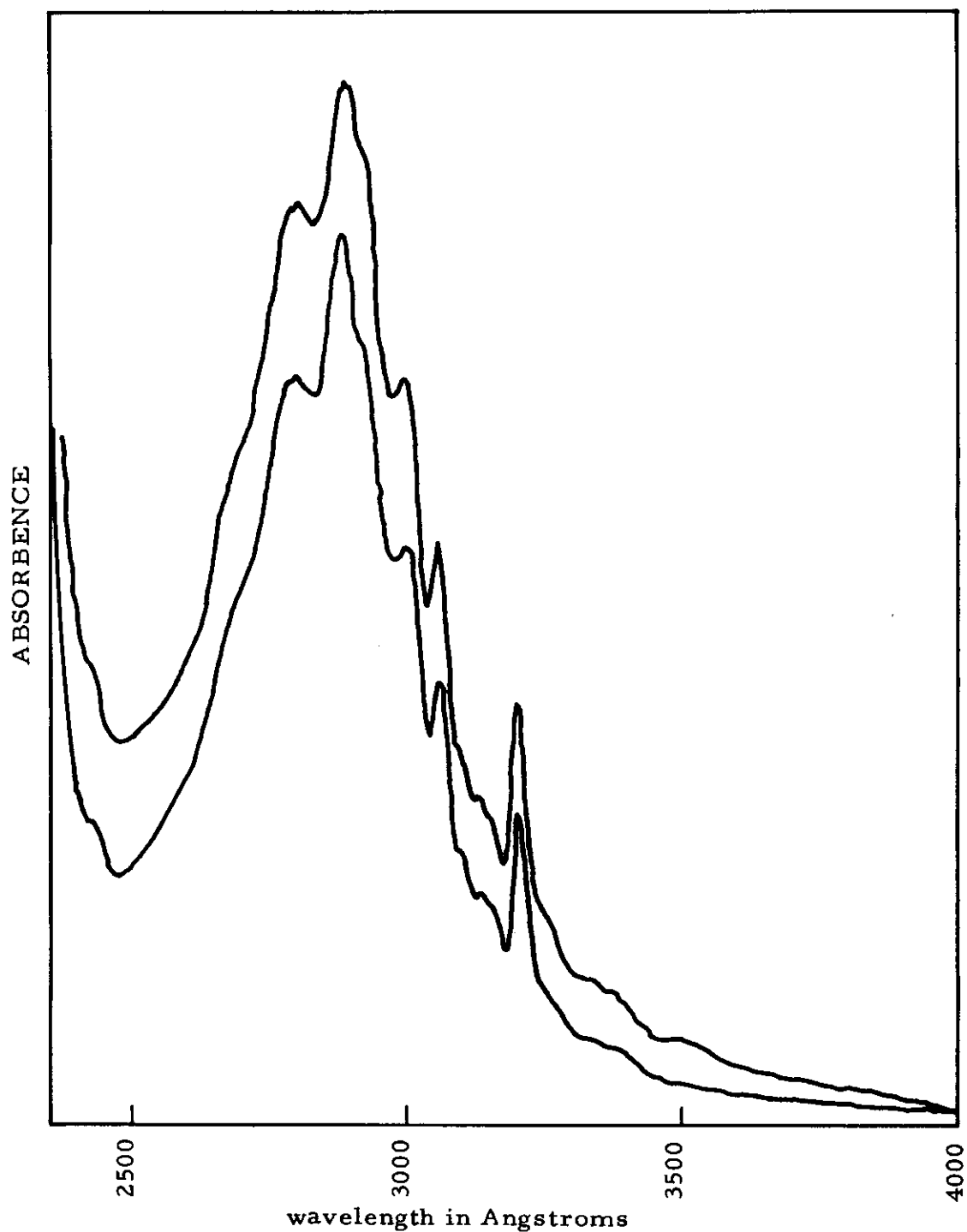RANGE (UPPER CURVE) FROM PITCH ONLY

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FIG. 15 - ULTRAVIOLET ABSORPTION SPECTRA OF TOTAL
PYROLYSIS PRODUCT COLLECTED IN THE 450°-
550°C RANGE (LOWER CURVE) AND 550°-650°C
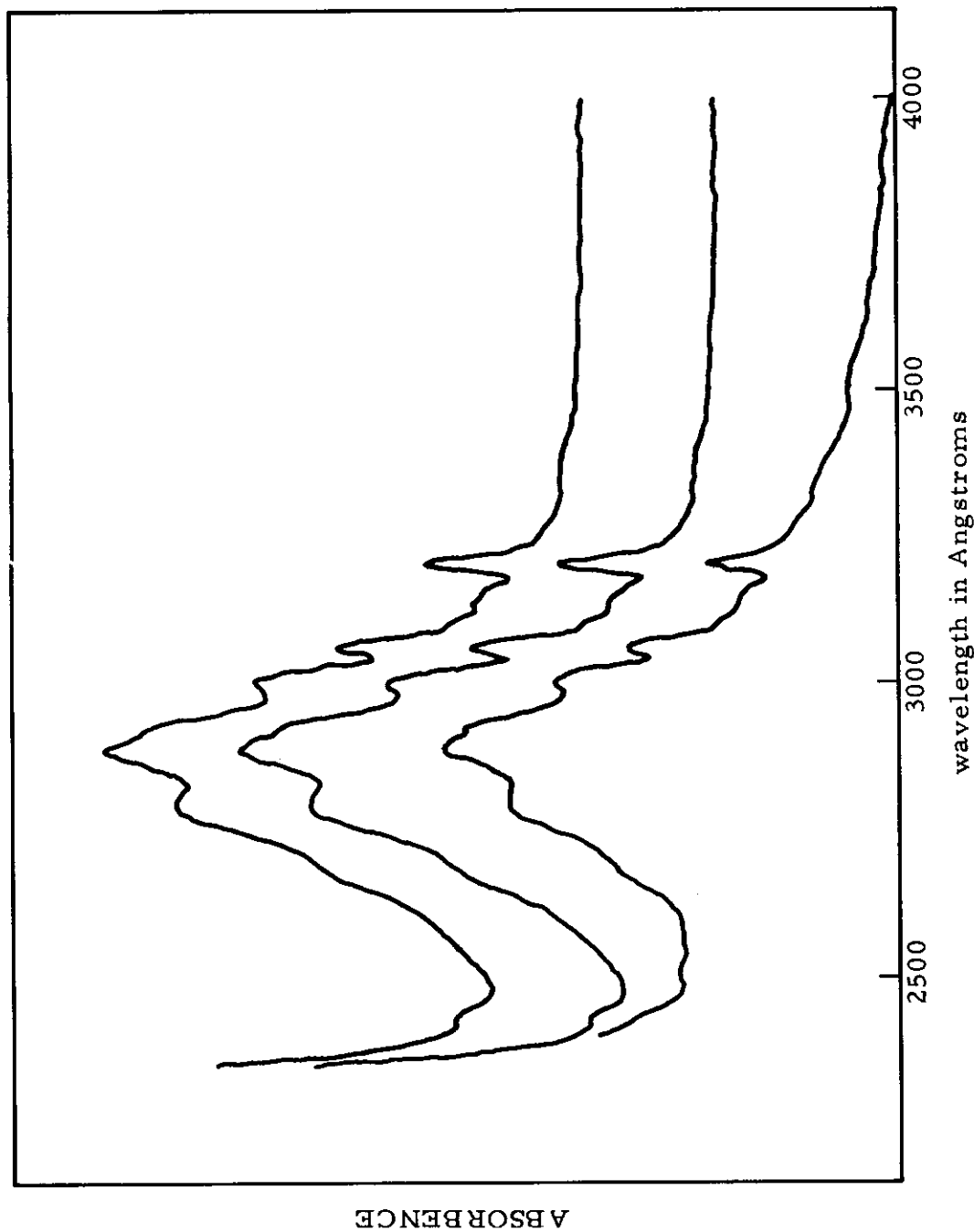RANGE (UPPER CURVE) FROM PITCH WITH COKE
FILLER

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FIG. 16 - ULTRAVIOLET ABSORPTION SPECTRA OF THE TOTAL PYROLYSIS PRODUCT COLLECTED IN THE 350°-450°C RANGE (UPPER CURVE), 450°-550°C RANGE (MIDDLE CURVE), AND 550°-650°C RANGE (LOWER CURVE)FROM PITCH WITH ALUMINA FILLER

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