

STRUCTURE DETERMINATION OF RESINS FROM PITCH OF
LOW-TEMPERATURE TAR BY COMBINED PYROLYSIS
AND GAS-LIQUID CHROMATOGRAPHY

Clarence Karr, Jr., Joseph R. Comberiat, and Patricia A. Estep

U. S. Department of the Interior, Bureau of Mines,
Morgantown Coal Research Center, Morgantown, W. Va.

This report is the second by this laboratory on investigations of the composition of the resins from pitch in connection with the Federal Bureau of Mines' research on the nature of coal and its products. The first report concerned the structure determination of resins by ring analysis and spectral characterization¹. The present work involves structure determination of resins from pitch of low-temperature tar by combined pyrolysis and gas-liquid chromatography.

Pyrolysis or thermal degradation of complex substances is one of the oldest methods of structure determination. Gas-liquid chromatography makes it possible to isolate the pyrolysis products immediately upon formation so that they can be identified before they are lost or altered in secondary reactions. There are apparently no previous reports in the literature on structure determination of resins from pitch by pyrolysis. The characterization of low-temperature tar resins is important, however, because they are major components of the pitch, and, in the case of some bituminous tars, make up as much as half the weight of the total tar.

The conditions of pyrolysis were chosen to yield, insofar as possible, primary products that would give the maximum information about the structure of the resin. The products of greatest interest were those large enough (C_5 and greater) to yield meaningful clues to structure. The pyrolysis temperature was generally in the range 520° - $530^\circ C.$, or above the temperature at which no volatile pyrolysis products are observed, and the heating time was only a few seconds. In addition, because the sample was heated in the absence of air in a glass container, catalytic effects should have been quite low if not non-existent. Under these conditions the pyrolysis products could be considered to represent primary fragments from the resin molecule.

EXPERIMENTAL

Many pyrolysis experiments were made under a wide variety of conditions to gain some insight into the behavior of the various resins from several pitches. This report has been limited to the experimental procedures and results that are of greater interest.

Apparatus

The pyrolysis apparatus consisted of a small coil (diameter, 1/8-inch) made from a 25.5-inch length of 28-gauge nichrome wire suspended in a stainless-steel chamber connected directly to a gas-liquid chromatographic unit by a short length of 1/8-inch stainless-steel tubing, as shown in Figure 1. The chamber, the connecting tubing, and a longer preheating section of tubing were all electrically heated to approximately the same temperature, which was a few degrees below the GLC column temperature. Helium carrier gas was passed through the preheat section and the pyrolysis chamber into the column. A 30-second maximum electrical timing switch and powerstat were used to control the firing period and voltage for the pyrolysis coil. The maximum temperature obtained during firing was determined in calibration runs with a thermocouple; the helium flow and other conditions were the same as during the pyrolysis runs. This thermocouple was placed inside a glass tube, which in turn was inside the coil. The thermocouple leads passed through gas-tight fittings in the lid of the pyrolysis chamber. In addition, the maximum temperature of the coil surface itself was estimated by means of thin films of materials selected to melt at specified temperatures.

Two different columns were used in order to determine the pyrolysis products under different conditions. One column was constructed of 15 feet of 1/4-inch diameter aluminum tubing and packed with 25 weight-percent polyphenyl ether on 30 to 60 mesh firebrick. The other column consisted of a 20-foot length of 1/4-inch copper tubing filled with 75 g. packing made from 25 percent Apiezon L grease on 30 to 60 mesh firebrick. A column temperature of 220 °C. was used so that relatively high-boiling products, such as phenols and naphthalenes, would be readily detected, if present.

Gas-liquid chromatographic fractions were collected for infrared spectra. The higher boiling fractions were collected in 6-inch 18-gauge needles cooled in powdered dry ice. A U-trap of 1/4-inch aluminum tubing was required for the lower boiling fractions (below benzene) in order to have enough cooling surface to condense this material from its dilute mixture in the helium carrier gas. This U-trap could then be warmed, and the evolved gas readily condensed in a 6-inch needle. The needles were stoppered at both ends with Teflon plugs and kept in Dewar flasks filled with powdered dry ice until the infrared spectra could be obtained. To determine the spectra, each needle was given a single rinse with 15 μ l. carbon disulfide introduced into the hub end with a micro syringe. The solution was allowed to flow from the point of the needle into a 0.5 mm. ultramicrocavity cell, which was then stoppered and placed in a liquid cell holder. The cell holder in turn was placed in the 6X beam condenser in the spectrophotometer. The details of this cell holder have been described elsewhere².

Pyrolysis results

The results of the pyrolysis of the semi-solid, benzene-soluble, petroleum ether-insoluble resin from Nugget, Wyoming, subbituminous coal tar pitch may be cited as an example. The resin was pyrolyzed at about 528 °C. in a chamber preheated to 175 °C., using a sealed glass tube technique. This procedure consisted of placing about 25 mg. of the finely divided resin in a glass capillary tube that was then evacuated,

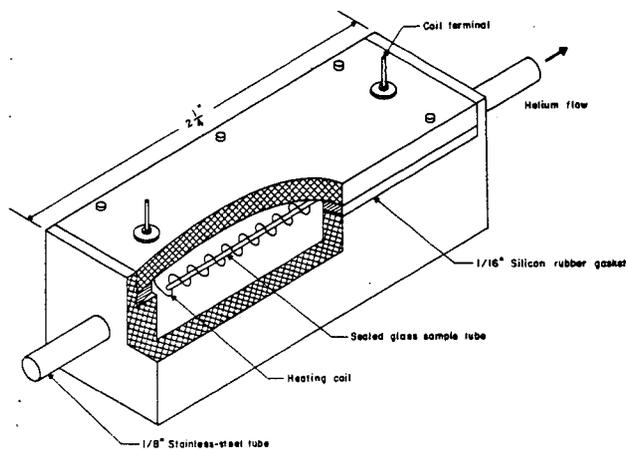


Figure 1. Pyrolysis apparatus for sealed glass tube technique.

sealed, and inserted in the coil. With this size sample and a setting of about 22.5 volts, the tube shattered at 8.4 seconds. The maximum temperature inside the glass tube after this length of time was determined from the calibration runs with a thermocouple. The volatile pyrolysis products were swept immediately and directly into the gas-liquid chromatographic column by the stream of helium. The pyrolysis residue appeared to consist of a mixture of char and an unknown amount of essentially unaltered resin.

Although the resin is subjected to a high pressure in the last few seconds before the tube shatters, this increased pressure has little apparent effect on the nature of the pyrolysis products as compared to heating a film of resin on the coil. This was shown by depositing a thin layer of the resin from solution on a coil and firing at various known maximum temperatures. At coil temperatures around 500°C., the low molecular weight resins (M, 400 to 500) simply evaporated from the coil and were deposited on the cooler walls of the pyrolysis chamber. A small peak was obtained on the chromatogram at the retention time for air, which had apparently been trapped in the semi-solid resin film. There were no other peaks, indicating that the resin had been distilled at about 500°C. without decomposition to lower boiling materials. [This suggests the possibility that at least some of the resins found in tars produced by low-temperature carbonization (500°C.) are essentially unaltered "coal molecules."] The medium molecular weight resins (M, 500 to 650) however, did not completely evaporate from the coil under these conditions, and at higher temperatures (around 530°C.), decomposition occurred. The chromatograms of these pyrolysis products were basically the same as those obtained with the sealed tube technique. The main difference between the two methods was the sharper, better resolved peaks with the sealed tube method. Pyrolysis of resins in evacuated sealed glass tubes thus had five distinct advantages: (1) no sample was lost from the pyrolysis zone by evaporation; (2) the resin was not heated on a metal surface so possible catalytic effects were avoided; (3) the pyrolysis products were swept into the gas chromatographic column during an exceedingly brief interval when the tube shattered; the resulting chromatogram had sharper and better resolved peaks; (4) the tube shattered so violently and into such small pieces that no sample remained in the pyrolysis zone; and (5) the little "spike" produced on the recording by this pressure surge was an accurate indication of zero time.

A typical chromatogram obtained with the subbituminous resin using the sealed tube technique and the Apiezon L column is shown in Figure 2. A recording with the methane peak 1 off-scale was chosen so that the minor component peak 12 would be evident. (All peaks were recorded at the same attenuation.) On other chromatograms, it was clear that peaks 4 and 5 were separate. The relative retentions of the pyrolysis products producing these peaks are compared with the relative retentions of pure compounds in Table 1. The wavelengths of some of the observed infrared absorption bands of the trapped fractions corresponding to peaks 7 through 14 are also shown in Table 1, as well as the quantities of pyrolysis products determined from corrected peak areas and spectra of trapped fractions. The identities of the pyrolysis products with relative retentions less than that for n-pentane were not considered pertinent to the present work. Nevertheless, evidence was obtained showing that peaks 1 through 4 are undoubtedly produced by the C₁ through C₄ hydrocarbons, all of which are gases. Several attempts were made to obtain evidence for pyrolysis

Table 1. Relative retentions and infrared-absorption bands of pyrolysis products

Compound	Relative retention ^a		GLC peak no.	Some observed I. R. bands, wavelength, μ	Weight percent ^b
	Pure	Pyrolysis product			
Methane	0.37	0.37	1		
		0.43	2		
		0.49	3		
		0.57	4		
1-Pentene ^c	0.60	0.59	5		9.7
2-Methyl-1-pentene ^c	0.70	0.71	6		2.7
2,2,4-Trimethylpentane	0.93	0.93	7	7.33, 7.81, 8.03, 8.32, 8.57, 10.21	24.7
Benzene	1.00	1.00	8	2.44, 3.20, 3.25, 5.12, 5.52, 9.65, 14.85	19.3
2,3,4-Trimethylpentane	1.15	1.15	9	7.25, 7.32, 8.93, 9.30, 10.07, 10.32, 10.92	26.9
2,2,4,4-Tetramethylpentane	1.23	1.23	10	8.03, 8.54, 10.28	7.0
Toluene	1.37	1.37	11	9.28, 9.71, 13.74, 14.43	3.5
2,6-Dimethyl-1,4-heptadiene ^c	1.53 ^e	1.55	12		0.5
p-Xylene)	1.92	1.93	13	8.95, 12.60 (para)	0.9
m-Xylene)				8.57, 9.13, 13.02, 14.53 (meta)	2.1
o-Xylene	2.14	2.15	14	7.22, 8.96, 9.53, 9.81, 13.46	2.7
					<u>100.0</u>

a Relative to benzene on Apiezon L grease at 220°C.

b On the basis of the total liquid pyrolysis products.

c This compound is typical of several equally likely possibilities.

d See text for discussion of olefin bands.

e Retention obtained from log retention-boiling point correlations.

products with retention times greater than that for o-xylene. However, even with the largest sample size of resin, the highest sensitivity setting of the GLC apparatus, and a more sensitive flame detector instead of a thermal conductivity detector, the recording beyond the o-xylene peak remained a straight line, including the region for higher boiling compounds such as phenol and naphthalene. Under the same conditions it was known that very small quantities of these compounds could be detected.

In addition to the infrared absorption bands listed in Table 1, there were several bands, characteristic of different types of olefins, which were readily observed. These were bands at 10.14μ and 11.06μ due to α -olefins, a band at 11.30μ due to branched (2-position) α -olefins, a band at 14.44μ due to cis-olefins, a band at 10.38μ due to trans-olefins, and a band at 12.32μ possibly due to branched internal olefins. The band at 6.1μ due to the C=C stretching vibration in olefins was detected, this being a weak band as is observed for non-conjugated compounds. No individual olefin compound could be identified with certainty. It appeared likely, however, that most of these olefins had the same highly branched carbon skeleton as the saturated hydrocarbons. This condition was verified by the complete absence of the band at 13.80μ due to the $-(CH_2)_4-$ group or larger. Conversely, the 8.57μ band for the "isopropyl" grouping of carbon atoms was frequently observed to be a major band. Bands at 7.23μ and 7.30μ also indicated the presence of the $(CH_3)_2CH-$ group.

DISCUSSION

From the large number of pyrolysis experiments that were made, it appeared from the repeated evidence of characterizing infrared absorption bands and the excellent agreement with relative retentions, that the 3 major liquid pyrolysis products of the subbituminous resin were 2,3,4-trimethylpentane, 2,2,4-trimethylpentane, and benzene, in that order of decreasing quantity. The large quantity of highly branched, relatively high carbon number (C_8) saturated hydrocarbons was of unusual interest.

As previously mentioned, it appeared reasonable to assume that, under the conditions adhered to in this work, these pyrolysis products represented primary fragments from the resin molecule. It was recognized that the actual fragments were very likely free radicals at the instant of formation, that is, that a free radical mechanism was involved in the thermal degradation around $500^\circ C$. It appears almost certain that the benzene rings found in the pyrolysis products existed as such in the resin molecule. These monocyclic aromatics (benzene, toluene, the 3 xylenes) are present in the same quantities at the threshold temperature for pyrolysis (slightly over $500^\circ C$.) as at much higher temperatures (up to about $650^\circ C$.). Non-catalytic aromatization is generally considered to become significant only for temperatures at or above about $650^\circ C$. In the absence of specific catalysts, the rate of formation of aromatics from non-aromatics at about $500^\circ C$. is presumably too slow to account for their production during the 2 or 3 seconds that the resin is heated above 300 or $400^\circ C$. DHONT has pyrolyzed a wide variety of pure compounds over "Chromosorb" at $550^\circ C$., the products being immediately analyzed by gas-liquid chromatography³. Compounds containing a benzene ring (such as benzyl alcohol) yielded benzene as a pyrolysis product. Aliphatic compounds yielded no benzene under these conditions.

From the pyrolysis results, it would appear that the resin molecule contains isolated benzene rings joined together by saturated, fused multi-ring systems with saturated bridge carbons, including quaternary carbons. From previous work on the resins as well as the non-resinous portions of the tar, it is known that the great majority of alkyl groups on aromatic rings are methyl groups, with very small amounts of ethyl and propyl groups, and negligible amounts of butyl groups. Thus alkyl groups could contribute products only to the permanent gases, in particular methane. The aliphatic compounds above C_4 in the pyrolysis products must therefore come from internal structures, that is, ring structures, rather than side chains.

A resin molecule containing as part of its structure a unit like 5,6,6a,7,8,12b-hexahydro-6,7-dimethylbenzo[c]phenanthrene could conceivably split up (with, of course, transfer of hydrogen from other structural units) to form 2,3,4-trimethylpentane, as shown in Figure 3. Only those methyl groups required for the formation of 2,3,4-trimethylpentane are shown; additional methyl groups would be present, as determined in previous work¹. One of the benzene rings in this unit could be released as such, or both benzene rings could be incorporated in the formation of the pyrolysis residue or char. The fact that the resins are rich in oxygen (10 to 15 weight-percent) whereas no oxygen-containing organic compounds could be identified in the volatile pyrolysis products would indicate that the oxygen-containing units in the resin (primarily benzene rings with phenolic hydroxyl groups) are involved in char formation. Under these circumstances, there would be a greater proportion of aliphatic compounds than aromatic compounds in the volatile products, such as was actually observed.

Although the pyrolysis results might appear unusual or unexpected, nevertheless the general structure of the resins indicated by these results is the same as that indicated by ring analysis (including ring arrangement), infrared spectra, and ultraviolet spectra¹.

REFERENCES

- 1 KARR, C., JR., COMBERIATI, J. R., and ESTEP, P. A. Fuel, Lond. 1962, 41, 167.
- 2 ESTEP, P. A., and KARR, C., JR. Applied Spectroscopy (accepted for publication).
- 3 DHONT, J. H. Nature 1961, 192, 747.

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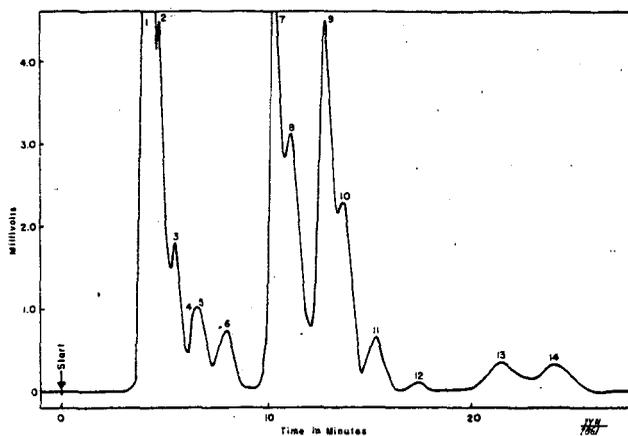


Figure 2. Chromatogram of pyrolysis products from a subbituminous resin.

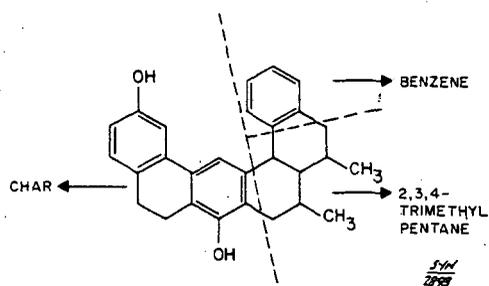


Figure 3. A representation of the pyrolysis of a hypothetical resin molecule.