

## Thermal Degradation of Polymers. II. Mass Spectrometric Thermal Analysis of Phenol-Formaldehyde Polycondensates\*

G. P. SHULMAN and H. W. LOCHTE, *Research Department,  
Martin Company, Baltimore, Maryland*

### Synopsis

The degradation of phenol-formaldehyde polycondensates has been investigated by mass spectrometric thermal analysis to 800°C. The thermal oxidative mechanism proposed by Conley and co-workers has been confirmed. Direct analysis of products at frequent intervals of a temperature-programmed heating cycle demonstrates the existence of postcuring, general degradation, and char-forming stages. Activation energies for formation of each product and for degradation of the polymer have been determined. Phenolic homologs, products of thermal scission of methylene-phenyl bonds, show high activation energies; oxidation products have activation energies comparable to or slightly higher than that for oxidation of methylene bridges to carbonyl groups. The tarry high molecular weight products found on pyrolysis at atmospheric pressure are not formed in high vacuum because recombination reactions of phenols and formaldehyde are minimized. Otherwise, no major change in product composition, as compared to the high heating rate pyrolysis-gas chromatographic investigation of Jackson and Conley, was observed.

### INTRODUCTION

The thermal degradation of phenolic resins has been the subject of numerous investigations. Until quite recently, little conclusive evidence to support a mechanism for the pyrolysis had been obtained, largely as a result of the complex nature of the materials, which creates difficult analytical problems. Beginning with the discovery that oxidative degradation begins during the curing process,<sup>1</sup> work directed toward an understanding of the sequential processes occurring during cure, postcure, degradation, and char formation has been facilitated. Techniques employed previously for study of the phenol-formaldehyde resin (prepared under identical, carefully controlled conditions) included infrared spectrophotometry of heated films,<sup>1,2</sup> pyrolysis-gas chromatography,<sup>2</sup> and elementary analysis of residues from various stages of a thermogravimetric analysis.<sup>3</sup> The current investigation was intended to secure data on the composition and kinetics of formation of the volatile products formed at various temperatures during a linearly programmed heating cycle.

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Mass spectrometric thermal analysis, the determination of total ion current as a function of temperature (and time), has been employed for the investigation of pyrolytic reactions.<sup>4</sup> We have extended this technique to obtain separate determinations of each pyrolysis product as a function of temperature (and time). This can be done continuously, by recording a characteristic peak for each product on an individual channel, or intermittently, by repeating scanning spectra, then plotting peak height as a function of temperature. The latter method has several advantages, provided that the heating rate is low enough to permit taking a spectrum over a limited range. Previously, mass spectrometric determinations of the volatile products from phenolic degradation have been reported, but fractions were collected over a temperature range of 100°C.<sup>5</sup> or 300–500°C.<sup>6a</sup>

By pyrolysis of the resin in the Knudsen cell inlet system of the mass spectrometer, analyses of products may be secured at frequent (<30°C.) intervals of a programmed heating cycle. Each spectrum is obtained over a small enough temperature range ( $\pm 8^\circ\text{C}$ . or less, depending on heating and scanning rates) that it can be considered an isothermal spectrum. In a rapidly pumped system, the response of the mass spectrometer at mass numbers corresponding to a particular species is proportional to its rate of formation. Thus, at each temperature, the rates of formation of the various pyrolysis products can be determined. This process gives results which are, in a sense, comparable to the rates of degradation determined by taking the slopes of a thermogravimetric trace at several temperatures of a programmed heating cycle such that the slope of a semi-logarithmic graph of rate versus reciprocal temperature is a function of the activation energy. The fraction of polymer remaining at any point can be determined from the ratio of the area under the MTA curve above that temperature to the total area, and can be used for calculation of specific rates (i.e., on a weight or molar basis). However, it is generally adequate merely to take the slope in the early stages of the decomposition, while the amount of polymer, or of the structure responsible for a particular product, is essentially constant. Details of the MTA method have been reported previously, indicating the validity of this technique as applied to polymer degradation kinetics.<sup>7</sup>

If a sample is maintained isothermally, peak height is again a measure of the rate of reaction. For first-order reactions, the rate is proportional to the amount of polymer remaining, and semilogarithmic peak height versus time graphs result. From these curves, half-lives and rate constants for formation of each product may be determined, and data from samples at several temperatures may be used to determine activation parameters.

## EXPERIMENTAL

### Mass Spectrometric Thermal Analysis

Two resole type phenolic resin systems were used in this investigation. Their preparation has been described previously (resins B and D).<sup>3</sup> Resin

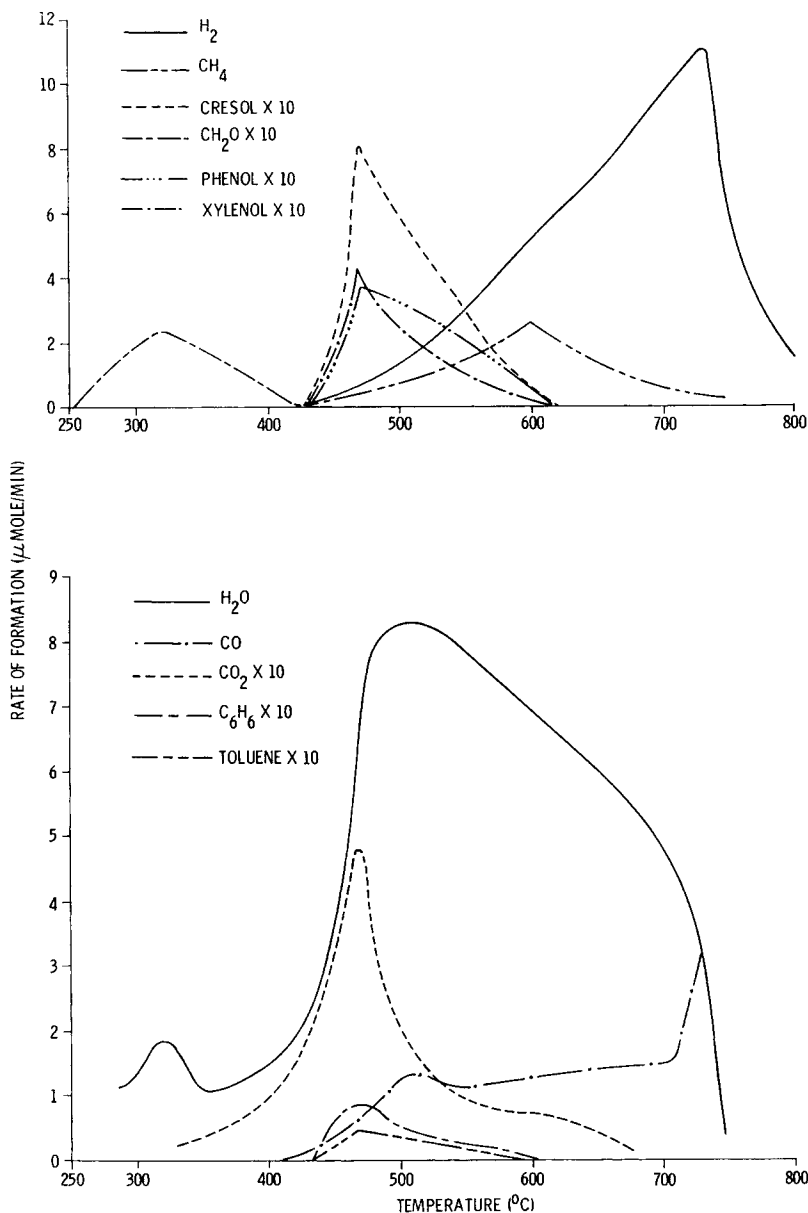


Fig. 1. Effect of temperature on product distribution from pyrolysis of phenol-formaldehyde polycondensates.

B was a polymer prepared with the use of a 2.36 molar ratio of formaldehyde to phenol (F/P ratio) and a calcium hydroxide catalyst (removed by precipitation as carbonate) in aqueous solution. It was cured for 118 hr. in stages up to 230 $^{\circ}\text{C}$ . (in air). Resin D was a polymer prepared at a 2.00 F/P ratio and with a sodium hydroxide catalyst, dried over molecular

TABLE I  
Characteristic Mass Numbers for Products of Phenolic Pyrolysis

Species	Mass no.	Ion	Interfering fragments (Source)
H <sub>2</sub>	2	H <sub>2</sub> <sup>+</sup>	None
CH <sub>4</sub>	15	CH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> <sup>+</sup> (cresol, xylenol)
H <sub>2</sub> O	18	H <sub>2</sub> O <sup>+</sup>	None
CO	28	CO <sup>+</sup>	CO <sup>+</sup> (CO <sub>2</sub> , phenol, cresol, xylenol)
CO	12	C <sup>+</sup>	C <sup>+</sup> (CO <sub>2</sub> )
CH <sub>2</sub> O	29	CHO <sup>+</sup>	COH <sup>+</sup> (xylenol)
CH <sub>2</sub> O	31	CH <sub>2</sub> OH <sup>+</sup>	None
CO <sub>2</sub>	44	CO <sub>2</sub> <sup>+</sup>	None
C <sub>6</sub> H <sub>6</sub>	78	C <sub>6</sub> H <sub>6</sub> <sup>+</sup>	C <sub>6</sub> H <sub>6</sub> <sup>+</sup> (cresol, xylenol)
Toluene	91	C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	None
Phenol	94	C <sub>6</sub> H <sub>5</sub> OH <sup>+</sup>	None
Cresol	107	C <sub>7</sub> H <sub>7</sub> O <sup>+</sup>	None
Xylenol	122	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> <sup>+</sup>	None

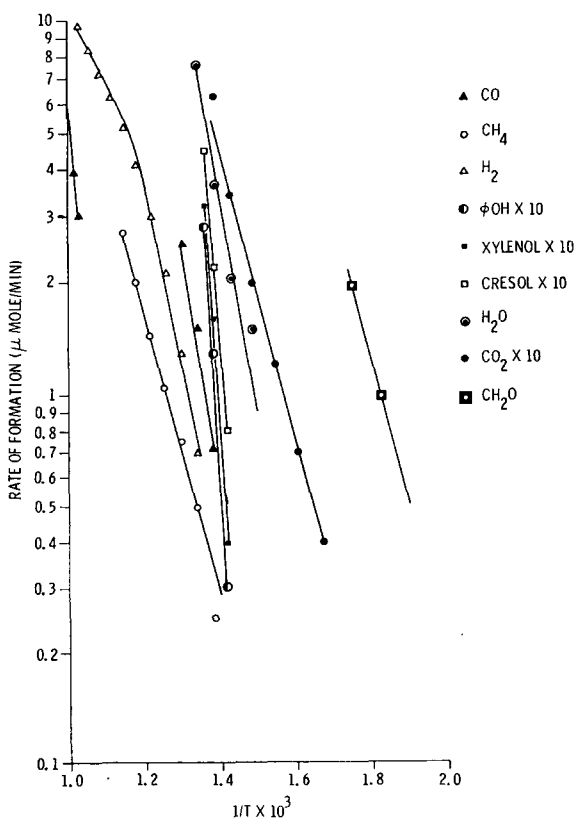


Fig. 2. Temperature dependence of formation rate of products from pyrolysis of phenol-formaldehyde polycondensates.

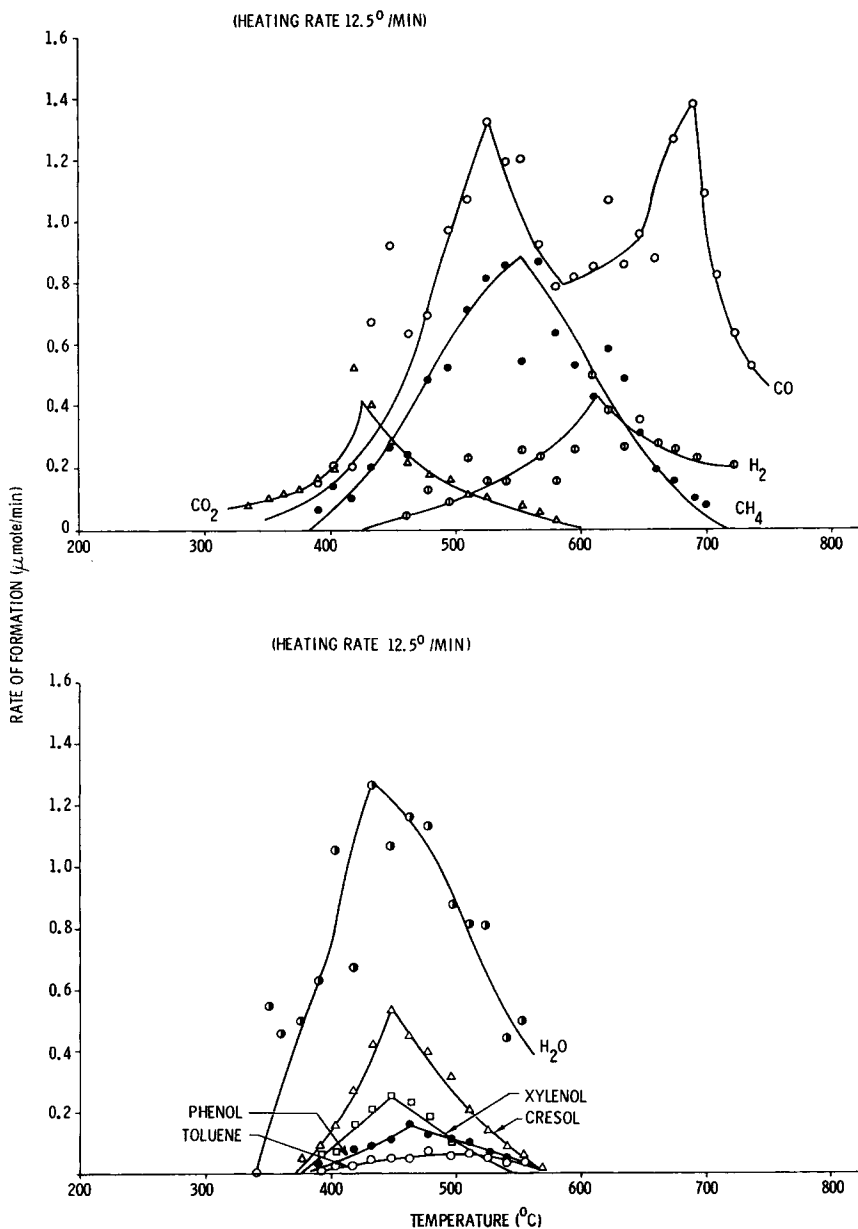


Fig. 3. Effect of temperature on product distribution from pyrolysis of phenolic resin B.

sieves in acetone solution, then cured for 3 hr. at 120°C. in air. A finely powdered sample of resin D weighing 14.9 mg. was placed in the tungsten crucible of the Knudsen cell inlet to the Bendix time-of-flight mass spectrometer, the system was evacuated, then heated at a linear rate of 29°C./min. Spectra from mass 1 to about 200 were determined each minute;

then the heights of the peaks characteristic of each major known product were determined (see Table I). These were corrected for contributions due to fragments of higher molecular weight products. Figure 1 shows the

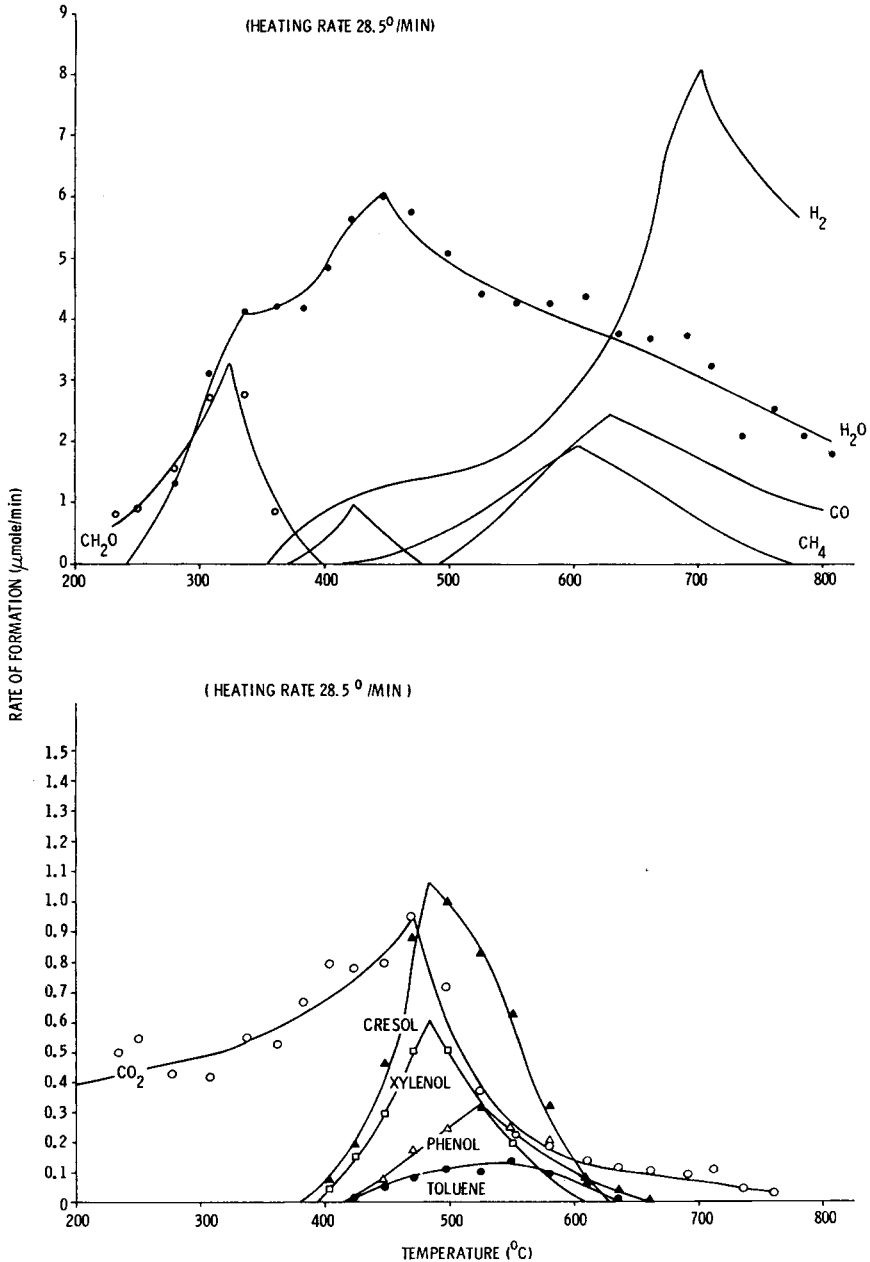


Fig. 4. Effect of temperature on product distribution from pyrolysis of phenolic resin B.

effect of temperature on product distribution; Figure 2 shows a typical Arrhenius plot for the reaction.

Similarly, 6.42 mg. and 6.0 mg. powdered samples of resin B were heated at linear rates of 12.5\* and 28.5°C./min, respectively. Data were recorded and treated in the same way. Figures 3 and 4 show the effect of temperature on product distribution.

TABLE II  
Yield of Products from Phenol-Formaldehyde Polycondensate Heated to 800°C.

Product	Resin D			Resin B		
	Activation energy, kcal./mole	Yield, % of volatile constituents		Activation energy, kcal./mole	Yield, % of volatile constituents	
		29°C./min. <sup>a</sup>	310°C./sec. <sup>b</sup>		12.5 °C./min. <sup>a</sup>	28.5 °C./min. <sup>a</sup>
H <sub>2</sub>	29	6.6	0	32	0.7	3.1
CH <sub>4</sub>	18	9.3	5.0	17	9.5	5.5
H <sub>2</sub> O	- <sup>c</sup> /27 <sup>d</sup>	37.0	<sup>e</sup>	17 <sup>c</sup> /— <sup>d</sup>	14.7	27.0
CO	28 <sup>f</sup> /56 <sup>g</sup>	14.6	8.0	40 <sup>f</sup> /45 <sup>g</sup>	30.0	14.6
CH <sub>2</sub> O	16	7.9	<sup>e</sup>	11	0	8.0
CO <sub>2</sub>	19	3.3	16.0	—	6.8	8.8
C <sub>6</sub> H <sub>6</sub>	—	2.0	3.0	—	0	0
Toluene	—	0.7	0.8	28	2.0	1.4
Phenol	99	4.0	<sup>h</sup>	57	5.5	3.8
Cresols	74	9.3	15.2	48	21.4	18.0
Xylenols	88	5.3	0.8	55	9.4	9.8
High mol. wt.	—	0	<sup>e</sup>	—	0	0
Char	—	52.8	≈50 <sup>e</sup>	—	<sup>e</sup>	<sup>e</sup>

<sup>a</sup> Determined from areas under rate of production versus time graphs (mass spectrometric thermal analysis).

<sup>b</sup> Pyrolysis-gas chromatography.<sup>2</sup>

<sup>c</sup> Temperature range 250–350°C.

<sup>d</sup> Temperature range 400–700°C.

<sup>e</sup> Not determined quantitatively.

<sup>f</sup> Temperature range 400–600°C.

<sup>g</sup> Temperature range 600–750°C.

<sup>h</sup> Included under cresols.

Activation energies for formation of each product were determined from the linear semilogarithmic graph of rate of formation versus reciprocal temperature and are given in Table II. The average activation energy, comparable to that derived from thermogravimetric analysis, was obtained as a function of temperature by averaging those of the various species, weighted by the product of molecular weight and molar rate of formation at the temperature under consideration (Table III).

Calibration factors were determined for these products. Experience indicates that uncontrollable day-to-day variations in detector sensitivity and adjustment of instrument settings limit their absolute accuracy to

\* This sample was held at 200°C. for 15 min. before start of the test.

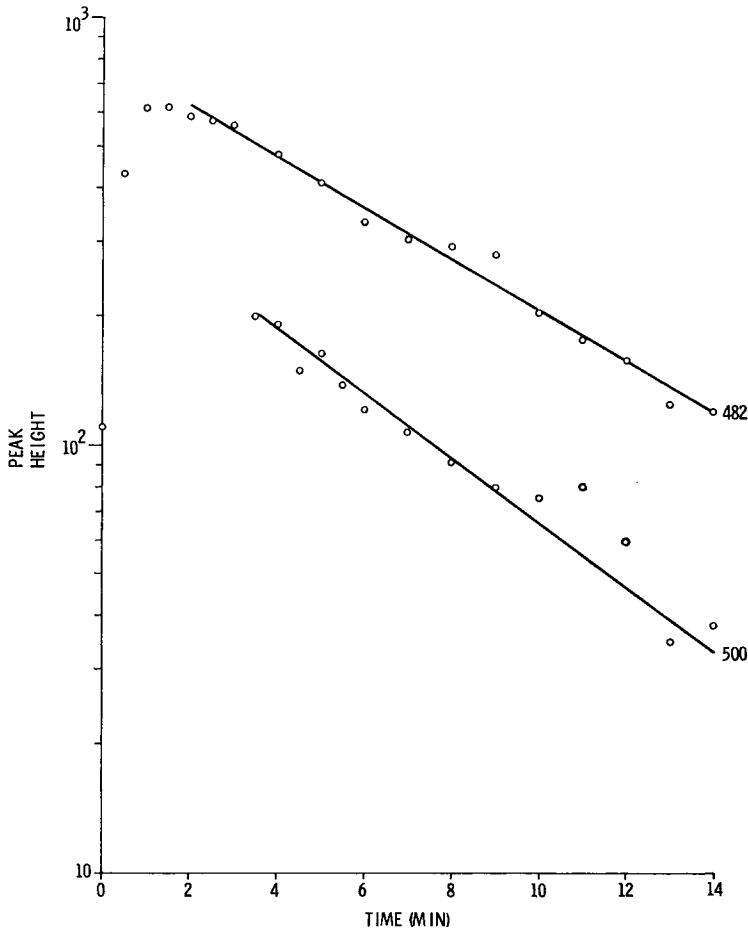


Fig. 5. Isothermal degradation of polytetrafluoroethylene.

rough calculations. Material balances of the resins included in this investigation range from 70 to 110%; thus, one can conclude that roughly 80% of the volatile products are accounted for. The calibration factors do provide a method for determining relative concentrations quite accurately (ca.  $\pm 5\%$ ). Relative yields were then calculated from areas under rate of reaction versus time graphs and are given in Table II.

#### Isothermal Kinetic Studies

To test the validity of the method, samples of molded Teflon cut into small chips were placed in the tungsten crucible of the Knudsen cell. The temperature was raised at the maximum rate (90–150°C./min), then maintained isothermally ( $\pm 2^\circ\text{C}.$ ) until peak heights dropped to a sufficiently small fraction of the original to permit accurate determination of the half life of the reaction. As shown in Figure 5, a linear semilogarithmic rate



TABLE III  
Temperature Dependence of Activation Energy

Temperature, °C.	$E_a$ , kcal.	Method <sup>a</sup>
300	16	A
350	19	A
400	26	A
450	44	A
500	48	A
550	38	A
600	34	A
650	43	A
700	42	A
725	43	A
331-380	18	B
405-428	22	C
400-600	55	D
500-700	13-20	E
140-220	16.7-19.5	F

<sup>a</sup> A = mass spectrometric thermal analysis; B = isothermal weight loss;<sup>6a</sup> C = isothermal mass spectrometric analysis; D = thermogravimetric analysis;<sup>12</sup> E = thermogravimetric analysis;<sup>13</sup> F = infrared spectroscopy.<sup>2,11</sup>

of formation versus time (first-order) relationship is observed. Rate constants were calculated from the relationship

$$k = \ln 2/t_{1/2} = 0.693/t_{1/2}$$

Similarly, kinetics were determined for phenolic resin D in the range of 405-428°C. All products except formaldehyde and water follow a linear semilogarithmic rate of formation versus time relationship with approximately equal half-lives (and hence, rate constants). Figure 6 shows a typical result.

### Pyrolysis-Gas Chromatography

The apparatus previously described<sup>2</sup> was used with a powdered sample of resin D. Pyrolysis was conducted at a heating rate of 310°C./sec. to 800°C., then isothermally for 30 sec.

## DISCUSSION

### Kinetics

Gravimetric methods for the determination of rate of degradation at constant or programmed temperatures are satisfactory only for polymers with insignificant nonvolatile residues. For char-forming polymers, the measurements must be confined to the first few per cent of weight loss to avoid complications introduced by assumption of an active weight fraction, with an inert char equal at all stages of degradation to the product of residual weight fraction and the active fraction which has reacted. This

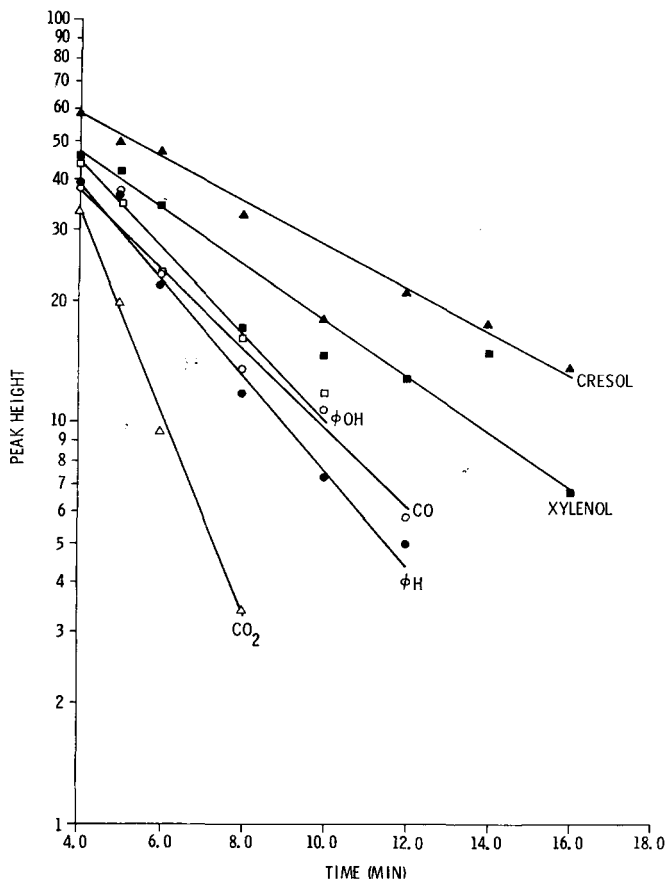


Fig. 6. Isothermal degradation of phenolic resin D at 405°C.

method is not applicable to phenolic resins with any reliability since the initial weight loss is due largely to postcuring rather than general degradation. The alternative assumption is difficult to justify in light of the mass spectrometric thermal analyses and the residue analyses of Lochte et al.<sup>3</sup>

Based on the proportional relationship of peak height to rate of formation, a determination of kinetic parameters is possible by mass spectrometric detection of effluent gases from a polymer maintained isothermally. The rate should then be proportional to the amount of reactive polymer remaining. To test this hypothesis, the rate of degradation of Teflon chips was determined in the range of 482–511°C. Figure 7 compares these data with those of several previous investigations.<sup>6b, 8–10</sup>

The agreement with the manometric measurements of Siegle et al.<sup>8</sup> is particularly good; in fact, both sets of data fit the same curve, with an activation energy of 83 kcal. An Arrhenius plot from a typical mass spectrometric thermal analysis of Teflon is also shown, based on the peak height of the mass 31 (CF) peak. Only trace amounts of C<sub>2</sub>F<sub>6</sub> and hydrogen

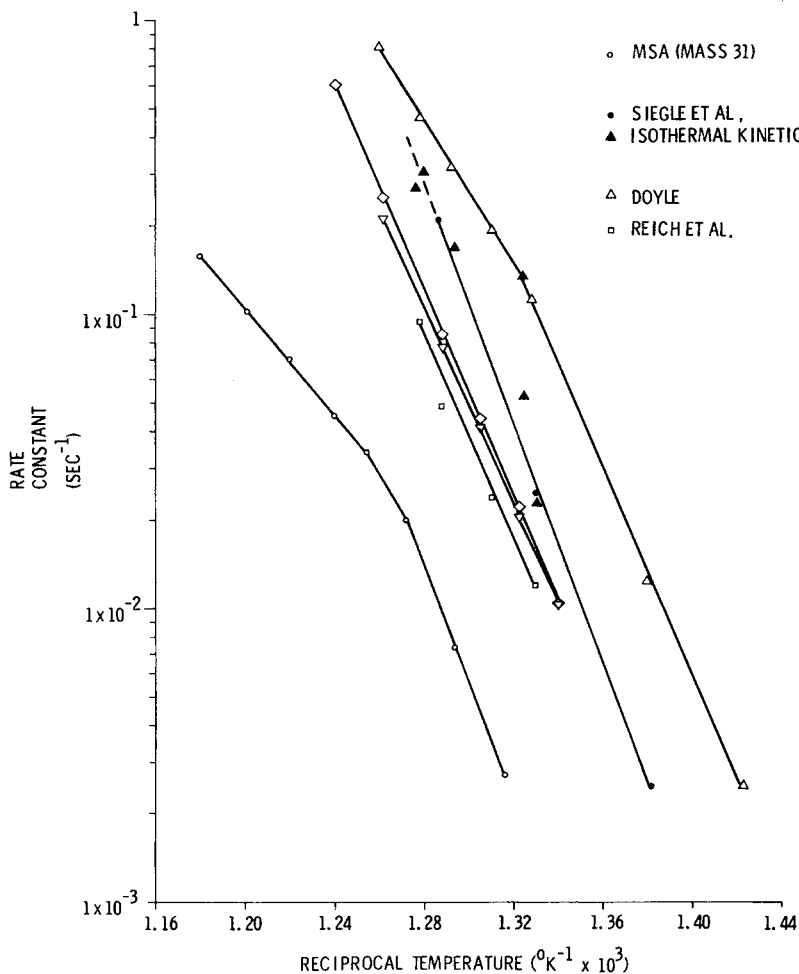


Fig. 7. Temperature dependence of polytetrafluoroethylene degradation.

fluoride were observed, so that the height of any tetrafluoroethylene fragment peak is proportional to the total ion current. Because of the high activation energy, the assumption that the amount of polymer is constant does not hold for long, and pronounced curvature results. However, inspection of Figure 7 shows that the initial portion of the curve is parallel to those determined by other methods.

The general degradation of phenolic resins is a first-order reaction; i.e., all products show a decay that is semilogarithmic in peak height versus time at constant temperature. The rates, and hence peak heights, must be proportional to the amount of active polymer remaining. Table IV shows the individual and average rate constants which were obtained. The activation energy, determined from the slope of an Arrhenius plot, is 22 kcal./mole.

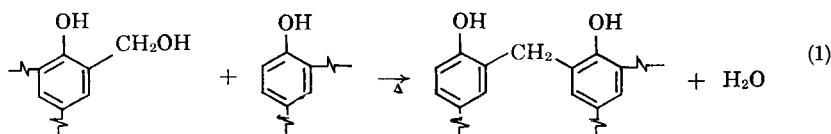
TABLE IV  
Rate Constants for Phenolic Degradation of Phenol-Formaldehyde Resin D

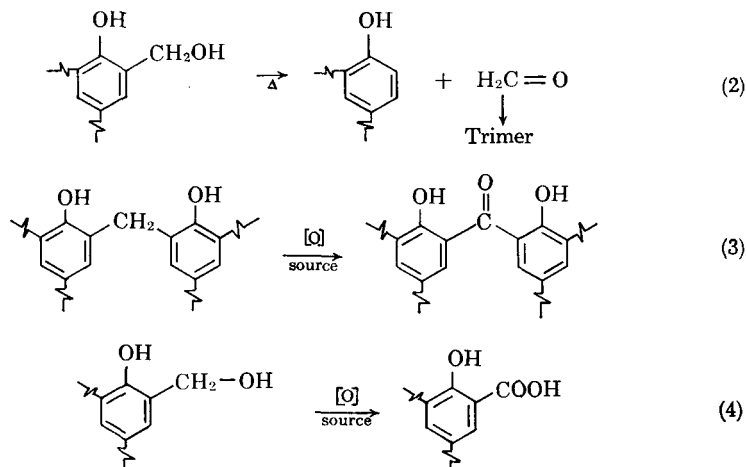
Product	Rate constants, min. <sup>-1</sup>		
	405°C.	415°C.	428°C.
H <sub>2</sub>			0.374
CH <sub>4</sub>		0.374	0.286
CO	0.263		
CO <sub>2</sub>	0.578	0.407	
C <sub>6</sub> H <sub>6</sub>	0.283	0.407	0.462
Toluene	0.250	0.427	
Phenol			0.513
Cresol	0.126	0.340	0.630
Xylenol	0.161	0.338	0.462
Average	0.28 ± 0.11 <sup>a</sup>	0.38 ± 0.04 <sup>a</sup>	0.48 ± 0.17 <sup>a</sup>

<sup>a</sup> Standard deviation.

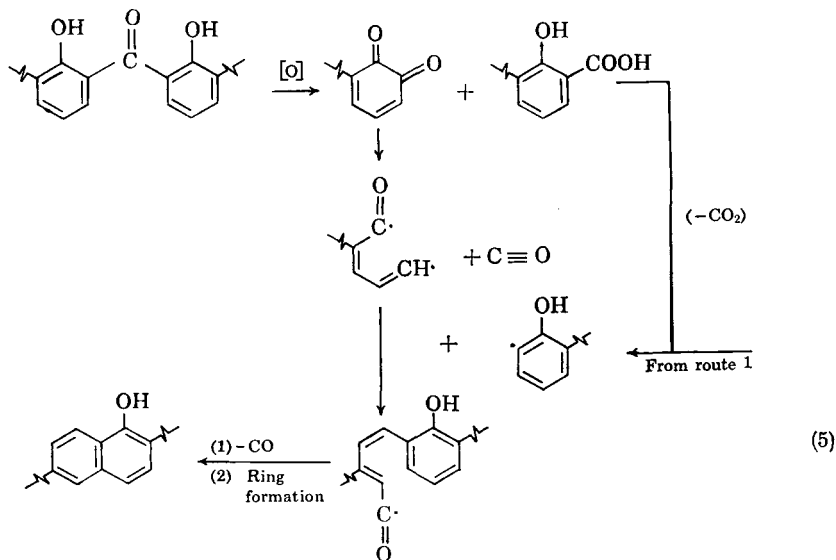
Activation energies for the various degradation products of resins B and D were also derived from mass spectrometric thermal analyses (Table II). Differences between the two resins probably reflect uncertainty in the data rather than variations due to different cures or formaldehyde:phenol ratios. Since the various products have quite different activation energies and are formed in different temperature ranges, the average activation energy is a function of temperature. At lower temperatures (300–400°C.), it is comparable in magnitude to values derived from isothermal kinetic studies described in this report, or by Conley<sup>2,11</sup> from infrared spectroscopy and by Madorsky<sup>6a</sup> from isothermal gravimetric measurements. For polymers with a high percentage of residual char, thermogravimetric kinetic methods are not very satisfactory (comparing data from methods D and E in Table III, for example). The difference between activation energies of 55 kcal. by Friedman<sup>12</sup> and 13–20 kcal. by Farmer<sup>13</sup> is caused principally by using different stages of cure as the basis for determining initial weight. These mass spectrometric kinetic methods can give much more reliable data in such systems, although infrared spectrophotometry is preferable for examination of initial stages of degradation.

A reaction scheme accounting for the decomposition products of phenol-formaldehyde polymers has been proposed.<sup>2</sup> At temperatures below 400°C., synthesis reactions are still occurring, with liberation of water by condensation (aromatic substitution) of methylol groups, and of formaldehyde by reversal of the synthesis as shown in eqs. (1) and (2). In competition with these are the oxidative reactions shown in eqs. (3) and (4). Methylene and methylol structures are oxidized to carbonyl and carboxyl groups, respectively, with liberation of water.





General degradation occurs in the range of 400–600°C. Thermal oxidative processes lead to carbon monoxide, carbon dioxide, benzaldehyde, benzene, and toluene (Fig. 8, routes I and III), while thermal fragmentation reactions account for formation of methane, phenol, and phenolic homologs (route II). At temperatures above 600°C., carbon monoxide liberation accompanies condensation to a fused-ring, deoxygenated char structure, as shown in the postulated char-forming reactions summarized in eq. (5).



The mass spectrometric thermal analyses generally confirm this mechanism. There is a direct demonstration of the postcuring stage at 250–400°C., involving water and formaldehyde as the only volatile products. Activation energies are 11–16 kcal./mole for formaldehyde (which must be a product of postcuring), 17 kcal./mole for water, and 16.7–19.5 kcal./mole

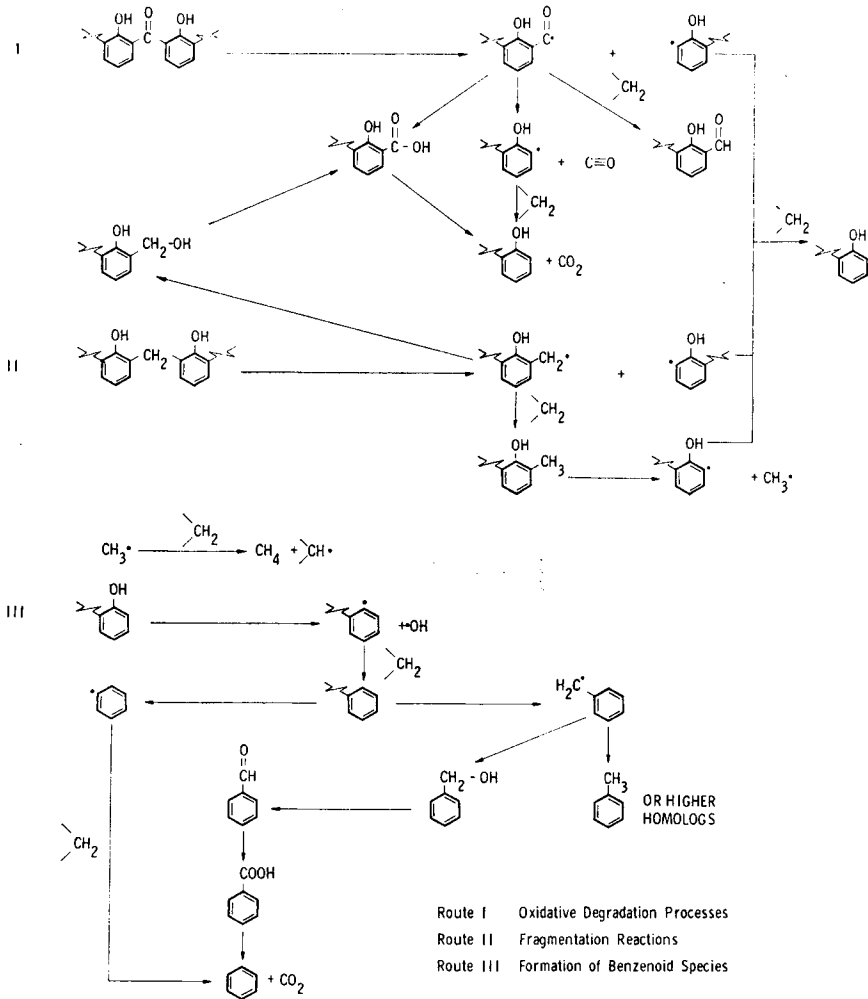


Fig. 8. Typical reactions proposed for resin decomposition at elevated temperatures.

for the low-temperature oxidation.<sup>2,11</sup> It is impossible to define the source of the water formed in this temperature range based on the evidence available, but most likely both oxidation and postcuring are taking place.

General degradation at 400–600°C. leads to all of the products observed except formaldehyde, which is no longer significant above 400°C., and hydrogen, which is not evolved until higher temperatures are reached. Water trapped in the polymer (observed in the infrared spectrum) is liberated when the physical structure of the polymer deteriorates. The activation energy might be expected to be about 10 kcal./mole, the heat of vaporization of water. The observed value of 27 kcal./mole is probably not related to any water-forming reaction, but instead represents the average activation energy for phenolic degradation. None of the products of

oxidative degradation has an activation energy lower than that for oxidation of methylene bridges. For carbon monoxide, which has a significantly higher activation energy, there must be a subsequent energy barrier. Evidence that phenolic products are formed by a thermal fragmentation process (Fig. 8, route II) is the high activation energies for formation of phenol, cresol, and xylenol ( $75 \pm 25$  kcal./mole) and the molar ratios in which they are formed.

In a polymer with little crosslinking, a 1:2:1 ratio of phenol:cresol:xylenol would be predicted, assuming random scission of methylene-phenyl bonds. This is the ratio for resin D. The 5:18:8 ratio of resin B is consistent with the higher formaldehyde:phenol ratio and more extensive cure. Two carbon monoxide peaks, corresponding to elimination of carbon monoxide from benzophenone linkages of the oxidized polymer (route I) at 400–600°C. and from phenolic functional groups (char formation) at 600–750°C., were observed. Hydrogen is also liberated during char formation.

There is surprisingly little difference between the composition of the volatile products from pyrolysis at 29°C./min. to 800°C. in the Knudsen cell and from pyrolysis at 310°C./sec. to 800°C. in the pyrolysis unit of the gas chromatograph.<sup>2</sup> The only major discrepancy is in the amounts of carbon monoxide and dioxide. That this is due to a difference in the nature of the polymer rather than in the reaction conditions was established by pyrolyzing a sample of this material under the same conditions employed by Jackson and Conley.<sup>2</sup> The ratio of carbon monoxide to carbon dioxide was high. The infrared spectrum did not differ markedly from that of the polymer used previously, although the carbonyl absorption at 6.03  $\mu$  was somewhat lower relative to the band at 6.25  $\mu$ , indicative of a lower degree of oxidation.

Differences between resins B and D are those expected from the changes in phenol to formaldehyde ratio and curing conditions. Resin B, with excess formaldehyde, must contain more methylol groups and/or methylene bridges. Consistent with the structural changes, yields of carbon dioxide (from methylol oxidation), toluene, cresol, and xylenol are significantly higher, while benzene and hydrogen yields have decreased.

A marked decrease in activation energy for pyrolysis in vacuum has been reported.<sup>8</sup> No significant products with masses above 122 were observed in the mass spectrum. At atmospheric pressure, appreciable amounts of tarry degradation products of low volatility are formed. These appear likely to be low molecular weight phenol-formaldehyde condensates.<sup>1,11</sup> The rate of reaction of phenol vapor and formaldehyde at the low partial pressures of the mass spectrometer would be negligible. The effect of higher pressure is to delay evaporation of marginally volatile pyrolysis products until higher temperatures are reached, causing a lower rate (by TGA) at low temperatures and a higher rate at elevated temperatures, and resulting in an artificially high activation energy.

In conclusion, we would like to emphasize the need for caution in inter-

preting mass spectra of unfractionated polymer degradation products. Previous reports on phenolic resins<sup>6a,14</sup> have included a number of products which could not be obtained in our laboratories, and have failed to include several of the major oxygenated products. These discrepancies are, perhaps, partially a result of variations in structure and purity of the resin, or in experimental conditions. While these factors might account for many of the minor products reported, it is not likely that variations of these types could account for failure to observe phenol or phenolic homologs. The authors recommend most strongly that, unless other confirmatory methods for identification of products are employed, definitive assignment of products from degradation of condensation polymers not be made by mass spectrometry.

The authors gratefully acknowledge the advice and assistance given by Dr. Robert T. Conley in the course of this work.

### References

1. Conley, R. T., and J. F. Bieron, *J. Appl. Polymer Sci.*, **7**, 103 (1963).
2. Jackson, W. M., and R. T. Conley, *J. Appl. Polymer Sci.*, **8**, 2163 (1964).
3. Lochte, H. W., E. L. Strauss, and R. T. Conley, *J. Appl. Polymer Sci.*, **9**, 2799 (1965).
4. Langer, H. G., and R. S. Gohlke, *Anal. Chem.*, **35**, 1301 (1963).
5. Ouchi, K., and H. Honda, *Fuel*, **38**, 429 (1959).
6. Madorsky, S. L., *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964, (a) p. 288; (b) p. 136.
7. Shulman, G. P., *J. Polymer Sci.*, **B3**, 911 (1965).
8. Siegle, J. C., L. T. Muus, T. P. Lin, and H. A. Larsen, *J. Polymer Sci.*, **A2**, 391 (1964).
9. Reich, L., H. T. Lee, and D. W. Levi, *J. Polymer Sci.*, **B1**, 535 (1963).
10. Doyle, C. D., *J. Appl. Polymer Sci.*, **5**, 285 (1961).
11. Conley, R. T., and J. F. Bieron, *J. Appl. Polymer Sci.*, **7**, 171 (1963).
12. Friedman, H. L., *J. Polymer Sci.*, **C6**, 183 (1964).
13. Farmer, R. W., Technical Documentary Report No. ASD-TDR-62-1043, Part I, February 1963, p. 32.
14. Friedman, H. L., *J. Appl. Polymer Sci.*, **9**, 651 (1965).

### Résumé

La dégradation de polycondensats phénol-formaldéhyde a été étudiée par analyse thermique au spectrographe de masse jusque 800°C. Le mécanisme d'oxydation thermique proposé par Conley et collaborateurs a été confirmé. L'analyse directe des produits à intervalles fréquents du cycle température-chauffage a montré l'existence de post-durcissements, de dégradation généralisée et d'étapes de résinification. Les énergies d'activation pour la formation de chaque produit et de dégradation du polymère ont été déterminées. Les homologues phénoliques, les produits de scission thermique des liaisons phényl méthyléniques montrent des énergies d'activation élevées; les produits d'oxydation ont des énergies d'activation comparables ou légèrement inférieures à celles de l'oxydation des ponts méthyléniques entre des groupes carbonyles. Les produits goudronneux de poids moléculaire élevé obtenu au cours de pyrolyses à pression atmosphérique ne sont pas formés sous vide élevé parce les réactions de recombinaison de phénols et formaldéhydes sont minimisées. Par ailleurs, aucun changement majeur de composition en produit n'a été observé, tel que cela a été décrit au cours de l'étude par



chromatographie gaseuse de Jackson et Conley concernant la pyrolyse, à vitesse de chauffe élevée.

### Zusammenfassung

Der Abbau von Phenol-Formaldehydpolykondensaten wurde durch massenspektrometrische thermische Analyse bis zu 800°C untersucht. Der von Conley und Mitarbeitern vorgeschlagene thermisch-oxydative Mechanismus wurde bestätigt. Direkte Produktanalyse in kurzen Intervallen eines temperaturprogrammierten Erhitzungszyklus zeigt das Vorhandensein von Nachhärtungs-, allgemeinen Abbau- und Verkohlungsphasen. Aktivierungsenergien für die Bildung aller Produkte und für den Abbau des Polymeren wurden bestimmt. Phenolhomologe, Produkte der thermischen Spaltung von Methylen-Phenylbindungen zeigen hohe Aktivierungsenergien; Oxydationsprodukte besitzen Aktivierungsenergien, welche vergleichbar oder schwach höher als diejenigen für die Oxydation von Methylenbrücken zu Carbonylgruppen sind. Die bei der Pyrolyse unter Atmosphärendruck auftretenden teerartigen hochmolekularen Produkte werden unter Hochvakuum nicht gebildet, da die Rekombinationsreaktionen von Phenolen und Formaldehyd auf ein Minimum gebracht werden. In andere Hinsicht wurde keine grössere Änderung der Produktzusammensetzung im Vergleich zur gaschromatographischen Untersuchung der Pyrolyse bei hoher Erhitzungsgeschwindigkeit von Jackson und Conley beobachtet.

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