

AN EVALUATION OF PYROLYTIC TECHNIQUES WITH REGARD TO THE APOLLO 11, 12 AND 14 LUNAR SAMPLES ANALYSES

BARTHOLOMEW NAGY, M. A. JABBAR MOHAMMED, and
VINCENT E. MODZELESKI

Dept. of Geosciences, The University of Arizona, Tucson, Ariz., U.S.A.

(Received 16 February, 1972)

Abstract. Two different pyrolysis techniques have been used in the analysis of lunar fines. The first technique involved pyrolysis at 700°C under an inert atmosphere in a flowing He system at normal pressure. The products were collected at liquid N₂ temperature and then allowed to pass instantaneously into a combined capillary gas chromatograph-mass spectrometer. The second technique consisted of a vacuum pyrolysis where the sample was first degassed at 150°C and then pyrolyzed at 500°C and 1000°C consecutively. The products were again collected at liquid N₂ temperature and then they were directly introduced to the ion source of the mass spectrometer through a modified gas inlet system.

An evaluation of the two techniques based on control experiments has shown that the probability of secondary reactions is greater in the inert atmosphere pyrolysis method. Pyrolysis of benzene in He under atmospheric pressure at 600°C showed the presence of small quantities of biphenyl and trace amounts of naphthalene. Biphenyl pyrolyzed under vacuum at 600, 700, 800 and 900°C by passing through a hot zone containing a quartz wool plug showed the presence of a wide range of synthesis and breakdown products as the temperature increased.

These experiments have shown the importance of taking into account the factors that influence pyrolytic degradation and/or the synthesis of products. These can be diffusion effects, involving sample size, sample form, pyrolysis pressure conditions; temperature, catalytic effects from the pyrolysis vessel, contamination, perhaps other factors. Pyrolysis is an effective method of analysis if used under carefully controlled conditions. Pyrolysis of Apollo 14 lunar fines and scrapings from an astronaut's glove gave different products by mass spectrometry and showed different looking flaky materials upon scanning electron microscopy.

1. Introduction

Pyrolysis has been extensively used during the last twenty-five years particularly as a standard technique to study the kinetics and mechanisms of the breakdown of macromolecular materials such as synthetic polymers and natural products [1, 2, 3, 4, 5]. Pyrolysis of polymers in vacuum has been carried out as early as 1860 by Williams [6] when natural rubber was degraded by destructive distillation and most of the products were identified. Polystyrene was first degraded in vacuum in 1935 by Staudinger and Steinhöfer [7]. In addition to elucidating molecular structures, this technique can also provide information about the bond strengths of the molecules. Degradation can be caused by any energy source such as heat, light, infrared, ultraviolet or gamma radiations, as well as by ultrasonic and mechanical stress. Thermal degradation appears to be experimentally the most convenient means, because the main requirements, a suitable heat source and accurate measurements of the temperature of the sample, are usually readily available. Pyrolytic degradation fragments may be identical, i.e. repetitive units, as is the case with polymethylmethacrylate, poly-

styrene, polyethylene, etc. or they may have no relation to the original structure as in the case of polyvinylchloride. The pyrolytic degradation products derived from coal are highly variable depending on the origin and rank of the coal.

Simmonds *et al.* [8] performed their pyrolyses experiments under a helium atmosphere in a system connected to a tandem gas chromatograph-mass spectrometer. Murphy *et al.* [9], on the other hand, used vacuum pyrolysis directly at the ion source of the mass spectrometer.

2. Factors Influencing Pyrolysis

To get meaningful information from the pyrolysis products, pyrolysis must be conducted under carefully controlled conditions in order to minimize or ideally eliminate secondary reactions. When a fragment is liberated from a molecule in the hot zone it must pass through the rest of the heated sample. Therefore, intra- or intermolecular chemical reactions may take place, and the pyrolysis products may interact with original material not yet pyrolyzed, particularly if these fragments are active free radicals. It is obvious, therefore, that in a very thin layer of sample, diffusion effects would be minimized, and that the thickness of the layer of the sample is a significant factor in pyrolysis (Figure 1). The form and shape of the sample, i.e. whether it is a powder or a film, are also important considerations (Figure 2). Diffusion effects in thin films are less likely to occur because there is less chance of the volatile

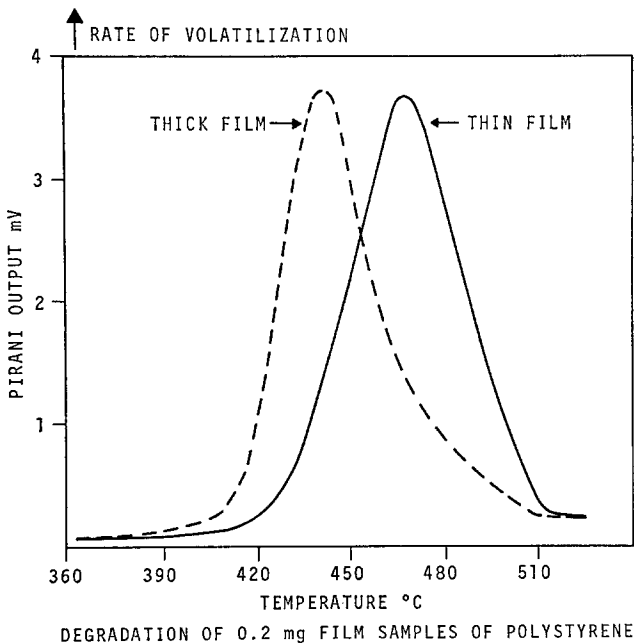


Fig. 1. Temperature programmed degradation of thick and thin films of polystyrene, [10]. Temperatures quoted in Figures 1 and 2 are sample temperatures.

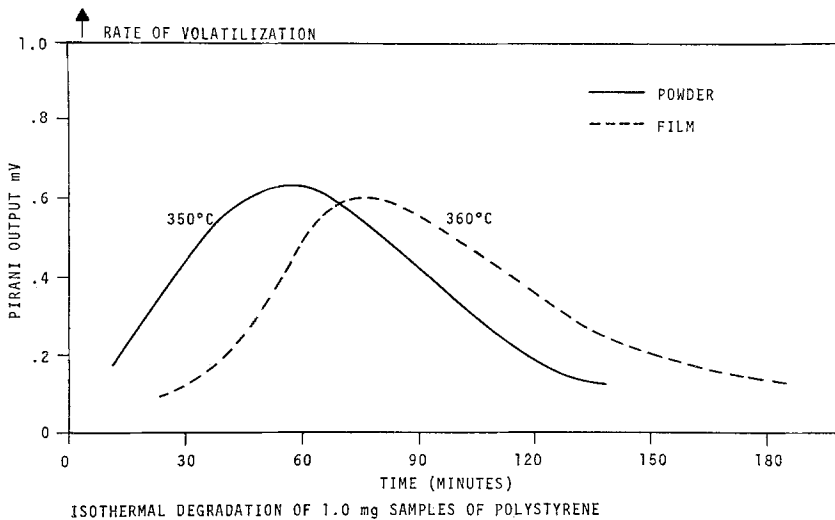


Fig. 2. Isothermal degradation of polystyrene, powder and film, [11].

products interacting with the unpyrolyzed material in the film. The rate of removal of fragments from the vicinity of the reaction zone may also affect secondary reactions. Elevated pressures, whether resulting from the pyrolysis products or from gases introduced into the system, will hinder the rapid removal of the fragments, thereby increasing the probability of secondary reactions. Catalytic effects may also influence the nature of the pyrolysis products. The sample chamber itself may have catalytic properties depending on its composition and its surface character. Copper has been found to affect the rate of volatilization during the pyrolysis of some polymers [3]. An additional example of metallic catalysts are iron, nickel and cobalt which are commonly used in the well-known Fischer-Tropsch synthesis. Contaminations on sample and reaction vessel surfaces may also affect the products. It is conceivable that lunar fines may have some catalytic properties, but this has not yet been proven.

The nature of the volatile products of organic substances depends to a large extent on the pyrolysis temperature. The higher the temperature the greater is the fragmentation of the original sample and of the resultant fragments themselves. Isothermal temperatures or programmed temperature increase may be additional factors in pyrolysis. The rate of formation of volatile products increases with temperature. For example, in the case of teflon, which is one of the most thermally stable polymers, the rate of volatile production at 500°C is about one percent per minute, whereas the rate is much higher at 1000°C. A knowledge of the previous thermal history of a given sample may reveal whether the material has already been partially degraded or polymerized prior to analysis.

Polymers degrade much faster under an atmosphere of air or oxygen. Oxygen may

react with the polymer and cause further fragmentation in the sample. It may also react with the gaseous degradation products causing secondary reactions.

It should be noted that an important factor in degradative type analyses is the nature of the activation energy and the strength of the chemical bonds of the molecules. The stereochemistry of the molecules may also be important in this connection.

3. Pyrolytic Techniques Used for Lunar Sample Organic Analyses

A Hamilton pyrolysis unit, modified for use for the lunar analyses consisted essentially of a fused quartz tube, a part of which was surrounded by a furnace.

Helium purified by passing it through a molecular sieve gas filter, flowed through the quartz tube at a rate of 3–5 ml min⁻¹. The effluent He was directly connected, by way of a heated transfer line and a small liquid N₂ trap, to a Perkin-Elmer Model 226, capillary column gas chromatograph. The He also served as the carrier gas for the gas chromatograph. The gas chromatograph in turn was connected by a Watson-Biemann molecular separator to a Hitachi RMU-6E single focusing mass spectrometer. For analysis, powdered samples were placed in the cool holding zone of the quartz tube of the Hamilton pyrolyzer and allowed to be purged of air by the helium stream. The pyrolyzer tube was then tipped in order to instantaneously transfer the sample into the hot zone where it formed a plug of powdered matter. Samples were pyrolyzed at 700°C for 7½ min. The pyrolysis products were collected in a capillary, stainless steel liquid N₂ trap and, upon completion of the pyrolysis, were flashed into the gas chromatographic column by heating the trap rapidly with a small oven to 250–300°C. Prior to each analysis, satisfactory blank runs were performed, and the quartz tubes were cleaned with a 85:15 v/v mixture of hot concentrated sulfuric and nitric acids.

Using this technique, a control experiment was performed by pyrolyzing benzene in helium at 600°C for 45s. After pyrolysis, a small biphenyl gas chromatographic peak and a trace of naphthalene were observed and identified by mass spectrometry in addition to the parent benzene. It may be of interest to note that it has been found by some workers [10] that when benzene is irradiated, biphenyl is formed together with a polymer and a wide range of other radiolysis products.

In order to evaluate the effectiveness of the Hamilton pyrolysis system, a vacuum pyrolysis technique was developed where the sample was pyrolyzed at isothermal temperatures as a thin layer in a quartz tube having a flat broad base. The system was connected with the modified mass spectrometer gas inlet system; the ion gauge, located near the ion source, registered a vacuum in the mass spectrometer of $\sim 10^{-7}$ mm Hg (Figure 3). The degradation products were collected in a cold trap at liquid N₂ temperature. Immediately after pyrolysis, as the trap was allowed to reach room temperature, the products were simultaneously passed into the ion source of the mass spectrometer for analysis.

A control experiment was performed to evaluate the vacuum pyrolysis technique. Biphenyl was passed over a plug of quartz wool heated to 500, 600, 700, 800 and 900°C respectively (Figure 3), and the products condensed in the liquid N₂ trap.

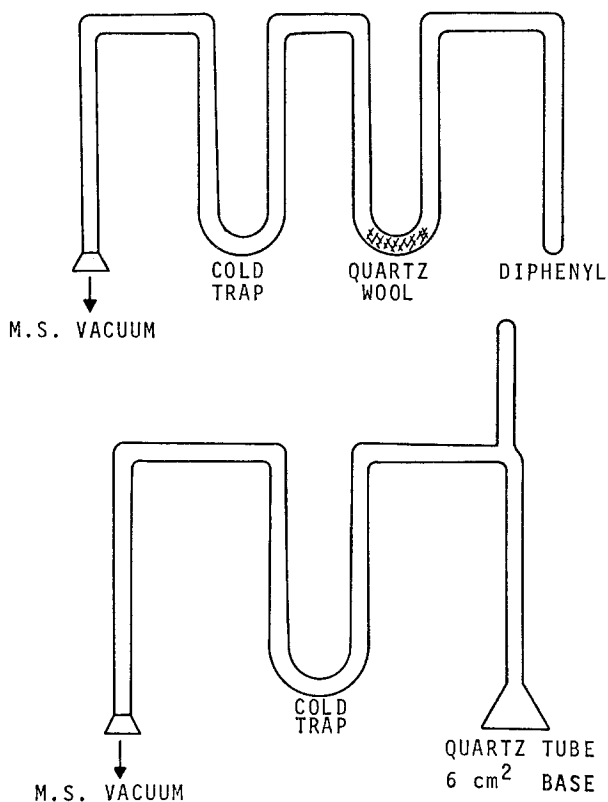


Fig. 3. Vacuum pyrolysis apparatus, for biphenyl degradation study (above), apparatus for lunar sample vacuum pyrolysis (below).

These products were then analyzed by mass spectrometry. A wide range of synthesis and breakdown products of biphenyl increased above 600°C ; some of these products were benzene, naphthalene and higher molecular weight products as well as substituted benzenes with a side group such as cyclopropene and cyclopentene. Consequently, both the vacuum pyrolysis and pyrolysis in an inert atmosphere can lead to secondary reaction products if they are not used under optimum conditions.

4. Discussion

Since in the vacuum pyrolysis method which was used for the Apollo 14 lunar samples the fines were distributed as thin layers on the flat base of the pyrolysis tube and degassed in high vacuum at 150°C for one hour, the chances of secondary reactions occurring are statistically much less than in the case of the He pyrolysis method. The thin sample distribution minimizes diffusion effects, degassing at 150°C in high vacuum lessens the possibility of catalytic effects from contaminations adsorbed on particulate surfaces, and vacuum allows the rapid removal of the degradation products

from the hot zone. However, the vacuum pyrolysis method as presently used in this laboratory does not permit the gas chromatographic separation of individual components which was possible with the Hamilton pyrolysis method. However, it was possible to obtain high resolution mass spectra on the vacuum pyrolyzates, which could not be performed with the atmospheric pyrolysis method.

The Hamilton helium pyrolysis method, while allowing for the gas chromatographic separation of individual components, has the disadvantage of pyrolyzing the sample as a plug which forces the degradation products to travel through substantial distances of hot powdered sample, increasing the chances of secondary reactions caused by diffusion effects. Atmospheric pressures within the pyrolyzer might hinder the rapid removal of the products from the hot zone. It should be noted, however, that pyrolysis by the Hamilton method takes place in a flowing system ($3\text{--}5\text{ ml min}^{-1}$) so that pressure effects might tend to be somewhat diminished as the He flow is constantly sweeping products away from the hot zone.

5. Preliminary Results of the Vacuum Pyrolysis of the Apollo 14 Lunar Fines

Apollo 14 lunar fines, including the SESC sample, have been pyrolyzed at 500° and 1000°C in the high vacuum system described previously. Care was taken that the samples were distributed in thin layers at the bottom of the flat pyrolysis tube. The samples had been degassed prior to these experiments at 150°C for one hour by connecting the pyrolysis tube to the mass spectrometer in which the ionization gauge registered vacuum of $3\text{--}4 \times 10^{-7}$ mmHg. The most common products of the lunar samples were carbon dioxide, carbon monoxide and methane. The total carbon contribution expressed in ppm, from these gases is shown in Table I. In addition, this

TABLE I
Apollo 14 – Gas Analyses

Sample	ppm C from the gases			
	CO	CO ₂	CH ₄	Total ppm C
14240 (SESC)	82.1	31.2	1.0	114.3
14003.55 (contingency)	72.1	28.3	1.4	101.8
14421.9 (fines)	88.6	22.6	2.0	113.2

Apollo 14 – Gas analyses

Sample	%C from gases		
	CO	CO ₂	CH ₄
14240 (SESC)	71.8	27.3	0.9
14003.55 (contingency)	70.8	27.8	1.4
14421.9 (fines)	78.3	20.0	1.7

table lists the percentage contributions of each of these gases to the total carbon content. Furthermore, much lesser quantities of higher molecular weight organic substances have also been detected. Ions at $m/e=78$, and 91 were always present at 500°C. At 1000°C, the $m/e=78$ ion was still noticeable and a number of low molecular weight sulfur containing ions appeared on the mass spectra. The SESC sample mass spectra had approximately the same abundance of organic ions as the other lunar samples, however, at 500°C, it was richer in benzene and in the tropylium ion. A control experiment conducted with an astronaut's training glove has shown entirely different spectra. Scrapings from the surface layer of the glove revealed different mass distribution, containing an abundance of many higher molecular weight ions than were present in the SESC sample. However, the glove pyrolyzate also contained the $m/e=78$ ion. The mass spectral results are interesting because the SESC sample contained an abundance of flaky, wrinkled polymer-like sheets which were originally thought to be derived from the astronauts' gloves. Scanning electron microscopy supported the mass spectrometric data and showed that the flaky material from the surface of the astronaut's glove and the SESC sample had different appearances.

Acknowledgment

This investigation has been supported by the National Aeronautics and Space Administration Grant NGR 03-002-237.

References

- [1] *Polymer Degradation Mechanisms*, National Bureau of Standards, Circular 525, Washington, D.C., 1953.
- [2] *Thermal Degradation of Polymers*, Monograph No. 13, Soc. Chem. Ind., London, 1961.
- [3] Grassie, N.: 1955, *Chemistry of High Polymer Degradation Processes*, Butterworths, London.
- [4] Jellinek, H. H. G.: *Degradation of Vinyl Polymers*, Academic Press, New York, 1955.
- [5] Madorsky, S. L.: 1964, *Thermal Degradation of Organic Polymers*, Interscience, New York.
- [6] Williams, C. G.: 1860, *Phil. Trans.* **150**, 241.
- [7] Staudinger, H. and Steinhofner, A.: 1935, *Ann. Chemie* **517**, 35.
- [8] Simmonds, P. G., Schulman, G. P., and Stembridge, C. H.: 1969, *J. Chrom. Sci.* **7**, 36.
- [9] Murphy, R. C., Preti, G., Nafissi-V., M. M., and Biemann, K.: 1970, *Proc. Apollo 11 Lunar Sci. Conf. Geochim. Cosmochim. Acta, Suppl. 1*, **2**, 1891.
- [10] Sherman, W. V.: 1969, in G. H. Williams (ed.), *Advances in Radical Chemistry*, Vol. III, Academic Press, New York.
- [11] Mohammed, M. A. J.: 1970, *Studies of Thermal Stability of Polymers by Thermal Volatilisation Analysis*, Ph.D. Thesis, Glasgow University, Scotland.