

Reacting Fluids Laboratory
Department of Chemical Engineering
Louisiana State University
Baton Rouge, Louisiana

Status Report

on

COMPARISON OF METHODS FOR DETERMINING
THE COMPOSITION OF PYROLYSIS
PRODUCTS FROM THE DEGRADATION OF ABLATIVE COMPOSITES

by

Simon Hacker, Student Assistant
Gary C. April, Graduate Associate
Eduardo G. del Valle, Graduate Associate
Ralph W. Pike, Associate Professor
Principal Investigator

ngl

NASA Grant NGR 19-001-059

Analysis of the Interaction of Ablative Protection
Systems and Stagnation Region Heating

NASA-RFL-9

February 15, 1970

70-24399 (ACCESSION NUMBER)
42 (PAGES)
CR-66929 (NASA CR OR TMX OR AD NUMBER)
1 (THRU)
06 (CODE)
06 (CATEGORY)

FACILITY FORM 602



TABLE OF CONTENTS

	page
I. SUMMARY	1
II. INTRODUCTION	2
III. METHODS FOR ESTIMATING PYROLYSIS PRODUCT COMPOSITIONS	4
Chemical Analysis of the Pyrolysis Gases	4
Comparison of the Experimentally Measured and Calculated Heat of Pyrolysis	5
Pyrolysis Product Composition by Relative Strength or Weakness	8
Restricted Equilibrium Analysis	12
IV. COMPARISON OF THE METHODS FOR ESTIMATING THE PYROLYSIS GAS COMPOSITIONS	15
Comparison of Experimentally Measured and Computed Heat of Pyrolysis	15
Restricted Equilibrium Analysis	24
Representative Pyrolysis Gas Compositions from Nylon-Phenolic Resin Ablative Composites	26
V. LITERATURE CITED	31
VI. NOMENCLATURE	32
VII. APPENDIX A: HEATS OF COMBUSTION AND FORMATION OF NYLON, PHENOLIC RESIN (CURED AND UNCURED) AND PHENOLIC MICROBALOONS	33
Theory	33
Description of Apparatus	37
Experimental Results	38
Sample Calculations of the Heat of Combustion	38
VIII. DISTRIBUTION	42

I. SUMMARY

An accurate description of the pyrolysis products formed from the degradation of ablative composites is required to accurately compute the energy absorbed by the heatshield during planetary entry. These products undergo chemical reactions as they pass through the char zone and are injected into the boundary layer. Key in the analysis of the energy transferred to the ablator surface is an accurate chemical model of the species entering the shock layer. This is particularly true for reentry speeds of 50,000 ft/sec where radiation from the shock heated gas to the surface is a significant portion of the energy transferred to the surface since the radiant energy is particularly sensitive to the ablative products distribution.

To obtain a representative composition of the pyrolysis products being given off in the decomposition zone from the degrading ablative composite a combination of four methods were used. These were 1. chemical analysis of the pyrolysis gases reported in the literature, 2. comparison of experimentally measured and calculated heats of pyrolysis, 3. relative strength or weakness of chemical bonds and 4. restricted chemical equilibrium. This report compares the results from among these methods for the prediction of the composition of the pyrolysis products. No one of the methods is clearly outstanding, but one and two above are definitely superior to three and four. Combining the results obtained for the four techniques a representative composition is proposed for the pyrolysis products from a nylon (40% weight)-phenolic resin (60% weight) ablative composite. This composition is stoichiometrically consistent with the elements present in the virgin plastic, but it is significantly different from the composition that would be predicted from chemical equilibrium due to the presence of high molecular weight carbon ring compounds.

II. INTRODUCTION

The knowledge of the composition of the pyrolysis products from the decomposition zone of a charring ablator is essential in the analysis of the heat transfer processes taking place in the char zone and in the boundary layer. The type and quantity of each species entering the char layer not only affects the convective and conductive heat transfer, but determines the chemical reactions that occur as the pyrolysis gases flow through the char. Therefore, in order to precisely model the non-equilibrium flow of these degradation products in the char zone and in the flow field adjacent to the body the pyrolysis gas composition must be accurately known.

The most obvious method for determining the composition of the pyrolysis products is to measure the composition directly. However, in early work by Madorski and others (1) difficulties were encountered in obtaining a representative sample of the degradation products. Consequently, most of the data reported in the literature presents only those components that were gases near room temperature. This nominally accounts for only about five percent by weight of the total material pyrolysed. Obviously these data can only be used as an indication of some of the chemical species formed by the pyrolysis of the material.

Other investigators (2-8) have analysed ablative plastic pyrolysis products with special emphasis on obtaining a representative sample. However, due to various experimental difficulties it was not possible to obtain a completely representative sample; and it would be most desirable to have alternate ways of evaluating the measured compositions for completeness and accuracy. Therefore, three alternate methods are presented and used for comparison with the compositions obtained from

the chemical analysis of pyrolysis products from ablative composites.

These methods are discussed in the next section.

III. METHODS FOR ESTIMATING PYROLYSIS GAS COMPOSITIONS

As previously mentioned there are four methods that can be used together to determine the composition of the pyrolysis products from ablative composites. These are:

- (1) Chemical analysis of the gases evolved during the thermal degradation of ablative composites.
- (2) Comparison of experimentally determined heat of pyrolysis with the heat of pyrolysis calculated knowing the composition and heat of formation of the ablative composite and estimating the compositions and knowing the heat of formation of the pyrolysis gases.
- (3) Qualitative inspection of the molecular structure of the plastic materials to determine the possible decomposition products based on the relative strength or weakness of bond energies.
- (4) Computation of pyrolysis gas composition using the concept of "restricted" chemical equilibrium.

Each of these techniques will be discussed in the following section.

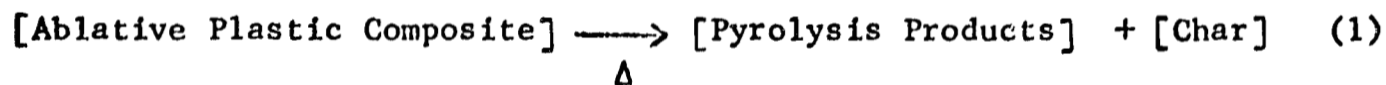
Chemical Analysis of the Pyrolysis Gases

The most direct method of determining the products of degradation is chemical analysis using pyrolysis gas chromatography. This technique has been employed by Sykes (2,3) in which the ablative composite was degraded in a furnace and the hot pyrolysis products were injected directly into a gas chromatograph. However, even with this careful procedure there is a certain amount of condensation of heavy molecular weight species in the heated line between the furnace and the chromatograph which remain unidentified, and this gives a source of error. The method has, however,

reduced the total amount of unidentified material pyrolysed from 50% (by weight) that was obtained with the more conventional methods (1) to 17% (by weight). Also the kind and concentration of the species were more precisely determined by this method. As a consequence these analyses will form the basis for quantitatively selecting a pyrolysis product composition used in the following method. The last two methods were used to make adjustments to the analytically determined composition, especially with regard to the species which would logically make up the unidentified portion of the pyrolysis products.

Comparison of the Experimentally Measured and Calculated Heat of Pyrolysis

The pyrolysis products are obtained by the thermal degradation of ablative plastic composites such as mixtures of nylon, phenolic resin etc. This is illustrated by the following equation.



The heat of reaction of the above reaction is the heat of pyrolysis, ΔH_{pyr} ; and it can be experimentally measured by differential thermal analysis. Also, it can be calculated knowing the heats of formation of the products (char and pyrolysis products) and reactants (the ablative composite) and knowing the heat capacity of both for the sensible enthalpy corrections of products and reactants from a reference temperature such as 25°C. The heat of pyrolysis can be computed using the following equation.

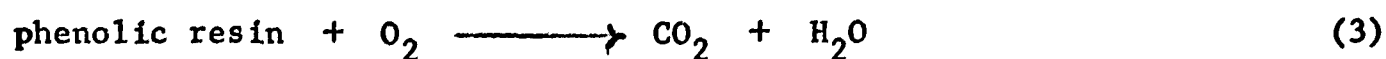
$$\Delta H_{\text{pyr}} = \sum_{i=1}^K \left[x_{p,i} \Delta H_{f,pi} + \int_{25^{\circ}\text{C}}^{T_p} x_{p,i} C_{p,pi} dT \right] - \sum_{j=1}^M \left[x_{r,j} \Delta H_{f,rj} + \int_{25^{\circ}\text{C}}^{T_r} x_{r,j} C_{p,rj} dT \right] \quad (2)$$

where K is the total number of species present in the pyrolysis products and M is the total components in the ablative composite. For nylon-

phenolic resin composites, the temperature, T_r , where degradation starts is approximately 250°C, and the temperature where the degradation ends is approximately 1000°C. Pyrolysis products are generated over this temperature range from 250 to 1000°C, and T_p is the appropriate average temperature which gives the correct energy associated with the pyrolysis products. It was determined to be 700°C as a weighted averaged based on the mass loss rate.

To be able to compare experimentally measured and calculated values of the heat of pyrolysis the weighted average temperature of 700°C based on mass loss rates from thermal gravimetric analyses and heats of formation at 25°C are listed in Table A-1 of Appendix A for compounds reported to be present during pyrolysis. Values of the heats of pyrolysis of nylon, phenolic resin and their composites were reported by Sykes (3) and Nelson (4). Heats of formation of nylon and phenolic resin as reactants were calculated from experimentally determined heats of combustion, and these are presented in Tables A2 and A3, respectively, of Appendix A. Details of the procedure for computing the heat of formation from the measured values of the heat combustion are contained in Appendix A as are the methods used for the measurement of the heat of combustion.

The combustion of an ablative plastic component such as phenolic resin forming carbon dioxide and water is represented by the following expression:



The heat of formation of phenolic resin is then simply:

$$\Delta H_{f,\text{phenolic resin}} = \Delta H_C - \sum_{i=1}^K x_{pi} \Delta H_{fpi} \quad (4)$$

Therefore, for a known composition of the various species in an ablative

composite, the heat of formation of the composite assuming no interaction is:

$$\Delta H_{f, \text{Composite}} = \sum_{j=1}^M x_j \Delta H_{f_j} \quad (5)$$

Now all of the pertinent data are now available to evaluate the heat of pyrolysis. In doing so, a selected composition determined by some analytical or numerical method is postulated to be valid. If the calculated value of the heat of pyrolysis is approximately equal to ($\pm 10\%$ of the desired value, for example), the composition is judged a representative composition. If, on the other hand, the experimental and calculated values do not agree within 10%, the composition that was proposed as valid is either in error or incomplete.

Correction of the postulated composition is made using any similar logic to that listed below:

(1) Inspect the literature data over a wide range of conditions by several authors, when available.

(2) Select those pyrolysis products which appear in a majority of the analyses.

(3) If the composition of various fractions are presented, weight each composition according to the size of each fraction.

(4) Superimpose these results and construct an overall species listing.

(5) Average values of species that appear within a reasonable range of values.

(6) Use the species that appear in only one analysis to make minor adjustments to the composition being corrected.

(7) Continue the evaluation until the calculated heat of pyrolysis agrees with the literature value within the accuracy of the data. Now,

based on the best possible literature composition, decide whether the corrections made in Step (6) to obtain the agreement are logical and reasonable. If so, the procedure is ended; if not, repeat the procedure with other more reasonable species.

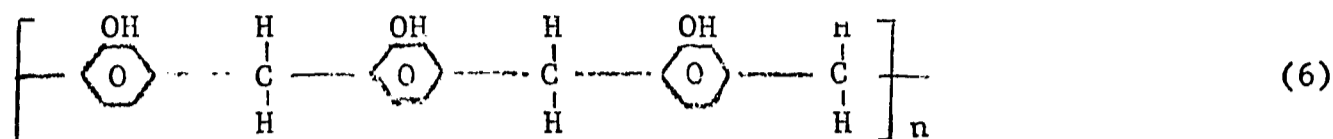
When little or no measured composition data are available, examining the polymer bond structure is suggested to arrive at pyrolysis products which are reasonable as discussed in the following section.

Pyrolysis Product Composition by Relative Strength or Weakness of Chemical Bonds

The thermal degradation of char forming ablative materials is a complex process. As indicated previously, little quantitative data on the decomposition mechanisms have been reported. The ability of the char layer to withstand aerodynamic stresses and high temperatures of reentry is well established. This ability is attributed, in part, to the highly crosslinked nature of the aromatic polymers such as phenolic resin. The already strong C-C bonds are reinforced by resonance effects resulting from the crosslinked structure. Therefore during thermal degradation these C-C bonds remain intact; and the weaker bonds (C-N, N-N, O-O, etc.) break producing the pyrolysis gas products. It is the purpose of this section to indicate the origin of likely pyrolysis products based on the bond energies of the polymers. A qualitative discussion for nylon and phenolic resin, and composites of these is presented in the following paragraphs.

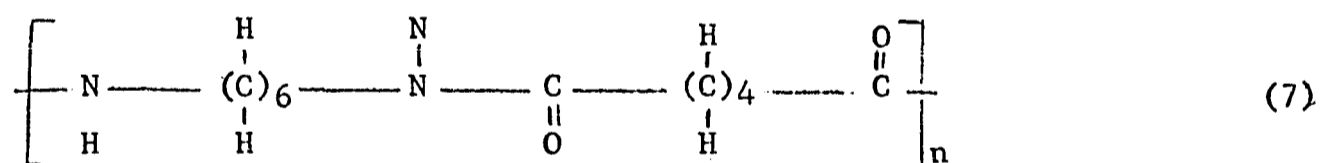
Decomposition of Phenolic Resin: Parker (10) presented a possible mechanism for the thermal degradation of phenolic novalac resins. Emphasis was placed on the final char structure; however, a great deal of information regarding the origin of some pyrolysis products was also reported.

Representing the phenolic novalac polymer as shown below:



Parker pointed out that the place where cleavage was most likely to be initiated was at the methylene bridge ($-\text{CH}_2-$) linkage. This resulted in the formation of a variety of free radicals including those of phenol, the cresols and many shorter polymeric units of the novalac resin which undergo still further degradation. A schematic diagram of the proposed mechanism is reproduced in Figure 1. In addition to the above mentioned products, water, hydrogen, carbon monoxide, and methane are also shown to be formed.

Decomposition of Nylon-66 (Hexamethylenediamine-Adipic Acid): The nylon-66 polymer is formed by the polymerization of one monomer of adipic acid with one monomer of hexamethylenediamine in alternating steps.



Inspection of the bond energies between atoms of the CHON system listed in Table 2, neglecting considerations of resonance and electronegativity effects that exist in the polymer, indicates that the most logical place for cleavage to occur is at the C-N bond. This essentially separates the polymer into shorter chain polymers and monomer units. From this point cleavage of bonds within the monomer structure can occur forming such species as NH_3 , CO , CO_2 , H_2O , H_2 , CH_4 , C_2H_6 , etc. In fact, reported experimental data shows that only about seven percent (by weight) of nylon-66 is degraded to residue (3,4). The remaining ninety-three percent forms gaseous products. From this analysis, it is evident that the char structure of a charring nylon-phenolic resin composite is primarily

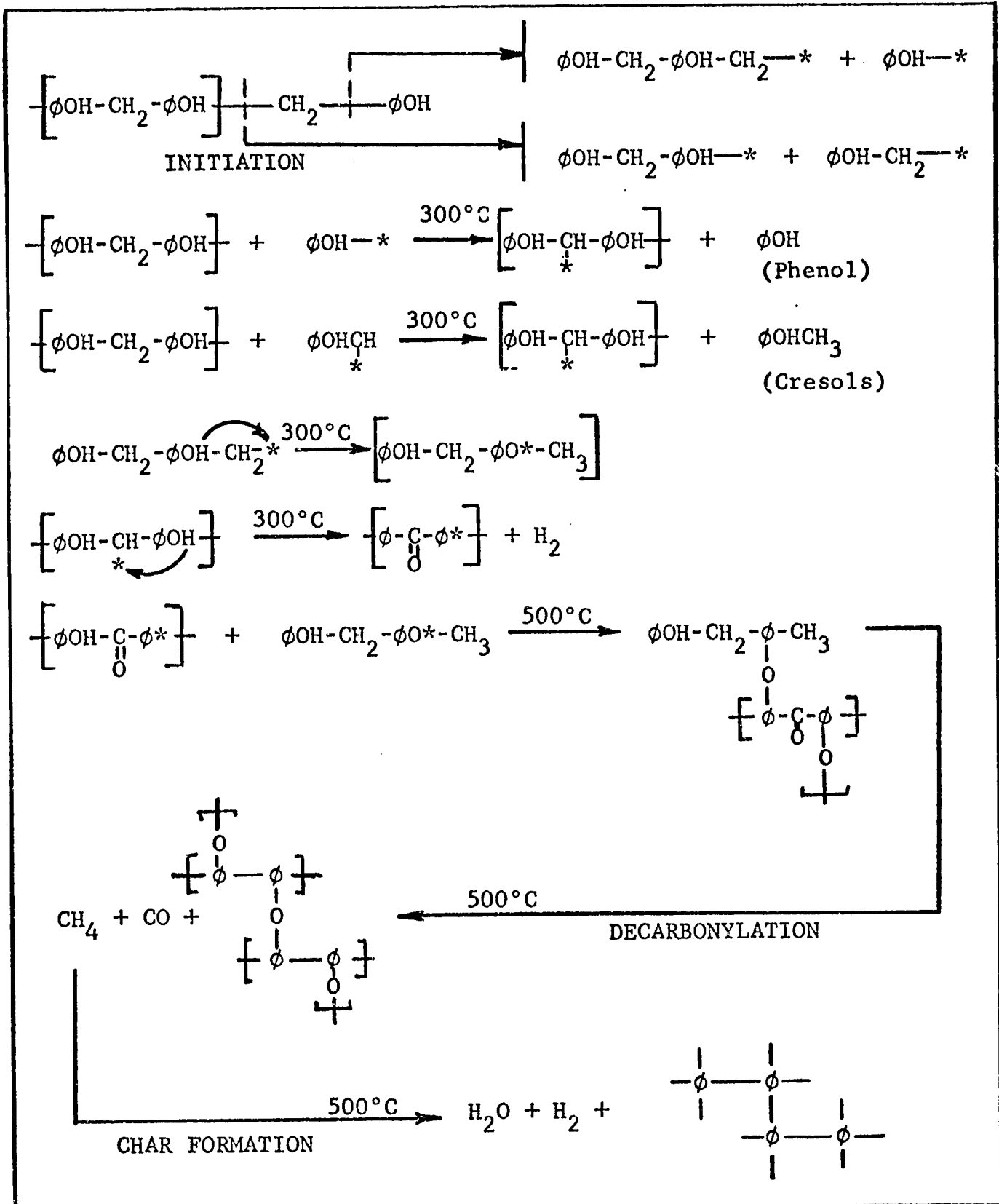


Figure 1. Mechanism of Phenolic Novalac Degradation to Char.

Table 2. Bond Energies Between Atoms in the CHON System (11).

Bond	Bond Energies, Kcal/gram
H - H	104
H - C	99
H - N	84
H - O	110
C - C	80
C - N	62
C - O	81
N - N	32
O - O	33
C = C	142
C \equiv C	186

composed of the phenolic degradation to carbon, while a major portion of the pyrolysis gases are formed from the nylon-66.

Decomposition of Nylon-Phenolic Resin Composites: Combining these two polymers with subsequent thermal degradation would result in all of the above mentioned products with relative quantities based on the weight fraction of each polymer in the composite if there is no interaction. A detailed listing of the various pyrolysis products identified by gas chromatographic and/or mass spectrographic analyses is presented in Table 3. Many of the species may only exist in small quantities; however, the large number formed is a very good reference of typical products which may be present when ablative composites undergo thermal decomposition.

Restricted Equilibrium Analysis

It has been suggested (12) that the composition of the degradation products from an ablative composite could possibly be computed accurately by considering them to be in a "restricted" thermodynamic equilibrium. The compositions predicted by considering the products to be in thermodynamic equilibrium assumes that sufficient energy is supplied or removed to equal the net heat of reaction of the chemical reactions that take place. The concept of restricted equilibrium proposes that the composition of the pyrolysis gases and char be constrained with the amount of energy supplied for the decomposition to be equal to the heat of pyrolysis.

The constraint equation is given by Equation (2), and this is an additional constraint on the composition of the reacting mixture. Equation (2) is rewritten below in a more meaningful form as Equation (8). Specifically ΔH_{pyr} is written as is the first term on the right hand side and the second term on the right hand side is the enthalpy of the ablative composite at T_r . The sum of these terms is a constant for a given ablative composite and the left hand side of this equation must be equal to this

Table 3. Various Species Identified as Pyrolysis Gas Products by Gas Chromatographic and/or Mass Spectrographic Analysis of Thermally Degraded Nylon-Phenolic Resin Composites. (1,2,3,5,6,7,8,10)

Hydrogen	Pentene	Methanol
Nitrogen	Pentane	Propyne
Oxygen	Benzene	Ethanol
Methane	Cyclohexane	Diacetylene
Carbon Monoxide	Hexadiene	Vinylacetylene
Carbon Dioxide	Hexene	Acrolein
Water	Hexane	Propanol
Ethylene	Toluene	Isopropanol
Ethane	Dimethyl Benzene	2-Pentene-4-yne
Propadiene	Dimethyl Phenol	Isopentanes
Propylene	Hexadiene	n-Butanol
Propane	Methyl Phenol	Phenyl Acetylene
Butadiene	Phenol	Styrene
Butene	2-Propanol	Xylenes
Butane	Acetone	4-Ethyl-1-Cyclohexane
Isoprene	Benzaldehyde	Methyl Phenyl Acetylene
Cyclopentene	Formaldehyde	Methyl Styrene
Cyclopentadiene	Ammonia	C ₉ Aromatics
Cyclopentanone	Acetylene	C ₁₀ Aromatics
Pentadiene	Hydrogen Cyanide	Dimethyl Styrene

constant. Examining the left hand side, the term in the brackets is a known constant and the compositions, x_{pi} , must be varied such that the equality holds.

$$\begin{aligned} \sum_{i=1}^K x_{pi} \left(\Delta H_{f,pi} + \int_{25^{\circ}\text{C}}^{T_p} C_{p,pi} dT \right) &= \Delta H_{pyr} \\ + \sum_{j=1}^M x_{rj} \left(\Delta H_{f,rj} + \int_{25^{\circ}\text{C}}^{T_p} C_{p,rj} dT \right) & \\ &= H(\text{a constant}) \end{aligned} \quad (8)$$

Thus Equation (8) becomes an additional constraint, along with the material balance constraints, on the free energy function which is minimized to obtain the equilibrium composition of the reacting mixture. This approach and computational procedure has been discussed in detail by de Valle (14), and results are given in the following section.

IV. COMPARISON OF THE METHODS FOR ESTIMATING THE PYROLYSIS GAS COMPOSITIONS

To illustrate the use of the above discussed methods, the results reported by Sykes (2,3), Nelson (4), Freidman (5), Ladachi et al. (6) and Jackson et al. (7) will be used. The ablative composites considered in these works were composed of phenolic resin, nylon and silica.

Comparison of Experimentally Measured and Computed Heat of Pyrolysis

Sykes (2,3) reported typical pyrolysis gas compositions for 83% of the total decomposition products evolved during the thermal degradation of nylon-phenolic resin composites. The techniques that were employed included differential thermal analysis, thermogravimetric analysis and pyrolysis gas chromatography of the hot gases evolved during rapid heating of the composite materials. The remaining 17% was reported to be an unidentified, dark, tarry substance. The composites from this research are presented in Tables 4 and 5. Also shown are the comparisons of the heat of pyrolysis calculations with the experimental values of Sykes (2). A very good agreement is obtained in Table 4 which indicates a high reliability in the reported compositions. The unidentified portion of the pyrolysis products was taken as phenol for calculating the heat of pyrolysis. In an earlier work on phenolic resin only the results were somewhat poorer as shown in Table 5. This is indicated by the larger difference in the calculated (110 BTU/lb.) and the experimental (146 BTU/lb.) heat of pyrolysis values. This was probably caused by either improper curing of the specimen resulting in the higher water content or inaccuracies in the analysis of the evolved pyrolysis products.

As a third example the pyrolysis products reported by Freidman (5) are compared in Table 6, for a nylon-phenolic resin composite. In this case the composition was determined from near room temperature samples

Table 4. Comparison of the Experimental Heat of Pyrolysis with Calculated Values Based on Heats of Formation of the Reported Pyrolysis Gas Components (2):

Component Name	Weight Fraction by:		Average Weight Fraction, x_i	A	B
	Flash	50°C Increments		$x_i \Delta H_{fpi}$ (BTU/lb)	$x_i C_{pmean} \Delta T$ (BTU/lb)
Phenol	0.124	0.112	0.118	- 49	34
Methylphenol	0.067	0.061	0.064	- 33	18
Dimethylphenol	0.049	0.052	0.051	- 29	14
Trimethylphenol	0.040	0.042	0.041	- 25	12
Benzene	0.004	0.001	0.003	2	2
Toluene	0.000	0.002	0.001	1	1
Cyclopentanone	0.019	0.039	0.029	- 18	9
Hydrogen	0.010	0.010	0.010	0	34
Methane	0.010	0.010	0.010	- 20	10
Carb. Monoxide	0.025	0.016	0.021	- 18	6
Carb. Dioxide	0.087	0.047	0.067	- 36	5
Water	0.059	0.066	0.062	-258	23
Ammonia	0.002	0.001	0.002	- 2	2
Unidentified*	0.173	0.173	0.181	- 72	51
Carbon Residue	-	-	<u>0.340</u>	<u>133</u>	<u>99</u>
			1.000	-742	320

Reactants	Weight Fraction, x_j	$x_j \Delta H_{rj}^C$ (BTU/lb)	$x_j C_{pmean}^D \Delta T$ (BTU/lb)	ΔH_{pyr} (Calculated) = A + B - C - D = 213 BTU/lb ΔH_{pyr} (Experimental) = 200 BTU/lb
Nylon	0.4	-384	250	
Phenolic Resin	0.6	-501	<u>250</u>	
	<u>1.0</u>	<u>-885</u>		

* Unidentified materials were considered to be phenol in the calculation of ΔH_{pyr} .

Table 5. Comparison of the Experimental Heat of Pyrolysis with Calculated Values Based on the Heats of Formation of Reported Pyrolysis Gas Components (3).

Component Name	Pyrolysis Gas Analysis		Average Weight Fraction, x_i	A	B
	Moles	Pounds		$x_i \Delta H_{fi}$ (BTU/lb)	$x_i C_{pmean} \Delta T$ (BTU/lb)
Carb. Dioxide	1.6	70.4	0.019	- 74	6
Carb. Monoxide	5.5	154.1	0.042	- 71	10
Benzene	0.2	15.6	0.004	2	2
Toluene	0.3	32.4	0.009	1	5
Phenol	7.1	668.2	0.181	- 75	52
Methylphenol	1.8	219.9	0.060	- 34	17
Methane	10.0	160.0	0.043	- 87	29
Water	23.4	421.0	0.114	-661	55
Hydrogen	50.1	100.2	0.027	0	91
Unidentified*	-	-	0.150	- 62	43
Carbon Residue	-	-	<u>0.350</u>	<u>137</u>	<u>101</u>
			1.000	-924	411

Reactant	C $x_j \Delta H_{frj}$ BTU/lb	D $x_j C_{pmean} \Delta T$ BTU/lb	ΔH_{pyr} (Calculated) = A + B - C - D = 110 BTU/lb
Phenolic Resin (Only)	-823	200	ΔH_{pyr} (Experimental) = 146 BTU/lb Ref (2)

* Unidentified materials were considered to be phenol in calculation of ΔH_{pyr} .

Table 6. Comparison of the Experimental Heat of Pyrolysis with Calculated Values Based on Heats of Formation of the Reported Pyrolysis Gas Components (5).

Component Name	Pyrolysis Gas Analysis		Average Weight Fraction, x_i	A $x_i \Delta H_{fi}$ (BTU/lb)	B $x_i C_{pmean} \Delta T$ (BTU/lb)
	Moles	Pounds			
Hydrogen	23.9	47.8	0.011	0	37
Methane	4.1	65.6	0.015	- 31	11
Ammonia	4.1	69.7	0.016	- 19	10
Water	15.3	275.7	0.064	-371	31
Acetylene	10.9	283.4	0.066	248	38
Hydrogen Cyanide	3.5	94.5	0.022	46	13
Carbon Monoxide	10.9	305.2	0.071	-121	17
Nitrogen	0.1	2.8	0.001	0	2
Ethylene	14.0	392.0	0.091	73	53
Ethane	0.2	6.0	0.001	- 2	1
Carbon Dioxide	2.2	96.8	0.023	- 87	7
Diacetylene	0.9	45.0	0.011	45	6
Acetone	0.7	40.7	0.010	- 21	6
Benzene	0.9	70.2	0.016	8	10
Toluene	0.5	46.2	0.011	2	6
Xylene	0.3	31.8	0.007	1	5
Isopropanol	1.3	78.0	0.018	- 10	7
Propane	1.5	63.0	0.015	- 7	5
Carbon Residue	-	2270.9	0.529	206	127
			1.000	- 40	392
Reactants	Weight Fraction, x_j	C = $x_j \Delta H_{fj}$ BTU/lb	D = $x_j C_{pmean} \Delta T$ BTU/lb	ΔH_{pyr} (Calculated) = A + B - C - D = 987 BTU/lb	
Nylon	0.4	-384	250	ΔH_{pyr} (Experimental) = 200-500 BTU/lb	
Phenolic Resin	0.6	-501	250		
	1.0	-885	250		

analysed by gas chromatography. The absence of the higher molecular weight species such as phenol and the cresols is evident. This resulted in a much poorer comparison between the calculated and experimental heat of pyrolysis as would be expected if important species were omitted from the composition. The inclusion of phenol and similar high molecular weight species which are liquids at room temperature where the particular samples were collected should be included. The quantity of each species added to correct the composition to a more representative value can only be determined by investigating the literature for the specific conditions of the experiment and subsequent analysis. If no such information is available, comparison with an analogous system (similar composite materials, for example) is a logical approach.

The results reported by Ladacki et al. (6) are reported in Table 7 for a silica, phenolic resin composite. In this work the heat of formation of the composite was calculated from the heat of combustion, and mass spectrometry was used to identify the pyrolysis products. The objective of this work was to calculate the heat of pyrolysis and compare it with experimentally measured values. This is the converse of the results given in this report but the same numbers should be obtained. This was the case as seen in Table 7 with the values being essentially the same i.e., 543 BTU/lb. and 550 BTU/lb.

The results reported by Jackson and Conley (7) on the thermal degradation of phenolic resin (base catalysed) were obtained by electrically heating the polymer in a quartz tube to 800°C. Helium flow from the pyrolysis oven to a gas chromatograph was through a heated line. Of the observer weight loss 50% was reported to be non-condensables e.g., water, paraformaldehyde and a high molecular weight, non-volatile residue. Referring to Table 8, an experimental value of the heat of pyrolysis was

Table 7. Comparison of the Experimental Heat of Pyrolysis with Calculated Values Based on Heat of Formation Data of the Reported Pyrolysis Gas Composition. (6)

Component Name	Pyrolysis Gas Fraction			Net Weight Fraction, x_i	ΔH_{fp} (BTU/lb)	A	B
	750°F	1110°F	1620°F			$x_i \Delta H_{fp}$ (BTU/lb)	$x_i C_{pr} \Delta T$ (1) (BTU/lb)
Hydrogen	0.04	0.43	0.95	0.014	0	0	34
Carbon Monoxide	0.04	4.45	8.16	0.127	-1697	-221	23
Water	4.70	3.25	1.05	0.090	-5780	-520	29
Methane	0.18	2.35	0.80	0.033	-2014	-66	16
Ethane	0.01	1.00	0.18	0.012	-456	-5	4
Nitrogen	0.61	2.40	1.41	0.044+	--	--	--
Carbon Dioxide	1.11	0.85	0.69	0.027	-3850	-116	7
Oxygen	0.00	0.95	0.41	0.014+	--	--	--
Benzene	0.03	0.75	0.23	0.010	456	5	4
Toluene	0.03	1.33	0.36	0.017	232	5	6
Xylenes	0.12	0.70	0.20	0.010	-415	-4	3
Phenol	0.61	2.25	0.27	0.031	-415	-12	9
Cresols	1.21	3.13	0.32	0.047	-415	-21	15
Dimethylphenol	0.48	1.18	0.00	0.017	-415	-8	6
2-Propanol	0.46	0.00	0.00	0.005	--	--	--
Acetane	0.37	0.00	0.00	0.004	--	--	--
Residue	--	--	--	0.500	390	195	105
TOTAL				1.000			

(1) For a temperature range from 25°C to 800°C.

(2) For a temperature range from 25°C to 25°C.

+ possible air contamination

$$\Sigma = \quad -768 \quad 261$$

Reactants	Weight Fraction	C $x_i \Delta H_{fr}$ BTU/lb	D $x_i C_{pr} \Delta T(2)$ BTU/lb
Silica- Phenolic Resin	0.7 0.3	-1050 measured experimentally	0

$$\Sigma = \quad -1050 \quad 0$$

$$\Delta H_{pyr} \text{ (Calculated)} = A + B - C - D$$

$$= 543 \text{ BTU/lb}$$

$$\Delta H_{pyr} \text{ (Ref (6)*)} = 550 \text{ BTU/lb}$$

* calculated using heat of formation and heat of pyrolysis data

Table 8. Comparison of the Experimental Heat of Pyrolysis with Calculated Values Based on Heat of Formation Data of the Reported Pyrolysis Gas Composition. (7)

Component Name	Pyrolysis Gas Fraction		Net Weight Fraction, x_i	A	B
	500°C	800°C		$x_i \Delta H_{fp}$ BTU/lb	$x_i C_{pm} \Delta T$ (1) BTU/lb
Methane	0.020	0.025	0.023	-46	13
Carbon Monoxide	0.000	0.050	0.025	-42	5
Carbon Dioxide	0.062	0.080	0.071	-273	20
Ethane	0.002	0.017	0.095	5	2
Toluene	0.005	0.005	0.005	1	1
Methylphenol	0.030	0.023	0.027	-14	7
Xylene	0.007	0.004	0.006	-3	1
Phenol	0.075	0.060	0.068	-28	16
Benzaldehyde	0.001	0.002	0.002	--	--
Water	0.058	0.067	0.060	-347	24
Unidentified	0.144	0.194	0.174	-72	42
Residue	0.596	0.468	0.532	208	128
Total	1.000	1.000	1.000		
				$\Sigma = -611$	259

- (1) For a temperature range from 25°C to 800°C.
 (2) For a temperature range from 25°C to 350°C.

Reactants	Weight Fraction	ΔH_{fr} BTU/lb	$C_{pr} \Delta T(2)$ BTU/lb	C	D
				$x_i \Delta H_{fr}$ BTU/lb	$x_i C_{pr} \Delta T(2)$ BTU/lb
Phenol-Formaldehyde	1.0	-835	248	-835	248
				$\Sigma = -835$	248

$$\Delta H_{pyr} \text{ (Calculated)} = A + B - C - D = 235 \text{ BTU/lb}$$

$$\Delta H_{pyr} \text{ (Experimental)} = 146 \text{ BTU/lb}$$

Reference 2

not reported so it was necessary to compare the results computed of 235 BTU/lb. with the experimental value reported by Sykes of 146 BTU/lb. This agreement is well within the accuracy of the experimental data, and it was necessary to assume the residue was carbon for the calculation.

The results reported by Shulman and Lochte (8) for the degradation of phenol-formaldehyde resin is summarized in Table 9 along with the calculation of the heat of pyrolysis. Experiments were conducted by pyrolysing the polymer in a tungsten crucible of the Knutsen cell inlet to a time-of-flight mass spectrometer. The sample was heated at a linear rate of 29°C/min., and the products analysed. The composition of phenol type compounds, gases such as CH₄, CO, and CO₂ were measured and there was 50.8% residue. Computing the heat of pyrolysis using the compositions reported gave a value of 110 BTU/lb. An experimental value was not reported. However, this comparable to the value reported by Sykes (2) of 146 BTU/lb. and within the accuracy of the computations taking the residue to be carbon

In summary, the comparison between the experimentally measured and computed heat of pyrolysis is within the accuracy of the data when a reasonably complete analysis of the pyrolysis products is available. Specifically the composition of the pyrolysis products used in the calculation must contain the higher molecular weight species such as phenol and other ring compounds from the degradation of phenolic resin. Agreement between the experimentally measured and computed heat of pyrolysis helps establish the accuracy and bounds the range on the composition of the species present in the pyrolysis products from the degradation of an ablative composite.

Table 9. Comparison of the Experimental Heat of Pyrolysis with Calculated Values Based on Heat of Formation Data of the Reported Pyrolysis Gas Composition. (8)

Component Name	Net Weight Fraction, x_i	$x_i^A \Delta H_{fp}$ BTU/lb	$x_i^B C_{pm} \Delta T$ (1) BTU/lb
Methane	0.054	-109	30
Carbon Monoxide	0.080	-136	16
Carbon Dioxide	0.160	-616	45
Benzene	0.030	14	7
Toluene	0.008	2	2
Methylphenol	0.008	-4	2
Xylene	0.152	-87	37
Residue	0.508	198	122
Total	1.000		
		$\Sigma = -738$	261

(1) For a temperature range from 25°C to 800°C.
 (2) For a temperature range from 25°C to 350°C.

Reactants	Weight Fraction	ΔH_{fr} BTU/lb	$C_{pr} \Delta T$ (2) BTU/lb	$x_i \Delta H_{fr}$ BTU/lb	$x_i C_{pr} \Delta T$ BTU/lb
Phenol-Formaldehyde	1.0	-835	248	-835	248
				$\Sigma = -835$	248

$$\Delta H_{pyr} \text{ (Calculated)} = A + B - C - D = 110 \text{ BTU/lb}$$

$$\Delta H_{pyr} \text{ (Experimental)} = 146 \text{ BTU/lb}$$

Reference 2

Restricted Equilibrium Analysis

A restricted equilibrium analysis, as previously discussed, was proposed as a computational technique which would give more accurate compositions of pyrolysis products than the usual chemical equilibrium analysis. Computations were made using Equation (8) as an additional constraint to the free energy minimization calculations. The details of these computations have been reported by del Valle and Pike (14) and the results are summarized here.

The chemical composition of the pyrolysis products resulting from the degradation of a 40% (by weight) nylon-60% (by weight) phenolic resin ablative composite was computed by the restricted equilibrium analysis. The computations have been done for two decomposition temperatures because of the uncertainty involved in the physical properties used to calculate the average temperature, T_p . In addition two different energy constraints were used because of uncertainties in the heat of pyrolysis. The limiting average temperatures were 600° and 700°C, and the energy constraints were -228 and -390 BTU/lb. of ablative composite.

In Table 10 a comparison of restricted equilibrium with the experimental data of Sykes (2) is given for two energy constraints (H = -228 and -390 BTU/lb.) at a temperature of 700°C. The results show an order of magnitude agreement with the low molecular weight species identified by Sykes (2). These are methane, hydrogen, carbon monoxide, carbon dioxide, water and ammonia. The agreement with the high molecular weight species, phenol, toluene, benzene, etc. was rather poor. The change in the energy constraint, H, from -228 to -390 BTU/lb of ablative composite has different and opposite effects on several of the species. For example, an increase in the value of H had the effect of decreasing the

TABLE 10. Comparison of Restricted Equilibrium Analysis Compositions with the Experimental Data of Sykes (2) for a 40% Nylon 60% Phenolic Resin Composite at a Temperature of 700°C.

<u>Species</u>	<u>Restricted Equilibrium Analysis (Mass Percent)</u>		<u>Experimental (Mass Percent)</u>
	<u>H = -390 BTU/lb</u>	<u>H = -228 BTU/lb</u>	
Phenol	10^{-11}	10^{-11}	11.8
Methylphenol	-	-	6.4
Dimethylphenol	-	-	5.1
Trimethylphenol	10^{-11}	10^{-11}	4.1
Benzene	10^{-11}	10^{-11}	0.3
Toluene	10^{-11}	10^{-11}	0.1
Cyclopentanone	-	-	2.9
Methane	3.9	3.6	1.0
Hydrogen	6.0	6.1	1.0
Carbon Monoxide	16.0	16.7	2.1
Carbon Dioxide	2.7	2.4	6.7
Water	3.8	3.6	6.2
NH ₃	10^{-2}	10^{-2}	0.2
N ₂	4.0	4.0	-
unidentified	-	-	18.1
Carbon	63.5	63.5	34.0
TOTAL	100.0	100.0	100.0

amount of hydrogen, and carbon monoxide, while increasing the concentrations of carbon dioxide and water. It should be noted that the mass fraction of unidentified plus that of carbon makes up 0.521 of the total mass fraction of the experimental composition, while the restricted equilibrium predicts a mass fraction of 0.635 carbon. It should be further noticed that the mass of nitrogen makes up about four percent of the mixture and no nitrogen was reported in the experimental results.

In Table 11 a similar comparison is made, but the decomposition zone temperature is taken to be 600°C. Again an order of magnitude agreement is observed among the composition of the lower molecular weight species. Changing H affects the composition in the same fashion as was for the 700°C. case.

In general, restricted equilibrium provided an order of magnitude agreement for the composition of low molecular weight compound. It failed to give any agreement with the higher molecular weight component.

In Table 12 a comparison of restricted equilibrium with the general equilibrium analysis is given. It is shown that the compositions are within an order of magnitude of each other. The only mass fraction that is the same is that of nitrogen, since it is practically an inert, and that of carbon is within one percent.

Representative Pyrolysis Gas Compositions from Nylon-Phenolic Resin Ablative Composite

An accurate description of the composition of the ablation products from the degradation of the composite is required to accurately compute the energy absorbed by a heat shield during entry. Furthermore these products undergo chemical reactions as they pass through the char zone and are injected into the boundary layer. Key in the analysis of the energy transferred to the surface of ablator is an accurate evaluation

TABLE 11. Comparison of Restricted Equilibrium Analysis Compositions with the Experimental Data Sykes (2) for a 40% Nylon 60% Phenolic Resin Composite at a Temperature of 700°C.

<u>Species</u>	<u>Restricted Equilibrium Analysis (Mass Percent)</u>		<u>Experimental (Mass Percent)</u>
	<u>H = -390 BTU/lb</u>	<u>H = -228 BTU/lb</u>	
Phenol	10 ⁻¹¹	10 ⁻¹¹	11.8
Methylphenol	-	-	6.4
Dimethylphenol	-	-	5.1
Trimethylphenol	-	-	4.1
Benzene	10 ⁻¹⁵	10 ⁻¹⁵	0.3
Toluene	10 ⁻¹¹	10 ⁻¹¹	0.1
Cyclopentane	-	-	2.9
Methane	2.5	2.4	1.0
Hydrogen	6.5	6.6	1.0
Carbon Monoxide	20.5	21.0	2.1
Carbon Dioxide	1.4	1.2	6.7
Water	2.1	1.9	6.2
NH ₃	10 ⁻²	10 ⁻²	0.2
N ₂	3.9	3.8	-
unidentified	-	-	18.1
Carbon	<u>63.1</u>	<u>63.0</u>	<u>35.0</u>
TOTAL	100.0	100.0	100.0

TABLE 12. Comparison of Restricted Equilibrium Analysis with the General Equilibrium Analysis for a 40% Nylon, 60% Phenolic Resin Composite, at 700°C and 1 Atmosphere Pressure.

<u>Species</u>	<u>Restricted Equilibrium (-390 BTU/lb)</u> <u>(mass percent)</u>	<u>Equilibrium Composition</u> <u>(mass percent)</u>
Phenol	10^{-11}	10^{-16}
Benzene	10^{-15}	10^{-11}
Toluene	10^{-11}	10^{-11}
Methane	2.5	4.3
Hydrogen	6.5	5.9
Carbon Monoxide	20.5	15.0
Carbon Dioxide	1.4	3.1
Water	2.1	4.3
NH ₃	10^{-2}	10^{-2}
N ₂	3.9	3.9
C	<u>63.1</u>	<u>63.5</u>
TOTAL	1.000	1.000

of the composition of the species entering the shock layer. This is particularly true for reentry speeds of 50,000 ft/sec where radiation from the shock heated gas to the surface is a significant portion of the energy transferred to the surface. The amount of radiant energy transfer is particularly sensitive to the ablation products distribution in the shock layer. Thus based on the four methods discussed in the report a composition of the pyrolysis products was estimated that was consistent with the experimental data, the heat of pyrolysis analysis, the molecular structure, and was also stiochiometrically consistent with the elemental composition of the composite.

In Table 13 is given the selected pyrolysis product composition arrived at from the decomposition of 40% (by weight) nylon-60% (by weight) phenolic resin ablative composite. Also shown in Table 13 is the elemental composition of the ablative composite. The composition shown in the table was arrived at by distributing the nitrogen, oxygen, hydrogen and carbon, in that order, among the species known to be present in the pyrolysis products. The composition of each species was selected by matching the experimental data as closely as possible as constrained by the heat of pyrolysis calculation and the molecular structure.

Table 13. Representative Pyrolysis Product Composition from the Degradation of a 40% (by weight) Nylon-60% (by weight) Phenolic Resin Ablative Composite.

<u>Component</u>	<u>Mass Percent</u>	<u>Mole Percent</u>
H ₂	2.60	20.92
CH ₄	3.87	3.90
C ₂ H ₂	3.89	2.41
C ₂ H ₄	3.90	2.24
C ₂ H ₆	0.65	0.35
C ₆ H ₆	2.59	0.53
C ₆ H ₅ OH	23.18	3.97
CO	4.18	2.40
CO ₂	4.62	1.69
H ₂ O	7.21	6.45
N ₂	3.83	2.20
Carbon(solid)	<u>39.48</u>	<u>52.94</u>
TOTAL	100.00	100.00

<u>Element</u>	<u>Mass Percent</u>	<u>Mole Percent</u>
C	73.03	41.54
H	7.29	49.76
N	4.96	2.42
O	<u>14.72</u>	<u>6.28</u>
TOTAL	100.00	100.00

V. LITERATURE CITED

1. Madorski, S. L., Thermal Degradation of Organic Polymers, p. 262, Interscience Publishing Co., Inc., New York (1964).
2. Sykes, G. F., private communication to R. W. Pike, (March 14, 1969).
3. Sykes, G. F., "Decomposition Characteristics of a Char Forming Phenolic Polymers Used for Ablative Composites," NASA TN D-3810, (February, 1967).
4. Nelson, J. B., "Determination of Kinetic Parameters of Six Ablative Polymers by Thermogravimetric Analysis," NASA TN D-3919 (April, 1967).
5. Freidman, H. L., "Pyrolysis of Plastic in a High Vacuum Arc Image Furnace," Journal of Applied Polymer Science, 9, 1005 (1965).
6. Ladachi, M., J. V. Hamilton and S. N. Cong, "Heat of Pyrolysis of Resins in Silica-Phenolic Ablators," AIAA Journal, 4, (10), 1798 (1966).
7. Jackson, W. M. and R. T. Conley, "High Temperature Oxidative Degradation of Phenol-Formaldehyde Polycondensates," Journal of Applied Polymer Science, 8, 2163 (1964).
8. Shulman, G. P. and H. W. Lochte, "Thermal Degradation of Polymers II. Mass Spectrometric Thermal Analysis of Phenol-Formaldehyde Polycondensates," Journal of Applied Polymer Science, 10, 619 (1966).
9. Perry, J. H., Editor, Chemical Engineering Handbook, 3rd Edition McGraw-Hill Inc., New York, N. Y., pp. 236-43 (1950).
10. Parker, J. A. and E. L. Winkler, "The Effects of Molecular Structure on the Thermochemical Properties of Phenolics and Related Polymers," NASA TR R-276 (1967).
11. Gould, E. S., Mechanisms and Structure in Organic Chemistry, p. 36-7, Holt, Rinehart and Winston, New York, N. Y. (1962).
12. Swann, R. T., private communication, (November 1968).
13. Hougen, O. A., K. M. Watson and R. A. Ragatz, Chemical Process Principles Part I Material and Energy Balances, 2nd Ed., John Wiley and Sons Inc., New York, N. Y., p. 305 (1954).
14. del Valle, E. G. and R. W. Pike, "Computation of the Equilibrium Composition of Reacting, Gas-Solid Mixtures with Material and Energy Balance Constraints NASA-RFL-10, Reacting Fluids Laboratory, Louisiana State University (March 1, 1970).

VI. NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>
C_p	Heat capacity of constant pressure
H	Enthalpy constraint defined by Equation (8)
ΔH	Heat of formation
ΔH_c	Heat of combustion
ΔH_{pyr}	Heat of pyrolysis
K	Total number of products
M	Total number of reactants
T	Temperature
T_p	Temperature of products
T_r	Temperature of reactants
x	Mass fraction

Subscripts

i	refers to species
pyr	refers to pyrolysis
r	refers to reactants
p	refers to products

APPENDIX AHEATS OF COMBUSTION AND FORMATION
OF NYLON, PHENOLIC RESIN (CURED AND UNCURED),
AND PHENOLIC MICROBALOONS

To compute the heat of reaction the heat of formation of the reactants and products of the chemical reaction must be known. The heat of pyrolysis is the heat of reaction of the degradation of a chemical species, and in this study the reactants were the polymer components of the ablative components. Although accurate values for the heat of formation of the products of the degradation are accurately known (Table A-1), the corresponding values for the reactants i.e., the polymer components are not accurately known. Thus it was necessary to measure the heat of formation for nylon-66, phenolic resin and phenolic microbaloons which are the components of the low density phenolic-nylon ablative composite.

The heat of formation for an organic compound is not measured directly, but it is computed from measured values of the heat of combustion. The heat of combustion of nylon-66, phenolic resin and phenolic microbaloons were measured as is subsequently discussed. Samples of these materials which are used to make ablative heat shields was furnished by Mr. George F. Sykes and Mr. James B. Nelson of the Entry Structures Branch of the Langley Research Center, N.A.S.A. and heat of combustion measurements were made with a Parr Adiabatic Bomb Calorimeter Model 2212. The calculations of the heat of formation from the measured heat of combustion for nylon-66 and cured phenolic resin are shown in Tables A-2 and A-3.

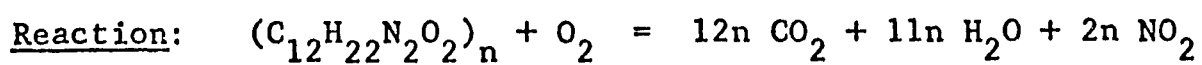
Theory

To measure the heat of combustion, a simple batch process (a bomb calorimeter) is generally used. In a bomb calorimeter, there is no accumulation of internal energy if the bomb is placed in a constant temperature

Table A-1. Heats of Formation and Heat Capacities of Various Pyrolysis Products. (9)			
Species	ΔH_f , BTU/lb	** C_{pmean} BTU/lb-°F	M_w
Phenol	-415.3	0.3*	94.1
MethylPhenol	-511.6	0.3	108.1
DimethylPhenol	-570.0	0.3*	122.2
TrimethylPhenol	-600.0	0.3*	136.1
Benzene	456.3	0.3*	78.1
Toluene	226.6	0.3*	93.1
Hydrogen	0.0	3.5	2.0
Methane	-2013.8	0.7	16.0
Carbon Monoxide	-1697.1	0.25	28.0
Carbon Dioxide	-3850.2	0.35	44.0
Water	-5780.0	0.5	18.0
Ammonia	-1160.5	0.67	17.0
Butylamine	-384.1		73.1
Acetone	-2214.7	0.44	42.1
Methylamine	-387.8		31.1
Formaldehyde	-1697.9	0.41	30.0
Ethylene	804.3	0.63	28.0
Ethane	-1212.0	0.6	30.0
Acetylene	3752.3	0.6	26.0
Butane	-923.2	0.7	58.1
Butene	9.7	0.74	56.1
Cyclohexane	-629.1	0.44	84.2
Cyclopentane	-475.0	0.47	70.1
EthylBenzene	120.3		106.2
Hydrogen Cyanide	2080.0	0.4	27.0
Methyl Cyclohexane	-676.8	0.46	98.2
Methyl Cyclopentane	-545.1	0.5	84.2
Pentane	-871.2	0.6*	72.2
Propane	-1012.2	0.6*	44.1
Xylene	76.3	0.3*	106.2
Amorphous Carbon	390.0	0.3	12.0

Note: * Estimated heat capacity by analogy with homolog(s).
 ** Mean heat capacity calculated over a temperature range from 250°-1000°C evaluated at a weighted average temperature of 700°C based on mass loss rates from thermal gravimetric analyses.

Table A-2. Heat of Formation of Nylon-66 from the Experimental Heat of Combustion Data.



Basis: 1 gram of nylon (Molecular weight of monomer = 226)

$$\frac{1 \text{ gram nylon}}{226 \text{ gr/gr mole}} = 0.00442 \text{ gm moles}$$

$$\text{gm moles } CO_2 = 0.00442 \times 12 = 0.053$$

$$\text{gm moles } H_2O = 0.00442 \times 11 = 0.049$$

$$\text{gm moles } NO_2 = 0.00442 \times 2 = 0.009$$

$$\Delta H_{fCO_2} = -94,052 \text{ cal/gm mole (0.053)} = -5004 \text{ cal/gm}$$

$$\Delta H_{fH_2O} = -57,800 \text{ cal/gm mole (0.049)} = -2815 \text{ cal/gm}$$

$$\Delta H_{fNO_2} = + 8090 \text{ cal/gm mole (0.009)} = 72 \text{ cal/gm}$$

$$\Sigma \Delta H_{fprod} = -7747 \text{ cal/gm}$$

$$\Delta H_C = -7214 \text{ cal/gm}$$

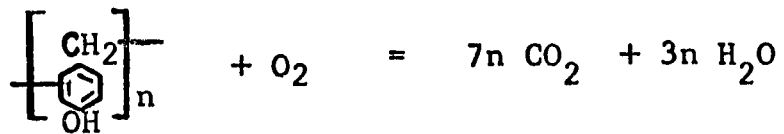
$$\Delta H_{fR} = \Sigma \Delta H_{fprod} - \Delta H_C$$

$$= -7747 - (-7214)$$

$$= -533 \text{ cal/gm } (-959 \text{ BTU/lb})$$

Table A-3. Heat of Formation of Phenolic Resin from the Experimental Heat of Combustion Data.

Reaction:



Basis: 1 gram phenolic resin (Molecular weight of monomer = 106)

$$\frac{1 \text{ gram phenolic resin}}{106 \text{ gram/gram moles}} = 0.00943 \text{ gm moles}$$

$$\text{gm moles CO}_2 = 0.00943 \times 7 = 0.0660$$

$$\text{gm moles H}_2\text{O} = 0.00943 \times 3 = 0.0283$$

$$\Delta H_{f\text{CO}_2} = -94,052 \text{ cal/gm mole (0.0660)} = -6207 \text{ cal/gm}$$

$$\Delta H_{f\text{H}_2\text{O}} = -57,800 \text{ cal/gm mole (0.0283)} = -1636 \text{ cal/gm}$$

$$\Sigma \Delta H_{f\text{prod}} = -7843 \text{ cal/gm}$$

$$\Delta H_C = -7386 \text{ cal/gm}$$

$$\Delta H_{fR} = \Sigma \Delta H_{f\text{prod}} - \Delta H_C$$

$$= -7843 - (-7386)$$

$$= -457 \text{ cal/gm (-823 BTU/lb)}$$

bath and the system volume remained constant. In this case the energy generation or consumption, Q , is equal to the heat of reaction per mole (or per unit mass) $\Delta H_{\text{rxn } A}$ of the reactant times the number of moles (or mass) of the specified material that disappears, m_A

$$Q = \Delta H_{\text{rxn } A} \times m_A \quad (\text{A-1})$$

When the reaction studied is the oxidation of a substance with oxygen, the heat of reaction is called also heat of combustion. Thermochemical data on organic compounds are ordinarily expressed in terms of the heats of combustion. The conventions used with the standard heats of formation are (13):

- i) the compound is oxidized with molecular oxygen to the products
 CO_2 (g), H_2O (l), HCl
- ii) the reference conditions are 25°C and 1 atmosphere pressure.
- iii) if other oxidizing substances are present, it is necessary to
 . make sure that states of the products are carefully specified
 and are identical to (or can be transformed into) the final
 conditions which determine the standard state.

Description of Apparatus

The Parr Adiabatic Bomb Calorimeter Model 2212 was used to measure the heat of combustion. The bomb is a heavy container in which the sample is placed, and oxygen is entered at a pressure of 24 to 30 atmospheres. Also a small amount of water is placed inside to saturate the oxygen so that all of the water formed by combustion ends up in liquid form.

This bomb is placed inside a water jacket which contains approximately 2 Kgm of water. A stirrer is used to maintain a uniform temperature in the

water jacket. This water jacket is immersed in a water bath in which temperature is maintained equal to that of the water jacket to make the process adiabatic. (This is done by introducing hot and cold water in the water bath until temperatures are equal.) The bomb is fired by an electrical current, and the temperature rise in the water jacket is recorded.

Experimental Results:

In Table A-4 the experimental results for the determination of the heat of combustion of nylon, phenolic resin (cured and uncured), phenolic microballoons and benzoic acid (a standard) are shown. Some difficulties with the phenolic microballoons arose when fabricating the sample pill required for the combustion experiment. The pill was noted to crumble because of the nature of the microballoon structure. As a result there is more scatter in this data. Also the heat of combustion of benzoic acid (a standard) was determined experimentally to within 0.5% of the actual value.

Sample Calculations of the Heat of Combustion

In these experiments an adiabatic bomb calorimeter was used and with data obtained the heat of combustion was calculated. To obtain ΔH_c the following formulae are used:

$$W = (\Delta H_c^B + C_{\text{wire}}) / \Delta T \quad (\text{A-2})$$

where:

- W = energy equivalent of calorimeter in calories per degrees F
- ΔH_c^B = heat of combustion of standard benzoic acid in calories per gram
- m = mass of benzoic acid in grams
- ΔT = temperature rise in °F
- C_{wire} = correction for heat of combustion of fuse wire in calories

Table A-4. Experimental Determination of the Heat of Combustion of Nylon 66, Uncured Phenolic Resin, Phenolic Microballoons, Cured Phenolic Resin, and Benzoic Acid.

Nylon 66

Run #	cal. due to wire used	T initial	T final	wt. used	ΔH_c (cal/gm)
1	4 cal	86.38	90.3	0.735 gm	-7232.0
2	13 cal	85.28	89.23	0.750 gm	-7124.3
3	19 cal	84.70	89.95	0.975 gm	-7282.0
4	17 cal	81.86	84.95	0.5782 gm	-7219.3
Average H_c					-7213.9

Uncured Phenolic Resin

Run #	cal. due to wire used	T initial	T final	wt. used	ΔH_c (cal/gm)
1	6 cal	84.60	91.00	1.105 gm	-7372.0
2	10 cal	76.15	81.20	0.998 gm	-6980.0
3	6 cal	86.91	92.66	1.076 gm	-7240.7
4	15 cal	75.92	81.62	1.082 gm	-7130.0
5	6 cal	84.74	90.74	1.1095 gm	-7327.6
Average H_c					-7210.0

Phenolic Microballoons

Run #	cal. due to wire used	T initial	T final	wt. used	ΔH_c (cal/gm)
1	12.5 cal	85.7	87.6	0.432 gm	-6570.3
2	12.5 cal	81.10	83.7	0.588 gm	-5974.7
3	15.0 cal	83.55	85.60	0.460 gm	-6010.9
4	12.0 cal	83.12	85.25	0.500 gm	-5752.2
5	15.0 cal	83.40	86.10	0.440 gm	-6287.0
Average H_c					-6119.5

Table A-4. Continued.

Cured Phenolic Resin

Run #	cal. due to wire used	T initial	T final	wt. used	ΔH_c (cal/gm)
1	10 cal	84.55	84.55	0.73 gm	-7442.3
2	15 cal	81.22	84.25	0.56 gm	-7313.8
3	10 cal	79.65	84.15	0.82 gm	-7402.7
Average H_c					-7386.3

Benzoic Acid (standardization)

Run #	cal. due to wire used	T initial	T final	wt. used	ΔH_c^* cal/gm
1	17.5 cal	79.65	83.0	0.722	-6318
2	23.0 cal	87.35	91.40	0.919	-6318

*Standard heat of combustion of Benzoic Acid (Parr Calorimeter Handbook).
is 6317 cal/gm.

and:

$$\Delta H_c = (w\Delta T - C_{\text{wire}}) / m \quad (\text{A-3})$$

where:

ΔH_c = heat of combustion in calories per gram

ΔT = temperature change in °F

C_{wire} = correction for combustion of fuse wire in calories

m = mass of the sample substance used in grams

The heat evolved by the combustion of the firing wire is given by the heat per unit length of wire, H_w , times the length of the wire used L . The wire used in this experimental study had the value of H_w of 2.3 cal/cm.

Using Equation (A-2) and the data on benzoic acid standardization experiment reported in Table A-4 gives:

$$W = \frac{0.722 (6318) + 17.5}{3.35} = 1356.44 \frac{\text{cal.}}{^\circ\text{F}}$$

The reported value by the Parr Calorimeter Handbook* for W is 1357 cal/°F, and this demonstrated the accuracy of the experimental procedure and apparatus.

The heat of combustion for nylon using the data in Table A-4 (Run 1) and Equation (A-3) gives:

$$\Delta H_c = \frac{1357 (3.92) - 4.0}{0.735} = 7232 \frac{\text{cal}}{\text{gm}}$$

*Parr Instruments Company, Moline, Illinois.