considerably simplified if the true bias K is known or is determined independently. If K is known, its value may be subtracted from the B_i in Eq. (19). The conditions for a least-squares data fit then become

$$\theta = \frac{\Sigma B_i \sin(\mathrm{Az}_i + \epsilon)}{\Sigma \sin^2(\mathrm{Az}_i + \epsilon)} \qquad (24)$$

$$F \triangleq \Sigma \sin 2(\mathrm{Az}_i + \epsilon)\Sigma B_i \sin(\mathrm{Az}_i + \epsilon) - 2\Sigma \sin 2(\mathrm{Az}_i + \epsilon)\Sigma B_i \cos(\mathrm{Az}_i + \epsilon) = 0 \qquad (25)$$

From Eq. (25)

$$F' \triangleq \frac{\partial F}{\partial \epsilon} = 2\Sigma \cos^2(\mathrm{Az}_i + \epsilon)\Sigma B_i \sin(\mathrm{Az}_i + \epsilon) - \Sigma \sin 2(\mathrm{Az}_i + \epsilon)\Sigma B_i \cos(\mathrm{Az}_i + \epsilon) \qquad (26)$$

The Newton-Raphson condition for determining ϵ may then be given as

$$\epsilon_{j+1} = \epsilon_j - F(\epsilon_j)/F'(\epsilon_j) \qquad (27)$$

where ϵ_0 is the initial guess and ϵ_j as the jth approximation to ϵ.

On Methods for Determining the Composition of Pyrolysis Products from Ablative Composites

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Nomenclature

C_p = heat capacity at constant pressure
$\Delta H_f, \Delta H_C, \Delta H_{\mathrm{pyr}}$ = heats of formation, combustion and pyrolysis, respectively
K, M = total number of products, and reactants, respectively
T = temperature
x = mass fraction

Subscripts

i,p,r = ith species, products and reactants, respectively
pyr = pyrolysis

Introduction

KNOWLEDGE of the composition of the pyrolysis products from the decomposition zone of a charring ablator is needed in the analysis of the heat-transfer processes taking place in the char zone and in the boundary layer. Direct measurement of the composition of the pyrolysis products is desirable, but there are difficulties in obtaining representative samples.[1-8] Consequently, most of the data reported in the literature present only those components that were gases near room temperature, which nominally account for only about 50% by weight of the total material pyrolyzed. Other methods are needed, and three alternative methods are presented and used for comparison with the compositions obtained from the chemical analysis of pyrolysis products from ablative composites.

Methods for Estimating Pyrolysis Gas Compositions

The total of four methods that can be used together to determine the composition of the pyrolysis products from ablative composites are discussed in the following subsections.

Chemical analysis of the pyrolysis gases

Sykes[2,3] degraded ablative composites in a furnace and injected the hot pyrolysis products directly into a gas chromatograph. However, even with his careful procedure, there was a certain amount of condensation of high-molecular-weight species in the heated line between the furnace and the chromatograph which remained unidentified. The method has, however, reduced the total amount of unidentified material pyrolyzed from the 50% level obtained with the more conventional methods[1] to 17% (by weight), and the species and their concentrations were more precisely determined. Therefore, results from Sykes' technique will form the basis for 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 measured and calculated heats of pyrolysis

The heat of pyrolysis, ΔH_{pyr}, which converts the virgin plastic composite ("reactants") to pyrolysis gases plus char (in total, the "products") can be experimentally measured by differential thermal analysis (DTA). Also, it can be calculated knowing the heats of formation and specific heat $C_p(T)$ of the products and reactants:

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

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 average temperature which gives the correct energy associated with the pyrolysis products. It was determined to be 700°C as a weighted average based on the mass loss rate. The heats of formation of nylon and phenolic resin, $\Delta H_{f,rj}$, were calculated from experimentally determined heats of combustion, ΔH_C, by the procedure reported in Ref. 9. Then the ΔH_{pyr} can be computed if the pyrolysis gas composition x_{pi} is known since $\Delta H_{f,pi}$ is tabulated in standard references e.g., Ref. 10.

If the value of ΔH_{pyr} calculated by the foregoing method does not agree within 10% of the value measured by DTA, the composition proposed is either in error or is incomplete. A recommended way to obtain an accurate composition is to inspect all of the available data as reported by various investigators and select those species to be present which are reported by a majority of the investigations. If the composition of various fractions are given, weigh each species composition according to the size of each fraction. Then superimpose these results and construct an over-all species composition listing. Average the values of species that appear within reasonable agreement, and use the species that are reported in a minority of the papers to make minor adjustments to the composition.

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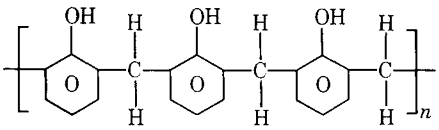
Deductions from relative strengths of chemical bonds

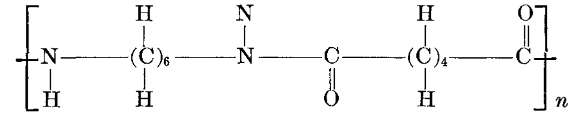
The ability of a char layer to withstand aerodynamic stresses, and high temperatures is attributed, in part, to the highly crosslinked nature of the aromatic polymers such as phenolic resin. The already strong C–C bonds are reinforced by resonance effects resulting from the crosslinked structure. Therefore, 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. We can speculate on the origin of likely pyrolysis products based on the bond energies in the polymers. Let us consider some information on a phenolic resin, a nylon, and composites of these.

Parker[11] 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. The phenolic novalac polymer may be represented as follows:



Parker pointed out that the place where cleavage was most likely to be initiated was at the methylene bridge ($-CH_2-$) 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 Fig. 1.

Nylon-66 (hexamethylenediamine-adipic acid) is formed by the polymerization of one monomer of adipic acid with one monomer of hexamethylenediamine in alternating steps:



$$\left[-\underset{\mathrm{H}}{\mathrm{N}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{(\mathrm{C})_6}}-\overset{\mathrm{N}}{\mathrm{N}}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{(\mathrm{C})_4}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\right]_n$$

Inspection of the bond energies between atoms of the CHON system reported in Ref. 12 and neglecting resonance and electronegativity effects that exist in the polymer, the most logical place for cleavage to occur is at the C–N bonds (62 kcal/g vs. 80 for C–C). This essentially separates the polymer into shorter chain lengths and monomer units. From this point cleavage of bonds within the monomer structure can occur forming NH_3, CO, CO_2, H_2O, H_2, CH_4, C_2H_6, etc. In fact, reported experimental data show that only about 7% (by weight) of nylon-66 is degraded to residue.[3,4] The remaining 93% forms gaseous products. Therefore, the char structure of a nylon-phenolic resin composite is formed from the degradation of the phenolic resin, while a major portion of the pyrolysis gases are formed from the nylon-66.

A nylon-phenolic resin composite yields all of the above mentioned products (some 53 organic compounds have been reported[1–8]). The relative quantities could be based on the weight fraction of each polymer in the composite if there is no interaction by the mixture on degradation.

Restricted equilibrium analysis

It has been suggested[13] 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. This concept proposes that the composition of the pyrolysis gases and char be computed from chemical equilibrium but be constrained by the amount of energy supplied for the decomposition to be equal to the heat of pyrolysis. The constraint equation is given by Eq. (1); specifically the sum of ΔH_{pyr} and the second term on the right-hand side of Eq. (1) (the enthalpy of the ablative composite at T_r) is a constant for a given ablative composite, and this constant must be equal to the first term on the right-hand side of Eq. (1). Thus Eq. (1) 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 are discussed in detail in Ref. (14). Results are given in the following section.

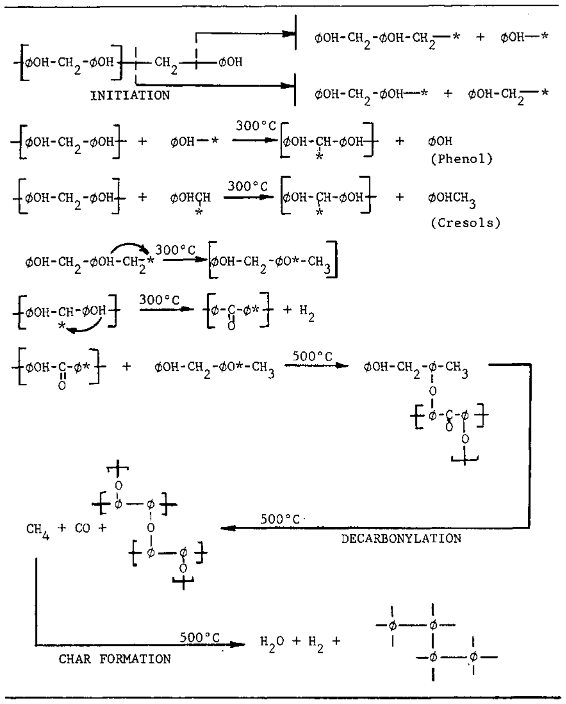


Fig. 1 Mechanism of phenolic novalac degradation to char.

Comparison of the Methods for Estimating the Pyrolysis Gas Compositions

Measured and computed heat of pyrolysis

Sykes[2,3] identified 83% of the total decomposition products evolved during the thermal degradation of phenolic resin and a nylon-phenolic resin composite during rapid heating of these materials. The remaining 17% was reported to be an unidentified, dark, tarry substance. The computed heat of pyrolysis is shown for phenolic resin and the composite in Table 1 and compared with the experimental values of Sykes. Agreement is well within experimental error for the composite, and this indicates the reported compositions are accurate. The unidentified portion of the pyrolysis products was taken as phenol for calculating the heat of pyrolysis. The results were somewhat, but not significantly, poorer for the phenolic resin only. This deviation could have been caused by either improper curing of the specimen resulting in the higher water content or inaccuracies in the analysis of the evolved pyrolysis products.

Similar calculations (not shown) were made with the data reported by Friedman[5] for a nylon-phenolic resin composite. In this case the composition was determined from near room temperature samples analyzed by gas chromatography. The higher molecular weight species such as phenol and the cresols were absent, and as a result a much poorer comparison between the calculated (987 Btu/lb) and experimental (200–500 Btu/lb) heats of pyrolysis was obtained. This would be expected if these important species were omitted, and the inclusion of phenol and similar high molecular weight species which are liquids and solids at room temperature is necessary.

Table 1 Comparison of measured and calculated heat of pyrolysis for nylon-phenolic composite[2] and phenolic resin[1]

Component Products	Composite x_i^b	Composite A_i^a	Composite B_i^a	Phenolic resin x_i^b	Phenolic resin A_i^a	Phenolic resin B_i^a
Phenol	0.118	−49	34	0.181	−75	52
Methylphenol	0.064	−33	18	0.060	−34	17
Dimethylphenol	0.051	−29	14	...		
Trimethylphenol	0.041	−25	12	...		
Benzene	0.003	2	2	0.004	2	2
Toluene	0.001	1	1	0.009	1	5
Cyclopentanone	0.029	−18	9	...		
H_2	0.010	0	34	0.027	0	91
CH_4	0.010	−20	10	0.043	−87	29
CO	0.021	−18	6	0.042	−71	10
CO_2	0.067	−36	5	0.019	−74	6
H_2O	0.063	−576	23	0.115	−661	55
NH_3	0.002	−2	2	...		
Unidentified[c]	0.173	−72	51	0.150	−62	43
Carbon residue	0.348	133	99	0.350	137	101
Σ	1.000	−742	320	1.000	−924	411
"Reactants"	x_i	C_i^a	D_i^a	x_i	C_i^a	D_i^a
Nylon	0.4	−348	250			
Phenolic	0.6	−501		1.0	−823	200
Σ	1.0	−885	250	1.0	−823	200
		$\Delta H_{\text{pyr,calc}}$ $(A + B - C - D)^a$			$\Delta H_{\text{pyr,exp}}$, Btu/lb	
Composite		213			200	
Phenolic resin		110			146	

[a] A_i and $C_i = x_i \Delta H_{fi}$, B_i and $D_i = x_i C_{pi}$, mean ΔT for products and reactants, respectively, and $A = \Sigma A_i$, $B = \Sigma B_i$, $C = \Sigma C_i$, and $D = \Sigma D_i$.

[b] Average of flash and 50°C increment compositions reported by Sykes.[2,3]

[c] Unidentified material was considered to be phenol for ΔH_f.

Ladachi et al.[6] computed the heat of pyrolysis of a silica-phenolic resin composite from the heat of formation (calculated from the heat of combustion) and the composition of the pyrolysis products (identified by mass spectrometry). Ladachi computed the heat of pyrolysis to be 550 Btu/lb, and our calculations gave 543 Btu/lb, i.e., essentially the same number as expected.

Jackson and Conley[7] thermally degraded phenolic resin (base catalyzed) 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 observed weight loss 50% was reported to be noncondensables, e.g., water, paraformaldehyde and a high molecular weight, nonvolatile residue. No experimental value of ΔH_{pyr} was reported, but the calculated value of 235 Btu/lb can be compared with the experimental value reported by Sykes of 146 Btu/lb. This agreement is probably within the accuracy of the experimental data, and it was necessary to assume the residue to be carbon for the calculation.

Shulman and Lochte[8] degraded phenol-formaldehyde resin by pyrolyzing 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 were analyzed. The composition of phenol type compounds, gases such as CH_4, CO, and CO_2 were measured, and there was 50.8% residue. Computing the heat of pyrolysis using the compositions reported gave a value of 110 Btu/lb. No experimental value was reported, but again,

Table 2 Comparison of restricted equilibrium and equilibrium compositions (weight %) with experimental data of Sykes[2] for a 40% nylon–60% phenolic resin composite

	Restricted equilibrium					
	−390 Btu/lb		228 Btu/lb		Equil. comp.	
Components	700°C	600°C	700°C	600°C	700°C	Experimental
Phenol	10^{-11}	10^{-11}	10^{-11}	10^{-11}	10^{-16}	11.8
Methylphenol	...	...	...	...	...	6.4
Dimethylphenol	...	...	...	...	...	5.1
Trimethylphenol	...	...	...	...	...	4.1
Benzene	10^{-11}	10^{-15}	10^{-11}	10^{-15}	10^{-11}	0.3
Toluene	10^{-11}	10^{-11}	10^{-11}	10^{-11}	10^{-11}	0.1
Cyclopentanone	...	...	...	...	...	2.9
Methane	3.9	2.5	3.6	2.4	4.3	1.0
Hydrogen	6.0	6.5	6.1	6.6	5.9	1.0
Carbon Monoxide	16.0	20.5	16.7	21.0	15.0	2.1
Carbon Dioxide	2.7	1.4	2.4	1.2	3.1	6.7
Water	3.8	2.1	3.6	1.9	4.3	6.2
NH_3	10^{-2}	10^{-2}	10^{-2}	10^{-2}	10^{-2}	0.2
N_2	4.0	3.9	4.0	3.9	3.9	...
Unidentified	...	...	...	...	...	17.3
Carbon (solid)	63.5	63.1	63.6	63.0	63.5	34.8
Total	100.0	100.0	100.0	100.0	100.0	100.0

Table 3 Representative pyrolysis product composition from the degradation of a 40% (by weight) Nylon-60% (by weight) phenolic resin ablative composite

Component	Mass percent	Mole percent
H_2	2.60	20.92
CH_4	3.87	3.90
C_2H_2	3.89	2.41
C_2H_4	3.90	2.24
C_2H_6	0.65	0.35
C_6H_6	2.59	0.53
C_6H_5OH	23.18	3.97
CO	4.18	2.40
CO_2	4.62	1.69
H_2O	7.21	6.45
N_2	3.83	2.20
Carbon (solid)	39.48	52.94
Total	100.00	100.00
Element	Mass percent	Mole percent
C	73.03	41.54
H	7.29	49.76
N	4.96	2.42
O	14.72	6.28
Total	100.00	100.00

this is comparable to the value of 146 Btu/lb experimentally measured by Sykes[2] 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, i.e., when the higher molecular weight species such as phenol and other ring compounds from the degradation of phenolic resin are included.

Restricted equilibrium analysis

Restricted equilibrium analyses were made[14] for the degradation of a 40% (by weight) nylon-60% (by weight) phenolic resin composite using Eq. (1) as an additional constraint to free energy minimization calculations. The computations were done for two decomposition temperatures (600° and 700°C) because of the uncertainty involved in the physical properties used to calculate the average temperature, T_p. In addition, two different energy constraints (-228 and -390 Btu/lb of composite) were used because of uncertainties in the heat of pyrolysis.

In Table 2 a comparison is given for the preceding cases with chemical equilibrium and the experimental data of Sykes.[2] The computations and experiments show an order of magnitude agreement with the low molecular weight species. The agreement with the high molecular weight species of phenol, toluene, benzene, etc., was rather poor. Changing the energy constraint and the temperature did not cause any dramatic changes in the computed compositions. In general, restricted equilibrium provided an order of magnitude for the composition of low molecular weight compound. It failed to predict the composition of the higher molecular weight component.

A Representative Pyrolysis Gas Composition

Accurate compositions of the pyrolysis products are required for computations of the energy absorbed by a heat shield during entry. This is particularly true where radiation heating is a significant portion of the energy transferred to the surface of the ablator. The radiant energy transfer is particularly sensitive to the ablation products distribution in the shock layer. Thus based on the four methods discussed in this Note a representative composition of the pyrolysis products from the degradation of a 40% nylon-60% phenolic resin composite was estimated. This composition is given in Table 3, and it is consistent with the experimental data, the heat of pyrolysis analysis, and the molecular structure. It is also stoichiometrically consistent with the elemental composition of the composite.

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Effect of Gas Composition on the Ablation Performance of Phenolic Nylon

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A NUMBER of recent experimental investigations[1–6] have considered the removal of surface char from the stagnation region of phenolic-nylon specimens exposed to high-temperature, arc-heated gas streams. The surface-

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