Outline

- Why this tutorial?
- Ablative TPS - early studies
- Organic resin composites
- **Surface recession mechanisms/modeling**
- High fidelity model development
- Testing approaches/requirements
- Future needs

Empirical Approach

- Potentially, very accurate (if data is well-behaved), but what parameter(s) does one correlate recession rate with?
  - Surface temperature
  - Pressure
  - Heat transfer-coefficient
- Empirical correlations do not provide any insight to ablation *mechanisms*
- Validity of correlations typically limited to range of ground test data
  - Extrapolation beyond data range carries significant *risk*
  - Capability to *simultaneously* simulate flight environment parameters (e.g., heat flux, pressure, enthalpy) in ground test is the exception rather than the rule

Empirical correlations

- Heat of ablation (Q*)
  - This approach has been/is being (erroneously) used to estimate surface recession
  - Typically, recession rate estimated from $\rho\dot{s} = \dot{q}_{cw} / Q^*_{cw}$
  - For environments other than very severe heating, this approach will overestimate recession
- Curvefits
  - Typical form: $\dot{s} = f(T_w)$ or $\dot{s} = f(p, T_w)$
  - Has been used with some success for materials that vaporize (e.g., glass) or sublime (e.g., teflon)
  - Not demonstrated to be a viable approach for reinforced organic resin composites
- Limited applicability
  - How to apply empirical correlations developed in ground test facilities operating on air (existing arc jet facilities) to performance in planetary atmospheres (e.g., N_2/CH_4, CO_2, H_2/He)

Ablation Mechanisms

- Melting (metals, glass, ceramics, etc.)
  - Heat of fusion (not very significant)
  - $M(s)^* \Leftrightarrow M(l)^*$
- Vaporization (liquid layer from melted metals, glass, ceramics)
  - Heat of vaporization
  - $M(l)^* \Rightarrow M(g)^*$
- Oxidation (graphite, carbon chars, etc.)
  - Exothermic
  - $M(s)^* + O_2(g) \Rightarrow MO_2(g)$
- Sublimation
  - Heat of sublimation (can be significant)
  - $M(s)^* \Rightarrow M(g)$
- Spallation
  - Mass loss with minimal energy accommodation

Melting

- Melting is a common ablation mechanism, but doesn't absorb much energy
- Rapid melt runoff due to aerodynamic shear results in significant (inefficient) ablation
- In contrast, a stable liquid layer on the surface can be attractive (due to the potential for vaporization)

Specie	Tmelt (K)	Heat of Fusion (J/g)
K*	336	60
Li*	454	432
Al*	933	397
Cu*	1358	206
Be*	1556	1297
Fe*	1809	247
Li_2O*	1843	1960
Ti*	1933	388
SiO_2*	1996	150
TiO*	2023	654
Zr*	2125	229
TiO_2*	2130	838
Al_2O_3*	2315	1159
Mo*	2896	375
ZrO_2*	2950	706
TiB_2*	3193	1443
W*	3680	192

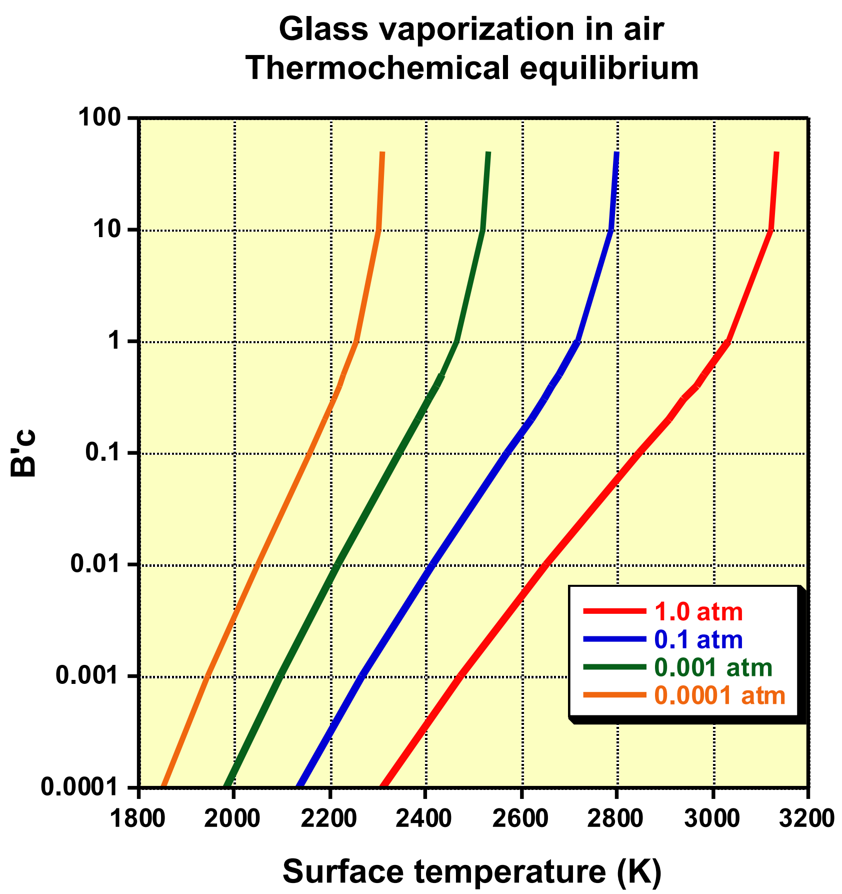
Vaporization

- Vaporization absorbs significant amount of energy
- Example:

$$SiO_2(l) \rightarrow SiO(g) + \frac{1}{2} O_2(g)$$

$$\Delta H_v \approx 12.5\ kJ/g_{SiO_2}$$

- However, typically, liquid layers have low-moderate hemispherical emissivity (reduces re-radiation)



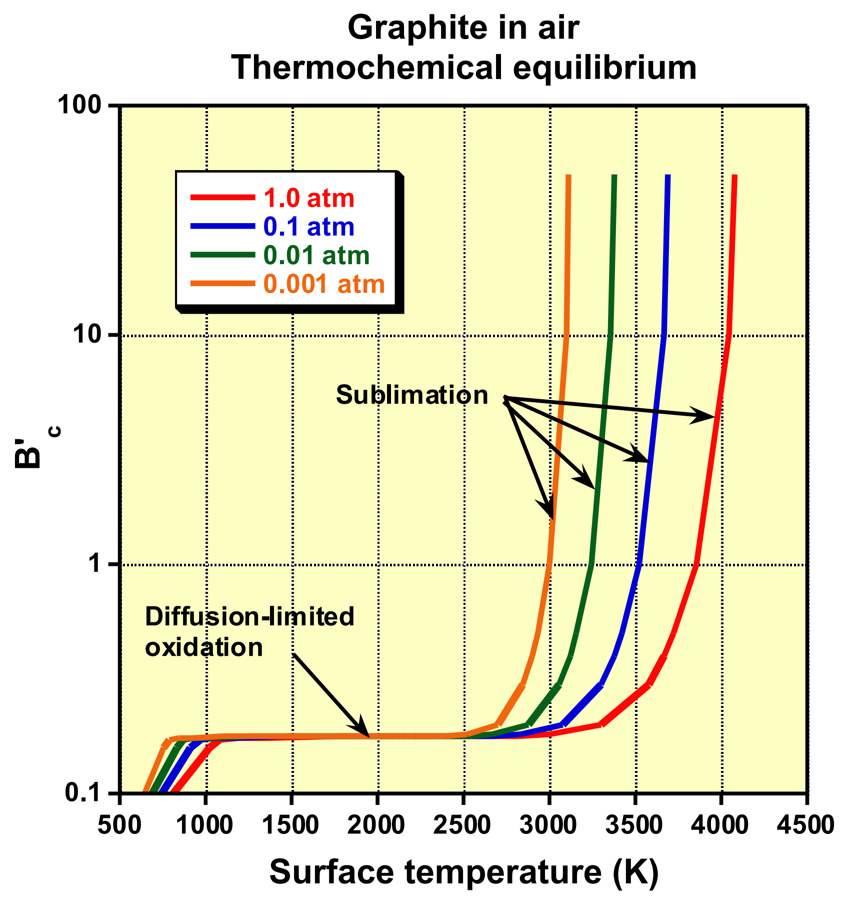
Oxidation - 1

- Oxidation is an *exothermic* process
- Example:

$$2C(s)+O_2(g)\rightarrow 2CO(g)$$

$$\Delta H_{comb} \approx -4170 \;\; kJ/g_{carbon}$$

- Note: the B' curve for carbon in air was generated with assumptions of thermochemical equilibrium, equal diffusion coefficients, etc.
- The "equilibrium" assumption allows the diffusion-limited plateau to extend to *unrealistically low* surface temperatures



Oxidation - 2

- The diffusion-limited value of B' can be calculated from the mass ratios of the reactants and products, i.e.,

$$2C(s)+O_2(g)+3.718N_2(g)\leftrightarrow 2CO(g)+3.718N_2(g)$$

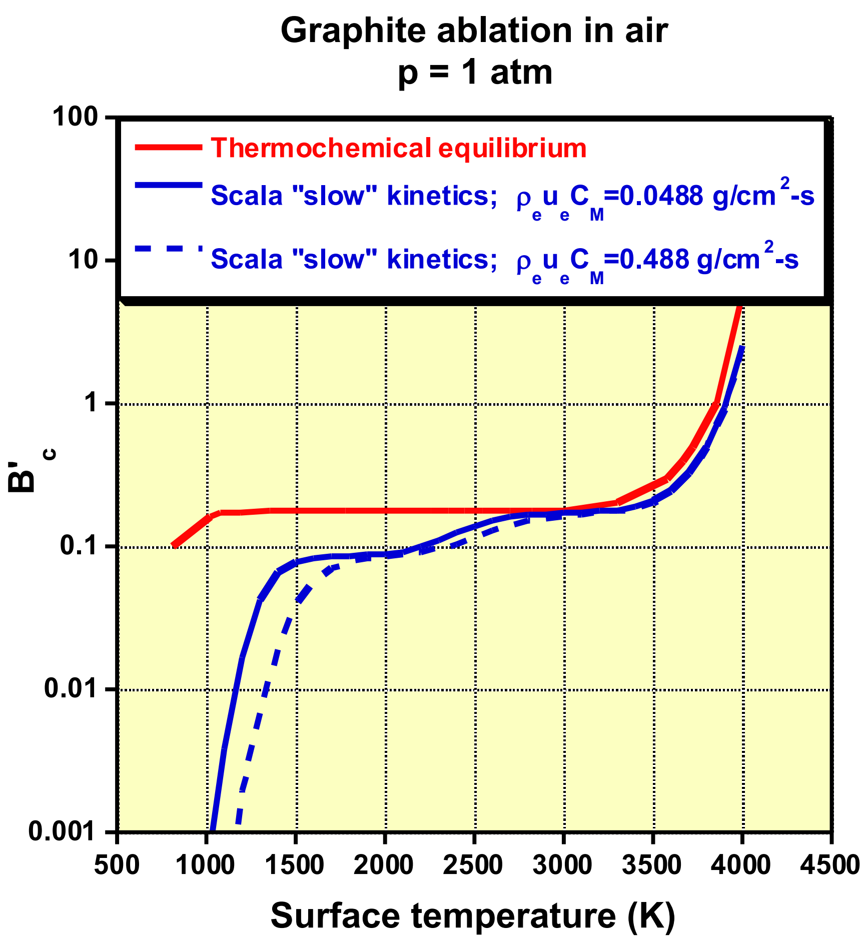
where there are 3.718 moles of N_2 for each mole of O_2 in air. The approximate value of B' for this reaction can be defined as the ratio of the mass of the solid reactants to the mass of the gaseous reactants, i.e.,

$$B' = \frac{mass\ of\ carbon}{mass\ of\ air} = \frac{2(12.011)}{[32.0+(3.718)28.014]} = 0.176$$

- Realistic estimates of carbon ablation at low surface temperatures requires consideration of reaction-rate limited oxidation processes
  - Complex problem where rates are dependent upon oxygen partial pressure, mass transfer coefficient, temperature, surface morphology, etc.

Oxidation - 3

- Comparison of equilibrium solution vs. rate-limited solutions for carbon oxidation demonstrates that equilibrium solutions will overestimate surface recession over much of the oxidation regime
- Developing kinetic rate constants requires careful experimentation
- Results will be material-specific since absorption/ desorption is dependent on surface morphology



Sublimation

- Carbon sublimation is a highly *endothermic* process

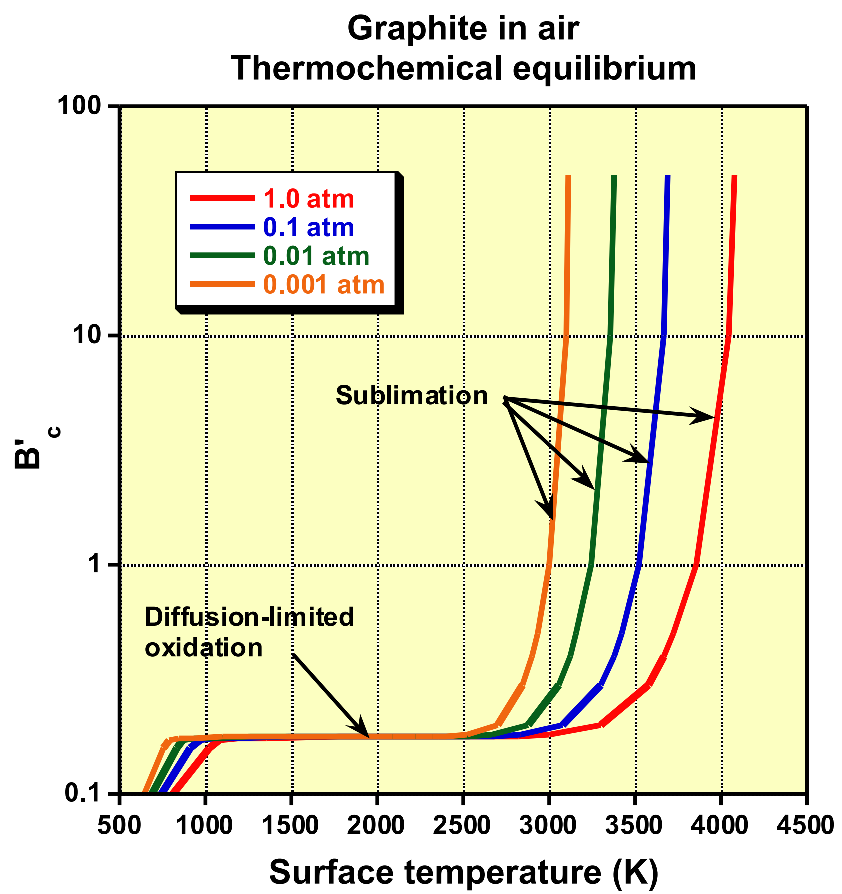
$$C(s) \rightarrow aC_1(g) + bC_2(g) + cC_3(g) + \dots nC_n(g)$$

- Example (for simplicity):

$$3C(s) \rightarrow C_3(g)$$

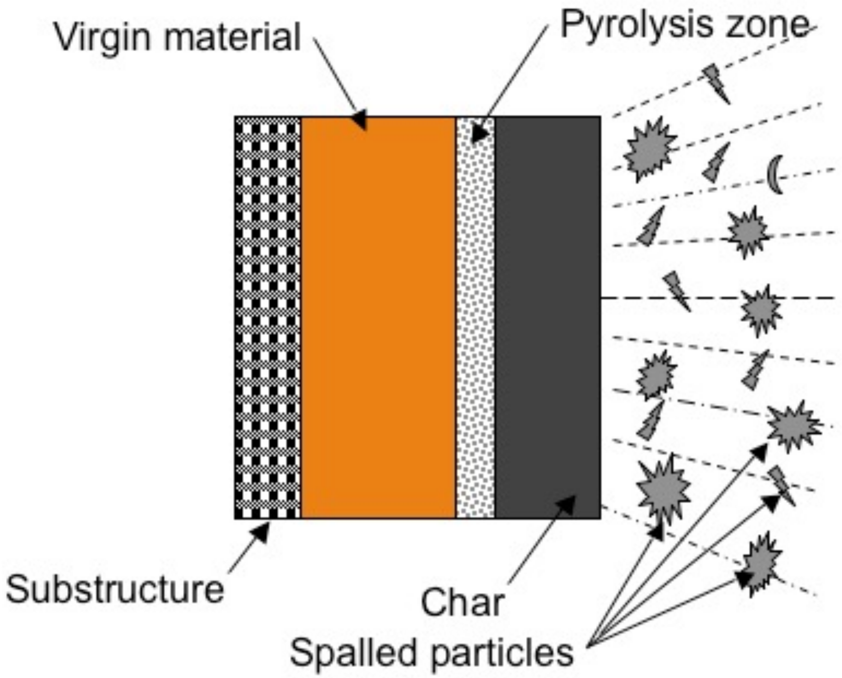
$$\Delta H_{sub} \approx 22.7\ kJ / g_{carbon}$$

- Carbon sublimation predictions exhibit some sensitivity to species thermochemical data (e.g., JANAF, Livermore, etc.)



Spallation

- Spallation refers to thermo-structural failure of the material and ejection of solid char and particulates[10,11,17,18,22]
  - More common in organic resin composites than homogeneous materials
- All organic resin composites have a spallation threshold = $f(\dot{q}, p)$
- Spallation threshold, in general, increases with increasing density

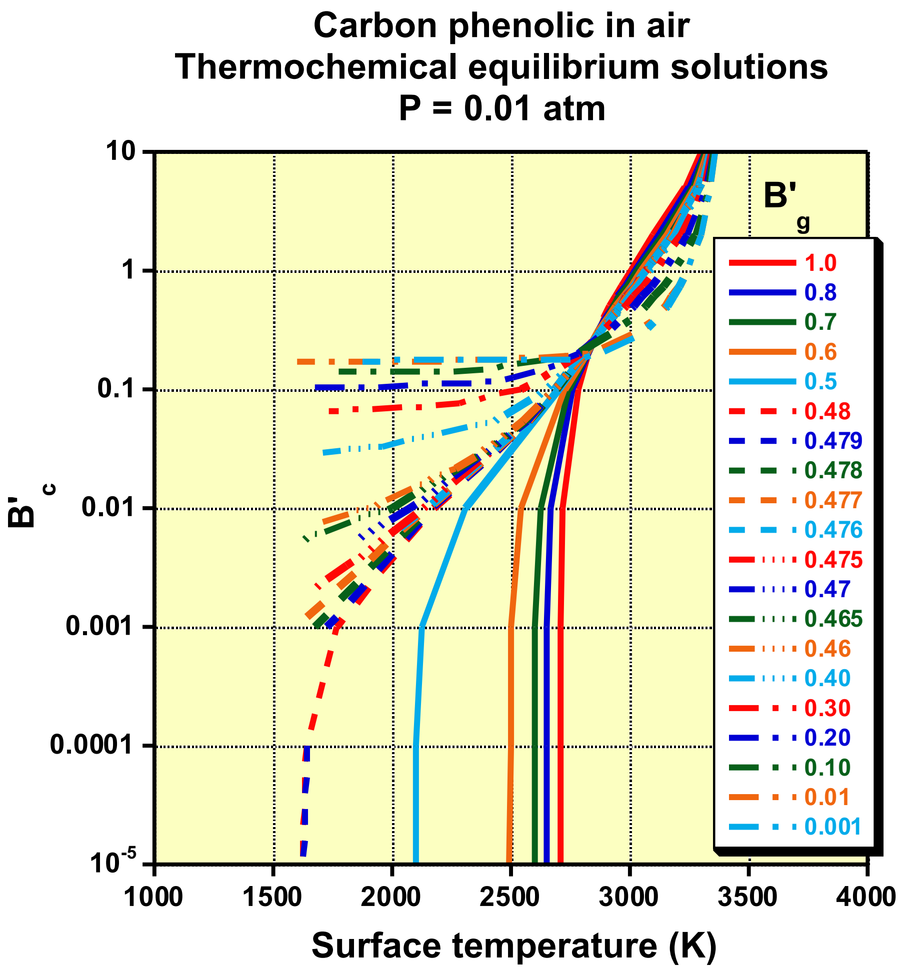


Organic Resin Composites

- Generating surface thermochemistry tables for organic resin composites requires thought and care

$$B'_c = f\left(p, T_w, B'_g\right)$$

- Useful to plot the solutions to ensure that the thermal response code is capable of interpolating between adjacent solutions with credible results
- Thermochemical equilibrium solutions are reasonably complex; incorporating rate-limited reactions is very complex



Summary

- Modeling surface ablation is best accomplished if the focus is on understanding ablation *mechanisms*
  - Requires careful experimentation
    - Film or video
    - Surface temperature (key discriminator)
    - Post-test inspection/autopsy
- Use theoretical models (e.g., thermochemical equilibrium) for pre-test/post-test predictions
  - Compare data with predictions (mass loss rate, surface temperature, surface species, etc.)
  - Identify other parameters that could influence performance (e.g., surface catalycity)
- Ability to model material performance mechanisms using thermochemical models allows extrapolation to conditions beyond ground test data base (within limits)

References

1. "JANAF Thermochemical Tables," Third Edition, *J. of Physical and Chemical Reference Data,* Vol. 14, 1985.
2. Anon., "User's Manual, Aerotherm Chemical Equilibrium Computer Program (ACE81)," Acurex Corporation, Aerotherm Division, Mountain View, California, August 1981.
3. Bethe, H.A. and M.C. Adams, "A Theory for the Ablation of Glassy Materials," *J. Aerospace Sci.,* Vol. 26, pp. 321-328, 1959.
4. Adams, M.C., Powers, W.E. and S. Georgiev, "An Experimental and Theoretical Study of Quartz Ablation at the Stagnation Point," J. Aerospace Sci., Vol., 27, pp. 535-543, 1960.
5. Scala, S.M., The Ablation of Graphite in Dissociated Air, Part I: Theory," General Electric Report R62SD72, Sept., 1962.
6. Diaconis, N.S. Gorsuch, P.D. and R.A. Sheridan, "The Ablation of Graphite in Dissociated Air, Part II" Experimental Investigation," General Electric Report R62SD86, Sept. 1962.
7. Beecher, N. and R.E. Rosensweig, "Ablation Mechanism in Plastics with Inorganic Reinforcement," *AIAA J.,* Vol. 31, pp 532-539, 1961.
8. Lundell, J.H. and R.R. Dickey, "The Ablation of Graphitic Materials in the Sublimation Regime," AIAA Paper No., 72-298, April 1972.
9. Milos, F.S. and Y.-K. Chen, "Comprehensive Model for Multicomponent Ablation Thermochemistry," AIAA Paper No. 97-0141, Jan. 1997.
10. Schneider, P.J., Dolton, T.A. and Reed, G.W., "Mechanical Erosion of Charring Ablators in Ground-Test and Re-Entry Environments, AIAA Journal , Vol. 6, No. 1.
11. Mathieu, Richard D., "Mechanical Spallation of Charring Ablators in Hyperthermal Environments", AIAA Journal, Vol. 2, No. 9, September 1964.

References (continued)

12. Stokes, Eric H., “Gas Permeability of RSRM Carbon Phenolic Composites as a Function of Across Ply Tensile Stress, Strain, and Temperature, 1992 JANNAF Rocket Nozzle Technology Subcommittee Meeting, Sunnyvale California.
13. Jortner, Julius, “Microstructures of Rapidly Heated Carbon-Phenolics”, SPIP Program, Document No. HI-054F/1.2.9, March 1993.
14. Koenig, John, “Solid Propulsion Integrity Program Exploratory Testing”, SPIP Program, Document No. H)-053F/1.2.9, March 1993.
15. Ross, R.B., Strobel, F.A., Fretter, E.F., “Plasma Arc Testing and Thermal Characterization of NARC FM5055 Carbon-Phenolic”, SPIP Program, Document No. HI-046F/1.2.9, April 1992.
16. Hercules Aerospace Company, “Solid Propulsion Integrity Program Final Report”, SPIP Program, Document No. HI-080F/1.2.9, December 1994.
11. Strobel, F.A., King, B.K., “ASRM Nozzle Thermal Analysis”, Aerotherm Final Report 7186-93-15, November 1993, Aerotherm Corporation, Huntsville, Alabama. Crose, J.G., Marx, D.A., Holman, R.L., “Solid Propulsion Program Mechanical Property Dependencies", SPIP Program, Document No. HI-079F/1.2.9, December 1994.
12. Kuhlman, Tim L., “Thermo-Chemical-Structural Analysis of Carbon-Phenolic Composites with Pore Pressure and Pyrolysis Effects”, SPIP Program, Document No. HI-017F/1.2.5, August 1992.
13. Stokes, Eric H., “Kinetics of Pyrolysis Mass Loss From MX4926 Standard Density NARC Based Carbon-Phenolic Composite” Volumes I, II, and III, SPIP Program, Document No. HI-063F/1.2.9, September 1994.
14. Poteat, R.M., Lundblad, W.E., Koenig, J.R., “Mechanical Property Evaluations Solid Propulsion Integrity Program Exploratory Testing” Volumes I and II, SPIP Program, Document No., HI-069F/1.2.9, November 1994.

References (concluded)

15. Ross, R.B., Strobel, F.A. “MX 4926 (HRPF) Thermal Response Model”, SPIP Program, HI-073F/1.2.9, December 1994.
16. Clayton, Fred I., “Derivation of New Thermal Decomposition Model for Carbon-Phenolic Composites”, SPIP Program, HI-065F/1.2.9, November 1994.
17. Koenig, John R., “Thermal Property Evaluations Solid Propulsion Integrity Program Exploratory Testing”, SPIP Program, HI-068F/1.2.9, November 1994.
18. McManus, Hugh L., “High Temperature Thermochemical Behavior of Carbon-Phenolic and Carbon-Carbon Composites”, A Dissertation submitted to the Mechanical Engineering Department of Stanford University, April 1990.
19. Stokes, Eric H., “Gas Compressibility of Carbon-Phenolic Pyrolysis Products”, SRI-MME-91-378-6672-003, April 1991.
20. Stokes, Eric H., “Vapor Pressure of Carbon Phenolic Pyrolysis Gas Products”, SRI-MME-92-295-6672.12, April 1992.
21. Stokes, Eric H., “Selection of Improved Acceptance Tests for Cured Carbon Phenolic Composites”, SRI-MME-92-836-6672.14, September 1992.
22. Koenig, J.R., Jackson, T.E., Stewart, D.J., Laughlin, W.T., “Evaluation of LHMEL Exposed Specimens”, Presented at the 1994 JANNAF RNTS Subcommittee meeting, Seattle Washington, 15-17 November 1994.
23. Clayton, J. Louie, “Thermal/Pyrolysis Gas Flow Analysis of MX4926 Carbon Phenolic Material Tested at the Laser Hardened Material Evaluation Laboratory”, Presented at the 1998 JANNAF Propulsion Conference, Salt Lake City, Utah, March 15, 1998.