Nonequilibrium Ablation of Phenolic Impregnated Carbon Ablator

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DOI: 10.2514/1.A32298

In previous work, an equilibrium ablation and thermal response model for Phenolic Impregnated Carbon Ablator was developed. In general, over a wide range of test conditions, model predictions compared well with arcjet data for surface recession, surface temperature, in-depth temperature at multiple thermocouples, and char depth. In this work, additional arcjet tests were conducted at stagnation conditions down to 40 W/cm² and 1.6 kPa. The new data suggest that nonequilibrium effects become important for ablation predictions at heat flux or pressure below about 80 W/cm² or 10 kPa, respectively. Modifications to the ablation model to account for nonequilibrium effects are investigated. Predictions of the equilibrium and nonequilibrium models are compared with the arcjet data.

Nomenclature

\( B' \) = dimensionless mass blowing rate
\( C_H \) = Stanton number for heat transfer
\( C_M \) = Stanton number for mass transfer
\( D \) = model diameter, m
\( E \) = fractional error defined by Eq. (1)
\( M \) = molecular weight, kg/kmol
\( p \) = pressure, N/m²
\( R \) = gas constant, 8314 J/kmol · K
\( R_c \) = model corner radius, m
\( R_n \) = model nose radius, m
\( r_f \) = forward reaction rate, kg/m² · s
\( T \) = translational–rotational temperature, K
\( T_v \) = vibrational-electronic temperature, K
\( u \) = gas velocity, m/s
\( \Delta S \) = recession, m
\( \eta \) = reaction probability
\( \rho \) = density, kg/m³

Subscripts

c = char or carbon
e = boundary-layer edge
g = pyrolysis gas
\( \omega \) = oxygen
\( (s) \) = solid phase

I. Introduction

PHENOLIC impregnated Carbon Ablator (PICA) is a low-density composite material made from a rigid, carbon fiber insulation impregnated with a phenolic resin [1]. PICA was the heat shield material on the Stardust sample-return capsule [2], which is to date the fastest man-made Earth-entry vehicle. PICA also is the heat shield material for the Mars Science Laboratory (MSL) [3], and it was one of two candidate materials for the Orion Crew Module [4]. A similar material, named PICA-X, is manufactured by SpaceX for the Dragon spacecraft§.

The Orion thermal protection system (TPS) Advanced Development Project conducted extensive thermal, mechanical, and other material property testing of PICA. Based on test results, the PICAv3.3 material property model¶ was developed specifically for use with the fully implicit ablation and thermal-response (FIAT) code that calculates ablation, pyrolysis, and thermal conduction in one dimension [5]. This code and the PICAv3.3 model have been used for analysis of ground tests as well as for thermal analysis and sizing of PICA tiles for flight applications on Orion, MSL, and Dragon.

A large number of stagnation arcjet tests were performed to acquire data on PICA thermal and ablative performance over a wide range of aerothermal conditions applicable to Orion low-Earth-orbit and lunar-return entries. The PICAv3.3 model was validated by comparison of numerical predictions with this large database of stagnation arcjet test data [6]. In general, the comparisons showed an excellent agreement between predictions and data for total recession, surface temperature, in-depth temperature at multiple thermocouples, and char depth. The error in recession predictions was less than 10% except for a few tests conducted at low heat flux or low pressure.

In [6], it was suggested that modifications to the modeling to account for nonequilibrium flowfield and ablation effects might improve the predictions at low test conditions. Since the development of the PICAv3.3 model, the MSL and Orion projects conducted additional stagnation arcjet tests of PICA including some environments with low heat flux or pressure. The purpose of this work is to describe modifications to the ablation model that account for nonequilibrium effects and to compare the model predictions with the arcjet data.

II. Arcjet Models, Data, and Test Conditions

PICA arcjet models were exposed to 15 test conditions that are plotted in Fig. 1 and listed in Table 1 in order of increasing heat flux. Four conditions, shown as triangles, were analyzed previously [6]. The circles are new test conditions. Based on previous experience with the arcjet facilities, the uncertainty of the stagnation pressure is considered to be less than ±5%, whereas the uncertainty in

\text{NASA-TM-2009-215377, 2018-12-29T22:07:04+00:00Z} \)
Table 1 was calculated by assuming that the three streams become the downstream electrode and the nozzle. The argon mass fraction in and had a 12.7-cm-diam iso-q shape. For environment 2 only, the two models direction parallel to the axis of symmetry. Twenty-nine models had a relatively constant over most of the front face of the iso-q shape. All geometry, is that, in the ARC arcjets, the heat advantage of the iso-q geometry, compared with a shape, the nose radius equals the diameter, the corner radius is the same external shape as the TPS samples to be tested [8]. For this combination slug-calorimeter/pitot-pressure device (Fig. 2) that had wall heat obtain calibration measurements of stagnation pressure and cold-condition, multiple runs and/or multiple swing arms were used to (AHF) at NASA Ames Research Center (ARC) [7]. For each test average measurement obtained from all runs at a given test condition.

stagnation heat flux is at least ±10%. The tabulated values are the average measurement obtained from all runs at a given test condition.

All tests were conducted in the Aerodynamic Heating Facility (AHF) at NASA Ames Research Center (ARC) [7]. For each test condition, multiple runs and/or multiple swing arms were used to obtain calibration measurements of stagnation pressure and cold-wall heat flux. For most runs, these quantities were measured using a combination slug-calorimeter/pitot-pressure device (Fig. 2) that had the same external shape as the TPS samples to be tested [8]. For this iso-q shape, the nose radius equals the diameter, the corner radius is 1/16 of the diameter, and the sides are cylindrical. The primary advantage of the iso-q geometry, compared with a flat-faced geometry, is that, in the ARC arcjets, the heat flux distribution is relatively constant over most of the front face of the iso-q shape. All PICA models were manufactured with the lower conductivity direction parallel to the axis of symmetry. Twenty-nine models had a 10.16-cm-diam iso-q shape. For environment 2 only, the two models had a 12.7-cm-diam flat-faced shape, and a flat-faced calorimeter was used to measure the stagnation conditions.

In the ARC facilities, argon is used to protect the upstream electrode, the main air is added along the length of the arcjet column, and finally additional air (called “add air”) may be injected after the downstream electrode. The purpose of add air is to increase the pressure. In the AHF, there is a mixing chamber for add air between the downstream electrode and the nozzle. The argon mass fraction in Table 1 was calculated by assuming that the three streams become thoroughly mixed, and noting that dry air contains about 1.3% argon by mass. The argon mass fraction varied from 8.6% to 27.6%. Argon is unreactive to TPS materials, and the primary effect of argon addition is simply to reduce by dilution the oxygen concentration in the flowfield. Because the ablation rate of carbon is a strong function of the oxygen concentration, it is important to include the argon mass fraction in the ablation calculations. In this work, ablation tables for each air/argon mixture were calculated using the Multicomponent Ablation Thermochemistry (MAT) code [9].

Table 2 provides a list of the models tested, the exposure time, the measured centerline recession, and the maximum surface temperature. The tabulated maximum temperature is the mean of the values obtained from multiple pyrometers after all corrections. Based on previous experience [6], the uncertainty of the centerline recession and the maximum surface temperature are considered to be ±0.5 mm and ±5%, respectively.

III. Flowfield Analyses

The Data Parallel Line Relaxation (DPLR) code [10] is used for computations of the nonequilibrium flow in the nozzle and around the calorimeter or TPS model. DPLR has been used extensively at ARC for hypersonic flight and planetary entry simulations, and its results have been compared against a wide variety of flight and ground-based experiments. In this work, the steady, axisymmetric Navier–Stokes equations are supplemented with equations for nonequilibrium kinetic processes. The thermochemical model includes six species (N2, O2, NO, N, O, Ar). The thermal state of the gas is described by Park’s two-temperature model [11,12] with translational–rotational temperature T and vibrational-electronic temperature Tν.

The flowfield in an arcjet facility, from the arc heater to the test section, is a complex, three-dimensional flow coupled to various nonequilibrium processes. To simulate the flowfield, several simplifying assumptions are made, and corresponding numerical boundary conditions are prescribed for the simulation. The DPLR simulations are started from the nozzle throat, where the flow properties are assumed to be in thermochemical equilibrium. At the model surface, the boundary condition is a fully catalytic cold wall, corresponding to flow around a copper calorimeter. The total enthalpy level and distribution at the nozzle throat are set such that the computations reproduce the facility and calibration data as well as possible. The facility data include measurements of total pressure (arc-heater pressure), mass flow rate, total bulk enthalpy, and test box pressure, whereas the calibration data include stagnation-point calorimeter heat flux and pitot pressure. Further details of the assumptions and numerical boundary conditions are provided in [13].

As an illustration of a typical simulation, Fig. 3 shows computed Mach contours of the AHF 45.7 cm conical nozzle flow with an

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### Table 1: Stagnation arcjet test conditions

<table>
<thead>
<tr>
<th>Test condition</th>
<th>Project</th>
<th>Stagnation cold-wall heat flux, W/cm²</th>
<th>Stagnation pressure, kPa</th>
<th>Centerline enthalpy DPLR, MJ/kg</th>
<th>Main air, g/s</th>
<th>Add air, g/s</th>
<th>Argon, g/s</th>
<th>Argon mass fraction</th>
<th>Exposure time, s</th>
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</table>

*This test used 12.7-cm-diam flat-faced models and calorimeter. All other tests used 10.16-cm-diam iso-q models.*
iso-q-shaped calorimeter placed 30.48 cm downstream of the nozzle exit. The solution is for test condition 1 of Table 1. The computed Mach number is approximately 8 at the bow shock in front of the calorimeter. The computed temperatures along the stagnation streamline are plotted in Fig. 4. The translational–rotational temperature increases greatly across the shock, but the vibrational temperature does not rise as quickly. However, the flow approaches thermal equilibrium near the boundary-layer edge, defined herein as the location where the total enthalpy is 99.5% of the freestream value. Table 3 lists the temperatures and species mass fractions, at the estimated location of the boundary-layer edge, for each test condition. For comparison purposes, the Chemical Equilibrium with Applications (CEA) code [14] was used to estimate the equilibrium species mass fractions at the pressure and temperature calculated by DPLR at the boundary-layer edge location. These quantities are provided in Table 4.

Figures 5–7 provide representative examples of species mass fraction profiles on the stagnation streamline. These profiles show three types of behavior, depending mostly on the value of the centerline enthalpy. Test conditions 1, 3, and 6 have the lowest enthalpy (<5.7 MJ/kg). There is no evidence of significant chemical reactions in the shock layer (Fig. 5). The species profiles are flat except for the boundary layer near the surface. The fully catalytic boundary condition forces the complete conversion of O to O2 at the wall. At the boundary-layer edge, the species are not in chemical equilibrium; specifically, there is a large excess of O2 and a deficiency of O. Nitric oxide (NO) also is significantly above the equilibrium value.

Test conditions 5, 8, and 9 have intermediate levels of enthalpy (5.9–6.4 MJ/kg). Results for these conditions are similar to the preceding, except that some chemical reactions occur in the shock layer (Fig. 6). O2 is greater than O, and there is some conversion of N2 and O2 to O and NO. Atomic oxygen is far below equilibrium value. NO is above the equilibrium value, but nevertheless increases as the flow approaches the boundary-layer edge.

Test conditions 2, 4, 7, and 10–15 have the highest enthalpy (>8.5 MJ/kg). Clearly, reactions are occurring in the shock layer (Fig. 7). Molecular oxygen is almost fully dissociated at the shock. The atomic oxygen is slightly below the equilibrium value because some oxygen is incorporated into NO. The relative amounts of N, NO, and O vary on a case-to-case basis (see Table 3).

Table 2 Measured quantities for arcjet models

<table>
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<tr>
<th>Test condition</th>
<th>Exposure time, s</th>
<th>Model ID</th>
<th>Centerline recession, mm</th>
<th>Maximum surface temperature, K</th>
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*Test conditions 10, 11, and 13 are denoted as a or b in order of increasing exposure duration.
For each model in Table 2, the average recession rate may be calculated. Because charred PICA is carbon, the recession rate should depend on surface temperature and on the partial pressure of O or O₂, depending on whether or not the dominant surface reaction is modeled as \( O + C(\alpha) \rightarrow CO \) or as \( O_2 + 2C(\alpha) \rightarrow 2CO \). The reaction rate depends quantitatively on temperatures and pressures at the ablating surface. Nevertheless, the average rate should approximately correlate with edge values of O and/or O₂ (from Table 3). As seen in Figs. 8 and 9, the average recession rate correlates well with atomic oxygen, but poorly with molecular oxygen. This result supports the first reaction model, rather than the second, and is consistent with the recommendations of Park [15].

IV. Material Response Analyses

The integration between DPLR and FIAT is based on an uncoupled approach. The DPLR solutions assume steady flow and axial symmetry with a fully catalytic, cold-wall boundary condition at the model’s surface. At the stagnation point, the recovery enthalpy and the unblown heat transfer coefficient are calculated from the DPLR solution, and then these parameters and pressure are passed as boundary conditions to FIAT. Surface thermochemical interactions and blowing effects are incorporated in the material-response code by use of ablation tables, a surface energy balance with heat transfer coefficient, and a blowing reduction parameter of \( 1/2 \). Further details on this coupling methodology may be found in [6,13].

For all test conditions, FIAT calculations were performed using the nominal aerothermal environment, and also with a \( \pm 10\% \) scaling factor applied to the heating. This factor is considered to be the minimum uncertainty of the arcjet environment. As an example, Fig. 10 presents the predicted recession histories for these three heating levels at test condition 15 at \( 183 \text{ W/cm}^2 \). The standard PICAv3.3 equilibrium ablation model was used. In all recession plots, the green, red, and blue curves are the FIAT predictions for 90%, 100%, and 110% of nominal heating, respectively.

Table 3: Boundary-layer edge quantities from DPLR solutions

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<th>Test condition</th>
<th>( T_e, K )</th>
<th>( T_{Tv}, K )</th>
<th>( N_2 )</th>
<th>( O_2 )</th>
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<td>0.03863</td>
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<td>0.17749</td>
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*Boundary-layer edge is defined as the location where total enthalpy is 99.5% of the freestream value.

Table 4: Estimated equilibrium quantities at boundary-layer edge

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<th>Test condition</th>
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<th>( \sqrt{T_{Tv}} )</th>
<th>( N_2 )</th>
<th>( O_2 )</th>
<th>( NO )</th>
<th>( N )</th>
<th>( O )</th>
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<td>2</td>
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<td>0.00450</td>
<td>0.17749</td>
<td>0.10500</td>
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</tr>
</tbody>
</table>
black circles are measured data points with uncertainty bars of ±0.5 mm. The range of recession that results from the environmental uncertainty is shaded yellow. For this example, the two data points fall within the yellow-shaded region, and the ablation model is not assigned an error.

If a data point falls outside the range of predictions, then a recession-prediction error may be defined as

$$E = \frac{(\Delta S_{\text{measured}} - \Delta S_{\text{FIAT}})}{\Delta S_{\text{measured}}}$$  \hspace{1cm} (1)$$

where the closest FIAT result is used in the formula. In previous work, the recession-prediction error was less than 10% except for a few tests conducted at low pressure and/or heat flux. The possible influence of nonequilibrium effects for these two regimes is examined in the next two subsections.

A. Nonequilibrium Effects at Low Pressure

Predictions and data for test condition 7 at 107 W/cm² and 2.3 kPa are shown in Fig. 11. In this case, although the data uncertainty bars intersect the yellow region, FIAT underpredicts the actual data points. The measured recession was about 2.3 mm, whereas FIAT predicts a recession range of 1.61–2.04 mm. The recession-prediction error is 12.7%, which was the largest disagreement reported in [6].

Underprediction of the recession data was also seen in the three other tests conducted at pressure below 7 kPa and heat flux above 100 W/cm² (test conditions 10, 12, and 13). It is unusual for carbon recession to exceed the predictions of an equilibrium model. At first, it was suspected that the measured recession could exceed the equilibrium prediction if, owing to the low pressure, there is an excess of O near the surface. To investigate this possibility, equilibrium ablation tables were calculated without the species O₂ and CO₂. That is, only O and CO were allowed. However, the equilibrium ablation rate was unchanged, because at equilibrium the ablated carbon becomes CO regardless of the state of the oxygen.

Equilibrium ablation $B'_c$ curves for this test condition are illustrated in Fig. 12. At very low $B'_c$, the curves show a plateau corresponding to diffusion-limited oxidation of carbon to CO. However, as $B'_c$ is increased, the plateau is suppressed, because the oxygen reacts with the pyrolysis gas as well as with the solid carbon.
For this test condition, the surface state is near the location indicated by the red dot on Fig. 12, which represents approximately a 15% reduction from the diffusion-limited plateau at $B_0^{c}/.0136^{0.129}$.

Indistinguishable curves are obtained whether the oxygen is modeled as an atomic or a molecular species.

An alternative approach, which increases the predicted recession, is to assume the pyrolysis gas is "inert" at low pressure. That is, the pyrolysis gas is assumed not to equilibrate with the boundary-layer gas if the pressure is sufficiently low. Pyrolysis gas is a multicomponent hydrocarbon mixture that may react with oxygen in the flowfield by a number of two- and three-body reactions. These homogeneous reactions have rates that are second or third order in pressure. At sufficiently low pressure, it is plausible that these reactions may become slow compared with the heterogeneous reaction for oxidation of solid carbon that is first order in pressure.

To investigate this alternative, new ablation tables were created by modeling the pyrolysis gas as one set of equilibrating species, and the test stream (air–argon) plus $C_{i0}$ and CO as a second set of equilibrating species. The modified ablation tables, depicted in Fig. 13, do not exhibit a suppression of the $B_0^{c}$ plateau regardless of the pyrolysis-gas blowing rate. Therefore the dimensionless ablation rate is 0.129 unless the temperature is sufficiently high to sublime carbon. Nevertheless, the pyrolysis gas flux still participates in the blowing correction to the heat transfer coefficient, and the gas enthalpy at the surface is a function of $B_0^{g}$.

Revised predictions of the surface recession for the three heating levels are presented in Fig. 14. The axis scales are the same as those used in Fig. 11. The recession predictions of the inert-pyrolysis-gas model are greater than for that of the full-equilibrium model and the level of agreement has been improved.

Figure 15 shows predictions of the temperature history at five locations along the axis of the model. The calculations were performed using the nominal (unscaled) heat flux and both ablation models. The results are so similar that it would be very difficult to distinguish between these two models based on temperature data.

Predictions from the two ablation models for all 15 test environments are listed in Tables 5 and 6. These predictions are compared with the surface temperature and recession data in Figs. 16 and 17, respectively. In these figures, the vertical colored bars show the range of the predicted quantity corresponding to the assumed environmental uncertainty of $\pm 10\%$. The red and blue bars show the predictions of the full-equilibrium and inert-pyrolysis-gas models, respectively. (The figures also have green bars for a kinetic ablation...
model that will be discussed in the next subsection. The predictions of the two equilibrium models (red and blue) are comparable; in most cases, the inert-pyrolysis-gas model gives just slightly greater recession and slightly lower surface temperature than the full-equilibrium model.

For surface temperature (Fig. 16), all predictions are within the uncertainty of the pyrometer data for all environments. The poorest agreement is test environment 9. For recession (Fig. 17), both equilibrium-based ablation models significantly overpredict the recession for most test conditions below 75 W/cm². Nonequilibrium modeling for low heat flux will be discussed in the next subsection. Considering only the tests above 100 W/cm², where surface equilibrium should be a good assumption, the inert-pyrolysis-gas model provides a slightly better match to the data for pressure environments below 7 kPa (test conditions 7, 10, 12, and 13), and the full-equilibrium model is slightly better for all cases above 13 kPa (test conditions 8, 9, 11, 14, and 15). The recession figure uses a log axis so that the relative (fractional) error between predictions and data may be observed. Although the absolute error is largest for test condition 10, the relative error is less than 10%, which is comparable to the relative error from other test conditions.

The available data do not provide a pressure upper limit for applicability of the inert-pyrolysis-gas ablation model. This model should be used cautiously for pressure above the values considered in this work. Alternatively, a hybrid ablation model is suggested, in which the inert-pyrolysis-gas ablation tables are used for pressure up to 7 kPa, and full-equilibrium ablation tables are used down to 13 kPa. Some additional tables are needed to obtain a smooth transition for pressures between these two values. For these transitional tables, the composition of the air–argon set is adjusted to include various amounts of reactive elements from the pyrolysis-gas set.

B. Nonequilibrium Effects at Low Heat Flux

Based on past experience with carbonaceous TPS materials, equilibrium ablation is a good assumption for surface temperature above 2000 K, which corresponds to a heat flux of approximately 85 W/cm² for a high-emissivity material such as PICA. For surface temperature below 2000 K, the ablation rate is typically below the calculated equilibrium rate, due to kinetic limitations to heterogeneous surface reactions. In Fig. 17, both equilibrium-based models (red and blue) overpredict the recession for test conditions 1, 3, 5, and 6 at 40, 45, and 73 W/cm².

Interestingly, the equilibrium predictions are close to the data for test conditions 2 and 4 at 42 and 65 W/cm², respectively. For these two conditions, the oxygen is highly dissociated in the shock layer (Fig. 7), and the pressure is too low for atom recombination to be significant within the boundary layer. Therefore, a high level of atomic oxygen reaches the surface, and the reaction $O + C_{(i)} \rightarrow CO$ approaches equilibrium even though the surface temperature is below 1800 K. The equilibrium models provide a good estimate for $B'_c$ despite their apparent inapplicability.

For the ablation of carbon in air–argon mixtures, three applicable heterogeneous reactions are oxidation, nitridation, and sublimation:

$$O + C_{(i)} \rightarrow CO \quad (2)$$

$$N + C_{(i)} \rightarrow CN \quad (3)$$

$$3C_{(i)} \rightarrow C_3 \quad (4)$$

The forward rate for the oxidation reaction may be expressed as

$$r_f = \eta p_o \sqrt{\frac{M_o}{2\pi RT}} \quad (5)$$

with a reaction probability from Park [15]:

$$\eta = 0.63 \exp(-1160/T) \quad (6)$$
The effective reaction probability may vary depending on the chemical state and roughness of the ablating material, but expression (6) is a good starting point for analysis. For the test conditions in this study, the rates for nitridation and sublimation were found to be negligible in comparison with the rate for oxidation.

Ablation tables that include reaction kinetics may be generated using the MAT code. The tables contain an additional dimensionless

<table>
<thead>
<tr>
<th>Test condition</th>
<th>Exposure time, s</th>
<th>Recession, mm</th>
<th>Maximum surface temperature, K</th>
</tr>
</thead>
</table>
|               |                 | 90% heating   | 110% heating                
|               |                 | 90% heating   | 110% heating                |
| 1             | 200             | 8.549         | 10.541                      |
| 2             | 200             | 3.376         | 4.215                       |
| 3             | 240             | 10.895        | 13.425                      |
| 4             | 200             | 5.455         | 6.780                       |
| 5             | 120             | 7.859         | 9.701                       |
| 6             | 120             | 10.222        | 12.585                      |
| 7             | 55              | 1.611         | 2.035                       |
| 8             | 80              | 8.681         | 10.708                      |
| 9             | 80              | 10.125        | 12.488                      |
| 10a           | 200             | 8.975         | 11.164                      |
| 10b           | 400             | 18.292        | 22.730                      |
| 11a           | 33              | 2.939         | 3.662                       |
| 11b           | 66              | 6.020         | 7.467                       |
| 12            | 50              | 3.127         | 3.916                       |
| 13a           | 33              | 1.658         | 2.097                       |
| 13b           | 60              | 3.132         | 3.933                       |
| 14            | 50              | 4.795         | 5.962                       |
| 15            | 50              | 6.040         | 7.492                       |

Table 6 Predictions of the inert-pyrolysis-gas ablation model

<table>
<thead>
<tr>
<th>Test condition</th>
<th>Exposure time, s</th>
<th>Recession, mm</th>
<th>Maximum surface temperature, K</th>
</tr>
</thead>
</table>
|               |                 | 90% heating   | 110% heating                
|               |                 | 90% heating   | 110% heating                |
| 1             | 200             | 8.991         | 11.020                      |
| 2             | 200             | 3.757         | 4.620                       |
| 3             | 240             | 11.412        | 13.984                      |
| 4             | 200             | 5.884         | 7.225                       |
| 5             | 120             | 8.232         | 10.090                      |
| 6             | 120             | 10.627        | 13.015                      |
| 7             | 55              | 1.824         | 2.247                       |
| 8             | 80              | 8.994         | 11.017                      |
| 9             | 80              | 10.435        | 12.780                      |
| 10a           | 200             | 9.379         | 11.508                      |
| 10b           | 400             | 18.885        | 23.181                      |
| 11a           | 33              | 3.104         | 3.810                       |
| 11b           | 66              | 6.257         | 7.672                       |
| 12            | 50              | 3.317         | 4.077                       |
| 13a           | 33              | 1.812         | 2.232                       |
| 13b           | 60              | 3.336         | 4.102                       |
| 14            | 50              | 4.984         | 6.113                       |
| 15            | 50              | 6.225         | 7.632                       |

Fig. 16 Range of maximum temperature predictions from three ablation models (colored bars) compared with data (black points).
parameter that is the ratio of the forward reaction rate \( r_f \) to the mass transfer coefficient \( \rho u C_M \), where both quantities have units of mass flux. Typically the heat transfer coefficient \( \rho u C_H \) is estimated from measured quantities and/or computational fluid dynamics solutions, and then \( C_M = C_H \) is assumed unless additional information is available.

For pyrolyzing ablators, these kinetic ablation tables contain four independent parameters: pressure, \( B_0^{c} \), \( B_0^{g} \), and \( \rho u C_M \). It is impractical to create and to interpolate tables with four or more independent variables. Furthermore, for the same material, different tables are needed for each atmospheric composition (i.e., argon mass fraction) to be analyzed. To circumvent these difficulties, the FIAT code was modified to enable calculation of the ablation rate without the intermediate step of table generation. This improved methodology is documented in [16].

For the full-equilibrium model, it is unclear how to properly implement the surface kinetics. If the pyrolysis gas is allowed to equilibrate with the edge gas, then most of the carbon in the pyrolysis gas is converted into CO and/or \( \text{CO}_2 \), and only a small amount of oxygen is available to react with the solid carbon. In other words, the suppression of \( B_0^{c} \) owing to pyrolysis, as seen in Fig. 12, always occurs in addition to kinetic limitations to surface reactions of any surplus oxygen. The net result is a large reduction in \( B_0^{c} \). If the Park surface kinetics are combined with the full-equilibrium model, then the ablation rate is underpredicted by more than an order of magnitude for all test conditions below 100 W/cm².

For the inert-pyrolysis-gas model, the finite-rate reactions may be implemented in the subset of species that includes the test stream (air–argon) plus \( \text{CO} \) and \( \text{CO}_2 \). Calculations were performed for all test environments using this combination of models. Also, for each condition, the edge fraction of atomic oxygen from Table 3 was specified as a boundary condition. This specification is required for two reasons: 1) the flowfields are not in chemical equilibrium, and 2) the primary source of atomic species (O and N) is from the boundary-layer edge.

Temperature and recession predictions of the kinetic model are listed in Table 7 and shown as vertical green bars in Figs. 16 and 17, respectively. For the higher enthalpy cases (above 8.5 MJ/kg, test conditions 2, 4, 7, and 10–15), the three models give comparable results for both quantities. The temperature predictions are within the uncertainty of the pyrometer data but usually on the high side of the error bars. The recession predictions show both positive and negative errors compared with the data. The kinetic model appears to be as accurate as the full equilibrium model, even for the highest pressures (conditions 11, 14, and 15) where some of the modeling assumptions may be questionable.

For the lower enthalpy cases (below 6.5 MJ/kg, test conditions 1, 3, 5, 6, 8, and 9), the results are inconclusive. The kinetic model predicts lower recession and higher temperature than the two equilibrium-based models. The surface temperature predictions (Fig. 16) of the kinetic model appear to be high, but within the error bars of the data except for test condition 9. The recession predictions

### Table 7 Predictions of the inert-pyrolysis-gas ablation model with surface kinetics

<table>
<thead>
<tr>
<th>Test condition</th>
<th>Exposure time, s</th>
<th>Recession, mm</th>
<th>Maximum surface temperature, K</th>
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<tr>
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temperature below 2000 K, which is a traditional value from past experience. Results for test conditions 2 and 4 suggest that the equilibrium models also may be used below 2000 K, if the edge oxygen is dissociated and the pressure is sufficiently low (<2 kPa) to prevent reactions of atomic oxygen in the boundary layer. This type of environment often occurs during the initial part of a hypersonic entry trajectory.

V. Conclusions

Data were presented from stagnation arcjet tests of iso-q- and flat-face-shaped Phenolic Impregnated Carbon Ablator (PICA) models. Thirty-one models were tested in the Aerodynamic Heating Facility at NASA Ames Research Center at 15 test conditions with stagnation-point heat fluxes from 40 to 183 W/cm² and pressures from 1.6 to 31.6 kPa. The surface temperature was estimated using multiple pyrometers, and the posttest recession was measured. Two modifications to the standard PICAv3.3 equilibrium ablation model were developed to address nonequilibrium effects that occur at low pressure and at low temperature. Predictions of the standard and the modified ablation models were compared with the test data. For heat flux above 85 W/cm² (surface temperature above 2000 K), two equilibrium-based models provided comparably good agreement with the recession data. The inert-pyrolysis-gas model was slightly better for stagnation pressure below 7 kPa, and the standard full-equilibrium model (PICAv3.3) was slightly better for pressure above 13 kPa. For heat flux below 85 W/cm² (surface temperature below 2000 K), in most cases, the equilibrium-based models overpredicted the surface recession. To obtain a good match to the recession data, a simple surface kinetics model was implemented with the inert-pyrolysis-gas assumption, and the atomic oxygen fraction at the boundary-layer edge was specified. This specification was critical, because otherwise the kinetics model underpredicted the recession in all environments.

Acknowledgments

This work was supported in part by the NASA Orion Insight/Oversight Project and through contract NNA04BG25C to ELORET Corporation. We acknowledge the NASA Strategic Capabilities Assets Program for their critical financial support of the arcjet operational capability at Ames Research Center. The authors greatly appreciate the assistance of P. Agrawal, D. Driver, M. Olson, and K. Skokova for arcjet test data.

References


G. Russell
Associate Editor