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PYROLYSIS MODELLING AND EXPERIMENTATION FOR THERMO-PHYSICAL PROPERTIES OF CHAR FORMED FROM ABLATIVE MATERIAL

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Abstract—Ablative materials are used in heat shields of spacecrafts re-entering the atmosphere to protect them from high aerodynamic heating. A computer program has been developed to predict the pyrolysis and thermal response in ablative materials. The computational results are verified by performing experiments conducted at the test facility in Vikram Sarabhai Space Centre. The properties and thickness of char formed are crucial to determine heat ingress. Using an inverse problem, the thermo-physical properties of char formed from the ablative material, which have not been determined earlier, are estimated. Thickness of char formed is also predicted using the program.

Keywords: Charring, Pyrolysis, Inverse-Conduction

I. INTRODUCTION

Ablative materials are designed to slowly burn away in a controlled manner, so that heat can be carried away from the surface by gases generated by the process, while the remaining solid char insulates a re-entry spacecraft from aerodynamic heating. Computer-based simulations have been crucial in rapid prediction of thermal response across the heat-shield thickness. Numerical solutions to predict the thermal response of charring ablators have been devised in the past by Swann et al. [1]. Deshpande et al. [2] have modelled the charring and ablation processes in one-dimension using a fixed mesh control volume and fully-implicit time integration. Different cases have been analysed and solutions with grid independence are obtained. Nair et al. [3] have developed low density ablative thermal protection material, for space-capsules with mass constraint. Silica fiber re-inforced phenloic syntactic foam composites of varying specific gravities were developed. Thermal properties of the ablative material was measured using standard tests. The thermal response of the ablative was studied and the low density ablative material was qualified for application in re-entry spacecrafts. Lattimer et al. [4] conducted an inverse analysis to find the thermal and physical properties for a glass-reinforced vinyl ester composite sample using an advanced experimental set-up. Best fits for properties like thermal conductivity, specific heat were obtained. Thermogravimetric Analyzer (TGA) and Differential Scanning Calorimeter (DSC) are used to validate the results. The predictions are within 10% of the data obtained. It has been observed that thermal properties for the char formed during pyrolysis of a low density ablative have not been estimated using any thermal analysis or experimental data.

The objectives of this paper are to develop a computer program which predicts char thickness formed due to pyrolysis for given ablative material specimen. Further, using the experimental results and the thermal response analysis, the thermo-physical properties of char formed from the ablative material are estimated.

A. The Pyrolysis Model

A one-dimensional transient heat flow normal to the surface is assumed. The model is divided into three major zones beginning at the surface with the pure char zone, where the material has completely degraded; the reaction zone, where material is undergoing depolymerization and pyrolysis; and the virgin material, where pure conduction exists and unrelated material is present. Pyrolysis happens at only one interface layer at a given instant of time. One moving boundary is assumed to exist, which is the pyrolysis of the char layer towards the virgin material. Pyrolysis occurs only after the fixed temperature of pyrolysis is attained at the interface node. At the beginning of pyrolysis, a very small char zone is assumed to exist on the surface of virgin material. This assumption has only a minimal effect on the thermal response at various nodes [1]. The thermo-physical properties of char have not been measured. Formation of pyrolysis gases and chemical reactions are not considered.

B. Energy-balance Equations

The governing equations of the conduction and pyrolysis model are differential energy conservation equations coupled with mass conservation.

C. Interface Model for Pyrolysis

In the one-dimensional char formation model, the energy-balance at the char-virgin material interface is given by

\[ k_A (T_{m-1} - T_m)\Delta x + k_B (T_m + 1 - T_m)\Delta x = 0 \]  

Energy-balance equations are developed for all other boundary conditions.

D. Model for Char Formation Rate

During char formation, the interface node is moving into the ablative material due to heat supplied. Swann [1] has developed the basic governing equations for pyrolysis and
char formation. The formation of char per second, per unit area, \( M_p \), can be defined as
\[
M_p = A_1 e^{-(B/T)},
\]
(2)

\( T \) = Temperature at the interface node.

The values of coefficients \( A_1 \) and \( B \) will differ with each material chosen. For each material, \( A_1 \) and \( B \) need to be found assuming typical values and by trial and error, which is tedious and need not be accurate. Therefore another approach is taken where char formation rate is calculated from the transient heat conduction equation. Here, the total input energy is equated to the product of mass formation rate and the heat of pyrolysis of the material under consideration. The temperature at interface is kept constant once the interface node attains the temperature of pyrolysis. Then, \( M_p \) is found using,
\[
k_A A (T_{m-1} - T_m)/Δx + k_B A(T_{m+1} - T_m)/Δx = M_p H_p
\]
(3)

This is used in equation (4) to find the new thickness of char layer,
\[
L_{p\text{New}} = L_p + \int 0^t M_p * Δt / (p_{\text{p2}} - p_1)
\]
(4)

Equations (3) and (4) are used for finding rate of growth of char layer. This thickness is compared with the distance from surface to the next node, i.e. the first node in virgin material. Once it crosses the limiting value, the number of nodes in char is increased by one. Since the total number of nodes is constant, the number of nodes in virgin material (ablator) decreases by one.

II. Analysis To Validate Char Formation

The problem is to find the thermal response and char formation when an ablative material specimen is exposed to variable heat flux and to observe a clear difference between slopes of char region and virgin material region in the thermal response. Typical properties were assumed for this analysis (shown in Tables I and II). The thickness of the virgin material specimen was taken to be 20 mm, with a surface emissivity of 0.85 and an ambient temperature of 303 K.

<table>
<thead>
<tr>
<th>Property (S.I Units)</th>
<th>Material : Ablator (Assumed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity (W/m-K)</td>
<td>1.0</td>
</tr>
<tr>
<td>Specific Heat (J/kg-K)</td>
<td>1288</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>480</td>
</tr>
</tbody>
</table>

| Heat of Pyrolysis (kJ/kg) | 21600 |
| Temperature of Pyrolysis (K) | 823 |

TABLE II. THERMO-PHYSICAL PROPERTIES FOR CHAR OF ASSUMED MATERIAL

<table>
<thead>
<tr>
<th>Property (S.I Units)</th>
<th>Material : Char</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity (W/m-K)</td>
<td>0.12</td>
</tr>
<tr>
<td>Specific Heat (J/kg-K)</td>
<td>901</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>128</td>
</tr>
</tbody>
</table>

A. Analysis and Results

A heat flux of 20 W/cm² is applied for 200 seconds. Assumed values of thermal conductivities for virgin material and char are 1.0 W/m-K, and 0.12 W/m-K respectively. The temperatures were plotted a time period of 0 - 200 seconds.

Figure 1. Thermal Response across Thickness, heat flux 20 W/cm²

Thickness of char formed at the end of 200 seconds is 1.43 mm. The program gives a thermal response which clearly shows the char layer (Fig 1) growing at different instants. The temperatures vary across thickness of specimen with different slopes for char region and ablative region. Thus it is established that the program is able to model the moving interface node and char layer growth.

III. Experimental Set-up and Procedure

The specimen is exposed to infrared heating from quartz-enveloped Infrared radiation (I.R) lamps. Thermal data was logged using a personal computer. A Gardon-type water-cooled heat flux sensor measures heat flux. The signal generated by the heat flux sensor is fed to the PLC controller as the feed-back.
An ablative material specimen of dimensions 150 x 150 x
25.5 mm is coated with a black coating with measured
absorptivity value of 0.749. Three calibrated K-type
thermocouples are bonded at the back wall of specimen
using a thermo-bond material. A thermocouple was inserted
to a distance of 12.75mm through the back-wall. The
instrumented specimen is fixed at a distance of 100 mm and
it is exposed to the required heating levels.

IV. RESULTS AND DISCUSSION

The Ablator-1 specimen was subjected to a variable heat
flux for 480 seconds, which has a triangular shape, reaching
a peak heat flux of 25 W/cm² at time 91 seconds and ending
the heat input at 182seconds. The thermo-physical properties
of the ablative material is given in Table III.

### TABLE III. THERMO-PHYSICAL PROPERTIES OF ABLATOR-1

<table>
<thead>
<tr>
<th>Property (S.I Units)</th>
<th>Material</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity (W/m-K)</td>
<td>0.1290</td>
<td></td>
</tr>
<tr>
<td>Specific Heat (J/kg-K)</td>
<td>1290</td>
<td></td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>380</td>
<td></td>
</tr>
<tr>
<td>Heat of Pyrolysis (kJ/kg)</td>
<td>10,000</td>
<td></td>
</tr>
<tr>
<td>Temperature of Pyrolysis</td>
<td>773 K</td>
<td></td>
</tr>
</tbody>
</table>

A. Results of Analysis After Change in Assumptions

The new analysis assumes that the thermal diffusivity
value for char is higher than that of virgin material. This
follows from a study on carbon-phenolic, an ablator with
known thermo-physical properties of char. It's thermal
conductivity and specific heat were both higher than those of
the virgin material by approximately 60 percent and 20
percent respectively [2]. So the thermal conductivity of char
of the present ablator and the specific heat were increased
accordingly as seen in Table IV.

### TABLE IV. Assumed Thermo-physical properties for char formed
from Ablator-1 (at 303 K)

<table>
<thead>
<tr>
<th>Property (S.I Units)</th>
<th>Material : Char formed from Ablator-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity (W/m-K)</td>
<td>0.2064</td>
</tr>
<tr>
<td>Specific Heat (J/kg-K)</td>
<td>1548</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>360</td>
</tr>
</tbody>
</table>

The char formation equation has the difference of two
densities in the denominator. Denominator could become
zero, if the two densities values were to be equal. So, the
denominator was changed to an average of both densities.

Fig.2 shows that the resultant graph with new values for
thermal conductivity and specific heat did result in better
concurrence of experimental and analysis results. For the
back-wall, at the end of 480 seconds, there is a deviation of
only 5.1 percent between analysis and experimental results.
There is also an under-prediction by 3.9 percent occurring at
215 seconds. This could be due to thermo-physical property
variation of char and also due to variation in absorptivity as
the surface layer turns to char. It is observed that the
temperatures for the second analysis and for the experiment
differ by 2.2K at the end of 480 seconds for the
thermocouple at a distance of 12.75mm from back-wall.
There is a deviation of only 0.52 percent between analysis
and experimental results. An under-prediction by 5.6 percent
is observed at 80 seconds into the test. For the
node, at a distance of 12.75mm from back-wall at 240 seconds, there is
a deviation of 8.8 percent between analysis and experimental
results.

The char thickness predicted in the second analysis
increased from 2.1 mm to 2.3 mm. The changed absorptivity
of the surface during charring, which changes the surface
composition, can result in different heat flux than expected,
which could result in higher temperatures and thus increase
the char formation. The char formation during experiment
exceeded the analysis prediction by approximately 4 mm.
The analysis accuracy can be improved by using
temperature-dependent absorptivity data for charred surface.

The variations observed between experimental and
analysis temperature profiles (Fig.3) is caused due to
following physical phenomena. Pyrolysis causes char
formation and releases gaseous species. As these hot gases
flow through the char layer, they may have transferred heat
to the porous layers through which they passed,
increasing temperatures at those nodes and increasing char
formation. Energy dissipated by gaseous species is not taken
into account and that can cause variations in char thickness
predicted by analysis.

The absorptivity of the specimen surface changes when
surface became charred due to exposure to heat flux of the
order of 15-25 W/cm² during the experiment. Variation in
surface absorptivity, results in variation of absorbed heat flux
and consequently in thermal response (Fig.3).

Further details of the dependence on absorptivity on
wavelength of radiation and on temperature can be found in
Incropera et al. [5].
B. Determination of thermo-physical properties of char

The reasonable concurrence between the analysis and experimental results is used to predict properties like thermal conductivity and specific heat of the char formed. It is difficult to experimentally determine these properties for char, given the extremely fragile nature of char and the difficulty of obtaining samples of char with uniform thickness and specified dimensions. An inverse problem is solved, to find the thermal properties of char and their variation with temperature, using the thermal response obtained from thermocouples, at two different locations. The assumed variation of thermal conductivity of char, with respect to temperature, is shown in Table V.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Thermal Conductivity (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>0.2064</td>
</tr>
<tr>
<td>503</td>
<td>0.2180</td>
</tr>
<tr>
<td>700</td>
<td>0.2500</td>
</tr>
<tr>
<td>850</td>
<td>0.2840</td>
</tr>
<tr>
<td>950</td>
<td>0.3100</td>
</tr>
<tr>
<td>1100</td>
<td>0.3250</td>
</tr>
<tr>
<td>1300</td>
<td>0.3320</td>
</tr>
</tbody>
</table>

V. CONCLUSION

A reasonable estimation of thermo-physical properties gives the estimated thermal conductivity, specific heat and density of char, formed from the given ablative material, to be 0.2064 W/m-K, 1548 J/kg-K, 360 kg/m³ respectively, at 303 K. Further concurrence between results could be achieved if chemical analysis, oxidation and gaseous products are taken into consideration.

Acknowledgment

This work was initiated with the kind permission of Dr. R.M. Jalnekar, Director, Vishwakarma Institute of Technology, Pune and and Dr. M.K. Nalawade, Head, Mechanical Engineering Department, Vishwakarma Institute of Technology, Pune. Crucial guidance and facilities were provided by Vikram Sarabhai Space Centre, Indian Space Research Organisation (I.S.R.O). S.V.A. Pulickel and M.B. Chaudhari is grateful for their support.

Nomenclature

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area of specimen, normal to direction of heat transfer</td>
<td>A</td>
<td>m²</td>
</tr>
<tr>
<td>Constant corresponding to specific reaction rate</td>
<td>A₁</td>
<td>-</td>
</tr>
<tr>
<td>Constant in corresponding to activation energy</td>
<td>B</td>
<td>-</td>
</tr>
<tr>
<td>Specific heat of a solid</td>
<td>Cp</td>
<td>J/kgK</td>
</tr>
<tr>
<td>Specific heat of char</td>
<td>Cp₁</td>
<td>J/kgK</td>
</tr>
</tbody>
</table>
Convective heat transfer coefficient at front wall \( h_1 \) W/m²K

Current time instant \( i \) seconds

Thermal Conductivity of char \( k_A \) W/mK

Thermal Conductivity of ablative material \( k_B \) W/mK

Initial thickness of char layer \( L_p \) m

New thickness of char layer \( L_{pNew} \) m

Mass formation rate of char \( M_p \) kg/s m²

Total number of nodes \( M+1 \) -

Temperature of previous node \( T_{m-1} \) K

Temperature of current node \( T_m \) K

Temperature of next node \( T_{m+1} \) K

Thickness of the finite element (Mesh Spacing) \( \Delta x \) m

Time-step used in explicit method iterations \( \Delta t \) seconds

Density of char formed \( \rho_1 \) kg/m³

Density of ablative virgin material \( \rho_2 \) kg/m³

REFERENCES


