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 ablatives 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

$$k_A A (T_{m-1} - T_m)/ \Delta x + k_B A(T_{m+1} - T_m)/ \Delta x = 0 \qquad (1)$$

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, Mp, can be defined as

$$Mp = A_1 . e^{(-B/T)} , \quad (2)$$

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, Mp is found using,

$$k_A \, A \, (T_{m-1} - T_m)/ \Delta x + k_B \, A(T_{m+1} - T_m)/ \Delta x = M_p . H_p \quad (3)$$

This is used in equation (4) to find the new thickness of char layer,

$$L_{pNew} = L_p + \int_0^t M_p \ * \Delta t / (\rho_{p2} - \rho_1) \quad (4)$$

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. ANAYLSIS 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.

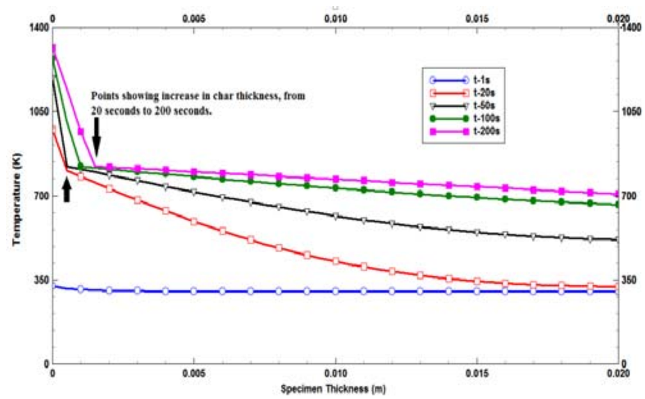
TABLE I. TYPICAL THERMO-PHYSICAL PROPERTIES FOR PROGRAM VALIDATION

Property (S.I Units)	Material : Ablator (Assumed)
Thermal Conductivity (W/m-K)	1.0
Specific Heat (J/kg-K)	1288
Density (kg/m^3)	480
Heat of Pyrolysis (kJ/kg)	21600
Temperature of Pyrolysis (K)	823

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

Property (S.I Units)	Material : Char
Thermal Conductivity (W/m-K)	0.12
Specific Heat (J/kg-K)	901
Density (kg/m^3)	128

A. *Analysis and Results*



A heat flux of 20 W/cm^2 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/cm^2

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/cm^2 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

Property (S.I Units)	Material : Ablator-1
Thermal Conductivity (W/m-K)	0.1290
Specific Heat (J/kg-K)	1290
Density (kg/m^3)	380
Heat of Pyrolysis	10,000 kJ/kg
Temperature of Pyrolysis	773 K

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)

Property (S.I Units)	Material : Char formed from Ablator-1
Thermal Conductivity (W/m-K)	0.2064
Specific Heat (J/kg-K)	1548
Density (kg/m^3)	360

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.

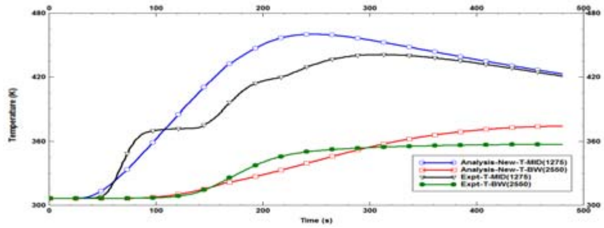


Figure 2. Experimental vs. Analysis Results

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 occuring 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.

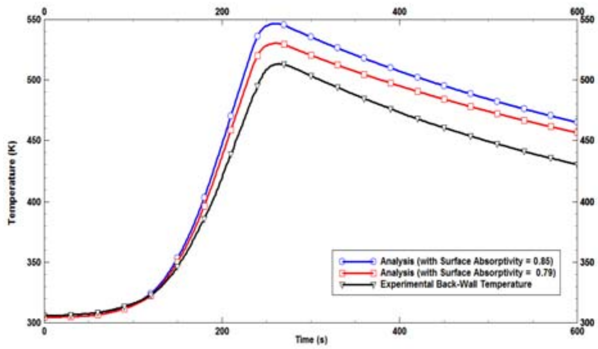
The variations observed between experimental and analysis temperature profiles (Fig.3) is caused due to following physical phenomena**.** Pyrolysis causes char formation and releases gaseous species. As these hot gases flow through the char layer, they may have transferred heat energy to the porous layers 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/cm^2 during the experiment. Variation in surface absorptivity, results in variation of absorbed heat flux and consequently in thermal response (Fig.3).

Figure 3. Graph showing dependence of analysis results on surface absorptivity

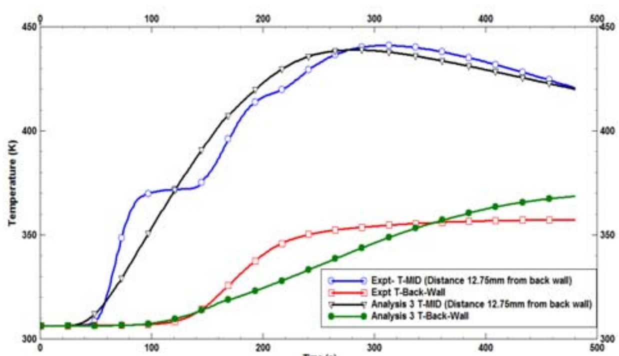
Further details of the dependence on absorptivity on wavelength of radiation and on temperature can be found in Incropera et al. [5].

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 V. Thermal Conductivity Variation of Char



Temperature (K)	**Thermal Conductivity (W/m-K)**
303	0.2064
503	0.2180
700	0.2500
850	0.2840
950	0.3100
1100	0.3250
1300	0.3320

ANALYSIS-2: COMPARISON OF EXPERIMENT AND ANALYSIS RESULTS

A very close match is observed as shown in Fig.4, especially for the temperature profile at distance 12.75mm from the back wall of specimen. At the end of test, the computed and measured temperatures are practically the same, validating the thermo-physical properties assumed for char. After 120 seconds into the test, for the mid-section, there is an over-prediction of temperatures by 4.3 percent. At the back wall, at the end of 480 seconds, the measured temperature is 358 K, whereas the computed temperature is 368 K, giving an over-prediction by 2.8 percent.

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/m^3 respectively, at 303 K. Further concurrence between results could be achieved if chemical analysis, oxidation and gaseous products are taken into consideration.

For charring of an ablator specimen, the temperatures predicted are within an acceptable range of variation. The program is able to predict increase in char thickness. The assumptions used in moving interface along with the formation and motion of gaseous by-products could be the cause of the under-prediction of char-thickness. The variation in absorptivity of surface of specimen which occurs during pyrolysis and oxidation is also a contributing factor to the variations observed.

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NOMENCLATURE

Name	**Symbol**	**Units**
Area of specimen, normal to direction of heat transfer	A	m^2
Constant corresponding to specific reaction rate	A_1	-
Constant in corresponding to activation energy	B	-
Specific heat of a solid	Cp	J/kgK
Specific heat of char	Cp_1	J/kgK

Convective heat transfer coefficient at front wall	h1	W/ m^2K
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	Lp	m
New thickness of char layer	LpNew	m
Mass formation rate of char	Mp	kg/s- m^2
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)	Δx	m
Time-step used in explicit method iterations	Δt	seconds
Density of char formed	ρ_1	kg/m^3
Density of ablative virgin material	ρ_2	kg/m^3

REFERENCES

[1] R.T Swann, C.M Pittmann and J.C Smith : "One-dimensional Numerical Analysis of the Transient Response of Thermal Protection Systems." NASA TN-D 2976, September 1965.

[2] S. Deshpande, S. Pavithran and V. Iyer, "A Finite Volume Model of Charring and Ablation", Journal of Engineering Research and Studies, Vol. II, Issue 1, Jan-Mar 2011.

[3] C.P.R. Nair, D. Mathew, B. John, G. Joseph, B. Deependran and N.K. Ninan, "Low Density Ablative Thermal Protection Systems for Recoverable Capsules : Mechanical and Thermo-physical Properties and Thermal Response Under Atmospheric Conditions", Materials and Structures Symposium, 59th International Astronautical Congress, 2008.

[4] Brian Y. Lattimer and Jason Ouellette, "Properties of Composite Materials for Thermal Analysis Involving Fires" Composites Journal, Part 37A, pp.1068-1081, 2006.

[5] Frank P. Incropera and David P. DeWitt, "Fundamentals of Heat and Mass Transfer", John Wiley and Sons, 1996.