Application of CMA Program to Wood Charring

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Experiments were conducted to test the ability of a computer program to describe the charring of ovendried wood.

TO EFFICIENTLY design structural wood members for fire endurance, it is necessary to be able to predict density and temperature distributions in a wood cross section. The Aerotherm Corporation Charring Material Thermal Response and Ablation (CMA)[a] computer program analyzes the transient thermal response of a one-dimensional charring material. The thermal properties of the material can be specified as a function of temperature, and the heat of pyrolysis is included in the internal energy balance equation. The CMA program was developed for the Air Force Rocket Propulsion Laboratory and has been used extensively for thermal performance studies of ablating heat shields, rocket nozzles, and spacecraft structures. This study evaluated the applicability of the CMA program to wood charring. The evaluation consisted of comparing CMA results with experimental data and investigating the effect of variation in the material parameters. on the CMA results.

BACKGROUND INFORMATION

Like most organic polymers, wood undergoes thermal degradation — pyrolysis — when subjected to fire exposure. Pyrolysis results in the reduction in the density of the wood, the generation of an outer char layer, which eventually ablates as it, undergoes combustion, and a gas mixture, which flows out of the wood and undergoes flaming combustion. A slow pyrolysis occurs in the temperature zone of 852°R to 996°R (200° C

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[a] A listing of the program is available from the U.S. Forest Products Laboratory or the NASA ADP Program Sharing Library.

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Approved Technical Article

to 280° C), until active pyrolysis begins suddenly in the 996°R to 1,392°R (280° C to 500° C) temperature zone.[1] Conflicting experimental results have shown the pyrolysis reactions to be endothermic and/or exothermic.

A temperature of 1,010°R (288° C) has been used to locate the base of the char layer.[2] After a more rapid char rate during the initial period of ASTM Standard E119[3] fire exposure, the char base penetrates into the wood at a fairly constant rate of about $1^1/_2$ in. hr^{-1}. The actual char rate will depend on the density, moisture content, and species of wood.[2] Above 1,392°R (500° C), the charcoal glows and is consumed.[1] The char surface recession due to the combustion is undocumented and is usually ignored in theoretical and experimental char rate studies. Increased internal temperature, as well as thermal degradation, reduces the strength of the wood member. The temperature gradient is steep. In Douglas fir, maximum temperatures of 820°R (182°C) and 680°R (104° C) develop at $^1/_4$ in. and $^1/_2$ in., respectively, below the char base of 1,010°R (288° C). This is generally attributed to the low thermal diffusivity of wood.

CMA MODEL

REVIEW

The CMA computer program is an implicit finite-difference computational procedure for describing the one-dimensional thermal behavior of a two-sided slab that can ablate at one surface and decompose in depth.[4,5,6] The three main events considered in the analysis are internal decomposition, internal energy balance, and the surface boundary energy balance. The results are internal density and temperature distribution, pyrolysis gas flow rate, and various energy terms.

The internal decomposition involves the pyrolysis of the virgin material into char and pyrolysis gases and is evaluated as a change in the density of the material. The rate of change in density is given by the Arrhenius equation:

$$\left.\frac{\partial \rho}{\partial \theta}\right|_y = -B \exp^{(-E/RT)} \cdot \rho_p \left(\frac{\rho - \rho_c}{\rho_p}\right)^{\psi} \tag{1}$$

Density changes are assumed to be only a function of changes in mass.

The in-depth energy balance is assumed to be governed by the differential equation:

$$\rho C_p \left.\frac{\partial T}{\partial \theta}\right|_x = \frac{1}{A}\frac{\partial}{\partial x}\left(kA\frac{\partial T}{\partial x}\right)_\theta + \left(h_g - \bar{h}\right)\left.\frac{\partial \rho}{\partial \theta}\right|_y + F\rho C_p \left.\frac{\partial T}{\partial x}\right|_\theta + \frac{m_g}{A}\left.\frac{\partial h_g}{\partial x}\right|_\theta \tag{2}$$

The physical meaning of the individual terms may be interpreted as (from left to right) the rate of storage of sensible energy, net rate of thermal conduction, pyrolysis energy release rate, convection rate of sensible energy due to coordinate system movement, and net rate of energy convected with pyrolysis gases passing a point. The internal energy balance equation is solved using the thermal properties of virgin plastic, char, and pyrolysis gas. Partially pyrolyzed material is evaluated as a simple mixture of virgin plastic and char.

The pyrolysis energy release rate term involves the energy consumed or produced by the pyrolysis reaction. The heat of pyrolysis, $h_g - \bar{h}$, is defined as:

$$h_g - \bar{h} = h_g + \frac{\rho_c}{\rho_p - \rho_c} h_c - \frac{\rho_p}{\rho_p - \rho_c} h_p \tag{3}$$

A positive $h_g - \bar{h}$ would indicate an endothermic reaction, while a negative value would indicate an exothermic reaction. The char enthalpy and virgin plastic enthalpy are computed as integrals of the specific heat input function from a datum temperature to the temperature of interest plus the heat of formation. An estimate of pyrolysis gas sensible enthalpy versus temperature and its heat of formation are required input.

USE OPTIONS

The CMA program has three options for defining the ablating surface boundary conditions: (1) general convective and radiative heating and thermochemical erosion; (2) specified surface temperature and surface recession rate; and (3) specified input radiant heat flux with zero surface recession rate.

The thermochemical ablation boundary condition of Option 1 has convection-radiation heating with coupled mass transfer. The procedure uses a transfer coefficient approach and requires surface thermochemistry tables as input. The Aerotherm Corporation Equilibrium Surface Thermochemistry (EST) computer program can be used to generate the thermochemistry tables which relate the surface state to arbitrary ablation rates. Chemical equilibrium is the basis for the EST program. A fissure model option can be used with this boundary condition option. In the fissure model option, the pyrolysis gas is assumed to escape directly through fissures and not be involved in the boundary layer events. As part of this option, the pyrolysis gas pickup of energy is suppressed by keeping the sensible enthalpy constant above a temperature exceeding the pyrolysis temperature.

In Option 2, the surface temperature and surface recession rate are specified. The specified surface temperature is inserted directly into the in-depth solution procedure. Thus, all surface energy balance and surface thermochemical considerations are bypassed.

Option 3 involves a simplified surface energy balance and no surface

thermochemical considerations. The surface energy balance involves the radiant heat flux to the surface, the reradiation from the surface, and the conduction of energy to the interior. A zero surface recession rate is assumed.

INPUT PARAMETERS

The CMA program requires the input of a number of material properties and boundary condition parameters. Values for the material properties were generally obtained from the literature. In some cases, the lack of adequate data required the use of a value selected from within a wide range of values given, the extrapolation to higher temperatures than the available data justified, or other debatable assumptions.

In-Depth Parameters: Prescription of specific heat levels is discussed by Knudson,[7] Widell,[8] Kollmann and Côté,[9] and Beall.[10] Dunlap[11] found it to be a function of temperature, T:

$$C_p = 0.266 + 0.00116T \tag{4}$$

for ovendry wood in kcal $kg^{-1}°C^{-1}$ and a temperature range of 0° C to 106° C. The Dunlap equation was used in this work for virgin wood without regard for the limited temperature range. Widell[8] has reported the specific heat of charcoal versus temperature. Some values are 0.275 Btu $lb^{-1}°R$ at 852°R, 0.449 at 1,932°R, and 0.446 at 2,292°R.

Variability of thermal conductivity with wood density, moisture content, and temperature are discussed in Knudson,[7] Widell,[8] Kollmann and Côté.[9] For a temperature of 545°R and moisture content values below 40 percent, MacLean[12] indicates the thermal conductivity (Btu in. ft^{-2} $h^{-1}°R^{-1}$) is given by:

$$k = 0.165 + S(1.39 + 0.028M) \tag{5}$$

Thermal conductivities at higher temperatures were obtained by multiplying MacLean's values by the ratio of the absolute temperatures.[13] Widell[8] gives the thermal conductivity for charcoal from Landolt-Bornstein's tables as 0.403 and 0.508 Btu in. ft^{-2} $h^{-1}°R^{-1}$ at 492°R and 672°R, respectively, for a charcoal density of 13.4 lb ft^{-3}. These values for charcoal were extrapolated to higher temperatures, and the effect of varying density was disregarded.

In the CMA model, the pyrolysis gas enthalpy is assumed to be a function of temperature only. For wood, the pyrolysis gas is a mixture of gases that has an ever changing composition. Possible factors that may influence the composition are history of exposure, degree of volatilization, and temperature. These changes affect the enthalpy of the partially pyrolyzed wood, char, and pyrolysis gas. For purpose of this CMA analysis, a fixed gas composition was assumed and the equation of Nielson and Tao[14] was employed for the specific heat (Btu $lb^{-1}°R^{-1}$) of the pyrolysis gas:

TABLE 1. *CMA Input Parameters*

Parameter	*Selected*	*Range*	*Reference*
B (s^{-1})	1×10^{10}	5×10^{8} to 5×10^{11}	Welker[15]
E/R (°R)	30,000.00	20,800. to 41,700.	Welker[15]
h_f cellulose (Btu lb^{-1})	− 2,700.00	− 1,800. to − 2,700.	Browne[1]
h_f char (Btu lb^{-1})	0.00	—	—
h_f pyrolysis gas (Btu lb^{-1})	− 3,604.00	—	Nielson & Tao[14]
ρ_c/ρ_p	0.23	0.15 to 0.50	—
ψ	1.00	—	—

$$C_p = 0.219 + 0.2377(10^{-3})\,T - 0.474(10^{-7})\,T^2 - \frac{2{,}030}{T^2} \qquad (6)$$

The sensible pyrolysis gas enthalpy at a given temperature is computed by integrating Equation 6 from 537°R to the desired temperature.

Some of the other input parameters (see Table 1) were adjusted within the indicated levels in order to obtain the best results. The selected values were used in the final analyses.

Using the char density to wood density ratio, specific heat and heat of formation, the heat of pyrolysis (Equation 3) can be computed. Figure 1 shows the total enthalpy curves and the resulting heat of pyrolysis. The graph indicates a reaction that becomes increasingly exothermic at higher temperatures; the exothermic heat of pyrolysis is 98 Btu lb^{-1} of pyrolysis gas (54 cal gm^{-1}) at room temperature (536°R).

Surface Parameters: At the unexposed surface or backwall, the movement of thermal energy by convection or radiation is defined in terms of the wall heat transfer coefficient, wall emissivity, and the constant temperature of the environment beyond the backwall. The emissivity of wood

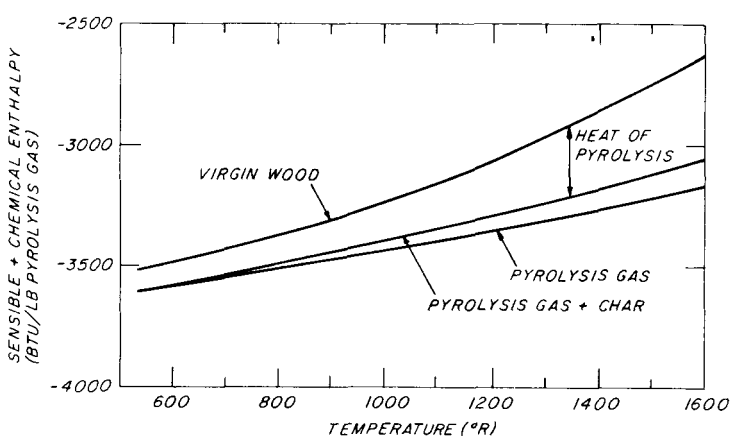

Figure 1. *Illustration of heat of pyrolysis computation* (ρ_c/ρ_p = *0.23).*

was taken as 0.85 and the convective heat transfer coefficient as 3.2 Btu $h^{-1}ft^{-2}°R^{-1}$. A reservoir temperature of 536°R was used.

For the ablating surface boundary condition involving surface energy balance and thermochemical erosion, the additional surface parameters required were the heat transfer convective film coefficient, recovery or boundary layer edge enthalpy, char emissivity, the ratio of the heat transfer and mass transfer Stanton numbers, and the surface thermochemistry tables parameters. Because the experimental tests used for comparison involved poorly defined boundary conditions, the ablating surface parameters were generally estimates. The Aerotherm Corporation EST computer program was used to generate the surface thermochemistry tables.

EVALUATION

Experimental results were compared with analytical results of the CMA program and the effects of varying some of the input parameters investigated. Comparison of the experimental and theoretical results was based on time-temperature curves and the 1,010°R isotherm. As noted before, experimental results have shown 1,010°R to be characteristic of the base of the char layer.

EXPERIMENTAL COMPARISON

Slabs of ovendried southern pine, 3¼ in. thick, were exposed on one face to burners in a small natural-gas-fired furnace at the U.S. Forest Products Laboratory. With an iron-capped thermocouple 2 in. away from

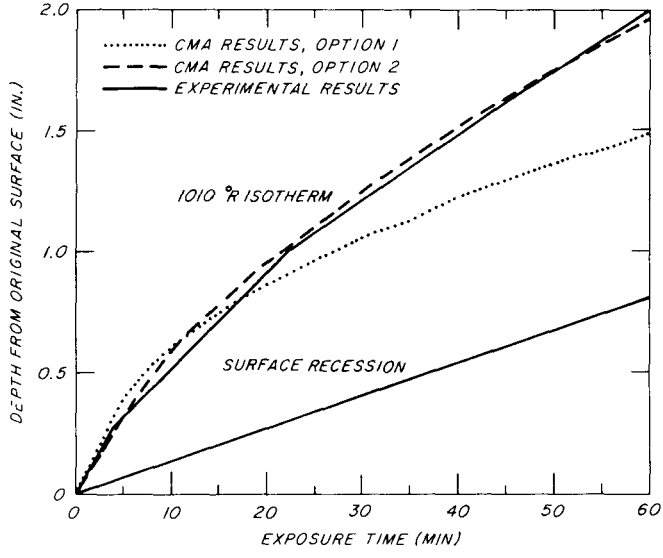

Figure 2. *Surface recession and depth of 1,010°R isotherm for wood slab subjected to a constant 1,960°R fire exposure. Experimental data are the average of two tests.*

the specimen surface, the natural gas was regulated to maintain a furnace temperature of 1,960°R. The natural gas was fed into the furnace and allowed to burn freely with air supplied naturally through vents along the base of the furnace.

The temperature distribution and the 1,010°R isotherm within the wood slabs were obtained by thermocouples at 1/4 in., 1/2 in., 1 in., 1 1/2 in., and 2 in. from the original exposed face. The thermocouples were inserted through 1/8-in.-diameter holes from the unexposed surface.[2] In addition, four bare thermocouples were inserted through holes and bent over on the fire-exposed surface. A ceramic rod was inserted through the backwall of the furnace, so the surface recession of the slab, $\dot{F}$, could be measured (see Figure 2). The average dry wood density was 32.7 lb ft^{-3}.

The initial CMA analysis was made using the general convective and radiative heating and thermochemical erosion surface boundary condition. The resulting 1,010°R isotherm is shown in Figure 2 as Option 1. All of the runs using this option indicated no surface recession. Similar results were obtained using the radiant heat flux and zero surface recession rate surface boundary condition option. The analysis was repeated using the specified surface temperature and surface recession rate option. The resulting 1,010°R isotherm is shown in Figure 2 as Option 2. The time-temperature curves for the thermocouples are given in Figure 3. The Option 2 results are in good agreement with the experimental data.

A 20-in. by 10-in. by 3-in. slab of red oak was tested in a manner similar to the southern pine tests, except that the furnace temperature fol-

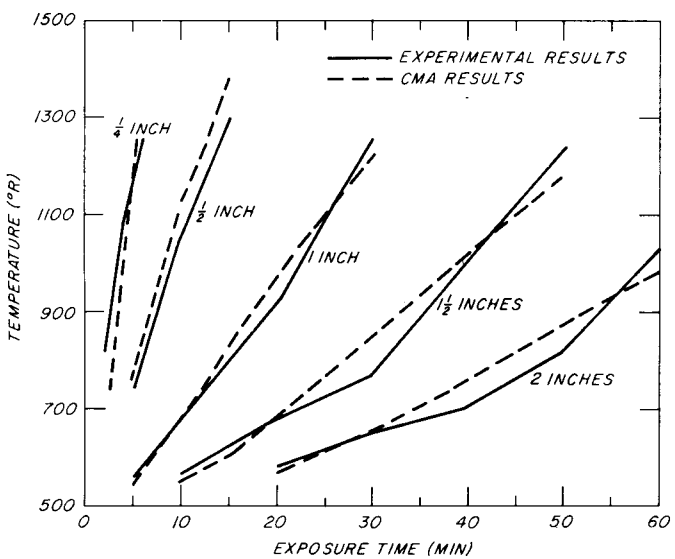

Figure 3. *Time-temperature curves at various depths from original surface for wood slab exposed to a constant 1,960°R fire exposure. Experimental data are the average of two tests.*

lowed the ASTM Standard E119 time-temperature curve. The ovendried wood density was 40.4 lb ft^{-3} and the moisture content was about 6 percent. CMA analysis indicated internal temperatures that were significantly higher than the experimental results.

Because the model does not include a heat of moisture vaporization term, the CMA results are for an ovendried slab. Thus, the 6 percent moisture content of the slab possibly would account for most of the difference between the theoretical and experimental results.

PARAMETER STUDY

The uncertainty in some of the input parameters allowed adjustments to be made in the input and the sensitivity of the results to them assessed. Some of these parameters were ratio of char density to wood density, activation energy, heat of formation of wood, specific heat, and thermal conductivity (see Figures 4 through 6). The standard was the Option 2 result for the southern pine slab.

The CMA model has options in considering the pyrolysis gas pickup of energy and surface recession. In the standard analysis, the pyrolysis gas enthalpy was kept constant above 1,572°R and a surface recession of 0.83 in. hr^{-1} was specified. Not suppressing the pyrolysis gas pickup of energy from the char resulted in a 0.06 in. hr^{-1} reduction in the 1,010°R

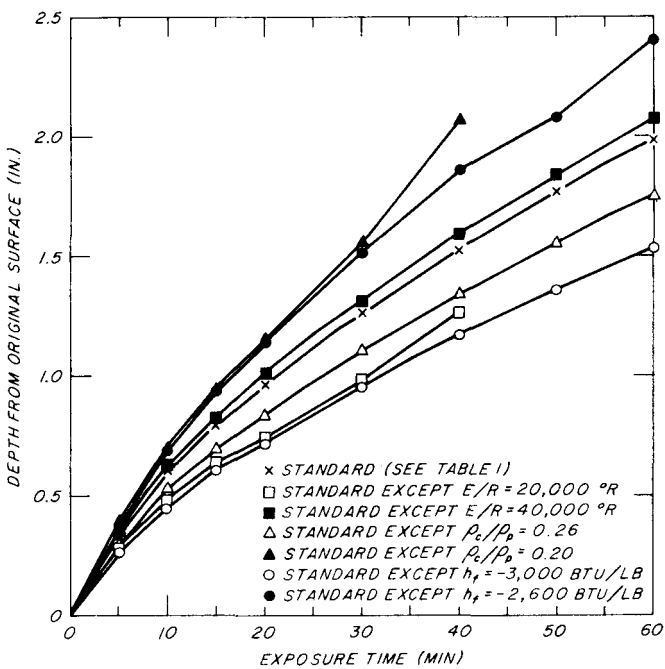

Figure 4. *Effect of changes in activation energy (E/R), char density (ρ_c/ρ_p), and heat of formation of virgin wood (h_f) on Option 2, 1,010°R isotherm for southern pine slab.*

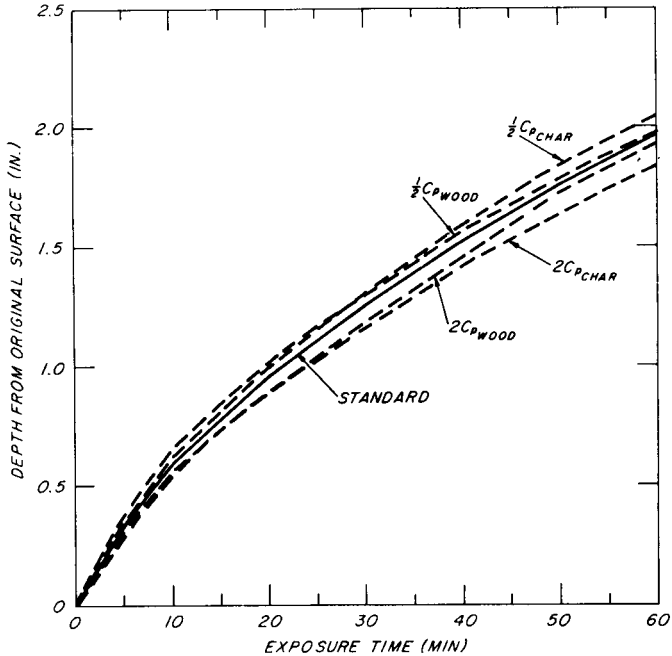

Figure 5. *Effect of changes in specific k a t of wood* ($C_{p_{wood}}$) *or char* ($C_{p_{char}}$) *on Option 2, 1,010°R isotherm for southern pine slab.*

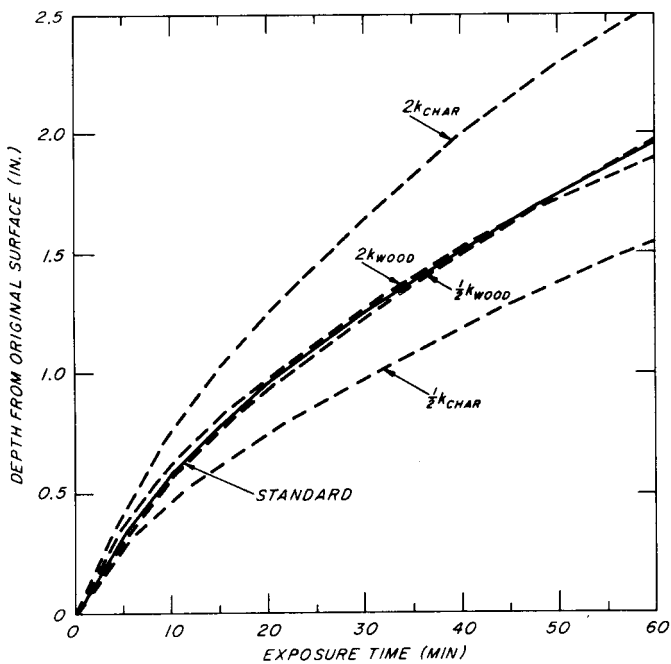

Figure 6. *Effect of changes in thermal conductivity of wood* (k_{wood}) *or char* (k_{char}) *on Option 2, 1,010°R isotherm for southern pine slab.*

isotherm. Assuming zero surface recession resulted in a 1,010°R isotherm 0.44 in. hr^{-1} below the isotherm for the standard analysis.

DISCUSSION

The CMA results were in good agreement with the experimental data for the southern pine slab. While some good results were obtained, there are limitations in using the CMA program to predict the charring of wood: (1) adequate data are not yet available for some of the material parameters; (2) when boundary condition Option 1 is used, no surface recession can be obtained; (3) the input required to define the boundary conditions of the experimental data are generally not available; and (4) a heat of moisture vaporization term is needed in the internal energy balance equation.

The CMA analysis proved to be very sensitive to the material parameters involved in the pyrolysis energy term of Equation 2. It is not that the "heat of pyrolysis" was critical in characterizing the charring of wood, but that small errors in the parameters comprising the term can result in the prediction of exaggerated exothermic or endothermic reaction. Some of the critical parameters are specific heat of wood and char, sensible enthalpy of pyrolysis gas, the heat of formation of wood, char, and pyrolysis gas, and the ratio of the char density to the initial wood density. Because some of these parameters are temperature dependent, the heat of pyrolysis of Equation 3 is also temperature dependent. Thus changes in the preexponential factor or activation energy of Equation 1, which change the temperature range at which pyrolysis occurs, can result in significantly different values for the pyrolysis energy term.

Particularly difficult to evaluate is the enthalpy and heat of formation of the pyrolysis gas. Though the gas enthalpy was computed from values for the pyrolysis gas composition, the relative proportions of gases, vapors, tar, and charcoal vary widely according to the condition of temperature, pressure, time, geometry, and environment under which pyrolysis occurs.[1] Using data giving the pyrolysis gas composition at different temperatures, a total enthalpy can be computed that will result in a highly endothermic heat of pyrolysis and a low char rate. The CMA model assumes that the pyrolysis gas enthalpy is only a function of temperature. But, Browne and Brenden noted that the heat of combustion of the volatilized material from wood depends little, if any, on the temperature at which pyrolysis takes place and that it increases as the degree of volatilization increases.[16] Further research is needed into these material parameters and reasons for differences in the available data.

No surface recession was obtained with the use of the general heating and thermochemical erosion surface boundary condition option. Charcoal glows and is consumed at 1,392°R (500° C). When the surface rises somewhat beyond 1,832°R (1,000° C), carbon is believed to be consumed at the surface as fast as the reaction zones penetrate into the wood.[1] Obtaining

surface recession is dependent upon the thermochemistry tables that are part of the input. Several possible explanations for this failure exist. The thermochemistry tables obtained using the EST program could be erroneous because of the required surface equilibrium assumption or poor specification of the elemental composition of the surface. The EST manual noted that equilibrium is an increasingly poor assumption at low surface temperatures (e.g., below 2,000°R).[6] Whether the equilibrium assumption is a poor one for burning wood is unknown, but the surface temperatures for wood are low in comparison with the conditions that the EST program was designed for. Another possible reason for the failure to obtain the surface recession is that the recession is more a physical phenomenon than a chemical one.

A problem in evaluating the CMA program is that the boundary conditions of the available experimental data are usually not consistent with the solution boundary conditions available for the CMA model. The general heating and thermochemical erosion surface boundary condition option requires the boundary condition to be defined in terms of the radiant heat flux, boundary layer edge enthalpy, heat transfer coefficient, mass transfer coefficient, pressure, and the blowing reduction parameter. The boundary condition Option 2 requires that surface temperature and the surface recession be specified.

The CMA analysis is limited to the case of ovendried wood. Inclusion of moisture would require adjustments in some of the material parameters. A heat of vaporization term would also have to be added to the internal energy balance equation.

CONCLUSION

The Aerotherm Charring Material Thermal Response and Ablation (CMA) program was investigated as an alternative to predict the temperature distribution of a wood slab exposed to fire. The CMA program can describe the charring of ovendried wood when the surface temperature and surface recession are specified and a proper selection of material parameters is made. There are, however, limitations to the use of this program in evaluating wood charring. The investigation has indicated the need for further research on the basic thermal properties of wood and char, the surface recession of the char layer, and the pyrolysis reaction.

NOMENCLATURE

A = Area, ft^2
B = Preexponential factor, s^{-1}
C_p = Specific heat, Btu lb^{-1} $°R^{-1}$ or kcal kg^{-1} $°C^{-1}$
E = Activation energy, Btu lb^{-1}-mole
h = Enthalpy (sensible + chemical), Btu lb^{-1}
$\bar{h}$ = Defined as $(\rho_p h_p - \rho_c h_c)/(\rho_p - \rho_c)$, Btu lb^{-1}
h_f = Chemical enthalpy or heat of formation, Btu lb^{-1}

k = Thermal conductivity, Btu - in. ft^{-2} hr^{-1} °R^{-1}
m = Mass flow rate, lb s^{-1}
M = Moisture content, %
R = Universal gas constant, Btu lb^{-1}-mole °R^{-1}
$\dot{F}$ = Surface recession rate, ft s^{-1}
S = Specific gravity, dimensionless
T = Temperature, °R
x = Coordinate normal to ablative surface, fixed to receding surface, ft
y = Coordinate normal to ablative surface, fixed in space relative to backwall, ft
θ = Time, s
ρ = Density, lb ft^{-3}
ψ = Decomposition reaction order, dimensionless

Subscripts

$_c$ = denotes char
$_g$ = denotes pyrolysis gas
$_p$ = denotes virgin plastic or wood

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GPO 821—329