MASS LOSS OF AND TEMPERATURE DISTRIBUTION IN SOUTHERN PINE AND DOUGLAS FIR IN THE RANGE 100 TO 800°C

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ABSTRACT

Southern pine and Douglas fir test specimens were placed in an over kept at either 100, 160, 245, 400, 600, or 800 °C, and the center point temperatures and the mass losses of the specimens were measured as functions of exposure time. A model is described for calculating the temperature distribution in and the mass loss of wooden beams having rectangular cross sections. Comparisons were made between the data and the results of the model, and reasonable agreements were found between the measured and calculated temperatures and mass losses. Some tests were also performed to assess the effect of ambient oxygen concentration on the mass loss.

INTRODUCTION

AN IMPORTANT PART OF THE PYROLYSIS OF WOOD IS THE HEATING up of wood and the evaporation of volatiles from the material. The evaporation of volatiles is represented by a mass loss. In this paper the temperature response and mass loss of wood were investigated at surface temperatures in the range of 100 to 800°. Data are presented for southern pine and Douglas fir. These types of wood were selected for the tests because of their wide use as structural timber. A model is also described which can be used to calculate the temperature distribution

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in and the mass loss of wooden beams having rectangular cross sections.

THE MODEL

Heat transferred to wood increases the temperature inside the wood, causing the wood to pyrolyze and to form volatile vapors. These vapors originate in the pyrolysis zone and flow out through the char layer, resulting in a mass loss. Here a simple model is described for calculating the temperature distribution and the mass loss as a function of time.

The model is developed for the following problem. A rectangular slab of thickness a and width b is exposed to radiant and convective heat fluxes (Figure 1). The slab is taken to be infinite in the z direction so that the temperature inside the slab varies only in the x and y directions (the problem is two dimensional). Initially, (time t=0) the temperature T at every point inside the slab is known and is sufficiently low so that no significant chemical or physical changes (i.e. no pyrolysis) occur in the material. The slab is then exposed suddenly to known heat fluxes q. Both convective and radiant heat fluxes may contribute to the total heat transfer. The slab is well ventilated so that the combustion products released during heating are removed from the vicinity of the surface.

The law of conservation of energy for a small volume element dv inside the slab can be expressed as:

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rate of change of Net rate of energy Net rate of energy Rate of energy energy in dv = transferred into + transferred into + liberated (or dv by conduction dv by convection absorbed) in dv
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The heat capacities of the vapor and the water are small compared to the heat capacity of the solid. The heat liberated by the vaporization of

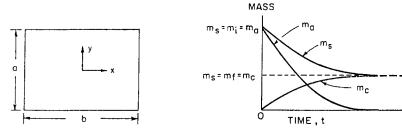


Figure 1. Geometry of the problem, and illustration of the variation of mass with time.

water is small compared to the heat generated by the pyrolysis of the "active" wood. Finally, the heat transfer through the wood by convection is small compared to the heat transfer by conduction. Accordingly, the law of conservation of energy may be written as [1-20]

$$\frac{\partial (m_s C_s T)}{\partial t} = \frac{\partial}{\partial x} K_x \frac{\partial T}{\partial x} + \frac{\partial}{\partial y} K_y \frac{\partial T}{\partial y} + \frac{\partial m_a}{\partial t} L \tag{1}$$

where T is the absolute temperature inside the material at the x,y coordinate, C_s is the specific heat (defined below), L is the heat of reaction, K_s and K_s are the thermal conductivities in the x and y directions. m_s is the mass per unit volume of the wood comprised of virgin ("active") wood (mass per unit volume m_a) and of wood which can not pyrolyze further at the given temperature ("inactive" wood, or "char", mass per unit volume m_s)

$$m_s = m_a + m_c \tag{2}$$

 m_s , m_a and m_c vary with time as illustrated in Figure 1. The water content is not included in m_s .

Following the suggestion of Kang [20], the specific heat and the thermal conductivities are expressed as

$$C_s = \frac{m_a}{m_s} C_a + \frac{m_c}{m_s} C_c \tag{3}$$

$$K_{x,y} = \frac{m_a}{m_i} K_{a_{x,y}} + \frac{m_c}{m_f} K_{c_{x,y}}$$
 (4)

where C_a , C_c and K_a , K_c are the heat capacities and thermal conductivities of the active wood and char, respectively. m_i and m_f are the masses (dry wood) at the beginning and at the end of the pyrolysis

$$\left\{ \begin{array}{ll}
 m_s = m_a = m_t = \varrho_a \\
 m_c = 0
 \end{array} \right\} t < 0 \qquad m_s = m_f = m_c \\
 m_a = 0
 \left\{ t \to \infty \right\}$$
(5)

 ϱ_a is the density of the dry, active wood. Note that ϱ_a is a constant for a given type of wood. The mass m_f depends upon the temperature. The value of m_f decreases with increasing temperatures. The mass m_s is related to m_i and m_f by the expression

$$m_s = (1 - \frac{m_f}{m_s}) m_a + m_f$$
 (6)

The expressions used for the specific heat, thermal conductivity, and mass (eqs. 3,4,6) are approximate only. The linear functions are adopted because detailed information on the behavior of these properties is unavailable. It is assumed that the volatile formation (and correspondingly the rate of change of mass of active wood) may be represented by a single step Arrhenius bulk reaction

$$\frac{\partial m_a}{\partial t} = -m_a k_a e^{-E_a/RT} \tag{7}$$

k is the frequency factor, E is the activation energy, and R is the universal gas constant. The reactions occurring during the pyrolysis are complex. Therefore, k_a and E_a may be taken to be constants only within narrow temperature ranges. Values of k_a and E_a appropriate to the temperature must be used in the calculations.

The rate of water vapor formation is also represented by a single step Arrhenius bulk reaction

$$\frac{\partial m_{w}}{\partial t} = -m_{w} k_{w} e^{-E_{w}}/RT \tag{8}$$

The total mass lost (volatile plus water vapor) by the wood during time t is

$$\Delta m = \int_{0}^{t} \left(\frac{\partial m_{a}}{\partial t} + \frac{\partial m_{w}}{\partial t} \right) dt$$
 (9)

In order to obtain solutions to eqns. (1)-(9) the initial and boundary conditions must be specified. Initially (time t=0) the temperature of the wood T, the density of the wood ϱ_a , and the mass fraction M of the water in the wood must be given

$$m_{s} = m_{i} = m_{a} = \varrho_{a} \qquad T = T,$$

$$m_{c} = 0 \qquad (10)$$

$$m_{w} = M\varrho_{a}$$

During pyrolysis (time t > 0) either the surface temperature T_o or the heat flux q must be known at every point on the surface.

Solutions to the above problem can be obtained by numerical methods. A "user friendly" computer code suitable for generating numerical results was developed and can be obtained from the Department of Aeronautics and Astronautics, Stanford University.

RESULTS

Initial mass fraction of water, M

Temperature distributions in and mass losses of southern pine and Douglas fir specimens were calculated using the material properties listed in Tables 1-4. The initial water content M was measured by drying 10 cm long, 2.54 cm wide, and 2.54 cm thick specimens in a circulating oven kept at 105 °C. The mass (weight) loss of each specimen during drying was followed by periodically weighing the specimens on a Mettler Analytical Balance. The moisture contents (average of 18 specimens) are listed in Tables 1-4.

The thermal conductivities of dry wood samples were measured at

Constant	Unit	Southern Pine	Douglas Fir	Source
Density of active wood, ϱ_a	kg/m³	547	365	measured
Final mass, m _f	kg/m³	496	340	from data
Specific heat of active wood, Ca	kJ/kg-K	2.30	2.30	Kung 1972
Specific heat of char, C _c	kJ/kg-K	1.013	1.013	Kung 1972
Thermal conductivity of active wood, Ka	kJ/m-sec-K	0.130	0.130	measured
Thermal conductivity of char, K _c	kJ/m-sec-K	0.188	0.188	Haven 1972
Heat of vapor generation, L	kJ/kg	2,510	2,510	from data
Frequency factor of active wood, ka	1/sec	100,000	100,000	from data
Frequency factor of water, kw	1/sec	2,000	2,000	from data
Activation energy of active wood, Ea	kJ/k mole	85,000	85,000	from data
Activation energy of water, E.,	kJ/k mole	45,000	45,000	from data

Table 1. Material constants used in calculating the mass loss at 100°C.

Table 2. Material constants used in calculating the mass loss at 160°C.

0.06

0.094

measured

Constant	Unit	Southern Pine	Douglas Fir	Source
Density of active wood, ϱ_a	kg/m³	547	365	measured
Final mass, m _f	kg/m³	496	340	from data
Specific heat of active wood, Ca	kJ/kg-K	2.30	2.30	Kung 1972
Specific heat of char, C _c	kJ/kg-K	1.013	1.013	Kung 1972
Thermal conductivity of active wood, Ka	kJ/m-sec-K	0.130	0.130	measured
Thermal conductivity of char, K _c	kJ/m-sec-K	0.188	0.188	Haven 1972
Heat of vapor generation, L	kJ/kg	2,510	2,510	from data
Frequency factor of active wood, ka	1/sec	60,000	60,000	from data
Frequency factor of water, kw	1/sec	10,000	10,000	from data
Activation energy of active wood, Ea	kJ/k mole	85,000	85,000	from data
Activation energy of water, E _w	kJ/k mole	45,000	45,000	from data
Initial mass fraction of water, M	-	0.06	0.094	measured

Constant	Unit	Southern Pine	Douglas Fir	Source
Density of active wood, ϱ_a	kg/m³	547	365	measured
Final mass, m _f	kg/m³	400	340	from data
Specific heat of active wood, Ca	kJ/kg-K	2.30	2.30	Kung 1972
Specific heat of char, C _c	kJ/kg-K	1.013	1.013	Kung 1972
Thermal conductivity of active wood, Ka	kJ/m-sec-K	0.133	0.133	measured
Thermal conductivity of char, K _c	kJ/m-sec-K	0.188	0.188	Haven 1972
Heat of vapor generation, L	kJ/kg	2,510	2,510	from data
Frequency factor of active wood, ka	1/sec	40,000	15,000	from data
Frequency factor of water, kw	1/sec	100,000	100,000	from data
Activation energy of active wood, Ea	kJ/k mole	85,000	85,000	from data
Activation energy of water, Ew	kJ/k mole	45,000	45,000	from data
Initial mass fraction of water, M	-	0.06	0.094	measured

Table 3. Material constants used in calculating the mass loss at 245°C.

Table 4. Material constants used in calculating the mass loss and the center point temperature at temperatures between 400 and 800°C.

Constant	Unit	Southern Pine	Douglas Fir	Source
Density of active wood, ϱ_a	kg/m³	547	365	measured
Final mass, m _f	kg/m³	125	125	from data
Specific heat of active wood, Ca	kJ/kg-K	2.30	2 30	Kung 1972
Specific heat of char, C _c	kJ/kg-K	1.013	1.013	Kung 1972
Thermal conductivity of active wood, Ka	kJ/m-sec-K	0.133	0.133	measured
Thermal conductivity of char, K _c	kJ/m-sec-K	0.188	0.188	Haven 1972
Heat of vapor generation, L	kJ/kg	1,255	1,255	Kung 1972
Frequency factor of active wood, ka	1/sec	7,700	9,400	from data
Frequency factor of water, k _w	1/sec	1,000,000	1,000,000	from data
Activation energy of active wood, Ea	kJ/k mole	85,000	85,000	from data
Activation energy of water, E _w	kJ/k mole	45,000	45,000	from data
Initial mass fraction of water, M	-	0.06	0 094	measured

100 and 160°C using a parallel plate apparatus and the procedures specified by ASTM C 518-76 standard.

Mass losses and center point temperatures were calculated for different frequency factors and activation energies. The mass losses and temperatures thus calculated were compared to data. The values of the frequency factors and activation energies were selected which gave the best fit between the results of the model and the measured mass losses and center point temperatures. The frequency factors and activation energies obtained by this procedure are given in Tables 1-4.

In the calculations the surface temperatures were taken to be constant at either 100, 160, 245, 400, 600, or 800 °C.

Comparisons between the Model and the Data

The results of the model were compared to center point temperatures $(T = T_c \text{ at } x = 0 \text{ and } y = 0)$ and to mass losses measured using southern pine and Douglas fir specimens. The mass loss is defined as

$$m^* = \frac{\Delta m}{m} \times 100 \tag{11}$$

where m, is the initial mass of the specimen and Δm is the mass loss (volatiles plus water vapor). The measurements were performed by placing 10 cm long specimens into a muffler oven. The mass loss was determined by keeping each specimen in the oven for a predetermined length of time and by measuring the weight before and after the exposure using a Mettler Analytical Balance. Each measurement was performed with a different specimen. Data were taken only with those specimens which did not flame in the oven.

The center point temperature was recorded by placing a chromelalumel thermocouple into the center of the specimen. Each data point in Figures 2 and 3 represents the average of two measurements performed using two different specimens.

Comparisons between the measured and calculated center point temperatures are presented in Figures 2 and 3. Comparisons between the measured and calculated mass losses are shown in Figures 4-11. The agreements between the measured and calculated center point temperatures and the measured and calculated mass losses are quite reasonable, especially when considering the limitations which, by necessity, were introduced in the calculations. The accuracies of the calculations are limited by simplifications in the analysis and by uncertainties in the physical constants. Nevertheless, the results of the model indicate the trend in the data and provide estimates of the mass loss.

This is of importance here since our primary goal in developing the model was to establish a tool which can provide a measure of the degradation process and can thus be used in estimate changes in the strength of the wood. For this purpose the results of the model appear to be adequate [22].

Effect of Oxygen Concentration

Tests were also performed to assess the influence of the ambient oxygen concentration on the mass loss. In these tests the oven was filled with either pure oxygen or with pure nitrogen. Mass losses were measured in these two environments at 100 and 245 °C. The results are shown in Figure 12. As one might expect, the mass loss is somewhat higher in the pure oxygen environment. However, the maximum dif-

ference in the mass loss in pure oxygen and in pure nitrogen environments is only about 25 percent. This suggests that a small (few percent) change in the oxygen concentration of the air may not affect significantly the mass loss.

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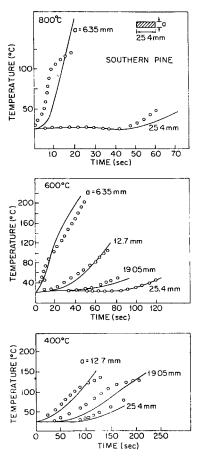


Figure 2. Center point temperature as a function of exposure time. Southern pine. o Data, _____ model.

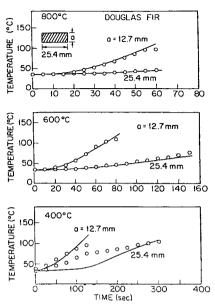


Figure 3. Center point temperature as a function of exposure time. Douglas fir. o Data, _____ model.

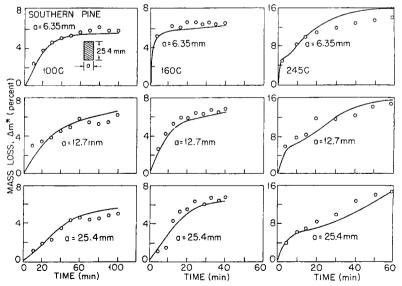


Figure 4. Mass loss as a function of exposure time. Southern pine at 100, 160 and 245°C. o Data, _____ model.

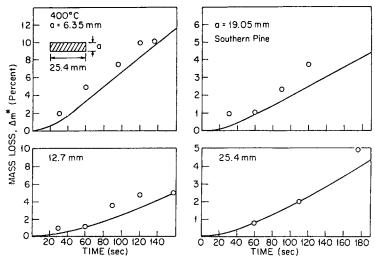


Figure 5. Mass loss as a function of exposure time. Southern pine at 400°C. o Data, _____ model.

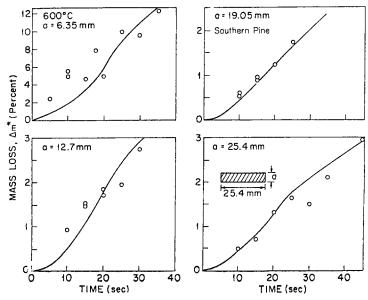


Figure 6. Mass loss as a function of exposure time. Southern pine at 600°C. o Data, _____ model.

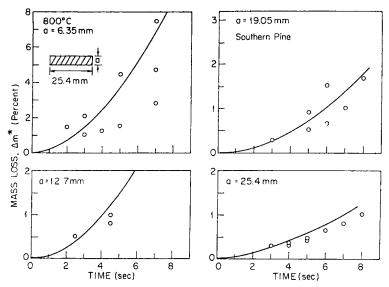


Figure 7. Mass loss as a function of exposure time. Southern pine at 800°C. o Data, _____ model.

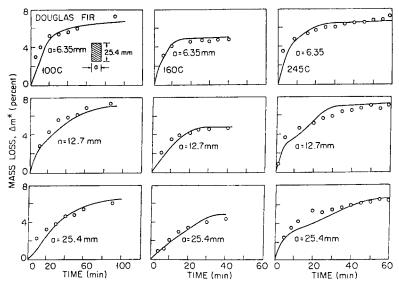


Figure 8. Mass loss as a function of exposure time. Douglas Fir at 100, 160 and 245°C. o Data, _____ model.

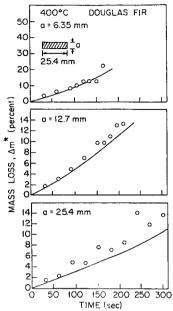


Figure 9. Mass loss as a function of exposure time. Douglas Fir at 400°C. o Data, _____ model.

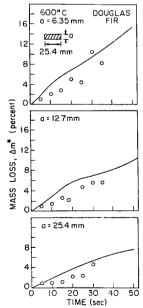


Figure 10. Mass loss as a function of exposure time. Douglas Fir at 600°C. o Data, model.

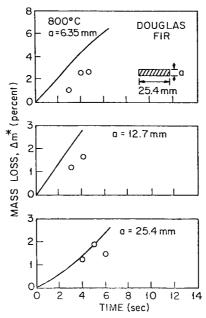


Figure 11. Mass loss as a function of exposure time. Douglas Fir at 800°C. o Data, _____ model.

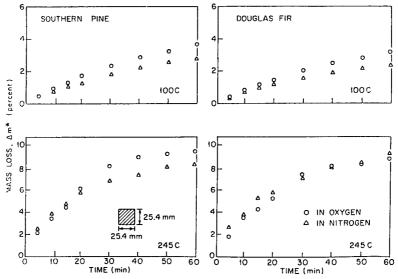


Figure 12. Mass loss as a function of exposure time with the wood immersed in pure oxygen or in pure nitrogen.

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