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A Radiative Ignition Model of a Solid Fuel

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Abstract—A theoretical model describing radiative ignition of a solid fuel is constructed and is numerically analyzed. The model includes the effects of gas phase reaction and a finite value of the absorption coefficient of the solid (in-depth absorption of incident radiation). It is found that the gas phase reaction must be included in the model in order to understand radiative ignition of a solid fuel and to find its ignition boundary. The in-depth absorption of the incident radiation by a solid fuel significantly affects the ignition delay time. The results indicate that there is a finite range of values for pyrolysis or gas phase reaction activation energy for which ignition will occur. This finding has a direct bearing on efforts to reduce material ignitability.

1. INTRODUCTION

The ultimate goal of fire research is to reduce fire hazards. Since ignition is the initiation of the fire, it is very useful to learn how to reduce the chances of ignition. If the ignitable domain of a solid fuel can be reduced, it would reduce the number of ignition accidents. The ignitable domain is the range of physical and chemical properties of the fuel and the atmosphere for which ignition can occur. However, previous ignition studies have not adequately examined the ignitable domain because of the lack of understanding of the ignition mechanism and the truly formidable complexity of the ignition process. This study looks in detail at two important aspects of ignition not previously treated well. These are gas phase reaction kinetics and fuel bed absorption of external radiation.

The complexity of the ignition process derives from the nature of the external energy source and the nature of the materials (Price *et al.* 1966, Kanury 1971). Since it is known that thermal radiation is a primary mode of energy transfer from a large open fire or a building fire, well-defined thermal radiation is used as the external energy source in this study. Note that the thermal radiation is required both to heat the fuel and to cause ignition. No pilot flame is used. Because of the growing use of plastics in building construction and furnishing, a plastic material was chosen for the model of the solid fuel used in the numerical calculations of this study.

Despite years of theoretical research, there are two important mechanisms in the radiative ignition of a solid fuel which are often neglected. One is the gas phase chemical reaction. Frequently this has been assumed *not* to be the rate controlling step during the ignition period. However, Martin (1965) reported that the gas phase reaction is the important process for ignition. Therefore, this assumption has to be examined carefully in the entire regime of ignition. The other important mechanism is the in-depth absorption of the incident radiation by a solid fuel with a finite value of absorption constant. This effect has been experimentally studied by changing the absorptivity of solid samples (Ohlemiller 1971). It is found that this has considerable effect on ignition. None of the previous works (Simms 1962, Martin 1965, and Anderson 1970) correctly included both of these important mechanisms. Ohlemiller (1968) developed the most sophisticated radiative ignition model, but other approximations of his model effectively excluded the gas phase reaction. Therefore, the main objective of this study is to construct the correct radiative ignition model including the above two important mechanisms and to find and understand the effects on ignition of physical and chemical parameters of the combustible material and the surrounding atmosphere. With this understanding, the conditions needed to reduce the ignitable domain of a solid fuel are studied. These conditions are theoretically predictable, and can provide ideas for experimentalists engaged in the development of fire resistive building materials.

2. THEORY

2.1 *Assumptions*

The theoretical model is described in Figure 1 as a semi-infinite solid fuel subject to one-dimensional radiative heating on the surface. As part of the radiation is reflected at the surface and part absorbed in-depth, the solid phase is heated up. The

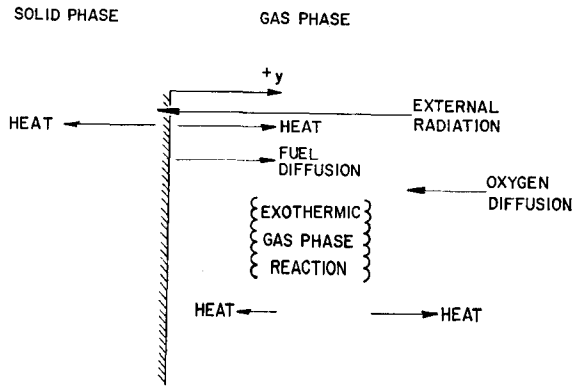

FIG. 1. Schematic illustration of the one-dimensional radiative ignition model of a solid fuel.

thermal degradation of the solid begins when surface temperature reaches the pyrolysis value. Following degradation, fuel vapor starts to diffuse away from the surface and to mix with surrounding oxygen in the gas phase. During the same time, the gas phase adjacent to the surface is heated, mainly by heat conduction from the warmer surface. As this gas phase heating and mixing between fuel vapor and oxygen near the surface continues, the rate of exothermic gas phase reaction increases rapidly and, consequently, the exothermic chemical heat release rates increases. This chemical heat release further heats the gas near the surface and accelerates the exothermic gas phase reaction. Finally a run away condition is achieved and ignition occurs.

In formulating the mathematical model described above the following assumptions are made.

1) Pressure is constant.

2) The gas phase chemical reaction is assumed to be a one-step irreversible chemical reaction subject to second-order Arrhenius kinetics.

3) The pyrolysis of a solid fuel occurs only at the surface and its rate is expressed by a single zero order reaction of Arrhenius law.†

4) The mixture of gases behaves like a perfect gas, and the specific heat is the same for all gaseous species and is constant.

5) The molecular weights of all species are equal, and the molecular diffusivities of all species are equal and constant.

6) The incident radiation is absorbed in-depth by the solid phase satisfying Beer's Law.

† Ohlemiller (1969) calculated that the temperature peak in the solid due to the in-depth absorption and heat loss from the surface to the gas phase was only several microns below the surface. The thermal layer thickness during the ignition period is at least two orders larger than this depth. Therefore, this assumption is reasonable.

7) All thermal properties of the solid phase are constant.

8) Reradiation from the solid is neglected.

It is recognized that this model involves several over-simplifications in the chemical reaction mechanism; however, it provides a reasonable basis for exploring the influences of material and process parameters. The complications which would be introduced by more sophisticated chemical reaction process models are hardly justifiable at the present state of knowledge of fire.

2.2 *Governing Equations and Boundary Conditions*

Using the above assumptions, the governing equations describing the model are as follows:

Continuity:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v)}{\partial y} = 0 \tag{1}$$

Energy:

$$\rho C_P\left(\frac{\partial T}{\partial t} + v\frac{\partial T}{\partial y}\right) = \frac{\partial}{\partial y}\left(K\frac{\partial T}{\partial y}\right) + Q\rho^2 C_f C_{ox} A_R e^{-E_R/RT} \tag{2}$$

Fuel Species:

$$\rho\left(\frac{\partial C_f}{\partial t} + v\frac{\partial C_f}{\partial y}\right) = \frac{\partial}{\partial y}\left(\rho D\frac{\partial C_f}{\partial y}\right) - \rho^2 C_f C_{ox} A_R e^{-E_R/RT} \tag{3}$$

Oxidizer species:

$$\rho\left(\frac{\partial C_{ox}}{\partial t} + v\frac{\partial C_{ox}}{\partial y}\right) = \frac{\partial}{\partial y}\left(\rho D\frac{\partial C_{ox}}{\partial y}\right) - n\rho^2 C_f C_{ox} A_R e^{-E_R/RT} \tag{4}$$

State:

$$\rho T = \rho_0 T_0 \tag{5}$$

Solid phase energy:

$$\rho_s C_s\left(\frac{\partial T_s}{\partial t} + v_s\frac{\partial T_s}{\partial y}\right) = \frac{\partial}{\partial y}\left(K_s\frac{\partial T_s}{\partial y}\right) + \frac{\partial I}{\partial y} \tag{6}$$

where

$$\frac{\partial I}{\partial y} = \beta I_0(1 - r)e^{\beta y} \tag{7}$$

The boundary conditions for the above governing equations are:
At $y = 0$:

$$-K\frac{\partial T}{\partial y} = -K_s\frac{\partial T_s}{\partial y} + \rho_s v_s L_v \tag{8}$$

$$-\rho D\frac{\partial C_f}{\partial y} + \rho v C_f = \rho_s v_s \tag{9}$$

$$-\rho D\frac{\partial C_{ox}}{\partial y} + \rho v C_{ox} = 0 \tag{10}$$

$$T = T_s \tag{11}$$

$$v_s = A_s e^{-E_s/RT_s} \tag{12}$$

At $y = \infty$:

$$C_{ox} = C_{ox,0} \tag{13}$$

$$C_f = 0 \tag{14}$$

$$T = T_0 \tag{15}$$

At $y = -\infty$:

$$T_s = T_0 \tag{16}$$

The initial conditions are:
At $t \leq 0$:

$$T = T_s = T_0 \tag{17}$$

$$C_{ox} = C_{ox,0} \tag{18}$$

$$C_f = 0 \tag{19}$$

It is often convenient in parabolic problems to express these equations in the so-called similarity space. The independent variables are transformed as follows:

$$\eta = \frac{\beta}{2\sqrt{\varepsilon\tau}}\int_0^y \frac{\rho}{\rho_0}\,dy \tag{20}$$

$$\tau = \alpha_s\beta^2 t \tag{21}$$

$$\eta_s = \frac{y}{2\sqrt{\alpha_s t}} = \frac{y}{2\sqrt{\tau}} \tag{22}$$

The transformation of equation (20) absorbs the continuity equation in the physical coordinates. The function $K\rho$ and $\rho^2 D$ are assumed to be constant in this analysis; this is analogous to the Chapman-Rubesin viscosity approximation in boundary layer theory and it permits realistically variable transport coefficients in the gas phase. Then, the governing equations and boundary conditions are expressed in terms of transformed coordinates as follows:
Energy:

$$4\tau\frac{\partial\theta}{\partial\tau} + 2\left(\gamma\sqrt{\frac{\tau}{\varepsilon}} - \eta\right)\frac{\partial\theta}{\partial\eta} = \frac{\delta}{\varepsilon\xi}\frac{\partial^2\theta}{\partial\eta^2} + 4C\tau\frac{C_f C_{ox}}{\theta}e^{-\theta_R/\theta} \tag{23}$$

Fuel species:

$$4\tau\frac{\partial C_f}{\partial\tau} + 2\left(\gamma\sqrt{\frac{\tau}{\varepsilon}} - \eta\right)\frac{\partial C_f}{\partial\eta} = \frac{\partial^2 C_f}{\partial\eta^2} - 4B\tau\frac{C_f C_{ox}}{\theta}e^{-\theta_R/\theta} \tag{24}$$

Oxygen species

$$4\tau\frac{\partial C_{ox}}{\partial\tau} + 2\left(\gamma\sqrt{\frac{\tau}{\varepsilon}} - \eta\right)\frac{\partial C_{ox}}{\partial\eta} = \frac{\partial^2 C_{ox}}{\partial\eta^2} - 4nB\tau\frac{C_f C_{ox}}{\theta}e^{-\theta_R/\theta} \tag{25}$$

Solid phase energy:

$$4\tau\frac{\partial\theta_s}{\partial\tau} + 2\left(\frac{\rho_0}{\rho_s}\gamma\sqrt{\tau} - \eta_s\right)\frac{\partial\theta_s}{\partial\eta_s} = \frac{\partial^2\theta_s}{\partial\eta_s^2} + 4G\tau e^{2\sqrt{\tau}\eta_s} \tag{26}$$

where

$$\gamma = \frac{\rho_s v_s}{\rho_0\alpha_s\beta}, \quad \varepsilon = \frac{\rho^2 D}{\rho_0^2\alpha_s}, \quad \xi = \frac{K_s\rho_s C_s}{K\rho C_P}$$
$$\delta = \frac{\rho_s^2 C_s^2}{\rho_0^2 C_P^2}, \quad C = \frac{Q\rho_0 A_R}{C_P\alpha_s\beta^2 T_0}, \quad B = \frac{\rho_0 A_R}{\alpha_s\beta^2} \tag{27}$$

$$G = \frac{I_0(1-r)}{\rho_s C_s T_0\alpha_s\beta}, \quad \theta = T/T_0, \quad \theta_s = T_s/T_0 \tag{28}$$

At $\eta = 0$:

$$-\frac{\partial\theta}{\partial\eta} = -\frac{1}{\xi}\sqrt{\frac{\varepsilon}{\delta}}\frac{\partial\theta_s}{\partial\eta_s} + \frac{2\rho_0\alpha_s\gamma L_v}{KT_0}\sqrt{\varepsilon\tau}\,\theta \tag{29}$$

$$\frac{\partial C_f}{\partial\eta} = -2\gamma\sqrt{\frac{\tau}{\varepsilon}}(1 - C_f) \tag{30}$$

$$\frac{\partial C_{ox}}{\partial\eta} = 2\gamma\sqrt{\frac{\tau}{\varepsilon}}C_{ox} \tag{31}$$

$$\theta = \theta_s \tag{32}$$

$$v_s = A_s e^{-\theta s/\theta} \tag{33}$$

At $\eta = \infty$:

$$\theta = 1$$
$$C_{ox} = C_{ox,0}$$
$$C_f = 0 \tag{34}$$

At $\eta_s = -\infty$:

$$\theta_s = 1 \tag{35}$$

The initial conditions are:
At $\tau = 0$:

$$\theta = \theta_s = 1$$
$$C_{ox} = C_{ox,0}$$
$$C_f = 0 \tag{36}$$

Note that the mathematical model is highly nonlinear and involves complicated couplings, and thus the equations are amenable to solution only by a numerical method. The calculation of the model was carried out numerically by using the National Bureau of Standards' UNIVAC 1108 computer. Due to the separated nature of their boundary conditions and the nonlinearity of the governing differential equations, the above equations are at first quasilinearized (Bellman 1965). Then, the quasilinearized differential equations were converted into finite difference equations using the Crank-Nicholson scheme. The dependent variables in the difference form can be expressed by tridiagonal matrices and calculated with great speed by the method of Isaacson and Keller (1966). Appropriate tests on stability and convergence were successfully satisfied. Physical and chemical values used in the calculation are listed in Table 1. Since values of chemical parameters of the gas phase reaction are not available during rapid ignition period, values of the gas phase are assumed, but ones of the solid phase are typical values of a plastic material.

TABLE I
Values of physical and chemical properties used in this study

A_R (cm³/g sec)	10^9
A_s (cm/sec)	5.5×10^8
K_s (cal/cm sec °C)	3×10^{-2}
L_v (cal/g)	-300
n	8
P (atm)	1
Q (cal/g)	7000
T_0 (°K)	298
ρ_0 (g/cm³)	1.2×10^{-3}
ρ_s (g/cm³)	1.18

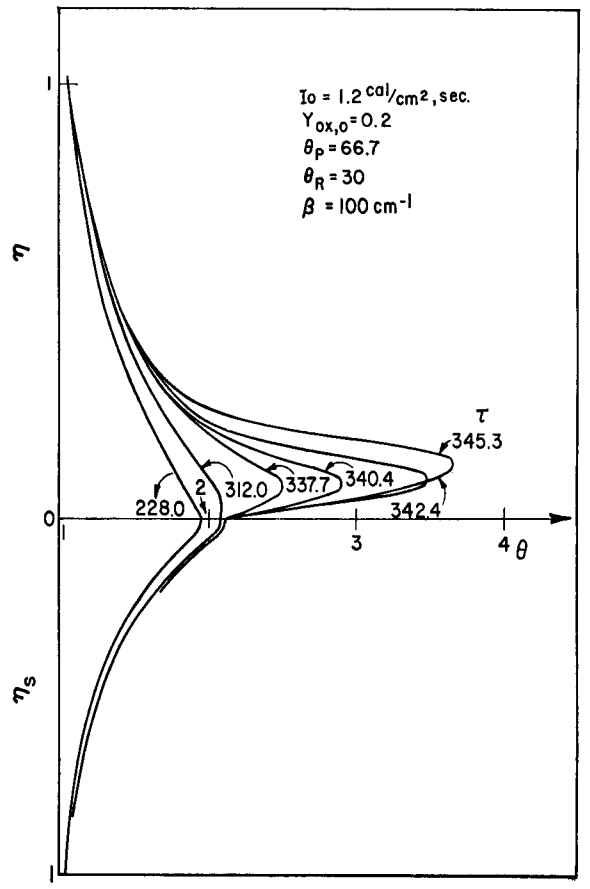

FIG. 2. Timewise temperature distribution in the gas phase and the solid phase.

3. CALCULATED RESULTS AND DISCUSSION

In the range of low radiant flux level, nondimensional temperature distribution in the gas phase and solid phase at various times is shown in Figure 2. A similar distribution is plotted in Figure 3 for a higher radiant flux. The nondimensionalized η coordinate is normalized with the traveled distance of the thermal wave, i.e. a characteristic point of the thermal wave is always at unity. Comparing these figures, it is evident that, under the high radiant flux, the reaction zone (near the temperature peak) moves away from the surface faster than the thermal wave. This is shown in Figure 3 as the value of η increases very rapidly in the short time. Under the low radiant flux, however, the reaction zone moves much slower than the thermal wave. In the former case, the large fuel injection rate due to higher surface temperature blows the reaction zone rapidly away from the surface. In the latter case, however, the small fuel injection rate due to low surface temperature cannot supply enough fuel for the reaction

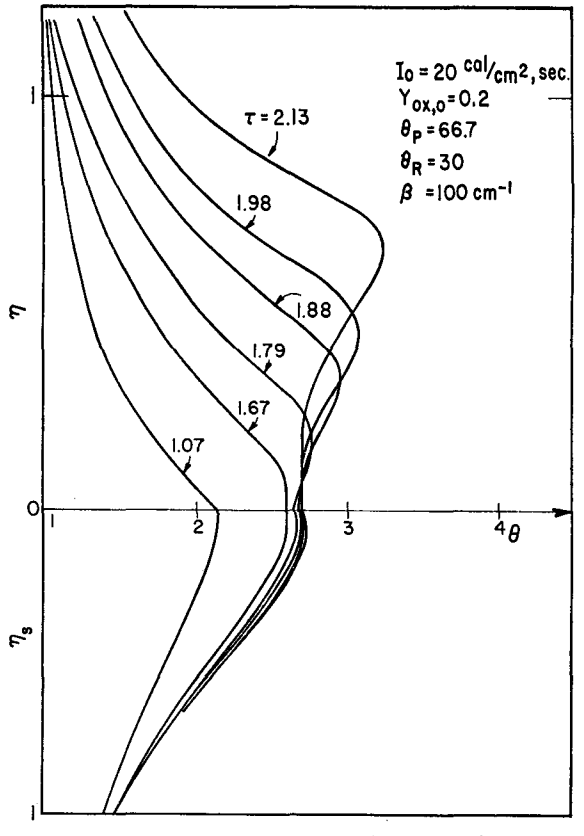

FIG. 3. Timewise temperature distribution in the gas phase and the solid phase.

zone to move rapidly away from the surface. In the physical coordinate y, the actual distance from the surface to the reaction zone is much shorter under the high radiant flux than under the low radiant flux due to short heating time for the surface to start to decompose.

A considerable problem in the study of ignition mechanisms is the question of the ignition criterion. The exact state of ignition is itself an ill-defined concept, but ignition delay can be evaluated only by defining in advance some criterion of runaway. In most experiments, the measurements of ignition delay time are based on the detection of light emission. However, this light emission criterion cannot be applied as the theoretical ignition criterion, unless detailed values of the physical parameters of the chemical reaction kinetics are well known. Although at present the available information related to complex chemical reaction kinetics is limited, it is believed that the ignition criterion should include the effect of the chemical reaction process with the addition of the conventional thermal criterion. For this reason, the following six ignition criteria are considered in this study.

1) $\int_0^\infty$ (Reaction Rate)$dy \geq C_1$
2) Maximum (Reaction Rate) $\geq C_2$
3) Maximum $(\theta) \geq C_3$
4) $Q\int_0^\infty$ (Reaction Rate)$dy \geq I_0(1 - r)$
5) $\partial(\int_0^\infty$ (Reaction Rate)$dy)/\partial t \geq C_4$
6) $(\partial\theta/\partial\eta)\eta = 0 \geq 0$

Since there is no steady state solution for the one-dimensional ignition model of a pure solid fuel, the so-called go no-go criterion is not considered. The physical meaning of each ignition criterion is as follows: (1) The total gas phase reaction rate becomes equal to or larger than a constant C_1, (2) The maximum local gas phase reaction rate becomes equal to or larger than a constant C_2, (3) The maximum local nondimensional gas phase temperature becomes equal to or larger than a constant C_3, (4) The total heat release rate of the exothermic gas phase reaction becomes equal to or larger than the rate of radiant energy absorption in the solid phase, (5) The acceleration of the total gas phase reaction rate becomes equal to or larger than a constant C_4, (6) The temperature gradient of the gas phase at the fuel surface becomes zero or positive. By giving an arbitrary but reasonable value for each constant, the ignition delay times based on each criterion are calculated and they are compared with each other in Figure 4. The calculated values of the ignition delay time as a function of the initial oxygen mole fraction are almost the same

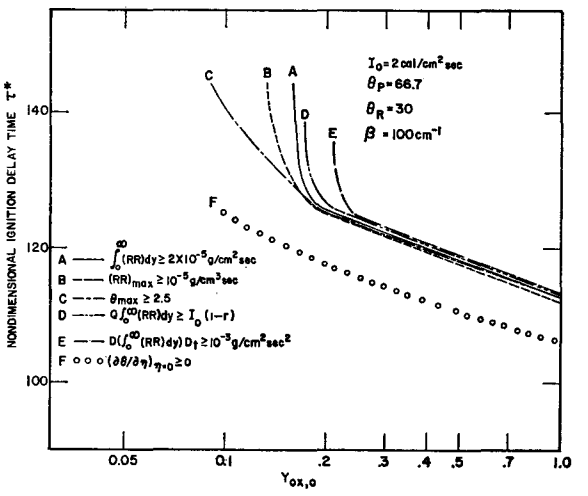

FIG. 4. The effect of ignition criterion on ignition delay time.

except when the $(\partial\theta/\partial\eta)\eta = 0$ criterion is applied. This trend is also observed with another physical parameters such as external radiant flux and environmental conditions. Therefore, the ignition criterion affects the ignition delay time and the ignitable boundary quantitatively, but not qualitatively. Since the objective of the analysis is to confirm the ability of the model to predict the qualitative dependence of the ignition delay time and ignitable boundary on incident radiant flux, physical properties, chemical properties and environmental conditions, any above ignition criterion is reasonable for the purpose of this study. For this reason, the ignition criterion (1), the total amount of the gas phase reaction, is used in this study and all results below are based on this ignition criterion.

In Figure 4, it is interesting to notice that, at low incident radiant flux $I_0 = 2$ cal/cm²sec, the dependency of the ignition delay time on the initial oxygen mole fraction is small above about 0.25, but it becomes very significant below 0.25. A similar behavior was experimentally observed by Alvares (1967) and Ohlemiller (1971). This behavior indicates that, under the low radiant flux and high initial oxygen, the rate controlling step of the ignition is the surface heat up but it becomes the gas phase reaction process for the low initial oxygen regime.

The effect of the incident radiant flux on the ignition delay time is one of the important characteristics of the radiative ignition of a solid fuel and is shown in Figure 5. It indicates that values of chemical parameters, such as pyrolysis activation energy and gas phase reaction activation energy, have significant effects on ignition delay time and the ignitable boundary. However, the effect of chemical parameters on the values of the slopes of the log–log plotted curves is small except near the ignitable boundary and the value of the slope is about −1.9. The often used thermal heat up model based on the constant heating of a thermally thick, opaque solid (Carslaw and Jaeger 1959) with an assumed constant ignition surface temperature yields a simple analytical expression for ignition delay time

$$t_i = \frac{\pi K_s \rho_s C_s}{4}\left[\frac{(T_s^* - T_0)}{I_0(1-r)}\right]^2 \tag{37}$$

which gives

$$t_i \sim \frac{1}{I_0^2} \tag{38}$$

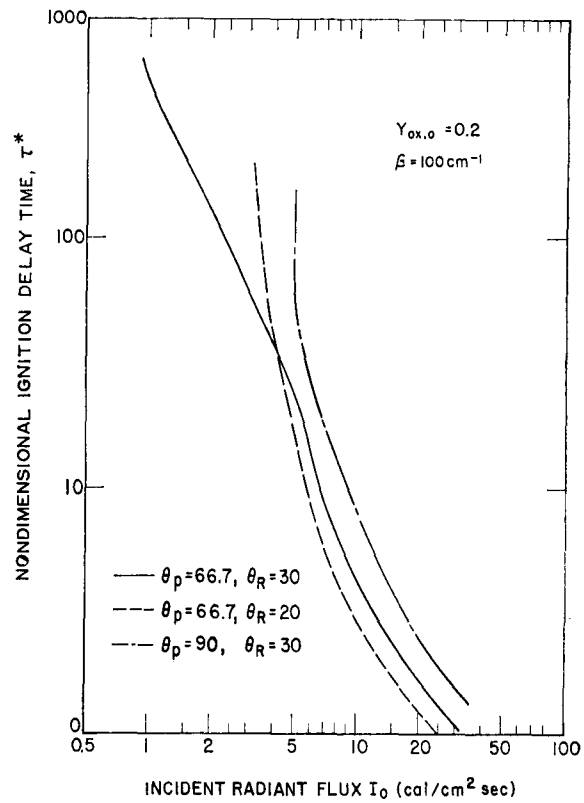

FIG. 5. The effect of values of activation energies on ignition delay time.

and the value of the slope of the log–log plot is −2.0, which is close to the predicted value in this study. On the other hand, the present calculation predicts that the surface temperature at ignition increases with increasing incident radiant flux, as shown in Figure 6.† With increasing radiant flux, the gas phase reaction becomes significantly closer to the surface due to the shorter ignition delay time. Therefore, with increasing radiant flux, the gas phase temperature distribution near the surface becomes steeper and the rate of heat loss from the gas phase reaction zone to the surface becomes greater. As a result, the gas phase

† Alvares and Wiltshire (1968) observed experimentally and concluded that the ignition surface temperature was independent of the incident radiation for alpha cellulose. However, their experimental results were based on only two different heat fluxes (~7 and ~14 cal/cm² sec) and their discussion suggests that their surface temperature measurement may not have been highly accurate. According to the present calculation, the difference in ignition surface temperature based on their experimental radiant flux is about 40 °C. Although the difference in the ignition surface temperature does seem to be small, $t_i \sim (T^* - T_0)^2$ the difference in the ignition delay time is not negligible. The experimental observation is not conclusive and further study is necessary to clarify this point.

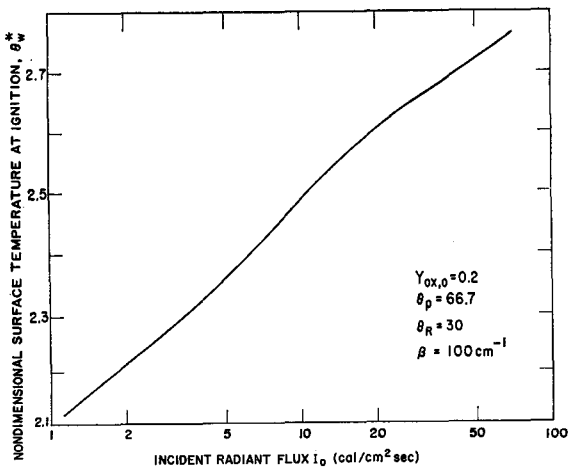

FIG. 6. Surface temperature at ignition instance vs. incident radiant flux.

reaction rate under the high radiant flux is less than that under the low radiant flux at the same ignition surface temperature. Hence, with increasing radiant flux, the ignition surface temperature should become higher in order to supply more fuel for the gas phase reaction to afford the larger heat loss. This tends to increase the ignition delay time and reduce the absolute value of the slope. However, with increasing radiant flux, the rate of heat feedback from the gas phase reaction zone to the surface increases and reduces the additional time required to reach the ignition temperature at the surface. Therefore, these two trends tend to cancel each other with increasing incident radiant flux and to predict the value of -1.9. Near the ignitable boundary, the effects of the gas phase reaction become dominant and the value of the slope becomes much larger. For this reason, although the value of the slope predicted by this study is close to that by the thermal heat up model, the detailed ignition mechanisms differ significantly from each other.

Another important parameter in the radiative ignition is the value of the absorption coefficient of the solid phase and its effect on the ignition delay time as shown in Figure 7. This figure indicates that the absorption constant does have significant effects on ignition delay time and on the value of the slope of the predicted curve. There are two effects: (1) the effectiveness of surface heating by incident radiation and (2) the amount of heat loss from the surface into the solid phase. The low value of the absorption constant reduces the effective surface heating which delays the pyrolysis process and tends to increase the ignition delay. On the other hand, the low value of the absorption constant causes a smaller heat loss into the solid phase due to the flatter solid temperature distribution, which tends to reduce the ignition delay time. Since the former is dominant at the low radiant flux regime and the latter is dominant at the high radiant flux regime, there are two distinct values of the slope for the lower value of the absorption constant as shown by the dashed line in Figure 7. Therefore, if the value of the absorption constant is small, a satisfactory model must include the effect of the in-depth absorption.

Other heat sinks and sources in the ignition process of a solid fuel are due to the pyrolysis. The pyrolysis may be either endothermic or exothermic (McCarter 1972, Roberts 1971). This effect of the endothermicity or the exothermicity of the pyrolysis of a solid fuel on the ignition delay time is examined in Figure 8. The result clearly indicates that this effect is negligible for the ignition delay time with reasonable values of the pyrolysis heat release. This illustrates that, during the ignition delay period, the total amount of pyrolysis is so small that the endothermicity or the exothermicity does not affect the ignition delay time significantly. During steady state burning the heat of pyrolysis will be significant.

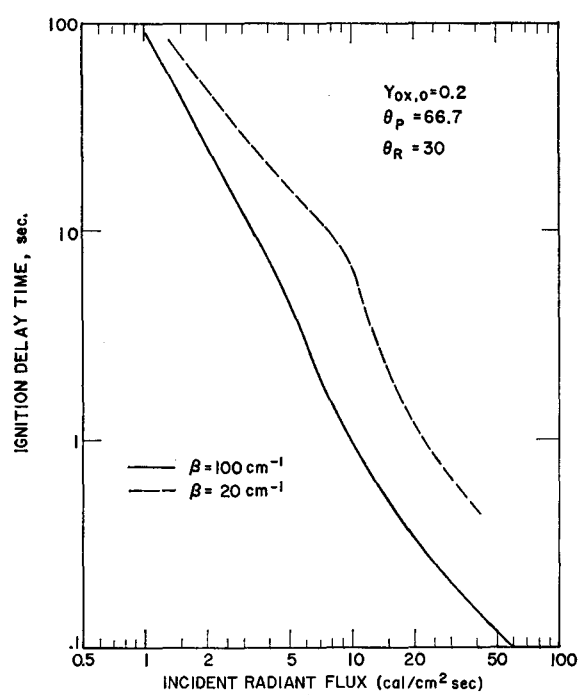

FIG. 7. The effect of the value of absorption constant on ignition delay time.

It is useful to study effects of the values of physical and chemical parameters on the ignitable domain to find how the ignitable domain can be reduced. Hence, the effects of the combination of values of the pyrolysis activation energy and the gas phase reaction activation energy on the ignitable domain were studied. This study might suggest specific combinations of values of the two activation energies which would reduce the ignitable domain. Figure 9 illustrates the change in the ignition delay time caused by varying the nondimensional pyrolysis activation energies of $\theta_R =$ 30 and 66.7. This figure indicates that there exists a lower limit and a upper limit in the value

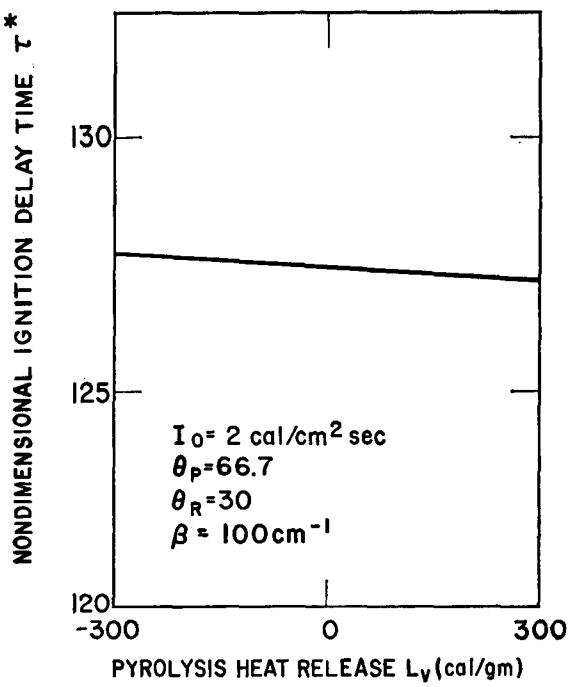

FIG. 8. The effect of the value of pyrolysis heat release on ignition delay time.

of the nondimensional pyrolysis activation energy required for ignition at a given value of the nondimensional gas phase reaction activation energy. With $\theta_R = 30$, the lower value is about $\theta_P = 52$ and the upper value is about $\theta_P = 75$. By increasing the value of θ_R, this ignitable domain shifts toward the higher values of θ_P. Also, the effect of the value of θ_R on the ignitable domain with a given value of θ_P is shown in Figure 10. Therefore, if the value of θ_P or θ_R is lower than the lower limit or higher than the upper limit, the ignition does not occur. The size of the ignitable domain increases as the incident radiant flux and the initial oxygen mole fraction increases. If these values are larger, the ignitable domain becomes

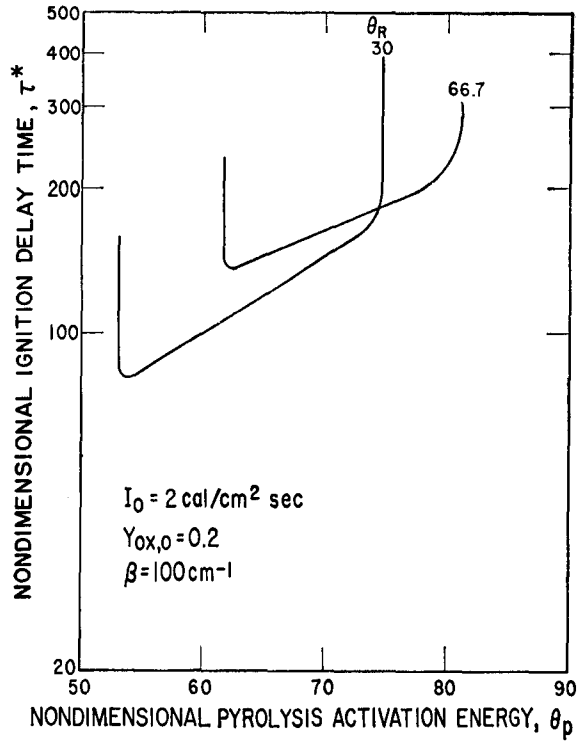

FIG. 9. The ignitable domain in the value of pyrolysis activation energy with given values of gas phase reaction activation energy.

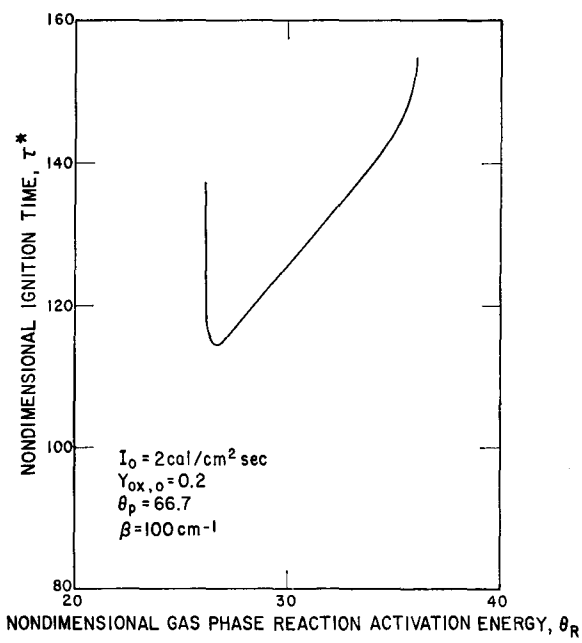

FIG. 10. The ignitable domain in the value of gas phase reaction activation energy with given value of pyrolysis activation energy.

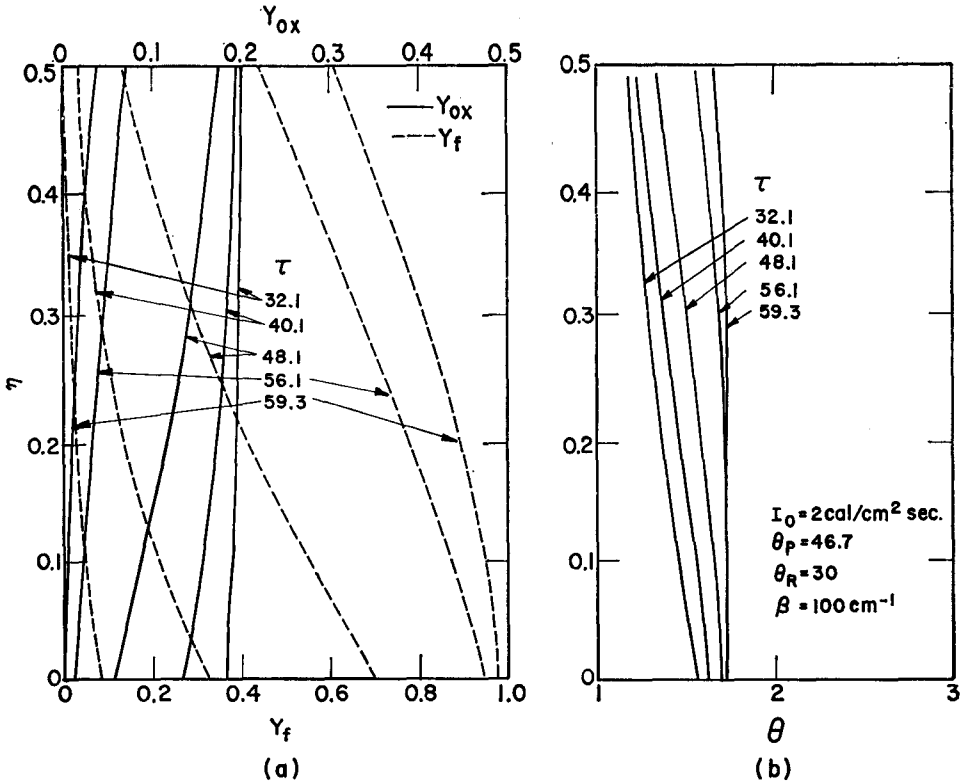

FIG. 11. (a) Timewise fuel and oxygen species distribution. (b) Timewise gas phase temperature distribution.

wider; if they are smaller, the ignitable domain becomes narrower. The important characteristic is that the values of physical and chemical parameters affect the ignitable domain quantitatively, but not qualitatively. The reasons why two limits for ignition exist in the value of θ_P with a given θ_R are explained by using Figures 11–13. Figure 11 illustrates the case in which the value of the nondimensional pyrolysis activation energy is too low for ignition to occur. In this case, the value of θ_P is so low that the pyrolysis of a solid fuel starts at a low surface temperature. Fuel species are then rapidly accumulated and oxygen species are diluted by them. Around $\tau = 48.1$, enough fuel and oxygen are available, but the gas phase is not hot enough to accelerate the gas phase reaction due to the addition of the cool fuel species into the gas phase. With increasing time, a large amount of fuel gas displaces oxygen away from the surface and ignition does not occur. Figure 12 is the case in which the value of the nondimensional pyrolysis activation energy is too high for ignition to occur. In this case, the value of θ_P is so high that the pyrolysis of the solid fuel requires the high surface temperature. Therefore, the gas phase temperature becomes high during the induction period, but the accumulation of the fuel species is very low although a sufficient amount of oxygen is available as shown in Figure 12. A small amount of the gas phase reaction is calculated to occur and produce a small amount of heat release, but the gas phase reaction does not accelerate to reach the runaway condition due to the lack of the sufficient fuel supply. While a small amount of the gas phase reaction continues during the induction period, the fuel supply gradually increases and the oxygen species are consumed fairly rapidly due to the high value of the stoichiometric constant. Therefore, the lack of the fuel supply at the early stage of the induction period and the exhaustion of the oxygen at the late stage of the induction period prevent ignition from occurring although the gas phase temperature is high enough to accelerate the gas phase reaction.

Figure 13 is the case in which the value of θ_P is in the right domain to cause ignition. From a study of Figures 11–13, it may be concluded that two conditions must be simultaneously satisfied

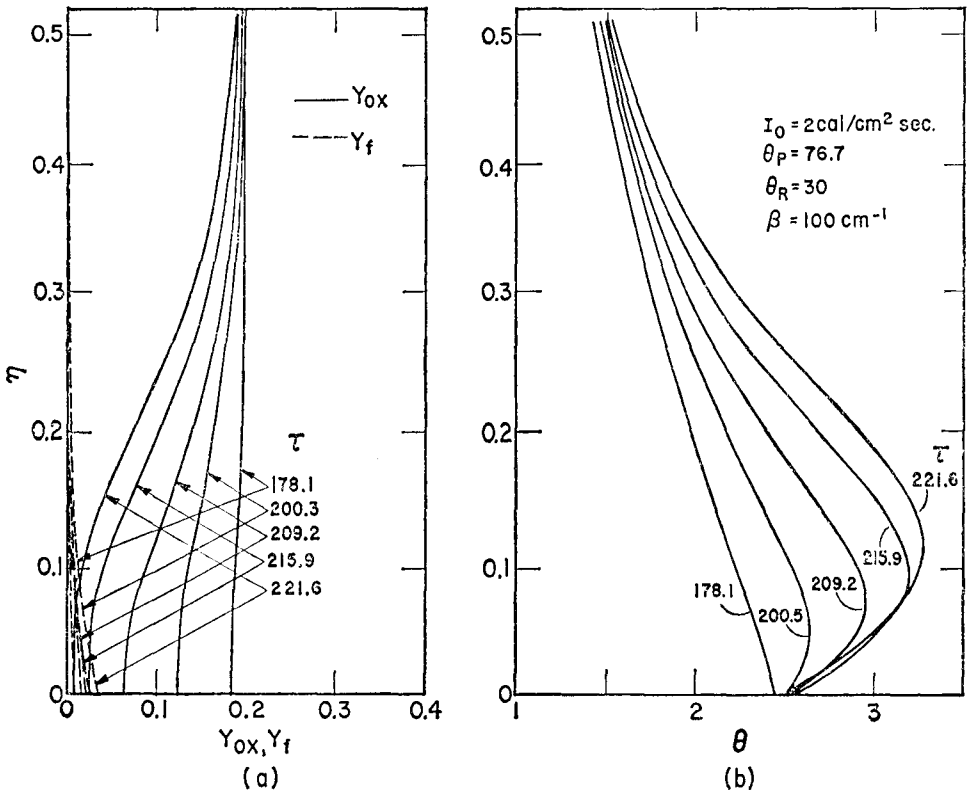

FIG. 12. (a) Timewise fuel and oxygen species distribution. (b) Timewise gas phase temperature distribution.

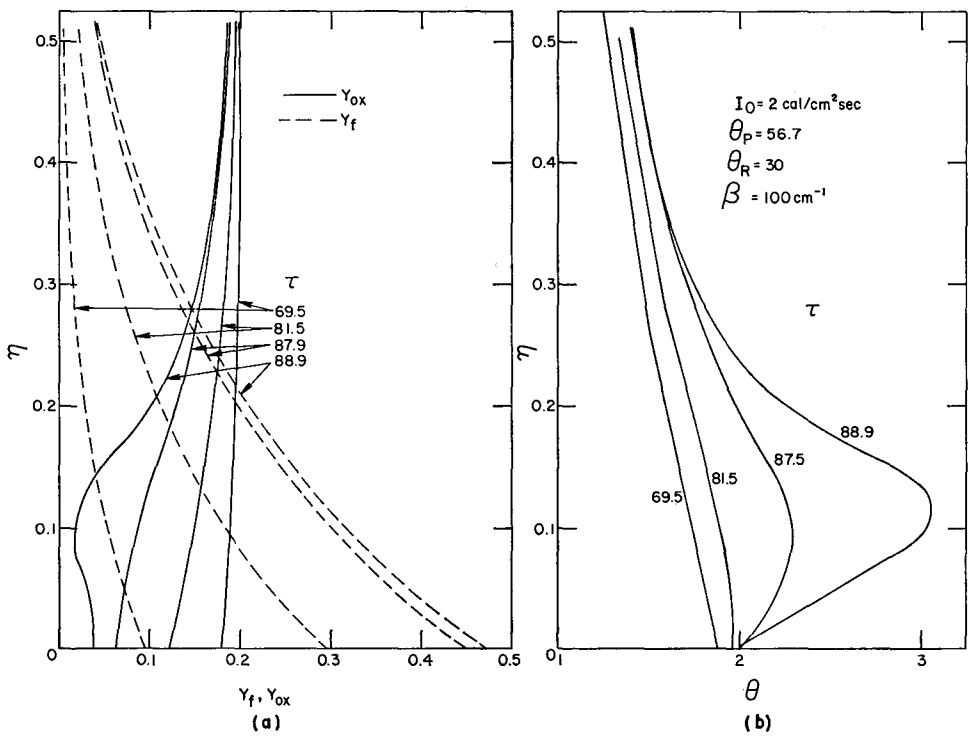

FIG. 13. (a) Timewise fuel and oxygen species. (b) Timewise gas phase temperature distribution.

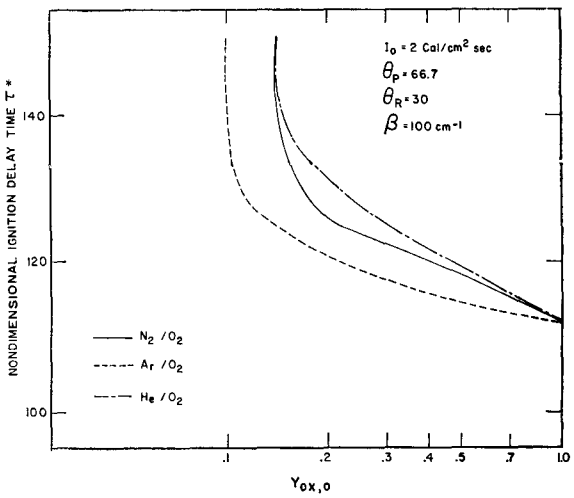

FIG. 14. The effect of diluent inert gas on ignition delay time.

for ignition to occur: (1) sufficient amount of fuel and oxygen are available in the gas phase, (2) the gas phase temperature is high enough to accelerate the gas phase reaction. Therefore, to understand the radiative ignition mechanism of a solid fuel and to find the ignitable domain, the model must include the gas phase reaction. For the purpose of ignition safety, the specific combination of values of θ_P and θ_R, such as described above, could be one way to reduce the ignitable domain. Since the above discussion is based on the reaction rate, the actual values of the activation energies would, of course, depend on frequency factors. Another possible way to reduce the ignitable domain is through the selection of diluent inert gases. Their effects on the ignition delay time and the ignitable domain were studied and are shown in Figure 14. It indicates that H_e/O_2 combination ignites with the longest delay time and with the highest minimum initial oxygen mole fraction. In the ignition safety point of view, the order of the safety is H_e/O_2, N_2/O_2 and A_r/O_2. Alvares (1967) observed experimentally a similar trend for H_e/O_2 and N_2/O_2 combinations with alpha-cellulose. The increase in ignition delay time with decreasing molecular weight is due to higher thermal diffusivity and conductivity of the lighter molecules.

4. CONCLUSION

A theoretical radiative ignition model of a solid fuel including the gas phase reaction and the in-depth absorption of the incident radiation by the solid phase is solved. The conclusion based on the calculated results are as follows:

1) The gas phase reaction must be included in the model in order to understand the radiative ignition of a solid fuel and to find its ignitable boundary. Particularly, the rate controlling process in the marginal ignition regime is the gas phase reaction.

2) The effect of the in-depth absorption of the incident radiation by a solid fuel on the ignition delay time is significant.

3) The effect of the endothermicity or the exothermicity of the pyrolysis of a solid fuel on the radiative ignition is negligible.

4) There are a lower limit and an upper limit in the value of the pyrolysis activation energy for ignition with given values of the gas phase activation energy and frequency factor. This is also true for the gas phase activation energy with given values of the pyrolysis activation energy and frequency factor. No ignition is predicted outside this domain.

5) The ignition delay time and the minimum initial oxygen mole fraction increase as the molecular weight of the diluent gas decreases in the case of A_r, N_2, and H_e.

NOMENCLATURE

A_R	Pre-exponential frequency constant of Arrhenius equation for gas phase reaction
A_s	Pre-exponential frequency constant of Arrhenius equation for pyrolysis
B	Constant defined by equation (27)
C	Constant defined by equation (27)
C_i	Mass fraction of species i
C_P	Specific heat of the solid phase
D	Molecular diffusivity
E_R	Activation energy for gas phase reaction
E_s	Activation energy for pyrolysis
G	Nondimensional incident radiant flux defined by equation (27)
I	Radiant flux
I_0	Incident radiant flux
K	Thermal conductivity
L_v	Pyrolysis heat release
n	Stoichiometric constant
P	Pressure
Q	Heat of combustion per gram of fuel
R	Universal gas constant
(RR)	Reaction rate: $\rho^2 C_{ox} C_f A_R e^{-E_R/RT}$
r	Reflectivity
T	Temperature
t	Time
v	Velocity

Y Mole fraction of species
y Coordinate normal to the surface
α Thermal diffusivity
β Absorption constant
γ Nondimensional fuel mass flux defined by equation (27)
δ Constant defined by equation (27)
ε Constant defined by equation (27)
η Nondimensional coordinate normal to the surface
θ Nondimensional temperature
θ_P Nondimensional pyrolysis activation energy E_s/RT_0
θ_R Nondimensional gas phase reaction activation energy E_R/RT_0
ξ Nondimensional thermal properties defined by equation (27)
ρ Density
τ Nondimensional time defined by equation (21)

Superscript

* At ignition

Subscript

f Fuel
ox Oxygen
s Solid phase
0 Initial condition

REFERENCES

Alvares, N. J. (1967). Oxygen concentration and pressure effects on the ignition of cellulosic fuels by thermal radiation, U. S. Radiological Defense Laboratory, USNRDL-TR-67-25.

Alvares, N. J. and Wiltshire, L. L. (1968). Ignition and fire splread in a thermal radiation field, U. S. Naval Radioogical Defense Laboratory, USNRDL-TR-68-56.

Anderson, W. H. (1970). Theory of surface ignition with application to cellulose, explosives and propellants, *Combustion Science and Technology* **2**, 213.

Bellman, R. E. and Kalaba, R. E. (1965). *Quasilinearization and Non-linear Boundary Value Problems*, Chap. 4, American Elsevier.

Carslaw, H. S. and Jaeger, J. C. (1959). *Conduction of Heat in Solids*, p. 72, Clarendon Press.

Isaacson, E. and Keller, H. B. (1966). *Analysis of Numerical Methods*, Chap. 2, John Wiley and Sons.

Kanuary, A. M. (1971). Ignition of cellulosic solid—a review, Factory Mutual Research Corporation Technical Report Serial No. 197211–7.

Martin, S. (1965). Diffusion—controlled ignition of cellulosic materials by intensive radiant energy, *Tenth Symposium (International) on Combustion*, p. 877.

McCarter, R. J. (1972). Thermal analysis of GIRCFF fabrics, unpublished report.

Ohlemiller, T. J. and Summerfield, M. (1968). A critical analysis of arc image ignition of solid propellants, *AIAA J.* **6**, 878.

Ohlemiller, T. J. (1969). Radiative ignition of polymeric fuels in an oxidizing gas, Ph. D. thesis, Aerospace and Mechanical Sciences, Princeton University.

Ohlemiller, T. J. and Summerfield, M. (1971). Radiative ignition of polymeric materials in oxygen/nitrogen mixtures, *Thirteenth Symposium (International) on Combustion*, p. 1087.

Price, E. W., Bradley, H. H. Jr., Dehority, G. L. and Ibiricu, M. M. (1966). Theory of ignition of solid propellants, *AIAA J.* **4**, 1153.

Roberts, A. F. (1971). The heat of reaction during the pyrolysis of wood, *Combustion and Flame* **17**, 79.

Simms, D. L. (1962). Damage to cellulosic solids by thermal radiation, *Combustion and Flame* **6**, 303.

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