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NATIONAL BUREAU OF STANDARDS REPORT

10 283

REVIEW OF INFORMATION RELATED TO THERMAL IGNITION OF COMBUSTIBLE SOLIDS

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NATIONAL BUREAU OF STANDARDS

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REVIEW OF INFORMATION RELATED TO THERMAL IGNITION OF COMBUSTIBLE SOLIDS

BY

J. B. FANG

ABSTRACT

The existing knowledge on the ignition of combustible materials subjected to an external heat flux is summarized. Information is included on the basic mechanisms of the ignition process, various analytical studies on the thermal decomposition of polymers, ignition phenomena in the gas phase, ignition criteria and factors affecting the ignition of materials. Suggestions for further theoretical and experimental efforts leading toward a better understanding of the ignition processes involved in a fire environment are presented. A comprehensive bibliography of seventy-five references, some of which are annotated, is included. The emphasis is on cellulosic materials.

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1. INTRODUCTION

The ease with which combustible materials such as wood, fabrics and polymer foams may be ignited is important in determining the initiation and growth of fires. It is essential to be able to characterize the degree of ignitability of combustible materials and to examine some of the parameters involved in fire build-up in order to predict the initiation and spread of primary fires under any existing conditions.

The ignition of cellulosic materials by thermal radiation has been the subject of intensive study, since radiation is recognized as a major means of heat transfer in a well-established fire and from a nuclear detonation, and cellulosic materials are the most commonly occurring combustibles in both urban and rural environments. In order to make reliable estimates of the fire hazards associated with nuclear attack and of the safe separation distances between buildings, considerable amounts of research work have been done in the areas of pyrolysis and ignition of representative fuels.

The purpose of this review is to present a summary of the current state of knowledge on the ignition of solid materials by external heating. It is hoped that this will be of value in the development of an appropriate test method on the ease of ignition for building materials and of improved techniques in fire prevention.

2. MATHEMATICAL ANALYSIS

The ignition of solid materials involves complex combinations of transient physical and chemical processes. When a solid such as wood or a synthetic polymer is heated, its temperature increases at a rate dependent on the rate of heat imposed at the surface and upon the rate of heat transferred into the interior of the solid. The absorption of heat by the solid causes temperature-dependent pyrolysis reactions and phase changes liberating flammable or non-flammable gases and in some cases leaving behind a rigid, porous carbonaceous residue. These gaseous products along with air present within the solid introduce an internal convection process, and may crack into lower molecular weight fragments while flowing through the high temperature carbonaceous residue zone. The volatile products issuing from the solid mix with the surrounding air, where they may or may not react with the oxygen present, and rise in the form of a plume. If the rate of emission of flammable gases is sufficient to create an appropriate fuel-air ratio within its flammability limits, the combustible mixture in the plume may ignite spontaneously or become ignited by an external heat source such as a pilot flame. The flame once initiated in the volatile stream travels back toward the exposed surface.

Whether ignition sustains is dependent upon a suitable distribution of temperature within the solid after removal of the external heat source, the transfer of sufficient heat from the flame to the solid to maintain a continuous supply of flammable gaseous decomposition products, and upon a sufficient supply of oxygen from the surrounding atmosphere. It follows that sustained ignition will not be obtained if solid nonflammable residues form on the surface and insulate the remainder of the flammable components from the heat source.

In a complex situation such as this, much can be learned by using an analytical model to study the major parameters involved in the process and to predict the ignition characteristics of the materials. Generally, most realistic models are too complicated to be solved, therefore the following simplifying assumptions are usually employed; (1) the material is isotropic, (2) its thermal properties are independent of temperature, (3) the heat loss at the exposed surface obeys the Newtonian cooling law, (4) the radiative interchange within the solid is negligible, and (5) the entire thermal decomposition can be represented by a first order reaction rate of the Arrhenius type.

With these considerations, the governing equation describing the distribution of temperature within a self-heat generating or heat absorbing solid subjected to an external heat source has the form

$$\rho C\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} (K\frac{\partial T}{\partial x}) + Q\frac{\partial \rho}{\partial t} + U - V \qquad (1)$$

where k, ρ and C are the effective conductivity, the density, and the specific heat respectively, T is the absolute temperature Q is the effective heat of decomposition, U is the rate of energy absorption in depth from external heating (this penetration is due to pores and diathermanacy), V is the rate of energy removal due to internal convection, x is the distance variable normal to the exposed surface, and t is the time variable.

Equation (1) is based on one-dimensional, transient heat conduction, a pyrolysis heat source or sink, external heating, and internal convection which opposes the inward conduction.

2.1 CHEMICAL HEATING

The generation or absorption of heat as the result of thermal decomposition or phase changes is a common occurrance. The rate of heat release depends on whether the reactions are exothermic or endothermic, and thus will determine the possible form the ignition process will assume. A number of researchers (1, 8, 16, 47, 70) have employed chemical reaction rates (expressed as one or more n-th order reactions) with Arrhenius temperature dependent rate constants to describe the rate at which an active material decomposes or changes phases. The rate of weight loss or volatile-generation rate may be expressed as

$$\frac{\partial \rho}{\partial t} = \frac{\partial (\rho u)_g}{\partial x} = -k\rho^n = -A\rho^n \exp(-\frac{E}{RT}) \qquad (2)$$

where $(\rho u)_g$ is the mass flux of pyrolysis gases, k is the rate constant, n is the order of the reaction, A and E respectively are the frequency factor and the activation energy, and R is the universal gas constant.

The rate constant (k) can be a combination of the rate constants of two or more elementary reactions for competitive or consecutive reactions.

Several investigators (9, 43) have expressed the rate of thermal degradation of a reactive material to char as

$$\frac{\partial \rho}{\partial t} = \frac{\partial (\rho - \rho_c)}{\partial t} = -A(\rho - \rho_c)^n \exp(-\frac{E}{RT}) \qquad (3)$$

which differs from the previous one in that the rate is considered a function of the difference between the degrading material's density and its final char density (ρ_c).

Wood has been in use since the beginning of time, and therefore a great deal of experimental work has been done on wood and its components. Browne (12) presented an excellent review of the information related to the combustion of wood up to 1958. In 1968, Shafizadeh (55) summarized the existing knowledge on the pyrolysis and combustion of cellulosic materials and on effects of flame-retardant chemicals.

Some researchers (8,52,70) have demonstrated that over a temperature range, cellulosic materials lose weight in a kinetically first order manner. Tang and Neil (64) on the basis of thermogravimetric analysis suggested that the initial stage of the thermal degradation of cellulose is controlled by pseudo zero-order kinetics and that the final stage is pseudo first-order. Lipska and Parker (28) observed by isothermal pyrolysis that after an initial rapid decomposition of about 10 percent, the rate of decomposition of cellulose was independent of time indicating a zero-order reaction. Thomas and Bowes (65) pointed out several experimental studies which concluded that at least two or more reactions are involved in the thermal decomposition of cellulosic materials and that a simple ignition theory based on a single reaction of the Arrhenius type may be inadequate to explain the available data. Thermogravimetric analysis experiments reported by Tang (63) indicated that a dual segment mechanism, involving two first order processes as suggested by Akita (1), successfully represents the actual kinetics of wood decomposition. From a number of cellulose pyrolysis observations made by thermogravimetric analysis (TGA), differential thermal analysis (DTA), mass spectrometric thermal analysis, and gas and paper chromatographic analysis, Kilzer and Broido (26) concluded that the pyrolysis of cellulose must be described by at least two competing endothermic reactions and a consecutive exothermic reaction.

Information pertaining to the pyrolytic decomposition of synthetic polymers was extensively reviewed by Madorsky (37). Levi (33) provided a comprehensive annotated bibliography on thermal degradation, thermal oxidation and thermal analysis of high polymers to about June of 1963. Welker (71) has recently reviewed the literature on the pyrolysis and ignition of cellulosic materials. Hilado (22) has summarized the existing information related to the flammability of plastics.

A quite general expression for the rate of density change of high polymers as a function of the degrading material's density and temperature only was employed by Wells (73). This expression is the sum of four similar terms, each of which is represented by a single n-th order reaction with Arrhenius rate constant and is significant in a given temperature range:

$$\frac{\partial \rho}{\partial t} = f(\rho, T) = -\sum_{i=1}^{4} A_i \left(\frac{\rho}{\rho_o}\right)^{n_i} \exp\left(-\frac{E_i}{RT}\right) \qquad (4)$$

where ρ is density at time t, ρ_o is initial density, A_i and

E_i are material frequency factor and activation energy respectively, and n_i is reaction order.

In a kinetic study of the rates of degradation of many plastic materials, Madorsky and Straus (38) found these rates to be closely first order with respect to the chemically active material fraction. Hilado (21) described the combustion process for urethane foams which have events similar to that seen in cellulose and other organic polymers.

2.2 EXTERNAL HEATING

Radiation and convection are the principal means of heat transfer in a well-developed fire. Consequently, numerous researchers (1, 16, 29, 43, 56) used either thermal radiation or forced convection to heat the materials for their ignition and pyrolysis studies.

For constant radiant heating applied to diathermanous solids, it is assumed that the energy absorbed at various depths within the solid follows the Lambert-Beer attenuation law. Therefore, the rate of radiation absorption can be described by

$$U_r = a\, H_o \exp(-ax) \qquad (5)$$

where a is the attenuation coefficient of the solid and H_o is the incident irradiance at the exposed surface.

For the constant convective heating condition, the rate at which heat is transferred from hot air to a solid boundary in accordance to Newton's law of cooling, may be expressed as

$$U_c = h_v(T_s - T) \tag{6}$$

where h_v is volumetric convective heat transfer coefficient, and T_s is the temperature of hot air.

The volumetric convective heat transfer coefficient which varies with depth depends on the properties of the hot air, the nature of the fluid motion past the surface, and the void fraction. The external energy absorption term in Equation (1) is then given by $U = U_r + U_c$.

2.3 INTERNAL CONVECTIVE COOLING

The gaseous products which are evolved in the pyrolysis zone within the solid, cause convective heat transfer while flowing through the other regions of the solid including the hot, porous carbonaceous char zone in char forming materials. If the solid is wholly converted into gaseous components, the mass flux of pyrolysis gases at a depth x, in terms of the rate of pyrolysis, is given by (58)

$$(\rho u)_g = -\int_x^{\ell_o} \left(\frac{\partial \rho}{\partial t}\right) dx \tag{7}$$

where ℓ_o is the depth at which the volatiles starts to genoerate, and depends on such factors as the temperature distribution of the solid.

With the assumption that a thermal equilibrium establishes between the porous interior of the solid and the gases flowing through it, the rate of heat loss due to convection from the solid to the pyrolysis gases can be expressed as

$$V = (\rho u)_g C_g \frac{\partial T}{\partial x} \tag{8}$$

where C_g is the specific heat of pyrolysis gases.

If the solid is considered to be at a uniform initial temperature and is subjected to one-sided heating with no heat loss from the back surface, the initial and boundary conditions are

$$\begin{aligned} &\text{(i)} \quad t=o,\ x>o;\ T=T_a \\ &\text{(ii)} \quad t>o,\ x=o;\ K\frac{\partial T}{\partial x}=h(T-T_a)+\varepsilon\sigma(T^4-T_a{}^4) \\ &\text{(iii)} \quad t>o,\ x=\ell;\ \frac{\partial T}{\partial x}=o \end{aligned} \tag{9}$$

where T_a is the temperature of ambient air, h is the convective heat transfer coefficient, ε is the average surface emissivity, σ is the Stefan-Boltzmann constant and ℓ is the thickness of the solid.

2.4 GENERAL SOLUTIONS

With these substitutions, the final energy equation has the form of a non-linear partial differential equation because of the exponential reaction rate term. Thus, the temperature and density distributions within the solid as a function of time and position can be predicted from the solution of this transient heat conduction equation with suitable initial and boundary conditions. The time to ignition is assumed to be the time at which the surface temperature reaches some fixed value.

Bamford, Crank and Malan (8) presented the first attempt at a comprehensive treatment of the combustion of wood in 1946. They solved the energy equation numerically for a finite slab with a constant heat flux boundary condition, neglecting internal convection and assuming a first order, Arrehenius-type pyrolysis reaction. Using a finite-difference method, and measured values of the heat of decomposition, the reaction rate constant and the activation energy of wood, they calculated the temperature distribution in the solid phase and the rate of mass loss of the slab.

By means of a similar technique, Weatherford and Sheppard (70) also computed the surface temperature and volatile generation rate. They pointed out that undulations which Bamford et al. found in the volatile-generation rate curves were caused by too large a step size in the finite difference approximation.

In an analytical study of combustion, Panton and Rittmann (47, 48) have recently included competitive and consecutive homogeneous reactions to describe the pyrolysis and have employed both constant, and density-dependent thermal conductivities in the mathematical treatment. They have developed a numerical technique to solve the resulting transient heat conduction equation for a porous slab of finite thickness subjected to a constant heat flux.

In order to predict the rate of burning and temperature histories, Blackshear, Murty and Wood (9) have proposed a unified model to describe the heat and mass transfer processes in the interior of charring organic and synthetic solids exposed to convective heating. The model was formulated based on the assumptions that (1) there exists a pyrolysis temperature and a charring temperature, at which the solid begins to gasify, and has lost all its volatiles, respectively, (2) the pyrolysis reaction follows first order, two-segment kinetics of the Arrhenius type, and (3) there are three different layers (virgin solid, pyrolysis and char layers) within the solid at different temperatures for various lengths of time. Currently, an effort is being made to find numerical solutions for the simultaneous, non-linear, partial differential equations derived from an energy and mass balance within an infinite slab for various time periods.

Numerous workers (18, 23, 58) have proposed correlations of the experimental results using dimensionless groups derived from the energy equation. Assuming that wood is an inert material, i.e. involving no heat generation during thermal decomposition, and no internal convection by gaseous products, Simms (58) employed dimensional analysis to derive the pertinent groups. His analysis considered two limiting cases; thermally thin material (the solid with a linear temperature gradient) and thermally thick material (the semi-infinite solid).

Koohyar, Welker and Sliepcevich (29) have suggested two mathematical models in which it is assumed that (1) the irradiated material is inert, opaque and has physical properties independent of temperature, (2) the penetration of radiant energy can be characterized by a single absorption coefficient and (3) no heat loss occurs at the exposed surface. One model assumes the material has a finite thickness and the other that it is semi-infinite. They correlated the ignition data on wood with two dimensionless groups derived from the solution of their simplified models.

Varma (68) performed a mathematical analysis of the heat transfer within a slab composed of randomly oriented, long cylinders of fuel with small diameters. He assumed that conduction of heat occurs only along the lengths of the individual fuel particles and neglected chemical heating and radiative interchange within the slab. His analytical model describes the ignition characteristics of high voidage fuels based on the constant surface temperature ignition criterion, conduction, diathermancy, internal convection and thermal inertia of a semi-infinite slab heated with radiant energy.

In the study of the ignition of cellulosic materials by intense thermal radiation, Martin (43) concluded that the actual unsteady-state temperature distribution in a reactive solid is not accurately represented by the classical heat conduction expression for an opaque, inert semi-infinite material since the boundary conditions are usually not perfectly satisfied and the experimental profile is perturbed by heats of reaction and phase changes.

Although most of the mathematical models are not yet sufficiently developed to provide a complete picture of the ignition processes involved, they have been shown to be appropriate for correlating the results of experiments under particular conditions.

3. GAS PHASE IGNITION PHENOMENA

The ignition of most combustible solids actually occurs in the gas phase since the volatile products of thermal decomposition lack the necessary oxygen when they issue from the surface and must travel some distance to mix with air in order to form a flammable mixture. Also the ignition must occur at distance sufficiently far from the surface to prevent excessive loss of heat and chain carriers to the solid. A gas phase oxidation starts immediately after these gaseous products mix with the air entrained from the surrounding provided the temperature is high enough. If the gas phase reaction proceeds at a high enough rate, ignition results. The necessary and sufficient conditions for ignition of the volatile-air mixture are that the relative concentration of gaseous fuel to air must lie between the lower and the upper flammability limits and some ignition temperature must be achieved.

The flammability limits of a gas mixture bears some relationships to the limits for each of the constituent gases alone, and can be predicted from Le Chateliers rule as below (19)

$$L = 1/(P_1/L_1 + P_2/L_2 + \text{etc.}) \qquad (10)$$

where L is the total volume percentage of flammable gases required for a lean limit mixture with air. P_1, P_2, etc., and L_1, L_2, etc. are the actual volume percentages and lean limits of each of the constituent gases.

Several factors such as static pressure, temperature and turbulence in the system, appreciably effect the flammability limits. A critical review and an excellent summary of the state of knowledge on flammability limits and ignition of gases can be found in the book by Mullins and Penner (46).

The attainment of a particular ignition temperature for a gaseous mixture is also an important threshold for gas phase ignition. Salooja (51) studied the effect of temperature on the ignition characteristics of hydrocarbons and concluded that the ignition lag decreases with an increase in temperature, and that increasing the fuel concentration markedly reduces the ignition lag around the minimum ignition point. This reduction gradually decreases and eventually tends to disappear as the temperature is raised.

The ignition of a combustible mixture requires the initiation of exothermic chemical reactions such that the rate of heat generation exceeds the rate of energy loss from the reaction zone. Once this condition is achieved, the reaction rate, which is determined by local reactant concentrations and local temperatures, will continue to accelerate so as to produce a self-propagating flame. In pilot ignition, the combustible mixture in the volatile stream is heated locally to a sufficiently high temperature by an external heat source to cause gas phase ignition.

Once a combustible mixture is ignited, the resulting flame will propagate down through the mixture toward the solid. Part of the heat liberated will be transferred back to the exposed surface by radiation and conduction to maintain the flow of volatiles required for sustained ignition. The rate of flame propagation is greatly influenced by oxygen concentration, the chemical composition of the gaseous mixture, velocity of gas flow and ambient pressure parameters as well as the ignition source and the physical environment.

In order to increase the fundamental understanding of the basic mechanism of ignition processes, an analysis of the mass and heat transfer in the gas phase is essential. Simultaneous solution of the energy and continuity equations under appropriate boundary conditions, which describe the rate of change of the surface temperature and the rate of evolution of gaseous products at the solid-gas interface, can provide useful information regarding the concentration and temperature distributions up to ignition.

4. IGNITION CRITERIA

Ignition commonly refers to the appearance of a luminous flame in the volatile stream issuing from a material undergoing thermal decomposition. Depending upon whether this gaseous mixture ignites with or without the aid of an external igniter, such as a pilot flame or an electric spark, placed in the volatile stream, ignition is accordingly classified as piloted or spontaneous. A special case of piloted ignition is termed as surface ignition if the gaseous mixture is ignited by a pilot flame in contact with the heated surface of a pyrolyzing material. Materials that have been ignited may or may not continue to burn. The condition in which the burning continues to total destruction or complete charring after the removal of original heating source is referred to as sustained ignition.

A number of criteria necessary for the occurance of ignition have been suggested by numerous investigators (1,58,70). The work done before 1962 has been well summarized by Simms (58). These postulated criteria for ignition are:

(1) Fixed Temperature Criterion: Ignition will occur when the temperature of the solid (mean temperature for "thin" materials or surface temperature for "thick" materials) reaches a certain fixed value. Martin (43) measured the temperature histories at various depths in α-cellulose sheets and extrapolated the internal temperature profile at the instant of ignition to the heated surface for a surface temperature. He concluded that the surface temperature at spontaneous ignition was independent of irradiance level and in excess of 600°C. Alvares (2) radiometrically determined the surface temperature for the spontaneous ignition of cellulose sheets and found a range of ignition temperatures from 600°C to 650°C for both 7 and 14 cal/cm^2-sec irradiances. Akita (1) performed experiments on ignition of wood by using hot air and a wide range of irradiances, and indicated that with an irradiance of up to 15 cal/cm^2-sec (62.7 w/cm^2), the surface temperature at ignition for various woods was about 500°C, which agreed with the ignition temperature obtained by heating with hot air only. Simms and Law (60) reported several experimental studies which concluded that a fixed surface temperature of about 545°C and

380°C as the criteria for spontaneous and piloted ignition can satisfactorily interpret their ignition data on wood. Koohyar, Welker and Sliepcevich (28, 29) used a radiometer to measure surface temperatures of wood at ignition, and indicated that the experimental ignition temperatures varied widely for all tests, and no remarkable trends were distinctly established. The lack of agreement among the measurements of the ignition temperature for cellulosic materials by various workers are due to differences in exposure conditions and temperature measuring techniques.

It is noteworthy that the spontaneous ignition temperature is higher than the pilot ignition temperature. In the case of pilot ignition, the sample temperature must raise high enough to support an active pyrolysis for production of enough volatile products to form a combustible mixture with the surrounding air. For spontaneous ignition, a higher surface temperature for heating the combustible mixture to attainment of a sufficient temperature for self-ignition is required in addition to maintaining a continuous supply of volatile products.

(2) Critical Rate of Volatile Evolution Criterion: Since ignition needs sufficiently hot combustible volatiles issuing into the surrounding atmosphere, it is likely that there is a minimum rate evolution of volatiles below which the gaseous mixture would be too lean to burn. Bamford, Crank and Malan (8)

first introduced this critical rate of volatile generation criterion in their ignition study on wood. Weatherford and Sheppard (70) suggested that a specified volatile-evolution rate of 2.5×10^{-4} g/cm^2-sec required for wood to achieve sustained ignition proposed by Bamford et al. did not appear to be valid because their conclusion was based on the probably erroneous undulating volatile-generation-rate curve. The results of finite-difference computations for the ignition of woodlike materials by Weatherford and Sheppard (70) indicated that for a constant source temperature, a constant volatile-generation rate corresponds approximately to a constant surface temperature, except for very thin slabs.

Experimental results by Simms (59) showed that the surface temperature and the ignition time for piloted ignition are a function of the position of the pilot flame. It would be more pertinent to consider the minimum rate of volatile evolution as the criterion for piloted ignition rather than a fixed surface temperature since the position of the pilot flame is not a very fundamental variable.

(3) Critical Irradiance: The lower limit of irradiance which will cause ignition in a combustible solid heated by thermal radiation is known as the "critical irradiance." Obviously the time to ignition depends upon the incident irradiance, but whether ignition will occur regardless of the

length of exposure is governed by whether the irradiance exceeds a certain critical value. By plotting H, the incident irradiance, against the function $H/\sqrt{t}$, where t is the ignition time, the critical irradiance, H_c is determined as the intercept on the irradiance axis when $H/\sqrt{t}$ is zero (31). Any factor such as a decrease in the size of the area irradiated or an increase in moisture content, which prolongs the time required for the exposed surface to reach its ignition temperature, tends to increase the critical irradiance required for ignition. The critical irradiance also depends upon the thickness and the optical properties such as the opacity and absorptivity of the material (44).

For the irradiance greater than the critical irradiance, the pilot ignition time for various species of wood was given by an empirical relation of the form (31).

$$(H-H_c)t^{2/3} = 0.025 \times 10^6 \ (K\rho C + 68 \times 10^{-6}) \qquad (11)$$

and the corresponding expression for spontaneous ignition was given by

$$(H-H_c)t^{4/5} = 0.05 \ X \ 10^6 \ (K\rho C + 35 \ X \ 10^{-6}) \qquad (12)$$

where H is the incident irradiance in cal/cm^2-sec., K is the thermal conductivity in cal/cm^2-sec-°C, ρ is the density in g/cm^3 and C is the specific heat of wood in cal/g-°C.

Assuming that RT_a/E (gas constant, the air temperature and activation energy) is much less than unity, and the gas flow in the volatile stream is turbulent, Akita (1) has derived an expression for the pilot ignition time, from an approximate treatment of the heat conduction equation for a semi-infinite slab heated by hot air as

$$\ell\eta t = \ell\eta B = E/RT_a \qquad (13)$$

where B is a constant and is approximately independent of temperature.

(4) *Attainment of Flammable Mixture Criterion*: Based upon considerations of the inflammability of volatile-air mixtures, Akita (1) suggested that pilot ignition could occur when the combustible gaseous mixture attains a certain composition and is not dependent on the surface reaching a fixed temperature. Weatherford and Sheppard (70) pointed out that for a given combination of ambient conditions, this criterion would be analogous to a fixed minimum volatile-generation rate at the heated surface.

(5) *Critical Ignition Energy*: A possible criterion for sustained ignition would be that the threshold for ignition occurs when a minimum amount of heat energy has been absorbed by a material prior up to ignition. Akita (1) found that the total energy absorbed by wood prior to ignition generally increases with increasing density and with increasing incident irradiance. He also used approximation techniques to derive

an expression for total energy required for ignition as

$$Q_s = (H/h)(2tK\rho C/\pi)^{1/2} \tag{14}$$

where h is convective heat transfer coefficient and H is the irradiance. Thus, he suggested that it is impossible to consider the absorption of a certain minimum energy as an ignition criterion.

5. FACTORS AFFECTING IGNITION OF SOLID MATERIALS

A number of factors can affect whether and when ignition by irradiation occurs. These may be divided into two groups:

(1) Environmental Factors: The irradiance level and its variation with time, the area of uniform energy flux, the spectral distribution of the incident radiation, the position and size of the pilot flame, the ambient conditions, including temperature, humidity and air movement, and the existance of cold areas surrounding the irradiated surface.

(2) Material Factors: The absorptivity, diathermancy, thermal properties, moisture content, surface area and thickness of the material, and the orientation of the irradiated area.

Some particularly important factors which affect the onset and occurrence of ignition are as follows:

1. Irradiance: The time to ignition decreases with increasing irradiance. Akita (1) pointed out that for irradiances greater than 15 cal/cm^2-sec the surface ignition temperature of cellulosic material generally increases with an increase in irradiance. This is possibly due to slow mixing of the decomposed volatiles with air, i.e., the surface reaches an abnormally high temperature before the critical combustible gaseous mixture is established. Also, as the depth of heat pentration decreases due to shorter ignition times, the temperature must be higher to produce the same amount of volatiles in the smaller volume and time interval.

2. Spectral distribution of the incident radiation: The ignition behavior of a flammable material not acting as a blackbody receiver is dependent upon the spectral distribution of the incident radiation. If H_λ is the spectral irradiance at wavelength λ from a non-blackbody source (whose spectral emittance is ε_λ) incident on a surface whose spectral absorptance is α_λ , the irradiance absorbed by the exposed surface can be expressed as

$$H_o = \int_o^\infty \alpha_\lambda H_\lambda d\lambda = \frac{\overline{S_1 S_2}}{A_2} \int_o^\infty \alpha_\lambda \varepsilon_\lambda W_{b\lambda} d\lambda \qquad (15)$$

Where $\overline{S_1S_2}$ is the interchange area between the radiant source and the exposed surface, A_2 is the total area of the surface, and $W_{b\lambda}$ is spectral emissive power of the blackbody. Thus, for a given source and surface temperatures, the incident energy absorbed by the material is a function of both the spectral absorptance of the material and spectral emissive power ($\varepsilon_\lambda W_{b\lambda}$ product) of the source.

Welker, Wisson and Sliepcevich (72) used a premixed gas flame and a tungsten filament lamp as heat sources to investigate the ignition behavior of cellulose and reported that the ignition time was much shorter for flame irradiation than for irradiation by a tungsten source at the same level of irradiance. This is attributed to the differnce in the spectral distributions of the radiation from the two sources. The ignition times for cellulose blackened with carbon black were in much better agreement between the two sources.

3. Position of the pilot flame: Piloted ignition can occur only when the pilot flame is within the thickness (boundary layer thickness) of the volatile stream rising from the irradiated materials (59). Simms (59) and Moysey and Muir (45) observed that the location of the pilot flame was important in determining ignition time. The ignition time for a given irradiance increases with an increase in distance of the pilot flame from the exposed surface. This variation in

the ignition time with the position of the pilot flame is due to the concentration gradient of the volatiles in the gas phase and implies that relatively little mass diffusion occurs, and that the flow in the volatile stream is mainly laminar not turbulent. With a pilot flame, 1.25 cm. long placed at 0.62 cm. to 1.9 cm. in front of the heated surface, Simms (59) reported that the surface ignition temperatures giving the best fit between the experimental points and the theoretical expression derived from a simple ignition model are 300° C to 410° C for wood.

4. External wind: The effect of an external wind is to induce turbulence and thereby lower the minimum irradiance required for ignition or the time to ignition. Turbulence increases the rate of heat release in the volatile stream by increasing the size of the zone in which the volatiles and the surrounding air mix as well as increasing the rate of mixing. Using air directed upward past an exposed vertical surface, Moysey and Muir (45) showed that air flowing at a velocity of approximately 25 cm/sec reduced the time required for piloted ignition when the material was exposed to low irradiance, but had little effect if the irradiance was high. Air velocities in excess of 100 cm/sec increased the time taken to produce piloted ignition, presumably due to the cooling effect.

5. Absorptivity: The spectral absorptance characteristics of the solid being irradiated affect the ignition properties of the material. The absorptivity of a surface varies with the wave length of the incident radiation early in the exposure. However, in heating a material to ignition in which the irradiated surface darkens, the absorptivity increases with the degree of charring (57).

6. Diathermancy: For an opaque solid, all the incident energy is absorbed at the surface. However, for a diathermanous solid; the incident energy is absorbed within the material. Thus, diathermancy causes a redistribution of the energy throughout the solid resulting in lower temperatures near the surface and higher ones in the interior than would occur if the solid were opaque. Hottel and Williams (23) studied the transient heat flow in organic materials exposed to high intensity of thermal radiation, and concluded that the effect of diathermancy becomes negligible at sufficiently large values of the exposure time or of the depth into the material. Gardon (18) found that the diathermancy effects are significant before cellulosic materials begin to char, and that once the surface irradiated has blackened, the natural materials become nearly opaque to thermal radiation.

7. Moisture content: The moisture content of a solid is a direct function of the ambient relative humidity for

solids which absorb and desorb moisture readily. Increasing moisture content increases the total energy required for ignition and also increases the time taken for both pilot and spontaneous ignition for any irradiance. The presence of moisture changes the heat transfer or the temperature rise within the solid in at least three ways (60): (a) Moisture increases the values of thermal conductivity and the volumetric specific heat. (b) Heat is transferred directly by molecular diffusion of water. (c) When phase changes occur, evaporation cools the hotter regions and condensation heats the cooler regions.

8. Size of the area irradiated: The critical irradiance required for ignition and the ignition time increase when the size of the area irradiated is decreased at low irradiances which are typical in a fire environment (56). The rate of surface cooling for the smaller area can be expected to increase due to decreased thickness of thermal boundary layer developed along the vertical exposed surface prior to ignition. This means that the smaller area requires a longer heating time to reach the ignition temperature and hence the ignition time is longer. Alvares, Blackshear and Murty (4) studied the influence of free convection on the ignition of cellulose by irradiation and concluded that the height of a vertically orientated sample became important

if the irradiance was less than 4.0 cal/cm^2-sec because the ignition time was long enough to allow a boundary layer to establish fully on the heated surface.

9. Voids in the solid: Variation in the voidage of the solid alters the mechanism of heat transfer within the solid phase in four ways (68): (a) Variation of conductive heat transfer, (b) Variation of absorption coefficient of the solid, thereby causing the incident radiation to be absorbed in various depths, (c) Variation of convective heat transfer within the solid, (d) Variation of thermal inertia (KρC product). As the void fraction of the solid increases, conductive heat transfer decreases, the radiation absorption coefficient decreases, thermal inertia decreases and internal convection increases up to a voidage of about 0.4 and then decreases.

6. CORRELATION OF RESULTS

Simms (59,60) correlated his ignition data in terms of two dimensionless groups; the energy modulus and the cooling modulus, derived from a simple heat transfer model. The solution to the conduction equation for an inert, opaque material with Newtonian cooling at the surface and a fixed temperature criterion for ignition, leads to the following equations:

(a) For a semi-infinite slab ("thick" material), the energy modulus is given by

$$(H/\theta_s)(t/K\rho C)^{1/2} = \beta/[1 - \exp(\beta^2)\ \mathrm{erfc}\ \beta] \qquad (16)$$

where θ_s is the surface temperature rise at ignition, $\beta = h\sqrt{t/K\rho C}$, the cooling modulus and h is the Newtonian cooling coefficient.

(b) For a slab with linear temperature gradient ("thin" material), the energy modulus is given by

$$Ht/\theta_m \rho C\ell = (2ht/\rho C\ell)/[1 - \exp\ (-ht/\rho C\ell)] \qquad (17)$$

where ℓ is the thickness of the slab, and θ_m is the mean temperature rise at ignition.

With an estimated value of Newtonian cooling coefficient (h), the temperature rise at ignition (θ_s or θ_m) can be determined by adjusting the best fit between the experimental points and the theoretical expression. Analysis by Simms seems to fit the data for spontaneous ignition better than for piloted ignition in the range of his experimental data. Several of his correlations include variables with time raised to the same power in both coordinates, this tends to make data look better than it really is.

Koohyar, Welker and Sliepcevich (29) have correlated their data on both spontaneous and pilot ignitions of wood by flame irradiation with two dimensionless groups: modified irradiance modulus ($\eta H\ell/K\theta_s$), and the square root of Fourier modulus ($\sqrt{\alpha t/\ell^2}$) derived from a modified model similar to that proposed by Simms (45), where η is a constant modifying factor.

Using a fixed surface temperature as the ignition criterion, Varma (68) has been able to correlate his experimental results for spontaneous ignition of high voidage celluosic fuels by irradiation in terms of three dimensionless groups: Effective fourier number ($a^2Kt/\rho C$), energy modulus ($H/Ka(1-\phi)\theta_s$), and cooling modulus (h_ϕ/a^2Kd) derived from an analytical model involving preheating of the fuel up to ignition. Here h_ϕ is the convective heat transfer coefficient within the sample, and d is the diameter of the fuel particles, and a is the absorption coefficient of the material.

7. EXPERIMENTAL FINDINGS

Lawson and Simms (31) determined the time required to ignite wood at various irradiances, with and without a pilot flame. They estimated the critical irradiance necessary for ignition by extrapolating graphs of irradiance versus the reciprocal of the ignition time out to infinite time and found that these critical irradiances were approximately constant for nearly all species.

Martin (43) heated cellulose slabs by radiation and measured the spontaneous ignition time, temperatures within the slab, weight loss and composition of the gaseous products for various irradiances. A maximum in the rate of evolution of volatile products occurred near the ignition time but no evidence was found for an ignition criterion based on a threshold rate of volatile evolution. He also pointed out that the persistence of ignition depends only upon the continued flow of flammable volatile products and not on any unique composition of the mixture.

An investigation on the ignition characteristics of high voidage slabs by Varma (68) showed that for a given ambient humidity and incident irradiance, with increase of voidage, the time taken to spontaneous ignition of cellulosic material increased up to a void fraction of about 0.4 and then continuously decreased. He also used high speed photography techniques to study the ignition processes involved, and found that the ignition occurred in the volatile stream and then the flame travelled down to the exposed surface and that the time elapsed for the flame to reach the surface from its first appearance was about 0.01 sec, giving a flame speed of about 500 cm/sec. Simms (57) also made high speed photographs which showed flaming to occur easily in the volatile stream where the laminar flow became turbulent, but Alvares et al. (4) suggested that the ignition may initiate at, or even within, the charred surface.

Sauer (52) analyzed the depth of char and weight loss data of cellulosic materials exposed to radiant flux and concluded that the rate of thermal degradation of the materials is governed primarily by the diffusion of heat into the interior of the solid as opposed to a kinetic reaction controlled process.

Lee, Loftus and Gross (32) conducted experiments to study the effect of moisture content on thermal inertia ($K\rho C$ product) and on surface flammability, and indicated that their data show a linear relation between the moisture content of cellulosic materials and their thermal inertia determined from the history of the surface temperature measured with a sensitive detector, and that the flame-spread factor is inversely proportional to the thermal inertia.

Simms and Law (60) studied the effect of moisture content on the ignition behavior of wood and found increased ignition times for higher moisture contents. They also satisfactorily correlated their data on the same basis as for dry wood, by accounting for variations in thermal properties due to the presence of moisture.

The experimental results by Koohyar, Welker and Sliepcevich (29) on spontaneous and piloted ignition of different species of wood exposed to irradiation from a buoyant diffusion flame showed that the rate of weight loss at ignition to be in the range of 1.0×10^{-4} to 21.7×10^{-4} gm/cm^2-sec. Thus, they concluded that a minimum rate of evolution of volatiles is a necessary, but not sufficient, condition for ignition to occur. They attempted to correlate the data using the actual experimental surface temperature rise along with the dimensionless groups as used by Simms (48) but obtained poor results. Consequently, they suggested that the constant surface temperature criterion is not adequate.

8. CONCLUSIONS

The mathematical analysis of the ignition of combustible materials has been limited to a consideration of the unsteady state heat conduction equation with heat generation from exothermic and endothermic reactions in the solid phase. No single analytical treatment provides complete information related to pilot ignition which is of practical importance in the initiation and spread of fire. Numerous ignition criteria derived either empirically or analytically have been proposed, yet there are still unsolved points in the correlation and interpretation of all of the available experimental results.

It appears that the significant factors which affect the occurrence of piloted ignition are the chemical properties, optical properties, moisture content, void fraction and thermal properties of the material; the flux density and the exposure time of the external heat source, and the position and the size of the pilot flame.

The ignition of a combustible material involves two separate and distinct processes: the decomposition of the solid into char and volatile products and a gas phase oxidation of these volatiles after mixing with the surrounding air at some distance from the solid. The rate of thermal degradation of polymeric materials heated by radiant energy has been shown to be diffusion-controlled rather than reaction rate - controlled for a wide range of exposure conditions. Ignition occurs in the volatile stream and then the flame travels towards to the heated surface.

9. SUGGESTIONS

A general mathematical analysis along with approximation techniques is needed to establish the relevant parameters controlling ignition events, to interpret the experimental observations and to provide better understanding of the basic mechanism of the pilot ignition process.

An extensive research study should be undertaken to study the influence of parameter variations on the pilot ignition responses of materials, which are heated by separate or combined, constant radiant and convective heat fluxes.

Pyrolysis kinetic data over a wide temperature interval is required in order to predict the ignition behavior of materials. Recent developments in thermal analysis techniques provide the means for attaining this information. More meaningful data can be obtained by isothermal pyrolysis than from TGA since the pyrolysis rate is in general dependent on the degree of decomposition as well as the time.

In order to obtain a complete picture of the ignition phenomena, a combined theoretical and experimental analysis of the mass and heat transfer in the gas phase is essential.

The conditions in the volatile stream should be analyzed to determine the temperatures and chemical composition of the volatiles as well as the rate of evolution of volatiles from the solid material. It is conceivalbe that a criterion for pilot ignition can be found from these quantities measured at the point of ignition.

The rate of weight loss of the heated material should be determined since it indicates the rate of release of volatile products which along with their composition and heat of combustion, determines the ignitability of the material and the rate of heat release.

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A unified model to describe the heat and mass transfer processes in the interior of pyrolyzing and charring cellulosic fuel elements exposed to a heat flux is proposed in order to predict the mass loss rate and temperature history as functions of the physical and chemical properties of the fuel. Equations are simplified by nodimensionalization.

Numerical analysis to obtain a computer scheme by forward differences is also presented in the first section. The second describes the experiments designed to simulate radiative/convective turbulent mass fires. Section three is involved with prediction of the smoulder propagation rate in a cellulosic fuel as a function of the physical properties of the fuel bed.

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Data on the spontaneous and piloted ignition characteristics of five different species of wood exposed to irradiation from a buoyant diffusion flame are presented.

Two mathematical models are proposed in which it is assumed that the irradiated material is opaque, inert, and with physical properties independent of temperature and no heat loss at the surface. One model assumes the material has a finite thickness and the other that it is semi-infinite. The data are well correlated by the solution to the differential equation when multiplied by a factor which represents the fraction of heat entering the material.

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Results have been correlated on the assumption that the material is inert and ignites at a fixed temperature. Simple heat transfer theory has been used to calculate this temperature, taking values for the thermal properties appropriate to the given moisture content.

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Mathematical and experimental studies are being conducted on the thermal processes involved in the ignition of slabs of woodlike substances. The results of extensive finite-difference machine computations suggest that the specified fuel-generation-rate criterion for sustained ignition, proposed by Bamford, Crank, and Malan is incorrect.

Experimental measurements of piloted-ignition thresholds have been conducted in an apparatus designed to simulate convective-source symmetrical heating of plane slabs. These experimental results and published data of prior investigators have been analyzed in terms of various ignition criteria.

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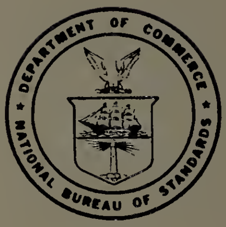

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